Baltic Conference Series

09 - 12 OCTOBER 2018, STOCKHOLM, SWEDEN

SESSIONS AND SYMPOSIA:

- Sensors & Actuators Conference
- Microfluidics and Nanofluidics Conference
- Biosensors and Bioelectronics Conference
- Tissue Engineering and Nanomedicine Conference
- Healthcare Technology Conference
ABOUT JOURNAL

Advanced Materials Letters is an international journal published 12 issues per year starting from June 2010. The journal is intended to provide top-quality peer-reviewed research papers in the fascinating field of materials science particularly in the area of structure, synthesis and processing, characterization, advanced-state properties, and applications of materials.

The journal provides an international publication platform for the broad spectrum of issues regarding theoretical and experimental advancements in materials science and engineering including molecular device materials, biomimetic materials, hybrid-type composite materials, functionalized polymers, supermolecular systems, information - and energy-transfer materials, bio- based and bio-degradable (environmental friendly) materials etc. at macro and nano levels.

The journal is focused to the interest of scientists and engineers from academia and industry who are participating in the materials engineering which is being formulated with the functional properties like thermal, electric, magnetic, optical and biological with the materials for the development of a wide range of smart, biocompatible and biodegradable materials for the food, adhesives, drug delivery, tissue engineering, gene delivery, biosensor, structural and other applications.

The journal includes review articles, research articles, notes and short communications. The peer-review and proof-ready editing is expected to be completed within 3 months and the online version will be published immediately.
**EDITORIAL BOARD**

**Editor-in-Chief**  
Ashutosh Tiwari  
Institute of Advanced Materials, Sweden  
editor-in-chief@vbripress.com

**Managing Editors**  
George Mishra  
VBRI Press  
editorialoffice@vbripress.com

Dharmesh Srivastava  
VBRI Press  
proof-desk@vbripress.com

**Academic Editors**

<table>
<thead>
<tr>
<th>USA</th>
<th>China</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bingqing Wei</td>
<td>Chee Wee Liu</td>
</tr>
<tr>
<td>Genxi Li</td>
<td>Qijun Sun</td>
</tr>
<tr>
<td>Lokman Uzun</td>
<td>Ravindra Pandey</td>
</tr>
<tr>
<td>Yogendra Kumar Mishra</td>
<td>Pavlo Mikheenko</td>
</tr>
<tr>
<td>Maroš Halama</td>
<td>Xuanhua Li</td>
</tr>
<tr>
<td>Rui Wang</td>
<td>Juan Escrig</td>
</tr>
<tr>
<td>Seiki Chiba</td>
<td>Yongmei Zheng</td>
</tr>
<tr>
<td>Tong Lin</td>
<td>Takanori Tsutaoka</td>
</tr>
<tr>
<td>Quang Hung Tran</td>
<td>Sinoj Abraham</td>
</tr>
<tr>
<td>Gyorgy Szekely</td>
<td>Xuesong Li</td>
</tr>
<tr>
<td>Nima Misra</td>
<td>Aleš Iglč</td>
</tr>
<tr>
<td>Valerio Voliani</td>
<td>Yaroslav Korpan</td>
</tr>
<tr>
<td>Yang-Fang Chen</td>
<td>Xiaogan Liang</td>
</tr>
<tr>
<td>Vasily Lutsyk</td>
<td>Abdel Hadi Kassiba</td>
</tr>
<tr>
<td>Hadar Ben-Yoav</td>
<td>Bin Zhu</td>
</tr>
<tr>
<td>Iwona Jasiuk</td>
<td>Aleksandr Lebedev</td>
</tr>
<tr>
<td>Jingan Li</td>
<td>Abderrazzak Douhal</td>
</tr>
<tr>
<td>Osman Adiguzel</td>
<td></td>
</tr>
</tbody>
</table>

*Note: This is a stylized version of the content, formatted for clarity and readability.*
ADVERTISEMENT POLICY

When you want to be seen with content that counts please try our advertising service. It will ensure that your product, service and/or brands are given the best possible visibility.

Advertising

Our journal and books are published online in the VPRI Press home page, www.vbripress.com, which is search engine optimized and regularly in the top rankings. We maintain almost 100% retention rates for visitors to our site.

• Indexed by multiple search engines
• High levels of qualified visitors
• Proven stickiness
• Quality as well as quantity
• High quality page views makers in your field
• Easily measurable results
• Industry standard inventory options
• Competitive pricing
• Flexible targeting of specific geographic regions or domains

Contact us

For your global advertising or sponsorship requirements please contact us to: contact@vbripress.com

The Advanced Materials Letters published by VBRI Press is carefully produced in Sweden. Nevertheless, authors, editors and publisher do not warrant the information contain in this journal to be free of errors. Readers are advice to keep in mind that statements, data, illustrations, procedural details and other items may inadvertently be inaccurate.
Author Guidelines

Please follow these instructions carefully to ensure that the review and publication of your papers are as quick and efficient as possible. The contents of papers are the sole responsibility of the authors and publication shall not imply the concurrence of the Editors or Publisher.

Manuscript

Authors have to submit manuscript electronically using online manuscript submission system as Microsoft Word files. Journal will not entertain any submission by e-mail. Authors are kindly advised to read journal policy before submitting manuscript.

Language

Articles must be written in clear, concise, grammatical English. Any author who is not fluent in idiomatic English is urged to gain assistance with manuscript preparation. Reviewers are not expected to correct grammatical errors and any deficiency in this area may detract from the scientific content of the paper.

Journal policy

Submission of an article implies that the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere, that its publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, without the written consent of the publisher. Authors accept full responsibility for the factual accuracy of the data presented and should obtain any authorization necessary for publication. As such the contents of the papers are the sole responsibility of the authors and publication shall not imply the concurrence of the editors or publisher.

All papers are submitted to referees who advise the editor on the matter of acceptance in accordance with the high standards required on the understanding that the subject matter has an element of novelty and has not been previously published and is not under consideration elsewhere. Referee names are not disclosed, but their views are forwarded by the editor to the authors for consideration. Authors are encouraged to suggest at least five names of experts in the field when papers are first submitted.

Copyright guidelines

Upon acceptance of an article, authors will be asked to sign a Copyright Transfer Agreement. Acceptance of the agreement will ensure the widest possible dissemination of information. If excerpts from other copyrighted works are included, the author(s) must obtain written permission from the copyright owners and credit the source(s) in the article. Neither the editorial committee nor the publisher are responsible for any copyrighted material from others work in the author(s) manuscript and any legal issues related to the same are the sole responsibility of the author(s).

On the Web

Any figure can appear free of charge in color in the Web version of your article regardless of whether or not this is reproduced in color in the printed version. Please note that if you do not opt for color in print, you should submit relevant figures in both color (for the Web) and black and white (for print).

In print

Color figures can be printed in the journal at minimal charge to the author.

Software

Software used as part of computer aided drug/agent design (e.g., molecular modeling, QSAR, conformational analysis, molecular dynamics) should be readily available from accepted sources and the authors may specify where the software can be obtained. Assurance of the quality of the parameters employed for the relevant potential functions should be detailed in the manuscript.
Preparation of supplementary Data

Advanced Materials Letters accepts electronic supplementary material to support and enhance your scientific research. Supplementary files offer the author additional possibilities to publish supporting applications, movies, animation sequences, high resolution images, background datasets, sound clips, and more.

Proofs

Proofs will be dispatched via email to the corresponding author and should be returned with corrections within 48 hours of receipt, failure to do so will delay the publication of the manuscript. This is possible due to the innovative use of the DOI article identifier, which enables the citation of a paper before volume, issue and page numbers are allocated. The Article in Press will be removed once the paper has been assigned to an issue and the issue has been compiled.

Electronic offprints

The corresponding author, at no cost, will be provided with a PDF file of the article via email. The PDF file is a watermarked version of the published article and includes a cover sheet with the journal cover image and a disclaimer outlining the terms and conditions of use.

Order, claim and journal enquiry:

Please contact to:

Editorial Office

VBRI Press
Teknikringen 4A, Mjardevi Science Park, 58330, Linköping, Sweden
Tel: (+46) 1313 2424
E-mail: editorialoffice@vbrypress.com
URL: www.vbrypress.com

Subscribe

The printed version can be subscribed and prices are available on request from the publisher by E-mail to: contact@vbrypress.com

Jurisdiction and applicable law

Our Terms are governed by Swedish law. The Swedish courts shall have exclusive jurisdiction over any dispute relating to our Terms.
## Table of Content

### Research Articles

1. **Coatings for sensing and protection in silicon sensors**  
   PJ French  
   392-399

2. **Polymer nanocomposites: Problems, preparation, mechanical properties**  
   Stoyko Fakirov  
   400-405

3. **Programming emissivity on fully integrated VO₃ windows**  
   José Figueroa, Yunqi Cao, Tongyu Wang, David Torres and Nelson Sepúlveda  
   406-410

4. **Fibril orientation and strength in collagen materials and adaptation to strain**  
   411-418

5. **Hydrogenated TiO₂, as efficient electron transport layer of planar perovskite solar cell**  
   Yulong Ma, Kaimo Deng, Bangkai Gu, Hao Lu, Yuyun Zhu, Liang Li  
   419-425

6. **Conjugate-like addition of soft nucleophiles to 8-alkenylBODIPYs**  
   Enrique Alvarado-Martínez, Eduardo Peña-Cabrera  
   426-431

7. **Microporous carbon spheres modified with EDA used as carbon dioxide sorbents**  
   Daniel Sibera, Joanna Sreńcsek-Nazal, Waldemar A. Morawski, Beata Michalkiewicz, Jaroslav Serafin, Rafal J. Wrobel, Urszula Narkiewicz  
   432-435

8. **Synthesis of rGO via UV-assisted photocatalytic reduction of graphene oxide**  
   Rui Liu, Wein-Duo Yang, Qiao Ying Jie, Ying Jin Song, Yan-Ru Li  
   436-438

9. **Synthesis and modelling of nanoparticles for chemical looping reforming**  
   439-443

10. **Nanoparticles-enabled low temperature growth of carbon nanofibers and their properties for supercapacitors**  
    Rickard Andersson, Amin M. Saleem, Ioanna Savva, Theodora Krasia-Christoforou, Peter Enoksson, Vincent Desmaris  
    444-449

11. **Mechanism of destruction of benzoyl peroxide on surface of sp²-type carbon nanomaterials**  
    Mykola Kartel, Liudmyla Karachevtseva, Wang Bo, Daryna Haliarnyk, Olga Bakalinska, Tetyana Kulyk, Borys Palyanytsya, Yevgen Demianenko, Anatoliy Grebenyuk, Volodymyr Kuts  
    450-455

12. **Plasmonic sensing through bioconjugation of Ag nanoparticles: Towards the development of immunoassays for ultralow quantification of antigens in colloidal dispersions**  
    Pablo A. Mercadal, Juan C. Fraire, Rubén Motrich and Eduardo A. Coronado  
    456-461
Coatings for sensing and protection in silicon sensors

PJ French

Ei-Ewi, TU Delft, Mekelweg 4, 2628CD, Delft, The Netherlands

DOI: 10.5185/amlett.2018.1892
www.vbripress.com/aml

Abstract

Silicon is an excellent material for sensing. Sensors for all signal domains can be realised, and in many cases, integrated with read-out electronics. However, in some applications an addition layer may be required for sensing and/or to protect the silicon device. Piezoelectric, polymers or magneto resistive layers can be added to expand the options of silicon. In the case of some implants, the polymer is used to protect the body from the device. In harsh chemical environments, the coating layer can be used to protect the silicon and in some cases also function as the sensor. Layers such as SiC represent a chemically resilient layer to protect the layers below, but this layer can also be used as a sensing layer. Atomic layer deposition (ALD) provides thin uniform, and pinhole free layers which can be used as protection and sensing. Other materials include graphene. In cases such as extreme temperature, it is more difficult to protect the silicon device, and in these cases the electronics must be isolated from the heat. This paper will show examples of how coating layers can enhance the sensing capabilities of silicon devices and also provide protection. Copyright © 2018 VBRI Press.

Keywords: Silicon sensor, coatings, harsh environments.

Introduction

Since the 1960s silicon has been an important material for sensors. The ability to integrate with electronics led to the “smart sensor”. Silicon displays many physical effects which cover all signal domains. However, some effects, such as the piezoelectric effect or magneto resistive effect are not found in silicon. Piezoelectric layers can be used for both sensors and actuators. The addition of these materials can therefore enhance the sensor possibilities. As long as the processes are compatible, these materials can be incorporated in smart sensors. Piezoelectric materials include ZnO [1-2], AlN [3-4], a range of polymers, such as pvdf [5-6] and ceramics, such as PZT [7-9]. Polymers have the advantage of being a low temperature process which can easily be spun, screen printed, or inkjet printed [10-12] onto a silicon substrate. Ceramic piezoelectric layers can also be screen printed on the substrates, but these require a higher firing temperature.

Piezoelectric materials are widely used for applications such as pumping [13-14] and energy harvesting [15-16].

Within the group of magneto-resistivity there are anisotropic magneto resistivity and giant magneto resistivity [17-19]. Giant magneto resistivity can be achieved by stacking extremely thin layers, which are usually deposited using MBE [20].

Other layers, such as polymers, can be used as layers for fluorescence devices [21]. An example of this approach is an oxygen sensor using fluorescence quenching for tissue and blood measurement [22].

In many harsh environments coating layers may be used to protect the device, whether it be a sensor or simply electronics. These layers are generally used for protecting against harsh chemical environments, or damaging radiation levels. SiC is an excellent protection layer for harsh chemical environments [23]. It can also be used as a sensing layer. Atomic layer deposition (ALD) is a technique for depositing a wide range of layers [24]. The advantage of this technique is that very uniform, pinhole-free layers.

Other materials include graphene [25]. Graphene, deposited on silicon presents many sensing opportunities, also in harsh environments. The development of CVD systems has also greatly expanded the possibilities [26]. These layers can be extremely effective in protecting against harsh chemical environments. Devices can also be protected from radiation through coating or in some cases through design. In cases such as extreme temperature, it is more difficult to protect the silicon device. This paper will show how coating layers can enhance the sensing capabilities of silicon devices and also provide protection. There will also be a description of applications.

Processing

This section will describe the materials and the processing of the required materials. These include low temperature process, such as spin-coating and printing and higher temperature processes such as CVD.
Spinning & inkjet printing

These techniques are widely used for polymer based materials [27-28]. Spin coating yields a uniform layer and will also planarize the surface. The thickness of the final layer is related, \(d\), to the spin speed, \(\omega\), by:

\[
t \propto \frac{1}{\sqrt{\omega}}
\]

Spin time is usually around 30 secs to 1 minute, depending on the material. A typical thickness curve as a function of spin speed is given in Fig. 1.

![Fig. 1. Example of film thickness as a function of spin speed [29]. Courtesy of Ossila Limited's spin coating guide.](image1)

In addition to spinning on the material, this technique can be used to deposit particle in a fluidic carrier, as shown in Fig. 2.

![Fig. 2. Depositing particle using spin technique [29]. Courtesy of Ossila Limited’s spin coating guide.](image2)

In recent years there has been increasing interest in inkjet printing for a range of materials including polymers for coating and organic electronic devices. The basic structure of such a device is given Fig. 3.

![Fig. 3. Illustration of a piezoelectric driven inkjet system. Adapted from [30].](image3)

Screen printing

Screen printing, in a recognisable form, can be traced back more than 1000 years in China [31]. The basic process is shown in Fig. 4.

![Fig. 4. Basic structure of a screen printing system A. Ink. B. Squeegee. C. Image. D. Photo-emulsion. E. Screen. F. [32].](image4)

This technique is widely used for materials such as polymers and ceramics. The main difference is that ceramics need a much higher temperature for the post deposition anneal, usually around 900C. This can be used on wafers, or on rolls of material.

Chemical vapour deposition (CVD)

The main forms of CVD are low pressure CVD (LPCVD), atmospheric pressure CVD (APCVD) and plasma enhanced CVD (PECVD). The use of plasma in PECVD greatly reduces the deposition temperature (usually below 400C), making it suitable for use on fully processed CMOS wafers. In standard processing, CVD is used for materials such as SiO\(_2\), SiN and polysilicon. Other materials of interest for coating on silicon include SiC and graphene. The basis of all these processes is to choose gasses which break down in the chamber to deposit the required material. For example, polysilicon is usually deposited using SiH\(_4\), which breaks down into Si + 2H\(_2\).
Molecular beam epitaxy (MBE)

MBE was invented in the 1960s at Bell Telephone Laboratories by JR Arthur and AY Cho [33]. The process takes place at high or ultra-high vacuum, typically \(10^{-8} - 10^{-12}\). This technique, shown in Fig. 5 is widely used for compound semiconductors, such as GaAs. It can also be used for deposition of multi-layers.

Atomic layer deposition (ALD)

As the name suggests, this is a technique to deposit layers at atomic level. Since the deposition is layer-by-layer at atomic level, the layers are extremely uniform and pinhole free [35-36]. It was developed in the 1960s by Prof. Kol’tsov from Leningrad Technological Institute, although the basic concept was proposed by Prof. Aleskovski in his PhD thesis in 1952. The important difference of ALD from other deposition techniques is self-limiting chemisorption of precursors in each half-cycle [36].

Sputtering & evaporation

These techniques are widely used for metals, although other materials are also deposited this way. With sputtering the ions are accelerated towards the substrate. The basic principle is illustrated in Fig. 7.

Evaporation systems use high vacuum to allow vapour of the required material to deposit on the substrate. There are a number of configurations, and one example, from Hivatec is given in Fig. 8.

Materials

There is a wide range of materials which can be combined with silicon as a protection layer or to expand functionality. In standard IC processing, layers such as SiO\(_2\) and SiN are widely used as surface passivation and insulation. Additional materials such as SiC can be used as a sensing layer and also a protection layer.

Protection layer

The main use for protection layer is for harsh chemical environments. For this SiC is an excellent choice it can be deposited using PECVD and is thus a suitable layer for coating processed IC devices [40]. This layer is extremely chemically resistant [41].

For medical implants the coating layers serve to protect the silicon device from this harsh environment, and also to achieve biocompatibility. For this, there are a number of materials. A wide range of polymers are available for this application. Polymers are composed of a large, chain-like molecular structure made of monomers, which are covalently linked in 3D networks. These layers can be used as coating and also sensing. There are both
natural and synthetic polymers [42]. As a protection layer, many are biocompatible and able to protect the device underneath. Examples of these polymers include the following:

- Natural
  - Plants: Cellulose, natural rubber
  - Animals: Collagen, heparin, DNA
- Synthetic
  - Parylene
  - Silicone rubber
  - Polyethylene (PE)
  - Polypropylene (PP)
  - Poly methyl methacrylate (PMMA)
  - Poly vinyl chloride (PVC)
  - Polyether ether ketone (PEEK)

Materials such as Parylene [43-48] and silicone rubber [49-50] are widely used as coating layers for medical implants.

**Sensing and actuating layers**

Although silicon is an excellent sensing material for many applications, there are some effects not found in silicon and in some cases additional layers are required to generate a reaction, such as in bio-chemical sensors.

The main effects not found in silicon are the piezoelectric effect and the magnetoresistive effect, although there are other effects found in silicon.

The piezoelectric effect transforms the mechanical signal directly into a voltage, and also a voltage into mechanical deflection. There are a number of materials which are suitable for integration with silicon. Frequently used materials include ZnO, AlN and a range of polymers. Other materials are quartz and GaAs. Both ZnO and AlN are usually deposited using sputtering [51-52] or CVD [53-54]. Quartz is usually bonded to silicon rather than being deposited, whereas GaAs is usually formed using techniques such as MBE.

The magnetoresistive effect is the change of resistivity of a material as a function of magnetic field. This was first discovered by Thomson in 1851, and can be divided into a number of forms: anisotropic [55], giant [56], colossal [57] and tunnelling [58]. In addition to integration with silicon, there are examples of GMR devices being formed on flexible substrates [59]. There are also many examples of integration of magnetoresistive layers with silicon [60-63]. Devices for anisotropic magnetoresistance use permalloys such as Ni-Fe. The giant magnetoresistive effect is found in multi-layers of alternating ferromagnetic and non-ferromagnetic conductive layers. This became possible when techniques were developed for depositing extremely thin and uniform layers. This development became extremely important in the massive increase in hard-disc capacity. The basic structure is shown in Fig. 9. Commonly used layers include Fe-Cr [64].

Colossal magnetoresistive devices usually is manganese-based perovskite oxides. The tunnel effect also requires the ability to deposit layers of a few nm, but the structure is quite different, as shown in Fig. 10.

Fluorescent devices mainly use materials such as polymers or hydrogels, which are either exposed directly to the environment, or covered with a membrane which allows the element of interest through. Examples of these devices, will be given in the next section.

**Applications**

**Piezoelectric devices**

As mentioned above, the piezoelectric effect can be used for both sensors & actuators. In the field of actuators, piezoelectric layers are commonly used for pumps, grippers and motors, etc. Although piezoelectric grippers and motors are not usually integrated into silicon. Micropumps use pressure differences to pull the fluid through, there are a number of actuation techniques, such as thermal, magnetic and electrostatic. Piezoelectric pumps [66-68] have a relatively simple structure needing only a piezoelectric layer on a membrane. The basic operation can be seen in Fig. 11.
In the field of sensors there are many examples of piezoelectric materials being integrated in silicon. One type of device which uses both the actuating and sensing properties of the piezoelectric material is the surface acoustic wave device [70-73]. The basic principle of the device (shown in Fig. 12) is to generate an acoustic wave using finger type electrodes. The wave passes along the surface of the device and is detected by a second set of electrodes. If, for example, the wave passes along a membrane, the speed of the wave can be modulated if the membrane comes into contact with a fluid. It is further dependent on the density and viscosity of the fluid. Using a reference path and a feedback, a frequency difference, as a function of the desired parameter can be produced. This basic structure is given in Fig.12.

![Fig. 12. Basic SAW device.](image)

The same basic principle can be used for a number of other parameters. Piezoelectric layers can also be used for measuring strain directly. Piezoelectric materials have also been used as actuation and sensing in gyroscopes. In other cases, the piezoelectric layer is used for actuation and another method used for sensing [74].

**Magnetic sensors**

Provided the magnetoresistive material can be deposited on silicon, at a relatively low temperature, it is possible to fabricate integrated magnetoresistive devices. In many cases, these resistors are formed in a Wheatstone bridge, as often used in mechanical devices. An example of this basic structure is shown in Fig. 13.

![Fig. 13. Illustration of the sensor geometry and the sensor stack with definitions of geometrical and electrical parameters.](image)

**Bio-chemical sensors**

Many chemical sensors require an additional layer to react with, or trap the element of interest. An early example of this was the ChemFET. First proposed by Prof. Piet Bergveld, in The Netherlands, this uses a standard MOSFET structure, but replaces the gate with a material which traps or reacts with the chemical or biological element [76]. From this first idea, a wide range of chemical and biological sensors have been developed.

Optical devices, such as waveguides can also be used when additional layers are added to trap elements. Once such example (Fig. 14), uses the evanescent wave along a thin waveguide. If the waveguide surface is coated with a layer to trap, in this case, a bacterium, the absorption of light, will increase with increasing presence of the bacteria. Therefore, the intensity of the out coming light will be reduced. The example given in Fig. 14 uses a TiO$_2$ waveguide. Similar structures have been made using materials such as SiC and SU8 [79]. All these devices we fabricated using a silicon substrate.

![Fig. 14. Waveguide bacteria sensor using the evanescent wave.](image)

Fluorescent techniques are also commonly used in chemical and biochemical devices. They require an additional layer, often polymer or hydrogel, which has been modified to fluoresce when in the presence of the compound of interest. One such example is to measure oxygen using fluorescence quenching. A porous polymer impregnated with ruthenium is used. When illuminated with blue light, it fluoresces with red. If oxygen enters the polymer, the fluorescence will be quenched. The more oxygen present, the faster the quenching. Measuring the speed of the quenching gives us the partial pressure of oxygen. This can be used to measure oxygen in tissue, blood and gasses [22]. For measuring CO$_2$, HPTS-(TOA)$_3$ can be added, although this is an intensity measurement and not fluorescence quenching [79]. These two sensors can be combined to make a tissue viability sensor. They can also be integrated into a silicon device using a single activating light source. The basic structure is given in Fig. 15.

Another example is a glucose sensor using a hydrogel. The device, shown in Fig. 16, using a membrane allowing glucose to pass through to reach a glucose responsive fluorescent hydrogel. The whole device can be implanted under the skin and uses wireless connection to a hand-held device. Ammonia is aggressive
to many materials, including silicon. In this application, SiC can serve as a protection layer, and also a sensing layer. Porous silicon carbide can be made to be sensitive to both humidity and ammonia depending on the structure of the pores [23].

![Cross-section of an O₂- CO₂ tissue vitality sensor.](image)

**Fig. 15.** Cross-section of an O₂- CO₂ tissue vitality sensor.

SiC can be deposited over the whole wafer, using PECVD and only made porous in the sensor area. This is achieved since the formation of porous SiC is an electrochemical process and is only formed above the bottom electrode. This way, it serves as both protection and sensor. The basic structure is shown in **Fig. 17**.

Graphene is also a material which is robust and can be deposited on silicon. Since the development of CVD systems for graphene, the possibilities for integration have become greater [81]. Just as in SiC, graphene can be used for humidity and gas sensing and a range of chemical sensors [82-85].

![Glucose-responsive fluorescent hydrogel and Wireless unit for CMOS image sensor.](image)

**Fig. 16.** Glucose sensor using a hydrogel on top of a CMOS image sensor. Adapted from [80].

Conclusions

Silicon is an excellent material for electronics and a wide range of sensors. However, in many applications we require additional functionality, or additional protection from the environment. Additional layers can be used to make piezoelectric or magnetoresistive layers. They can also be used to react with the environment to generate fluorescence, change colour, or increase optical absorption. As a protective layer material such as SiC serve as an excellent chemical protection for the surface of the silicon. In medical implants, it is important not only to protect the silicon from this harsh environment, but also to ensure no adverse reaction from the surrounding tissue. For this material such as paylene, polymers and silicone are often used. This combination of silicon with additional layers can greatly expand the options for silicon sensors and smart sensors.

Acknowledgements

Many colleagues have contributed to the research work over the years. In addition, much of the research has been funded by the Dutch Science Foundation, STW. Also thanks to the colleagues who provided some of the figures.

References


Copyright © 2018 VBRI Press
Polymer nanocomposites: Problems, preparation, mechanical properties

Stoyko Fakirov*

Leibniz-Institut fuer Polymerforschung Dresden e.V. (IPF), Hohe Strasse 6, 01069 Dresden, Germany

DOI: 10.5185/amlett.2018.1850
www.vbripress.com/aml

Abstract

The main target of this review article is to try to find the reasons for the drastic difference between expected and observed mechanical properties of polymer nanocomposites prepared via blending the matrix and the nano-reinforcement. Additional target is to recommend thereafter ways for solving of this problem. Based on the published materials the conclusion is drawn that the main reason for this discrepancy is the poor dispersion resulting in formation of particles with sizes in the micrometer but not in nanometre range. For this reason, it is assumed further that these nanocomposites hardly exist. Since currently are missing techniques and instrumentation for a proper dispersion of the reinforcement to single nanoparticles, it is recommended to avoid the dispersion step during manufacturing of polymer nanocomposites. Two techniques are described for this purpose, representing application of the rather new concept of “converting instead of adding” for preparation of polymer nanocomposites. Copyright © 2018 VBRI Press.

Keywords: polymer nanocomposites, mechanical properties, reinforcement dispersion, concept of converting instead of adding

Introduction

During the last decades revolutionary changes happened in the material science – a new type of materials were created - the nanomaterials. Nanomaterials are materials with morphological features on the nanoscale, and their special properties are stemming from their nanoscale dimensions, which usually are defined as smaller than a one tenth of a micrometer in at least one dimension. Recently [1], the European Commission offered a more precise definition, namely, 50% or more of the particles in the number size distribution are in the size range 1–100 nm. A common characteristic feature of all nano-size materials, regardless of their chemical composition and method of manufacturing, is the extremely high ratio of surface area to volume. For example, 1 kg of particles of 1 mm$^3$ has the same surface area as 1 mg of particles of 1 nm$^3$. The natural tendency to reduce this free surface is the driving force for agglomeration of nanoparticles in larger formations approaching the micrometer range.

Although nanoparticles are generally considered a discovery of modern science, they actually have a very long history. Nanoparticles have been used by artisans as far back as the ninth century in Mesopotamia for generating a glittering effect on the surface of pots.

A milestone in the development of nanomaterials was the discovery of carbon nanotubes, which usually is credited to Iijima [2]. It turned out that carbon nanotubes are the strongest material ever created – with an elastic modulus in the terapascal range carbon nanotubes (CNTs) overcome any known material. The idea to use CNTs as reinforcement of plastics arose immediately because simple model calculations demonstrated that small amounts of this reinforcement will result in some 10-fold increase of the elastic modulus, and so started the “era of polymer nanocomposites”.

Problem: why the mechanical performance of polymer nanocomposites does not justify the expectations?

The expectation formulated two decades ago, that the most common polymer composites comprising about 30% glass fibers will be replaced by nanocomposites having as reinforcement only 2–5 wt. % nano-size minerals turned out to be elusive.

Discussing the mechanical behavior of polymer nanocomposites it should be stressed that an improvement of 20% (for tensile strength) and 50% (for the modulus of elasticity) is quite typical for all polymer nanocomposites [3]. According to Bousmina [4], only in exceptional circumstances can one observe an improvement greater than 30% in the mechanical performance of nanocomposites. More specifically, Zhang et al. [5] studied thoroughly the case of polypropylene (PP)/SiO$_2$ nanocomposites in which nanoparticles have been coated by various polymers to improve the interfacial adhesion. They reported mechanical properties (Young’s modulus and tensile strength) only 20 – 25% higher than those of the neat PP [5].
The above conclusions were supported by the statements of Schaefer and Justice in their review “How Nano Are Nanocomposites?” [6]: “Composite materials loaded with nanometer-sized reinforcing fillers are widely believed to have the potential to push polymer mechanical properties to extreme values. Realization of anticipated properties, however, has proven elusive”.

As mentioned above, such systems have attracted enormous interest from the materials community because they theoretically promise substantial improvement of mechanical properties at very low filler loadings. In addition, nanocomposites are compatible with conventional polymer processing, thus avoiding costly layup required for the fabrication of conventional fiber-reinforced composites. The appeal of nanocomposites is illustrated by considering single walled carbon nanotubes (SWCNTs). With tensile moduli in the terapascal range and lengths exceeding 10 μm, simple composite models predict order-of-magnitude enhancement in modulus at loadings of less than 1%.

“Introductory paragraphs similar to the above can be found in hundreds of nanocomposite papers. With the exception of reinforced elastomers, nanocomposites have not lived up to expectations. Although claims of modulus enhancement by factors of 10 exist, these claims are offset by measurements that show little or no improvement. The lacklustre performance of nanocomposites has been attributed to a number of factors including poor dispersion, poor interfacial load transfer, process-related deficiencies, and others” [6].

And finally, let mention in this respect the statement in a very recent review on the practical applicability of polymer nanocomposites [7]: “Initial developments of nanocomposite thermosets focused on high aspect ratio nanoparticles such as nano-clays, carbon nanotubes and more recently graphenes. Generally, these systems showed 10 – 35 % improvement in mechanical properties with 0.2 – 5 wt. % filler. However, the translation of these improvements to prepregs or laminates proved to be difficult due to processing issues, including extremely high viscosity, nanoparticles filtration, nanoparticles agglomeration, and void formation.”

It seems rather realistic to assume that polymer nanocomposites prepared via melt blending of the two basic components, the matrix and the reinforcement, are characterized by a maximum improvement of their mechanical properties by 30 – 35% as compared with the respective neat isotropic matrix. Such a result is quite far from the expected 10-fold (at least!) improvement.

An interesting question regarding the reasons for this drastic discrepancy arises.

The concept of polymer nanocomposites, that is, the expectation that using 1–5% of nanofiller instead of the common 30–40%, it will be possible to realize improvements of magnitude of order as compared with the traditional composites materials as well as to enhance the environmental impact of these materials failed for the following reasons:

(i) Poor dispersion
(ii) Poor interfacial load transfer
(iii) Process-related deficiencies
(iv) Poor alignment
(v) Poor load transfer to the interior of filler bundles
(vi) The fractal nature of filler clusters.

Do polymer nanocomposites prepared via blending a polymer with nanomaterial really exist?

Such question sounds rather provocative but if we remember the criteria according to which the composite materials are categorized, we will see that the question is justified. Depending on the sizes of the reinforcing filler we distinguish between macrocomposite (the common ones), microcomposites, when the sizes are in the micrometer range and nanocomposites if the single reinforcing particles are nano-size particles, i.e. with dimensions below 100 nm or around this size.

Dealing with this “terminological” issue, it seems important to remind how the polymer nanocomposites are prepared. The most common practice is to blend a polymer (the matrix) with nano-size material (reinforcement) and to add to the title of paper the modern word “nanocomposite”. In rare cases attempts are undertaken to determine the degree of dispersion and if this is done, it is by means of electron microscopy. Usually, 2 – 3 micrographs are shown comprising a couple of nano-size particles, which demonstrate how these particles look but, by no means, they offer any information about their amount in the sample. The question regarding the degree of dispersion still remains without answer. Such information can be obtained by using scattering techniques – X-ray, neutron scattering, etc. On this important detail is also stressed in the recent review on polymer nanocomposites [7].

The electron microscopes reveal also rather large aggregates of nanoparticles with sizes sooner closer to the micrometer range rather than to the nanometre sizes. Their existence is to be expected taking into account the extremely strong tendency of nano-size material to reduce the surface energy via agglomeration. The question is if these aggregates dominate in the sample. The answer can be found if we return to the scattering techniques, for example light scattering.

There are polymers which are completely transparent, i.e. they let the light trough on 100% as, for example, atactic poly(methyl methacrylate) (at-PMMA), atactic polystyrene (at-PS) and, to some extent, polycarbonates (PC) and polyyarylates (PAR) do. They can be used as a matrix for preparation of nanocomposites via blending with nano-size fillers.

The nanomaterials of inorganic origin have typical sizes below 100 nm and in many cases around 2 – 5 nm. If the dispersion during mixing with the matrix is a good one, i.e., up to single nanoparticles, the transparency should not be different from that of the matrix, that is, the...
transmission of the light has to be 100%. This situation is due to the known fact that light scattering can be observed only if particles have sizes in the range of the size of the wave length of the used light, which for the common light is 500 – 600 nm.

Let look at the results of such studies. Nanocomposites have been manufactured from completely transparent at-PMMA (100% transmission of the light) and nano-size ZnO (particles of 75 nm in concentration 1 wt. %). The used light was with wave length $\lambda = 600$ nm. The measured amount of transmitted light is only 2 % but it increases up to 50 % if the concentration of the filler drops to 0.01 % [8].

Similar nanocomposite has been prepared using the same matrix and ZrO$_2$ with particles size of 4 nm and concentration of 15 %. The transmission of the light ($\lambda = 600$ nm) was 80 % [9]. Even finer ZnO filler (2.3 nm) in concentration of 0.5 % showed 90 % transmission of the light [10].

Practically the same are the results of another completely transparent matrix, the at - PS - when as reinforcement is used CeO$_2$ (size 20 nm, concentration 20 wt. %) the light transmission decreases to 75 % [11]. In cases when as matrix is used PC the observed results are similar. For example, whiskers of AlO$_2$ in concentration of 2 wt. % cause reduction of light transmission up to 80 % [12], while Al$_2$O$_3$ (size 96 nm, concentration 1 wt. %) shows 50 % transmission of the light [13].

It should be mentioned that in all cited cases the thickness of the samples subjected to light transmission measurement has been between 1 and 4 mm.

The observed [8-13] serious decrease in light transmission of the cited nanocomposites as compared with their completely transparent matrices leads to the conclusion that in these blends the dispersed particles by far are not nano-sized. Taking into account the fact that they scatter the common light ($\lambda = 500 - 600$ nm), their sizes should be in the same range, which, in many cases, is some 100 times larger than the real sizes of the single particles introduced to the polymer matrix.

At such a situation it is hardly correct to call these composites “nanocomposites” because they, as a matter of fact, belong to the category of microcomposites. If we agree with this statement a quite important conclusion can be derived – the answer of the very basic question about the drastic difference between expected and observed mechanical properties of the polymer nanocomposites prepared via blending matrix and reinforcement. They do not justify the expectations derived for nanocomposites because they are not nano - but microcomposites. The situation is really interesting because it could be considered from its reverse side – the lack of agreement between observed and predicted mechanical properties support the conclusion that these composites are not of nano type. And this can be proven if we succeed to prepare real polymer nanocomposites and measure their mechanical properties.

**Solution of the problem: Avoiding the dispersion as manufacturing step**

Nowadays a rather large number of nano-size materials are available and nevertheless the preparation of true nanocomposites is not an easy task. The basic problem in manufacturing of polymer nanocomposites is the dispersion of the reinforcing component to single nanoparticles in the matrix material. Due to the inherent property of the nano-size materials, namely, the extremely high specific surface, they tend to agglomerate and their further dispersion in the matrix component is practically impossible. In this respect, it seems useful to cite here the opinion of Greiner and Wendorff [14] expressed in their excellent review of electrospinning as a method for preparation of ultrathin fibers and their application as reinforcing material for nanocomposites. After listing the advantages of the electrospin nanofibers as reinforcement over macroscopic fibers as owing to their extremely high aspect ratio, little refraction of light (due to the small diameters) resulting in transparent reinforced matrices, the authors [14] conclude: “Given the advantages of nanofibers for reinforcement, the number of investigations on this topic is rather small. The main problems, to which there are no convincing solutions yet, are the dispersion of the electrospin nanofiber webs and the control of the nanofiber orientation in the polymer matrix.”

The felt-mat structure of the nonwoven is for the most part maintained upon the incorporation of the nanofibers into the matrix. Attempts to disperse single nanofibers from the nonwoven mats using ultrasound, kneaders, or high-speed stirrers have only been marginally successful.

Very similar problems occurred in matrix reinforcement with carbon nanotubes and nanofibers [15]” [14].

It appears that currently we do not have reliable tools and/or techniques for a proper dispersion of nanomaterials in polymer melts in order to reach the dispersion degree of single nanoparticles what is the requirement for having true nanocomposites. Obviously, so far such techniques for preparation of these composites are missing we have to create methods free of the dispersion step in the manufacturing process. Such an opportunity is offered by the new concept of “converting instead of adding” [16], that is, converting the bulk polymer into nano-size material instead of blending it with nanofillers. In this way it is possible to avoid the practically non-soluble problem of proper dispersion and to create true polymer nanocomposites distinguished by perfect distribution of nanoparticles in the matrix.

The realization of the new concept means that instead to take the two basic composite components, the matrix and the reinforcement, in their final form and blend them, one takes one component only in its final form and during the processing creates the missing second component. For example, starting from blend of two thermodynamically non-miscible polymers, we can convert the minor blend component into nanofibrils playing later the role of
reinforcement of the nanofibrillar polymer-polymer composite (PPC).

![Diagram of manufacturing process](image)

**Fig. 1.** Manufacturing of nanofibrillar PPCs (NFC) (Route A) and nanofibrillar SPCs (Route B) via the concept of converting instead of adding.

In the second case, instead of having the matrix in its final form we can use neat polymer nanofibrils and during the subsequent processing to create the missing matrix. This can be done by subjecting the nanofibrils to thermal treatment close but below the temperature of complete melting when a small amount of the same polymer is converted in isotropic matrix (playing the role of binder of nanofibrils). In this way a nanofibrillar single polymer composite (SPC) is prepared.

A characteristic feature of the two approaches is that a perfect distribution of the nano-filler is observed, i.e. each single nanoparticle is surrounded by matrix material and no aggregates of nanoparticles are observed.

The manufacturing process of nanofibrillar PPCs and SPCs is schematically shown in **Fig. 1.** It should be noted that this process can be performed on common equipment for polymer processing. The two thermodynamically non-miscible polymers in a usual ratio A/B = 70/30 by wt. are melt blended, extruded and cold drawn as shown on the upper part of **Fig. 1.** Again there, two micrographs of scanning electron microscope (SEM) are added. They demonstrate the drastic morphologic change in the minor component (reinforcement) from spheres (left) to nanofibrils (right). This transition takes place during the cold drawing via necking. The result so far is preparation of a drawn blend comprising nanofibrils of the minor component.

It seems important to note here that the prepared material is still not a composite material because it would be hardly correct to call the synthetic textile yarns prepared from polymer blends “composites” – both blend components are in a highly oriented state. Additional treatment step is needed in order to convert the dominating (but with lower melting temperature) component from highly oriented into isotropic state. For this purposes the drawn bristle is wound on a metal plate and subjected to compression molding at melting temperature of the matrix polymer A, which has to be at least 40°C below the melting of the reinforcing polymer B (**Fig. 1, Route A**). In this way a nanofibrillar polymer-polymer composite is prepared.

For preparation of nanofibrillar single polymer composites one has to select the Route B (**Fig. 1**), according which from the drawn bristles has to be removed the matrix polymer A using a selective solvent. The rest of nanofibrillar bunch of B has to be wound on a metal plate and compression molded at temperature at least 20°C below the melting temperature of B (**Fig. 1, Route B**). This treatment results in creation of small amount of isotropic matrix (binder of nanofibrils (**Fig. 1, Route B**).

If we analyze the prepared two materials, the PPC and the SPC, by means of SEM, we can get important information regarding the sizes of the reinforcing nanofibrils and, what is more interesting in the current case, the distribution character of the reinforcing nanofibrils in the matrix. Such results for the two materials under discussion are shown in **Fig. 2.**

The photographs taken from the cryofractures perpendicular to the nanofibril orientation (**Fig. 2a and c**, as well as from cryofracture parallel to the nanofibrils orientation (**Fig. 2b**) demonstrate rather homogeneous distribution of the reinforcing nanofibrils in the polymer matrix, i.e. practically, no aggregates of nanofibrils can be observed. Such a situation is quite different from the case of polymer nanocomposites prepared via blending of the two starting components as demonstrated in the previous paragraphs.
Mechanical performance of nanofibrillar polymer-polymer and single polymer composites

The nanofibrillar polymer-polymer composites, prepared according to the concept of converting instead of adding demonstrate superior mechanical performance. Let mention two examples, the linear low density polyethylene/poly(vinylidene fluoride) (LLDPE/PVDF) [17] and the polypropylene/poly(buthylene terephthalate) (PP/PBT) [16]. In both cases the two components are taken in weight ratio 70/30. The observed improvement in the elastic modulus in the first case is 165 % and in the second case – 45 % while the improvements in the tensile strength are much higher, 230 % in the first case and 190 % in the second.

This impressive mechanical performance of the nanofibrillar polymer-polymer composites originates from the very high aspect ratio of nanofibrils, their better adhesion then the mineral fillers to the matrix and mostly from the perfect distribution of nanofibrils in the matrix.

Even higher are the reinforcing effects in tensile experiments of the true nanofibrillar (diameter of nanofibrils between 10 and 250 nm) SPCs, prepared via one-constituent approach. The comparison is done with isotropic film of the same polymer prepared via compression molding with a thickness similar to that of the SPC samples.

For the nanofibrillar single polymer composite based on PVDF the improvement in elastic modulus is 40 % and of the tensile strength - 330 % [16], for poly(ethylene terephthalate) (PET) – 350% and 300 %, respectively [18], for LLDPE - 112 % and 325 %, respectively [19], and for PP - 70 % and 440 %, respectively [19].

The improvements in the tensile mechanical properties of all SPCs so far reported [20 – 25], and particularly the superior mechanical properties of the new nanofibrillar SPCs [16-19] prepared by hot compaction using only one constituent are evident. What could be the reason for this impressive mechanical performance? There are at least four reasons: (i) in the current SPCs the reinforcing constituent dominates strongly, and has much better mechanical properties when compared with the isotropic matrix of the same polymer, (ii) excellent adhesion between matrix and reinforcement because they have the same chemical composition, (iii) better orientation of the macromolecules in nanofibrils as compared to that in microfibrils and textile filaments of the same polymer, and (iv) in the test specimen of SPCs the nanofibrils are uniaxially aligned and the testing has been performed so far in the drawing direction only.

Conclusions and outlook

Nowadays it seems generally accepted that the concept of polymer nanocomposites did not justify the expectations – a drastic difference in mechanical properties between the theoretically derived and the experimentally obtained results is observed. The most probable reason for this discrepancy is the poor dispersion – reinforcements are not the single nanoparticles but their aggregates with sizes in the micrometer range. This situation is since currently there are not reliable techniques for proper dispersion of nanomaterials aggregates into polymer matrix. For this reason, so long such techniques are missing we should avoid the dispersion step in the preparation of true polymer nanocomposites as the concept of converting instead of adding does.
Two techniques being the essence of the new concept are described, where instead to take the matrix and the reinforcement in their final form and blend them one takes one component only and during the processing creates the missing second component [16-18, 24-27].

Both techniques are free of the dispersion step and, what is more important, one always observes a perfect distribution of the reinforcing nanomaterial in the polymer matrix, i.e. each nanofibril is individually characterized by perfect nanoparticles distribution in the prepared by means blending of matrix and reinforcement.

The properties of these polymer nanocomposites, prepared by means of dispersion-free methods and characterized by perfect nanoparticles distribution in the matrix, can be further improved attacking the rest of their drawbacks as: poor interfacial load transfer, process-related deficiencies, poor alignment, and poor load transfer to the interior of filler bundles.

Acknowledgements
The author gratefully acknowledges the financial support of the Alexander von Humboldt Foundation in the frame of the Program “Re-invitation of Humboldt Research Awardee” enabling his stay at the Leibniz-Institut fuer Polymerforschung Dresden e.V. (IPF), where this paper was prepared.

References

5. Zhang, M.Q.; Rong, Z.; Friedrich, K. Application of non-layered nanoparticles in polymer modification, In Polymer composites: from nano-to macro-scale; Friedrich, K.; Fakirov, S.; Zhang, Z. (Eds); Springer; USA, 2005, pp. 25-44.

Copyright © 2018 VBRI Press

Advanced Materials Letters 2018, 9(6), 400-405
Programming emissivity on fully integrated VO$_2$ windows

José Figueroa$^1$, Yunqi Cao$^1$, Tongyu Wang$^1$, David Torres$^1$ and Nelson Sepúlveda$^{1*}$

Department of Electrical and Computer Engineering, Michigan State University, East Lansing, Michigan, 48824

DOI: 10.5185/amlett.2018.1848

www.vbripress.com/aml

Abstract

The programmability of emissivity states in a monolithically integrated micro window based on vanadium dioxide (VO$_2$) thin film is demonstrated. The 400 $\mu$m window features a VO$_2$ thin film with integrated electrodes for actuation and sensing. The phase transition was induced by resistive heating, while the electrical resistivity and optical transmittance (for near IR wavelength of 1550 nm) of the VO$_2$ thin film were monitored simultaneously. Abrupt drops in electrical resistance and optical transmittance confirmed the quality of the VO$_2$ thin film. Electronic pulses were used to program emissivity states in the VO$_2$ window. The emissivity programmed state was shown for a specific DC current over imposed with the programming pulse; but any emissivity state that belongs to the minor hysteretic curves can be obtained by choosing different electronic inputs. The fully monolithically integrated device presented here can be used for IR cloaking applications, where different emissivity values can be programmed with electronic pulses. Copyright © 2018 VBRI Press.

Keywords: Emissivity, smart materials, vanadium dioxide.

Introduction

In the last few years, adaptive camouflage has seen an increase interest for its wide array of applications. Many animals have natural camouflage capabilities for survival and hunting. Species such as cephalopods and reptiles, use a form of visual coloration to adapt to any surroundings [1–3]. Numerous past studies have tried to discern and incorporate such adaptive camouflage for commercial and military grade applications [4]. Similarly, infrared cloaking is of equal importance due to the ability to cloak and shape shift in thermal imaging which allows to incorporate any camouflage system on arbitrary surfaces [5–7]. In order to create a thermal cloaking device, either the temperature or the emissivity of the material must be modulated [8,9]. Emissivity modulation is more advantageous over thermal controlling, since it would not involve a real temperature change of the object and it will eliminate the need to compensate for heat dissipation limitations when controlling the temperature. However, emissivity modulation would require materials with tunable optical properties, especially for the thermal infra-red (IR) region.

Vanadium dioxide (VO$_2$), has shown to be a suitable candidate for such applications. It undergoes an insulator to metal phase transition above 68 $^\circ$C [10], which can be done either by simple conductive, resistive heating, or photo-thermal heating [11–13]. Along with the phase transition, VO$_2$’s optical and electrical properties simultaneously change as well [14–15]. The material’s optical constants (n, k) suffer a significant change across the phase transition, abruptly causing a drop in transmittance. This change is more evident for near-IR (NIR) region up to 2500 nm [16,17], thus allowing VO$_2$ to be incorporated in smart window designs [18–21]. This was cleverly used by Xiao et al., when they reported the use of VO$_2$ for thermally adaptive camouflage. [8]. VO$_2$ also behaves as a highly disordered material for emissivity modulation, due to its change in emittance along the phase transition [22,23]. Furthermore, unlike most materials, VO$_2$’s emissivity decreases as the temperature increases through the phase transition region. This means that the material “looks colder” as the temperature is raised. Since the transition region of VO$_2$ extends only about 10 $^\circ$C, inducing the change in emissivity of a VO$_2$ thin film coating requires much less energy than changing the emissivity of the coated element by a large increase in temperature. This makes VO$_2$ a great candidate for adaptive camouflage windows.

Here we propose a micro variable optical window based on VO$_2$ thin film. The window can be actuated via resistive heating which allows to program states in both transmittance and emissivity via electronic modulation. Via this change in transmittance and emissivity we can developed a smart VO$_2$ window that could act as a cloaking device. The intrinsic hysteresis of VO$_2$ allows for multiple optical states for a single temperature within the transition region. In this work, we exploit this to demonstrate electronically programmable emissivity states in a monolithically integrated VO$_2$ window.
Experimental

Device Fabrication

The fabrication of the VO$_2$-based window consisted of a 4-mask lithography process, with a minimum feature size of 10 μm. The fabrication process is shown in Fig. 1. A double sided polished SiO$_2$ wafer (2-inch diameter, 500 μm thick, SOF50D05C2, MTI) was used as the substrate. The metal layers (titanium/platinum (Ti/Pt) with thicknesses of 400 Å/1500Å, respectively) used for the heater and electrodes were deposited by evaporation and patterned using lift-off technique. The Ti layer was used only for adhesion purposes. The width of the heater loop was 10 μm and the electrodes was 15 μm. The gap between the heater loop and the electrode was 10 μm as well.

An insulating layer of SiO$_2$ of approximately 400 nm thick was deposited by plasma enhanced chemical deposition (PECVD). This was done in 3 steps of ~130 nm each to avoid possible voids through the SiO$_2$. After deposition, the SiO$_2$ layer was etched by reactive ion etching (RIE) to open vias to the Pt electrodes to the VO$_2$ thin film that was going to be deposited next. A layer of VO$_2$, approximately 170 nm thick was deposited by pulsed laser deposition (PLD). A KrF laser operated at 10 Hz with a laser fluence of ~2 J/cm$^2$ was used, with a deposition time of 25 minutes. The substrate was maintained at 595 °C in an oxygen environment at 15 mTorr pressure. After deposition, an annealing process under the same pressure and temperature conditions was performed for 30 minutes. To avoid any undesired material residual accumulation that would have affected the results for transmission experiments, the backside of the wafer was covered during the deposition. This was followed by the patterning of the VO$_2$ windows through photolithography process and RIE using [24]. Finally, another SiO$_2$ etching step was performed to open contact pads to the heater and electrodes. The 2 inch wafer was then diced into individual dies, each measuring 4 mm$^2$.

![Fig. 1](image1.png)  
**Fig. (1).** Fabrication process for the VO$_2$ based window. (a) SiO$_2$ substrate, (b) metallization of heater and electrodes. (c) SiO$_2$ insulating layer, (d) opening of the electrodes. (e) VO$_2$ deposition and window patterning, and (f) opening of contact pads for electrical connections.

Experimental setup

Fig. 2 (a) shows the electro-optical setup used to test the VO$_2$ window. The die containing the four micro VO$_2$ windows was mounted and wire-bonded into a circular package which has a hole in the middle to facilitate the transmittance measurements. The package was then mounted to a custom built printed circuit board (PCB) with a centered hole and electrical connections for both the heater and electrodes. Once wired and mounted, the PCB was placed on an X-Y-Z translational stage to align the IR laser beam with incidence normal to the window. A Thorlabs NIR laser diode (λ = 1550 nm, ML925B45F) was operated below its stable power of 5 mW for measurement taking. To make sure that the beam spot was properly aligned with the window, a Thorlabs NIR laser diode (λ = 980 nm, L980P010) was used. Both laser diodes were passed through a 50:50 NIR beam splitter (Thorlabs, BS015- 50:50, 1100 nm – 1600nm), then coupled into a single mode optical fiber and focused with a lens of 15 mm focal length. The lens was mounted on a micro positioner rail to control the diameter of the beam. A laser beam profiler (LBP, Newport, Model number LBP-4-PCI) was used to assist in the alignment of the focused laser beam and to obtain an approximate value of the beam diameter. After passing through the sample, the laser beam was focused into an optical sensor (S144C, Thorlabs) connected to a power meter (PM100D, Thorlabs), which communicates with a LabVIEW computer interface to facilitate data gathering.

For measurements, the electrical contacts on the PCB were connected to a National Instruments data acquisition (NI USB-6001) control for data acquisition. To actuate the window, a heater current I$_H$ was used while the voltage across the VO$_2$ ($V_{VO_2}$) was measured. Using a voltage divider and $V_{VO_2}$, the resistance of VO$_2$ was calculated (see insert in Fig. 2). For the voltage divider, a series resistor of R$_S$ = 6.67 kΩ and a supply voltage of V$_C$ = 10 V were used to measure the VO$_2$ resistance. Thus, the setup allows to simultaneously measure and drive the device.

![Fig. 2](image2.png)  
**Fig. (2).** Optical set-ups used to measure the VO$_2$ window: (a) Electro-optical setup used for measurement taking. (b) IR camera setup.
The electro-thermal actuation, temperature distribution and emissivity were investigated by IR thermal imaging (OptoTherm, Infrasight MI320) as shown in Fig. 2 (b). Emissivity measurements were taken as a function of both temperature (i.e. conductive heating) and current (i.e. resistive, or Joule heating). For the temperature measurements, the die containing the window was attached to a Peltier heater. In order to obtain the value of the thermal emissivity, it is necessary to have a material with a well-defined emissivity (i.e. a benchmark). To this end, a piece of masking tape with a known value of emissivity (E = 0.95 [25]) was placed near the window of VO$_2$. Then the emissivity of the VO$_2$ was modified in the thermal camera until the temperature measured by the IR thermal imaging system in the VO$_2$ region was equal to the temperature measured in a selected region inside the masking tape.

Results and discussion

Characterization of both optical and electrical transitions were performed simultaneously for the 400 $\mu$m sized VO$_2$ window as shown in Fig. 3. In order to obtain the major hysteretic loops, current steps of increasing amplitude (0.1 V, or 0.63 mA) were applied to the heater electrodes until the phase transition was complete. This resulted in the major heating hysteretic loop. Then, current steps of decreasing amplitude were applied until reaching 0 mA, which resulted in the major cooling hysteretic loop. Each current step lasted 1 s, and the measurement was taken after waiting 900 ms from the beginning of the step. During this input to the heater, the VO$_2$’s resistance and transmittance were being monitored. A drop of approximately 3 orders in magnitude is visible for the resistance of VO$_2$ across its phase transition. This drop in resistance of VO$_2$ is to be expected and confirms the overall good quality of the sample. The average resistance drop for the sample was from $R_l = 631$ kΩ to $R_f = 676$ Ω, having an average $R_l/R_f$ ratio of $\sim 9.35$. For the optical transmittance, the power of the IR laser before the sample (1.22 mW) was used to normalize the transmitted power through the sample. A transmittance drop from $T_l = 0.36$ to $T_f = 0.14$ was observed for the 400 $\mu$m window, giving a ratio of $T_l/T_f = 2.57$ for the infrared region ($\lambda = 1550$ nm). To demonstrate the programmability stages of VO$_2$, several minor loops were measured for both electrical and optical transitions. Fig. 4 shows the plots for resistance and transmittance. The input used for obtaining these minor loops is shown in the insert of Fig. 4.

Obtaining the minor loop plots allows for a more reliable way to program the desired values for transmittance and therefore emissivity. For this case, the same current-increase input steps used to obtain the major heating hysteretic loop was used, until reaching 15 mA.

This was used as the pre-heating current, from which the first electrical/optical state was measured. Programming of a second electrical/optical state was achieved by applying an electrical pulse (also following the same step input) up to 16.97 mA (see Fig. 3). Since this value of current is not enough to complete the phase transition of VO$_2$, once the pulse is over, the resistance was...
and transmittance comes back to the pre-heating current, but following one of the minor hysteretic loops. The resulting pre-heated and programmed states in electrical resistance and optical transmittance are shown in Fig. 3, and the corresponding minor loop is identified in Fig. 4. It should be noted that there is a DC shift in transmittance between the minor loops and the programming pulse, which is most likely due to a small difference in the background light when measurements were taken. Although this shows only one programmed state, essentially any electrical resistance/transmittance value that belongs to the minor loops can be programmed by simply using a different pulse magnitude or pre-heating current.

In order to know the required minimum sampling rate for the 400 μm window, the device’s thermal time constant was measured. This was done by measuring the voltage in VO₂ (V_VO₂) resulting from a single current step input I_H. Fig. (5) shows the thermal time constant (t_{eff} = 21.68 ms) for the device for the case when the step was released (see Fig. 5). This measured time constant of ~ 20 ms is much faster than the 100 ms used for the current step input pulses, which indicates that the pulses will be enough to reach steady-state.

The change in VO₂’s optical properties across its phase transition is larger for wavelengths in the infra-red (IR) region [18]. The material’s ability to radiate thermal energy (i.e. emissivity) also changes abruptly during the material’s phase change, which allows for selective thermal emission. Fig. 6 shows the VO₂ emissivity as a function of both temperature and current. For both plots, VO₂ shows negative differential emissivity at the onset of the phase transition, which occurs around T_{PT} ≈ 68 °C and I_{PT} ≈ 19.9 mA. The VO₂ window shows a large thermal emissivity change from 0.76 below the transition point to 0.54 above the transition point. To measure emissivity as a function of current, the temperature of the VO₂ window was first measured as a function of current. Given that the emissivity of VO₂ changes with temperature, we needed a benchmark for calibration. Using the masking tape mentioned earlier for conductive experiments from Peltier heater would not work in this case, since it would require increasing the temperature of the tape by Joule heating through the same resistive heater used for the window. Therefore, we used the platinum heater as a temperature sensor, by monitoring its resistance as the current was applied. The heater’s temperature as a function of current was used to obtain the VO₂ window’s temperature. This allowed for mapping VO₂’s emissivity to obtain figure (6-b). On comparing the transition point for the plots on Fig. (4) to the plot in Fig. (6-b), there is a difference in current of I_{PT} ≈ 4.5 mA. This is most likely due to the method for measuring the emissivity as a function of current as previously mentioned. It should be noted that the hysteresis curves have similar shapes, which suggests that the difference is most likely a “DC offset”, which would be corrected by an additional integrated device that can be used as a benchmark for calibration.

Fig. 7 shows a thermal image for a 400 μm window before and after actuation using an electric pulse (1 mA), supplied in the form of short current steps –as depicted for the electrical and transmissivity experiments. Although both states correspond to the same temperature –since after the pulse the current returns to the pre-heated value–, the thermal image after the pulse clearly shows a lower irradiance, which is mapped to a lower temperature. This is due to the lower emissivity of the VO₂ after the programming pulse.
Conclusion

We have developed a VO$_2$ based window of 400 $\mu$m$^2$ that can be used as a smart window or thermal camouflage system. The electrical and optical transition in VO$_2$ where investigated, and hysteretic curves for minor loops where obtained. The minor loops inside the hysteresis of the VO$_2$ allows to program any state for transmissivity inside the window. Since the optical properties of VO$_2$ change greatly in the IR- region, then the emissivity will change during the transition. The emissivity for the VO$_2$ film as a function of both temperature and current was determined, and confirmed that the film shows a negative differential emissivity with the phase change. Emissivity states were programmed by electronic pulses to change the window's thermal radiation, which can be used for real-time thermal cloaking. The rapid tune-ability of both transmissivity and emissivity in VO$_2$ suggest that the film could be incorporated in the use of adaptive thermal camouflage devices.

Acknowledgements

This work was supported in part by the National Science Foundation (USA), Award Number: 1744273. The authors are thankful to N. Davila and E. Merced for assistance in the VO$_2$ window design.

Author’s contributions


References

Fibril orientation and strength in collagen materials and adaptation to strain

Hannah C. Wells¹, Hanan R. Kayed¹, Katie H. Sizeland¹,², Susyn J.R Kelly¹, Melissa M. Basil-Jones¹, Richard L. Edmonds³, Richard G. Haverkamp¹,²

¹School of Engineering and Advanced Technology, Massey University, Riddet Road, Palmerston North 4410, New Zealand
²SAXS/WAXS, Australian Synchrotron, 800 Blackburn Road, Clayton, VIC 3168, Australia
³Leather and Shoe Research Association, Dairy Farm Road, Palmerston North 4414, New Zealand

DOI: 10.5185/amlett.2018.1844
www.vbripress.com/aml

Abstract

Collagen based soft materials are important as medical materials and as consumer products. Strength is a crucial parameter. A better understanding of the structural factors that contribute to strength is sought. Synchrotron based small angle X-ray scattering was used to characterize the collagen fibril structure and structural arrangement in a range of collagen based materials including leather, surgical scaffold materials and glutaraldehyde stabilized pericardium. Structure was compared with strength and was also characterized during strain. When collagen fibrils are orientated in a highly layered structure (with a high orientation index) the materials exhibit higher tear strength. This applies to leather, surgical scaffolds derived from dermis and pericardium. A more layered structure is found in stronger leather, and depends on the species of the source animal and processing conditions. For surgical scaffolds and stabilized pericardium stronger material is found also to have a more layered structure. In pericardium it is affected by the age of the source animal with younger animals having a more layered fibril arrangement in the pericardium. When collagen based soft materials are strained, the material responds first by a reorientation of the fibrils then by extension of individual fibrils, and this enables them to withstand high stresses. Copyright © 2018 VBRI Press.

Keywords: Collagen; leather; orientation; SAXS; structure.

Introduction

Type I collagen is a fibrillar protein that is the major component of many soft tissues in animals [1]. These tissues include skin, pericardium, stomach, and tendons. Other types of collagen form important components of bone, cartilage and other organs. In tissues dominated by type I collagen other components are present which contribute to the structure and function of the tissues. These include other collagen types (e.g. type II and III), elastin, and glycoaminoglycans (GAGs) such as dermatansans and hyaluronan. Collagen is essential to the existence of animals by providing structural support and form and performs some of the functions in animals that cellulose does in plants and chitin does in insects. Collagen based soft materials have also been coopted into service in medical materials and consumer products. Examples of these are surgical scaffolds made from decellularised dermis [2], heart valve leaflets made from pericardium [3] and shoes made from leather.

One of the main functions of type I collagen in tissues is to provide structural form. Both strength and elasticity are needed [4]. Strength is derived from the fibrillar nature of collagen. Collagen fibrils may be many hundreds of nanometres long, with a diameter in the range 30-100 nm. The fibrils have a high tensile strength along their length. However connections between the fibrils may be less strong. The fibrils are ordered into bundles, which in turn make up fibres. Animal tissues are fibrous materials comprised of these collagen fibres. Strength and elasticity are also important for the technical applications of collagen materials. Strength may be measured in a variety of ways, some of which provide similar information. The methods have often been developed to mimic in-service performance. These include tensile strength [5], tear strength [6], bending stiffness, ball burst test [7], suture pull-out force or stitch tear testing. For leather, tear strength is the most routinely used measure of strength and correlates well with performance in shoes and upholstery. For surgical scaffolds, tear test or the similar ball burst test give information that is relevant to in-service performance. These tests reproduce the normal failure mode of these materials, which is not by catastrophic failure of a large portion of tissue at one time, but rather by a propagating failure at a point stress.

The dynamic properties of tissue and tissue derived materials are also important for their performance. Skin has to stretch and contract to accommodate movement of the body, pericardium has to expand and contract with
each heartbeat, stomach tissue has to expand with each meal. Leather in shoes must flex with each footstep, surgical scaffolds must duplicate the expansion and contraction of the tissue it replaces. Therefore collagen materials must have mechanisms to accommodate this dynamic behavior. These mechanisms may be at the scale of the molecule, fibril, fibre or tissue structure.

The structure of collagen in tissues has been characterized by a range of techniques. Optical microscopy, including staining with picrosirius red, is useful in getting a macroscopic view of the collagen organization [8]. Scanning electron microscopy and transmission electron microscopy (TEM) can show the organization of the fibrils and the structure of the fibrils. It has the disadvantages that these methods normally require chemical staining and dehydration which may alter the structure and these methods only show small areas of sample which comes with a risk of not being representative. Atomic force microscopy provides structural information at a similar scale to TEM [9] with the similar sampling representation risk, but avoids the need for transformational sample preparation. Small angle X-ray scattering (SAXS) is also useful [10] and has advantages over these other techniques in that it may be performed on samples without chemical modification, it can sample a larger volume of sample while providing structural information at a range of scales (e.g. from 1-200nm), and it can be easily and directly quantified [11]. SAXS also has the advantage that these measurements can be made while a tissue sample undergoes strain or other mechanical transformations[12-13].

Here the structural aspects of collagen based materials that contribute to strength are investigated. The investigation includes the correlation of measured mechanical properties with nanostructure and also the dynamic changes in collagen structure and structural arrangement under strain. It is hoped that a better understanding of the mechanism of collagen in providing strength and elasticity may both enable manufacture of improved collagen based materials but also provide a better understanding of the performance of natural tissues.

Experimental

Sample source and sample preparation

Leather. The following procedure was used to produce leather from animal skins. Adhering fat and flesh was removed from the skins before a conventional lime sulfide paint (140 g/L sodium sulfide, 50 g/L hydrated lime, 23 g/L pre-gelled starch thickener) was applied to the flesh side of the skin at 400 g/m². After an incubation period of 16 h at 20 °C the skins were washed to remove the lime and the pH was lowered to 8 by adding ammonium sulfate. A commercial bate enzyme called Tanzyme (0.1 % w/v) was then added and the skins were held at 35 °C for 75 min before being washed and pickled (20% w/v sodium chloride and 2% w/v sulfuric acid). The pickled skins were then degreased using a 4% nonionic surfactant (Tetrapol LTN, Shamrock, New Zealand) at 35 °C for 90 min before being washed. To neutralize the skins they are then washed for 10 min in 8% NaCl, 1% disodium phosphate solution (Feliderm DP, Clariant, UK) and 1% formic acid. The mix was then made up to 5% chrome sulfate using Chromosal B (Lanxess, Germany) and processed for 30 min. 0.6% magnesium oxide is then added based on the weight of the skins to fix the chrome and is processed over night at 40 °C. The resulting wet-blue pelts are neutralized again, using 1% sodium formate and 0.15% sodium bicarbonate for 1 h. The pelts are then washed and retanned with 2% synthetic retanning agent (Tanicor PW, Clariant, Germany) and 3% vegetable tanning (mimosa; Tanac, Brazil). 6% mixed fatsliquors were added and the leathers were held at 50 °C for 45 min, followed by fixing with 0.5% formic acid for 30 min and washing in cold water.

Pericardium. Fresh bull (Charolais Cross) pericardium samples were sourced within 2 h of slaughter from John Shannon, Wairapara, New Zealand. The tissue was cut into rectangular sample pieces (50 mm × 6mm) with the long axis being parallel to the long axis of the heart. The pericardium was washed for 24 h in 1% octylphenol ethylene oxide condensate (Triton X-100, Sigma) and 0.02% EDTA solution made up in phosphate buffered saline (Lorne Laboratories Ltd). Finally, the samples were stored in phosphate buffered saline up until experimental analysis.

Surgical scaffold materials. Commercial acellular dermal matrix (ADM) materials were obtained. These included Strattice Firm porcine ADM (LifeCell Corporation, US), Alloderm human ADM (LifeCell Corporation, US) and a range of SurgiMend bovine ADM (TEI Biosciences, US). The range of SurgiMend bovine ADM included third trimester fetal ADM and neonatal ADM (animals less than 5 months old). Strattice and Alloderm were transported as sterile hydrated materials whereas the SurgiMend materials were transported dry and required hydrating with distilled water prior to SAXS analysis and physical testing.

Synchrotron SAXS

SAXS diffraction patterns were recorded on the SAXS/WAXS beamline at the Australian Synchrotron (Melbourne, Australia). A high-intensity undulator source was used with an energy resolution of 10⁻⁴ obtained from a cyro-cooled Si(III) double-crystal monochromator. The beam size was 250 × 80 μm (FWHM focused at the sample) with a total photon flux of around 2 × 10¹² ph.s⁻¹. Diffraction patterns were recorded with an X-ray energy of 12 keV using a Pilatus 1 M detector that had an active area of 170 × 170 mm and a sample-to-detector distance of 3371 mm. Exposure time for diffraction patterns ranged between 1 and 5 s and initial data processing was carried out using Scatterbrain software.

SAXS data was recorded in two directions through the samples. The X-ray beam either passed through the
flat (top) surface of the sample, normal to the surface or edge-on to the sample (referred to as edge-on or cross sections). For edge-on analysis, the structure was analysed every 0.1 – 0.2 mm through the sample, since the structure is known to vary through the thickness.

![Image](image_url)

*Fig.1. SAXS experimental setup. (a) Samples of leather or tissue mounted for measurement without strain. (b) Samples mounted for SAXS measurement during strain. (a) Reprinted with permission from Basil-Jones, M. M. et. al., J. Agric. Food Chem. 2010, 58, 5286. ©2010 The American Chemical Society.*

Samples were strained with apparatus using a linear motor, Linmot PS01 48 _ 240/30_180-C (NTI AG, Switzerland), mounted on a purpose-built frame. Clamps to hold the pericardium were fitted between the linear motor and a L6D OIML single-point loadcell (Hangzhou Wanto Precision Technology Co., Zhejiang, China). Samples were mounted horizontally without tension and strained in 1mm increments and maintained for 1min at each extension to stabilize before SAXS patterns, the extension and the force information were recorded. This process was repeated until the sample failed, with the interval between strain increments around 8–13 min.

**Fibril Diameter.** The Irena software package, running on Igor Pro, was used to calculate fibril diameters from collected SAXS data. The data were fitted at the wave vector, \( q \), between 0.01 – 0.04 Å\(^{-1}\) and at an azimuthal angle which was approximately 90° to the long axis of most of the collagen fibrils. The long axis of most of the collagen fibrils was determined as the azimuthal angle that had the maximum intensity for the D-spacing diffraction peaks. The “cylinderAR” shape model with an arbitrary aspect ratio of 30 was used for all fitting. We did not attempt to individually adjust the aspect ratio for all samples, and the unbranched length of collagen fibrils could in fact exceed this ratio.

**Orientation Index.** The orientation index (OI) is a measure of the spread of fibril orientation. The spread is quantified to a value between 0 and 1, where 0 indicates isotropically orientated fibrils and 1 indicates parallel fibrils. The OI is defined by the equation \( (90° – OA)/90° \), where OA (orientation angle) is the minimum azimuthal range that contains 50% of the microfibrils, using the spread in azimuthal angle of D-spacing diffraction peaks, converted to an index. The peak area is measured above a fitted baseline, at each azimuthal angle.

**Electron microscopy**

**SEM.** To carry out scanning electron microscopy, samples were cut into small cube-shaped pieces and fixed for at least 8 h at room temperature in Modified Karnovsky’s fixative. This fixative contains 3% glutaraldehyde and 2% formaldehyde in 0.1 M phosphate buffer (pH 7.2). Following fixing, the samples were washed three times in phosphate buffer (0.1 M, pH 7.2) for 10 – 15 min before being dehydrated in a graded series of ethanol washes (25, 50, 75, 95 and 100%). Each dehydration stage was carried out for 10 – 15 min, and this was followed by a final wash for 1 h with 100% ethanol. Critical point (CP) drying was carried using the Polaron E3000 series II critical point drying apparatus. Liquid CO\(_2\) was used as the CP fluid and 100% ethanol as the intermediary fluid. The samples were then mounted on to aluminium stubs and sputter coated with gold using the Baltec SCD 050 sputter coater. Samples were viewed in the FEI Quanta 200 environmental scanning electron microscope at an accelerating voltage of 20 kV.

**TEM.** For transition electron microscopy, samples were fixed with 20 g kg\(^{-1}\) formaldehyde and 30 g kg\(^{-1}\) glutaraldehyde in 0.1 mOlL\(^{-1}\) phosphate buffer (pH 7.2) for 2 h at room temperature. Samples were washed and fixed with 10 g kg\(^{-1}\) OsO\(_4\) in buffer for 1 h at room temperature. After a further three washings for 10 min each, the samples were dehydrated using acetone/water series (150, 500, 750, 950, 1000 g kg\(^{-1}\)). Each stage was carried out for 10 – 15 min each and was followed by two pure acetone washes for 1 h each. Samples were first embedded with an acetone resin 50:50 mixture (Procure 812 ProSciTech, Australia), left on a stirrer overnight, then were left for another 8 h in pure acetone and stirred; this step was repeated twice. Lastly, the samples were embedded in pure resin at 60 °C for 48 h.

**Atomic Force Microscopy (AFM)**

Small square sections of sample were cut and mounted onto 12 mm diameter magnetic metal discs using double-sided tape. Sample were left to air dry for a few h before being imaging. Sample were viewed using a Nanoscope E (Veeco) atomic force microscope with a JV scanner. An x-y calibration to ±3% was completed just prior to imaging. CSG01 cantilevers (NT-MDT, Russia) were used for contact mode imaging, with a force constant of about 0.05 Nm\(^{-1}\).
Optical Imaging with Picosirius Red Staining

Samples were frozen and cut in a Leica CM1850 UV cryogenic microtome at -30 °C before being mounted on microtome discs using an embedding medium. Cross-sections of samples were cut, each being 10 μm thick, and transferred on to glass microscope slides. The mounted samples were then stained following the procedure given with the Picosirius Stain Kit (Polysciences, Inc.) and placed in 70% ethanol for 45 s, before being left to air dry for several h. A Nikon Digital Sight DS-Fi2 camera was used to view the samples and collect images with cross-polarised filters.

Tear Tests

Tear strength for each material was determined using standard methods for double-edge tear testing [6]. Samples were cut to size and stored at 20 °C and 65 % relative humidity for 24 h before testing. Thickness of each sample was measured prior to testing, using method BS EN ISO 2589:2002. An Instron 4467 was used to carry out the tear tests.

Results and discussion

Images of materials

The structure of ovine dermis (in the form of leather) and pericardium at a range of scales and with a range of imaging techniques are shown in Fig. 2. The materials are not of uniform composition throughout, and this reflects the function of the native materials. Leather has a smooth upper surface that forms a barrier to the environment. In leather the top half (approximately) is referred to as grain and this is the portion that formerly contained hair follicles. The lower half is referred to as corium. Similarly in pericardium the internal side is lubricated and slides against the heart with every beat, whereas the external side is the interface with the abdominal cavity. An optical image of a cross section (Fig. 2a) demonstrates the gross differences between grain and corium. A stained cross section of pericardium (Fig. 2b) highlights the arrangement of collagen in pericardial tissue. At higher magnification the fibrils in bundles can be seen in a SEM image of ovine leather (Fig. 2c), with the banding of collagen fibrils in pericardium visible in an AFM image (Fig. 2d) or in a TEM image of bovine leather (Fig. 2e).

SAXS patterns

The imaging techniques provide a good insight into the structure of collagen tissues and a variety of scales, however, SAXS provides quantitative information on these structures in a volume averaged sample, although not in such a visually intuitive manner [11]. A typical scattering pattern of a collagen material (Fig. 3a) gives a series of partially aligned diffraction rings, and a central region of scattering aligned at 90° to the alignment of the diffraction rings. This scattering pattern can be processed
in a variety of ways. Two useful methods are to plot the intensity with radial angle integrated over all azimuthal angles (Fig. 3b) or the intensity with azimuthal angle integrated over a small range or radial angle corresponding to one diffraction ring (Fig. 3c).

**OI and tear strength**

The orientation index was measured both with the X-rays edge on to the tissue or leather materials (giving a measure of the layering of collagen fibrils in planes) and perpendicular to the surface of the tissue. For the edge on measurements a correlation is found between the tear strength and the OI. With a large number of samples of ovine and bovine leather a strong correlation is found between tear strength and a relatively small range of OI [14]. The ovine leather was selected on the basis of one group of low tear strength material (n = 15, with 228 diffraction patterns) and one group of higher strength material (n = 14, with 249 diffraction patterns) and one random group of bovine leather (n = 10, with 167 diffraction patterns). While the spread in OI values for each sample group is quite high (σ = 0.03, 0.03, 0.016 respectively) giving a low $r^2$ of 0.20 the fit is robust with a $p < 0.0001$ (Fig. 4a) [14].

Taking a much smaller sample set, but with a much wider range of tear strengths, this time of leather from a range of different animal species, an extended correlation is found between tear strength and OI [15]. The leather from the mammals falls in a straight line with an $r^2$ of 0.98 and $p < 0.0001$ (Fig. 4b).

Acellular dermal matrix materials used for surgical scaffolds made from neonatal bovine dermis (5 months old), while stronger than their leather counterparts made from adult animals, also show a correlation between OI and tear strength (Fig. 4d) [16].

If the strength is due to the sum of the components of the fibrils that lie in the direction of applied force then the OI is given by

$$OI = \frac{\int_0^{2\pi} \int_0^{\pi/2} \cos^4 \theta F(\theta, \phi) \, d\theta \, d\phi}{\int_0^{2\pi} \int_0^{\pi/2} F(\theta, \phi) \, d\theta \, d\phi}$$

where $F(\theta, \phi)$ is the angular distribution function where $\theta$ and $\phi$ are orthogonal [16].

While the structuring of collagen fibrils into a more layered structure may result in leather with higher tear strength, one may propose a thought experiment where this is extended to an OI = 1 where the fibrils are perfectly aligned. Then there are no fibrils traversing layers and providing a strong fibre connection to tie the layers together. The connections between layers are then due only to the connections between fibrils. Connections in native tissues are generally believed to result from GAGs [17-18], however these are known to be weak and recently this crosslinking effect has been challenged [13, 19]. In leather these GAGs have been removed and replaced by chromium or tannins, which are believed to form a similar role. Nevertheless, the bonds holding fibrils together are much weaker than the strength provided along the length of a fibril. Therefore, in a material where the fibrils are arranged perfectly in planes it might be imagined that the layers would separate. This has been identified, and it is known as looseness in leather.

Looseness may occur in bovine and other strong leather. Looseness is defined as the appearance of wrinkles on the surface (grain) of leather when it is folded grain side inwards. It is an undesirable attribute and results in a downgrade of the leather [20]. The OI through a cross section of tight (good) and loose (poor) leather
found that loose leather has a higher OI throughout the cross section [21]. The loose leather in this example also had a higher tear strength (130 ± 61 N mm⁻¹ compared to 73 ± 10 N mm⁻¹ for tight leather, with P <0.001 for the difference), in agreement with the correlation found between OI and tear strength in general for leather, but even with the higher strength the appearance of looseness substantially reduces the value of the leather. Looseness therefore is an example of a high OI continuing to increase strength but causing other undesirable properties. The correlation of strength and looseness with OI also provides a reason why looseness is mainly observed in leather from animals that typically produce high strength leather.

Age of donor animal and OI

The correlation between OI and tear strength in leather made from the skins of mammals also applies to other tissues. Pericardium, the membrane that encloses the heart and separates it from the other organs, is used in medical devices, especially in heart valve leaflet replacement. Pericardium is rich in type I collagen (Fig. 2b, d) and in contrast to collagen in dermis the collagen contains a strong crimp when not under tension. The strain at failure for bovine pericardium derived from neonatal animals is found to be 33 ± 4 MPa whereas from adult animals it is 19 ± 2 MPa. The stronger neonatal pericardium also has a higher OI, measured with X-rays edge on, of 0.78 compared with 0.63 for adult pericardium (with a p < 0.0001 for a comparison between these two OI values) [22-23]. The correlation between tear strength and OI is probably fairly universal for a range of tissue types, although the specific factors leading to high OI may vary.

Processing conditions

The structural arrangement of collagen fibrils in an animal derived material depends on both the native structure and also on the processing that the material has undergone. Changes that are caused by processing should be considered separately to those that occur naturally, in order to understand the inherent natural strength and the strength changes derived from processing conditions. Leather is prepared from skins through a series of processes to remove most non-collagenous components. This is followed by “cross linking” of the collagen with chromium or tannin followed by incorporation of fatliquors. Surgical scaffolds will typically be decellularised tissue with no cross linking agents or preservatives added. Heart valve leaflet replacements are normally decellularised tissue which has subsequently been treated with glutaraldehyde.

The OI varies during the stages of tanning from a salted skin (the normal starting material for a tannery) through to the dry crust staked (finished leather before the final stage of fatliquoring) (Fig. 5). While the variation in OI is quite large, so is the variation in thickness of the leather and of the moisture content. The OI can be adjusted for changes in thickness. If the materials containing a fibril expands in thickness uniformly, and the fibril is at an angle θ₁ from the base, then the new angle of the fibril, θ₂, depends on the change in thickness by:

\[
\frac{T_2}{T_1} = \tan \theta_2 \tan \theta_1
\]

where T₁ is the original thickness, and T₂ is the new thickness. Rearranging for θ₁ gives the new angle of the fibril after the leather has increased in thickness:

\[
\theta_2 = \tan^{-1}\left(\frac{T_2}{T_1}\tan \theta_1\right)
\]

Once corrected for thickness the remaining difference in OI is only due to water content with the wet samples having a higher OI (0.8 in the leather example) compared with dry leather (0.66) [24].

Tissue adapting to strain

When collagen based materials are strained, the collagen fibrils respond to the strain in a number of ways. The collagen fibrils first reorient to the direction of strain (Fig. 6a). This is apparent in the shift in orientation of the features in the scattering pattern. The diffraction rings become centred on the direction of applied strain while the low q region of the pattern reflecting the form factor of collagen, importantly the fibril diameter, becomes aligned at right angles to this direction. As the orientation changes, the OI increases which is apparent as a narrowing of the azimuthal angle – intensity plot (Fig. 6a) [12-13]. This reflects the process of fibrils turning to the direction of applied strain, with those furthest from the direction of strain reorienting the most. In some materials such as pericardium (but not dermis) crimp may be present, and this is straightened in the early stages of stretching and reflected in both an increase in OI and an apparent decrease in fibril diameter (since the SAXS form factor gives an average diameter for the fibril). Finally the individual fibrils begin to stretch. This can be measured...
by the increase in D-spacing, this change being directly proportional to the increase in length of the fibrils (Fig. 6b). The fibril diameter, measured from SAXS as a tissue is strained, decreases at the same time as the D-spacing increases. These changes can be plotted together for a collagen material as it is strained (Fig. 6c). From this, a Poisson’s ratio for collagen fibrils can be calculated, which turns out to be large (2.1 ± 0.7) [25]. This variety of mechanisms for accommodating strain gives collagen materials great strength and toughness [26-27].

Conclusion

The arrangement of collagen fibrils in tissues has been characterized by synchrotron based small angle X-ray scattering supported by microscopy techniques. There was a strong correlation between tear strength, which is a good indicator of in-service performance, and the spread of fibril orientation (orientation index, OI). A highly layered structure provides the greatest tear strength. The OI of a natural material was found to depend on the individual source animal (with considerable variation between animals), the species of the source animal, the age of the animal, and processing conditions from the raw material to the finished product. The correlation between tear strength and OI appears to be universal for a range of tissue types. When collagen based materials are strained, the collagen fibrils respond to the strain by reorienting to the direction of strain with an increase in OI, then the individual fibrils begin to stretch. From this, a Poisson’s ratio for collagen fibrils can be calculated. This variety of mechanisms for accommodating strain gives collagen materials great strength and toughness.

Acknowledgements

This work was supported by grants from the Ministry of Business Innovation and Employment LSRX0801 and LSRX1301 (MMB-J, KHS, HSW, SJRK), a Massey University Scholarship (HRK) a Royal Society of New Zealand NZ-Taiwan Nanotechnology Research Student Travel grant (HCW) and the Australian Synchrotron for travel funding and accommodation. Samples were provided by Southern Lights Biomaterials (NZ), TEI Biosciences (USA) and Tasman Tanning Ltd (NZ). This research was undertaken on the SAXS/WAXS beamline at the Australian Synchrotron, Victoria, Australia and the SAXS/WAXS beamline at NSRRC, Taiwan.

Author’s contributions

Conceived the plan: RGH; Performed the experiments: HCW KHS HRK SJRK, MMB-J, RLE, RGH; Performed the data analysis: HCW KHS HRK SJRK, MMB-J, RLE, RGH; Wrote the paper: HCW, RGH. Authors have no competing financial interests.

References


Hydrogenated TiO$_2$ as efficient electron transport layer of planar perovskite solar cell

Yulong Ma, Kaimo Deng, Bangkai Gu, Hao Lu, Yayun Zhu, Liang Li

College of Physics, Optoelectronics and Energy, Jiangsu Key Laboratory of Thin Films, Center for Energy Conversion Materials & Physics (CECMP), Soochow University, Suzhou 215006, P. R. China

DOI: 10.5185/amlett.2018.1944
www.vbripress.com/aml

Abstract

The electron transport material has the great effect on the performance of hybrid perovskite solar cells. TiO$_2$ is widely chosen as the electron transport layer due to its facile synthesis and excellent charge extraction capability. Here, for the first time, we utilize the hydrogen treated TiO$_2$ as the electron transport layer for improving the performance of perovskite solar cells. The hydrogen treatment increases the Fermi level and conductivity of TiO$_2$, and the device based on hydrogen treated TiO$_2$ exhibits a power conversion efficiency of 13.15% compared with 9.45% for the reference device with untreated TiO$_2$. The results highlight the importance of optimizing the electron transport material and provide a new route to fabricate highly efficient planar perovskite solar cells. Copyright © 2018 VBRI Press.

Keywords: Electron transport layer, hydrogen treatment, TiO$_2$, perovskite, atomic layer deposition

Introduction

Since the first application of inorganic-organic hybrid perovskite in the field of solar cells by Miyasaka in 2009 [1], it has attracted tremendous attention due to its advantage as photovoltaic materials such as the high absorption of visible light, simple production process and large carrier mobility [2-9]. Particularly, the power conversion efficiency (PCE) of the CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) perovskite solar cells (PSCs) increases from 3.8% to over 21% just within several years [1,10]. The typical PSCs include several parts: the transparent anode layer (FTO or ITO), electron transport layer (ETL), perovskite as light absorption layer, hole transport layer (HTL) and metal cathode (Au or Ag). ETL plays an important role in achieving a high PCE since it not only efficiently extracts and transports electrons from perovskite to electrode but also suppresses the recombination with holes generated in the perovskite [11,12]. TiO$_2$ thin film has been widely used as ETL in PSCs because of high light transmittance, matched energy level and thus efficient electron injection from the perovskite film to TiO$_2$ layer [13-17]. There are many methods developed to deposit TiO$_2$ thin film, such as spin coating [18], spray pyrolysis [19], sputtering [20], and atomic layer deposition (ALD) [21].

However, TiO$_2$ has a relatively low electron mobility and conductivity which may lead to a higher recombination rate and deteriorate the performance of PSCs [17]. Many efforts have been made to solve this concern. On one hand, alternative materials with a higher electron conductivity such as ZnO, SnO$_2$ and CdS have been chosen as ETL to replace the traditional TiO$_2$ layer and comparable PCEs have been achieved [22-24]. On the other hand, modified TiO$_2$ films have also been used to improve the performance of PSCs. Snaith et al. adopted Al-doped TiO$_2$ as ETL to figure out this problem [25]. The conductivity of TiO$_2$ increased after Al doping, resulting in a better performance. Chen et al. employed Li to modify the TiO$_2$ surface, which resulted in increased conductivity of TiO$_2$ and improved PCE of devices from 14.2% to 17.1% [26]. Plenty of works indicate that modifying TiO$_2$ can obviously increase the performance of planar PSCs [27-30].

Hydrogen treatment is a simple and practical tactic that can effectively increase the conductivity and Fermi level of TiO$_2$. The hydrogenated TiO$_2$ (H:TiO$_2$) has been broadly applied in some fields such as water splitting, photocatalysis, photoelectrochemical sensor and lithium-ion rechargeable battery due to its excellent conductivity and optical property [31-33]. However, there are no reports about the application of hydrogen treated TiO$_2$ in perovskite solar cells. In this paper, to the best of our knowledge, we firstly employed the H:TiO$_2$ as ETL to improve the performance of PSCs. By optimizing the time and temperature of hydrogen treatment, a higher PCE of 13.15% was obtained compared to 9.45% for the reference TiO$_2$ PSCs without hydrogenation. The enhanced performance was mainly ascribed to the increased open circuit voltage and fill factor. The mechanism for the improved performance was illustrated by the systematical characterization of absorption spectra, Mott-Schottky curves, electrochemical impedance spectra and photoluminescence spectrum.
Experimental

Device fabrication

The FTO substrates were cleaned with detergent, acetone, ethyl alcohol and DI water in an ultrasonic bath. After the FTO substrates were treated with the O3 bath for 15 min, a 10nm thick TiO2 film was deposited on the FTO substrate by ALD and annealed at 500 °C in air for 2 hours. Once cooling to room temperature, the TiO2 substrates were annealed under a 5% H2:95% Ar gas flow with various temperatures of 250-500 °C for 5 hours. The TiO2 substrates without hydrogenation serve as the reference devices. The perovskite films were deposited on the TiO2 and H:TiO2 substrates by a modified two-step vapor-assisted method. A 461 mg mL⁻¹ PbI2 precursor was spin coated onto the substrate at 3000 rpm for 40 s, followed by annealing at 100 °C for 10 min. After cooling down to room temperature, the PbI2 film was kept in a closed vessel containing CH3NH3I (MAI) powder for 15 min at 150 °C (the vessel was preheated for 20 min in advance). After the vapor reaction, the films were rinsed with 2-propanol afterwards and dried at 70 °C for 30 min. The spiro-OMeTAD used as the hole-transport layer was deposited on the perovskite film by spin coating at 2000 rpm for 45 s. The precursor of spiro-OMeTAD solution was prepared by adding 72.3 mg spiro-OMeTAD, 28.8 μL 4-tertbutylpyridine, and 17.5 μL lithiumbis-(trifluoromethanesulfonyl) imide (Li-TFSI) (520 mg of Li-TFSI in 1 mL acetonitrile) in 1 mL chlorobenzene. Finally, a 100 nm thick silver electrode was deposited by thermal evaporation with a shadow mask (0.12 cm² active area).

Characterizations

The morphology of the samples was measured by a field-emission scanning electron microscope (FE-SEM) (Hitachi SU8010). The crystallization of products was checked using an X-ray diffractometer (XRD) (D/MAX-III-B-40KV, Cu Kα radiation, λ = 1.5418 Å). X-ray photoelectron spectroscopy (XPS) (ESCALAB, 250Xi) was recorded for valence states.

Property measurements

The current-voltage (J-V) was characterized using a Keithley source meter with a Newport solar simulator calibrated to AM1.5G (100 mW/cm²) by a standard silicon solar cell. A metal mask of 0.06 cm² was used to define the exact illumination area. External quantum efficiency (EQE) was measured with a Newport quantum efficiency system. The absorption spectra were collected by a UV-vis spectrophotometer (Shimadzu, UV-3600). The electrochemical impedance spectroscopy (EIS) was acquired with an electrochemical workstation (Autolab, PGSTAT 302N) under light at zero-bias voltages with an alternative signal amplitude of 5 mV and in the frequency range of 400 KHz to 0.01 KHz. The photoluminescence (PL) spectrum was detected with a spectrofluorometer (Horiba, Fluoromax-4) with a 525 nm excitation wavelength at room temperature.

Result and discussion

Fig. 1 presents the top-view scanning electron microscopy (SEM) images of bare FTO glass (Fig. 1a), 10 nm-thick TiO2 (Fig. 1b), H:TiO2 (Fig. 1c) and MAPbI3 perovskite (Fig. 1d) films on FTO substrates. TiO2 film was deposited by ALD technique and the hydrogenation reaction was conducted at 450 °C for 5 h under a mixed (5% H2:95% Ar) gas flow. The MAPbI3 perovskite film was fabricated by a two-step vapor assisted synthesis method. The synthetic details can be found in the experimental section. It can be observed from the SEM images that the surface morphology of 10 nm-thick TiO2 with ALD process is almost the same with the bare FTO due to the highly uniform ultrathin coating of ALD, and no obvious difference is found between the hydrogen treated and the pristine TiO2. Perovskite film is smooth and pin hole free with a large grain size.

Fig. 2 XRD patterns of FTO, FTO/H:TiO2, and FTO/H:TiO2/perovskite.
Fig. 2 shows the corresponding X-ray diffraction (XRD) patterns for FTO, FTO/H:TiO$_2$, and FTO/H:TiO$_2$/MAPbI$_3$. No distinct peaks of TiO$_2$ or H:TiO$_2$ appear because the 10 nm thickness of deposited TiO$_2$ or H:TiO$_2$ is too thin to be detected. In addition, the typical PbI$_2$ peak mainly at 12.6° is not found, indicating the complete conversion of PbI$_2$ to CH$_3$NH$_3$PbI$_3$. The diffraction peaks of perovskite at 14.2°, 20.0°, 23.5°, 28.5°, 31.9°, 40.7° and 43.2° are in accordance with previous report [34]. To further confirm the existence of TiO$_2$ and change of surface bonding induced by hydrogen treatment, X-ray photoelectron spectroscopy (XPS) measurement was carried out. Fig. 3a shows the XPS survey spectra of O 1s core-level. The peak at 529.8 eV can be attributed to the lattice O$^{2-}$ in TiO$_2$. The peak at 531.6 eV is assigned to Ti-OH which has been reported with a 1.5-1.8 eV higher binding energy than the lattice O$^{2-}$ core level [31]. Besides, the hydrogenated TiO$_2$ has relatively higher OH peak intensity than the TiO$_2$ without treatment, which proves the hydrogen treatment is beneficial to the formation of OH group on TiO$_2$ surface. The XPS spectra of Ti 2p core-level is shown in Fig. 3b. Both of the samples have an identical pattern with Ti$^{4+}$ peaks located at 458.6 and 464.5 eV, which is similar to other reports [31].

![Fig. 3. XPS measurement of H:TiO$_2$ film. (a) and (b) are survey spectra for the O 1s and Ti 2p core-levels.](image-url)

<table>
<thead>
<tr>
<th>Devices</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 °C</td>
<td>0.89</td>
<td>18.59</td>
<td>64.46</td>
<td>10.71</td>
</tr>
<tr>
<td>350 °C</td>
<td>0.92</td>
<td>19.49</td>
<td>64.78</td>
<td>11.59</td>
</tr>
<tr>
<td>450 °C</td>
<td>0.99</td>
<td>19.69</td>
<td>66.27</td>
<td>12.94</td>
</tr>
<tr>
<td>500 °C</td>
<td>0.85</td>
<td>16.78</td>
<td>56.51</td>
<td>8.09</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.89</td>
<td>17.16</td>
<td>61.31</td>
<td>9.45</td>
</tr>
</tbody>
</table>

Table 1. Summary of photovoltaic parameters for devices with different hydrogenated temperatures and the reference TiO$_2$.

![Fig. 4. (a) The cross-section SEM image of device. (b) J-V curves of the reference TiO$_2$ and H:TiO$_2$ based PSCs with different hydrogenated temperatures measured under AM 1.5G irradiation (100 mW/cm$^2$).](image-url)

The typical cross-sectional SEM image of H:TiO$_2$ based planar PSCs is shown in Fig. 4a, and corresponding J-V performance of PSCs based on H:TiO$_2$ ETLs with different hydrogen treated temperatures is shown in Fig. 4b together with the devices based on TiO$_2$ without hydrogenation for comparison. The corresponding photovoltaic parameters are listed in Table 1. The power
conversion efficiency of reference PSCs is 9.45%, with $V_{oc}$ of 0.89 V, $J_{sc}$ of 17.16 mA/cm$^2$ and FF of 58.93%. The performance of H:TiO$_2$ based PSCs is enhanced gradually with the hydrogenated temperature from 250 to 450 $^\circ$C and then largely degraded at 500 $^\circ$C. The highest performance of PSCs obtained at 450 $^\circ$C has the corresponding $V_{oc}$, $J_{sc}$, FF and PCE of 0.99 V, 19.69 mA/cm$^2$ and 66.27%, respectively. Compared with the PCE of the reference TiO$_2$ sample, all the physical parameters after hydrogen treatment are increased obviously. The definition of theoretical $V_{oc}$ in PSCs is the difference between the Fermi level of ETL and the highest occupied molecular orbital level of HTL. The Mott-Schottky ($M$-$S$) was used to measure the Fermi level of TiO$_2$ and H:TiO$_2$ ETLs, as shown in Fig. 5a. A positive slope in $M$-$S$ plots are observed for both samples, demonstrating the feature of $n$-type semiconductor. More importantly, it shows that the Fermi level of TiO$_2$ drops from -0.633 to -0.826 V by fitting the curves, suggesting that the Fermi level of ETLs is increased after hydrogen treatment. This phenomenon agrees well with the increase in $V_{oc}$ for the PSCs. Moreover, the H:TiO$_2$ sample shows a smaller slope of $M$-$S$ plot compared to the reference TiO$_2$, which means the donor densities of TiO$_2$ after hydrogen treatment are increased. According to the equation [35]

$$N_D = \left( \frac{2}{\varepsilon \varepsilon_0 e} \right) \left[ d(1/C^2)/d(V) \right]^{-1}$$

where $N_D$ is the donor density, $\varepsilon$ is the dielectric constant of TiO$_2$, $\varepsilon_0$ is the permittivity of vacuum, $e$ is the electron charge, $C$ is the capacitance of the space charge region and $V$ is the applied voltage at the electrode, the donor density of TiO$_2$ and H:TiO$_2$ samples are calculated to be $4.09 \times 10^{20}$ and $7.82 \times 10^{20}$ cm$^{-3}$, respectively. Obviously, the donor density is increased due to the increased OH groups after hydrogen treatment, and thus the electrical conductivity of TiO$_2$ is improved. To further confirm the increased oxygen vacancies, the $J$-$V$ curves of TiO$_2$ and H:TiO$_2$ films were measured in hole-only devices under the dark condition (Fig. 5b). Clearly, the current increases linearly with voltage at the lower bias voltage, which indicates the ohmic response of devices. At the higher bias voltage, the current increases nonlinearly, suggesting that the trap states are fully filled. The trap filled limit transition points ($V_{TFL}$) linearly vary with the trap-state density and is determined by the equation [36]

$$V_{TFL} = \frac{en_l L^2}{2 \varepsilon \varepsilon_0}$$

where $e$ is the electron charge, $n_l$ is the trap-state density, $L$ is the thickness of TiO$_2$ film, $\varepsilon$ is the dielectric constant of TiO$_2$ and $\varepsilon_0$ is the permittivity of vacuum. The $V_{TFL}$ value of H:TiO$_2$ is 0.84 V, larger than that of 0.48 V of TiO$_2$, indicating that the trap density increases after hydrogenation, considering the other parameters are the same. In other words, the oxygen vacancies increase after hydrogen treatment, which agrees well with XPS results above. To further confirm the increased conductivity of samples after hydrogenation, the resistance of TiO$_2$ and H:TiO$_2$ based substrates were measured. The resistance of H:TiO$_2$ is 5.2 $\Omega$, significantly lower than 26 $\Omega$ for the pristine TiO$_2$.

![Fig 5](image)

**Fig 5** (a) $M$-$S$ curves of TiO$_2$ and H:TiO$_2$ electrodes. (b) Dark $J$-$V$ curves of the hole-only devices.

When the hydrogenated temperature exceeds 450 $^\circ$C, the performance of devices decreases dramatically, which is primarily attributed to the increased resistance of FTO substrate as the hydrogenated temperature is higher than 450 $^\circ$C. The corresponding resistance of the FTO substrate after hydrogen treatment at 500 $^\circ$C is 398 $\Omega$, which is much higher than the pristine FTO. The same phenomenon was also observed in the previous report [31]. Therefore, 450 $^\circ$C is served as the optimal hydrogenated temperature in our work. The PCEs from 30 devices with the optimum hydrogenated temperature were obtained to evaluate the reproducibility of PSCs. As
shown in Figs 6a and 6b, the champion device has a PCE of 13.15% and the average value is 12.32%. The output current density at the maximum power point of the champion device is shown in Fig. 6c. The corresponding stable PCE is 12.95%, which is consistent with the PCE from the J-V curve.

The ultraviolet-visible (UV-vis) absorption spectra of FTO/TiO$_2$/MAPbI$_3$ and FTO/H:TiO$_2$/MAPbI$_3$ were carried out to explore whether the optical properties of devices were changed after the hydrogen treatment. In Fig. 7a, the intensity of the absorption curves is almost the same in the whole wavelength range for two samples. In contrast, the external quantum efficiency (EQE) curves (Fig. 7b) of PSCs show a significant difference with the integrated $J_{sc}$ to be 15.80 and 18.14 mA/cm$^2$, respectively. It is well known that the EQE as well as the $J_{sc}$ values are intimately related to the light harvesting and charge collection efficiencies. Since there is little influence on the light absorption after the TiO$_2$ hydrogenation, the dynamics of charge transport may be responsible for the different EQE.
Electron impedance spectroscopy (EIS) was measured to uncover the charge transport and recombination process in PSCs. Fig. 8a shows the Nyquist plots of TiO$_2$ and H:TiO$_2$ (450 °C) based PSCs under AM 1.5G illumination, and the corresponding equivalent circuit model is inserted in the top-right corner. Two main arcs are observed clearly from the Nyquist plots with one at the high-frequency range and the other at the lower-frequency range. Three components constitute the equivalent circuit: the series resistances ($R_s$), $Z_1$ consisted of $R_1$ and the relevant capacitors (CPE1), and $Z_2$ including $R_{rec}$ and capacitor (CPE2). The $R_1$ at the high-frequency region stands for the transport resistance at the ETL/perovskite or HTL/perovskite interface. In our work, the $R_1$ represents the transport resistance at the ETL/perovskite interface since both the architecture of PSCs have the same perovskite/HTL interface. The $R_{rec}$ at the lower-frequency region represents the recombination resistance. The values of resistances extracted from Nyquist plots are summarized in Table 2. It is shown that the series resistances of devices decrease from 54 to 16 Ω after hydrogenation compared with the untreated TiO$_2$ based PSCs. The series resistance directly affects the FF of PSCs, and a lower series resistance favors a larger FF which is consistent with the above $J$-$V$ test. The $R_1$ of H:TiO$_2$ based device decreases from 484 to 170 Ω compared with the untreated sample, demonstrating that the electron transport and extraction become more efficient at the ETL/perovskite interface after hydrogenation. To further confirm this result, steady-state photoluminescence (PL) was performed to investigate the electron transport process at the ETL/perovskite interface. Fig. 8b shows the PL of FTO/TiO$_2$/MAPbI$_3$ and FTO/H:TiO$_2$/MAPbI$_3$. The emission peak for both samples is observed at around 790 nm consistent with the previous study. The peak quenching effect for H:TiO$_2$ based device is more serious than the reference TiO$_2$, implying more effective electron transfer at the H:TiO$_2$/perovskite interface. The $R_{rec}$ is inversely proportional to the recombination rate in PSCs. It is worthy to note that the values of $R_{rec}$ increase distinctly from 731 to 2140 Ω. Therefore, the recombination rates are reduced by hydrogenating the TiO$_2$. Furthermore, the EIS of PSCs based on TiO$_2$ hydrogenated at different temperatures was studied under the light illumination (Fig. S1) and the corresponding values of $R_s$, $R_1$ and $R_{rec}$ are listed in Table S1. Increasing the hydrogenated temperature, the values of $R_s$, $R_1$ decrease and $R_{rec}$ increase gradually, because the higher temperature makes the hydrogenation more efficient, except for the H:TiO$_2$ (500 °C) based devices because of the damaged FTO substrates at this temperature. Based on the above analysis, we propose that the facile hydrogen treatment of TiO$_2$ ETLs is an efficient route to obtain a more efficient charge transport and a lower recombination rate in planar perovskite solar cells.

![Nyquist plots](image)

**Fig. 8.** Nyquist plots of (a) H:TiO$_2$ and reference TiO$_2$ based PSCs measured under AM 1.5G illumination. (b) PL spectra of the pristine perovskite films deposited on TiO$_2$ and H:TiO$_2$ coated FTO substrates.

<table>
<thead>
<tr>
<th>Devices</th>
<th>$R_s$ (Ω)</th>
<th>$R_1$ (Ω)</th>
<th>$R_{rec}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H:TiO$_2$</td>
<td>16.1</td>
<td>170</td>
<td>2140</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>54</td>
<td>484</td>
<td>731</td>
</tr>
</tbody>
</table>

**Table 2.** Summary of EIS parameters of H:TiO$_2$ (450 °C) and reference TiO$_2$ devices.

**Conclusions**

In summary, we have demonstrated a new hydrogenation method to treat the TiO$_2$ ETLs for enhancing the performance of planar PSCs. A champion PCE of 13.15% is achieved at the optimum hydrogenated temperature (450 °C) compared with 9.45% for the reference TiO$_2$ based device. The enhanced performance after hydrogenation is attributed to more efficient charge extraction and lower recombination rates existed at the ETL/perovskite interface, which is related to the raised Fermi level and conductivity of TiO$_2$. Our results open a new and promising method to engineer the ETL/perovskite interface and improved performance can be manipulated from the point of interface energy band engineering.
Acknowledgments

This research was supported by the National Natural Science Foundation of China (51772197, 51422206, 51372159), 1000 Youth Talents Plan, Key University Science Research Project of Jiangsu Province (17KJA430013), 333 High-level Talents Cultivation Project of Jiangsu Province, Six Talents Peak Project of Jiangsu Province, Distinguished Young Scholars Foundation by Jiangsu Science and Technology Committee (BK20140009), and Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

References

8. Dong, Q.; Fang, Y.; Shao, Y.; Mulligan, P.; Qiu, J.; Cao, L.; Huang, J.; Science 2015, 347, 967.
Conjugate-like addition of soft nucleophiles to 8-alkenylBODIPYs

Enrique Alvarado-Martinez¹, Eduardo Peña-Cabrera¹*

¹Departamento de Química. Universidad de Guanajuato. Noria Alta S/N. Guanajuato, Gto. 36050, Mexico

DOI: 10.5185/amlett.2018.1859
www.vbripress.com/aml

Abstract

Meso-phenylethenylBODIPY 8 was prepared using the Liebeskind-Srogl cross-coupling reaction. The reactivity of 8 was evaluated in the addition of soft nucleophiles observing that, in all the cases studied, the addition took place exclusively at the β-alkene position with good chemical yields under mild conditions. While the starting BODIPY 8 was non-emissive, all of the adducts were highly fluorescent in MeOH, except for meso-coumarinBODIPY 11. However, when the fluorescence of 11 was measured in EtOAc, a 41-fold increase was observed. This behaviour was explained in terms of a photoinduced electron-transfer phenomenon. Copyright © 2018 VBRI Press.

Keywords: BODIPY, meso-alkenylBODIPY, conjugate addition, fluorescence

Introduction

Borondipyromethenes (BODIPYs) 1,[1] are a type of fascinating small molecules.

They possess several chemical and photophysical[2] properties that render them amenable for numerous applications.[3][4] In addition to having narrow absorption and emission bands, some have high quantum yields (Φ), and excellent solubility in most organic solvents. Moreover, there are many chemical transformations that can be carried out at the different BODIPY positions thereby controlling not only the emission properties, but also their solubility, even in water. The typical preparation involved and acid-catalyzed condensation of pyrrole with an aromatic aldehyde, followed by DDQ oxidation of the intermediate dipyrromethane, and finally, treatment of the resulting dipyrin with BF₃·OEt₂ in the presence of triethylamine.[5] In 2006, Biellmann et al.[6] reported the synthesis, photophysical properties, and preliminary reactivity of 8-methylthioBODIPY 2. Over the last ten years, our group has demonstrated that such compound is a privileged building block. We have shown that 2 engages in completely new modes of reaction through which novel derivatives, with previously unknown properties, have been prepared. Thus, BODIPY 2 can react with: boronic acids, organostannanes, organozinc derivatives, alcohols, phenols, 1,3-dicarbonyl compounds, amines, phosphines, carbohydrates, polyarylamines [7].

Using the so-called Liebeskind-Srogl cross-coupling reaction,[8] we reported the preparation of a family of 8-alkenylBODIPYs (eq. 1).[9]

These compounds have interesting optical properties. When there is a Csp² directly connected to the 8-position, the chromophore is non-emissive, however, when there is a Csp³ at the same position, the product displays very highly intense fluorescence (Fig. 1).

© 2018 VBRI Press
We reasoned that the double bond at the 8-position of the BODIPY core would behave as an activated double bond, just like that of an α,β-unsaturated ketone (Fig. 2).

Knowing that there are many biologically important nucleophiles, we set out to investigate the addition of soft nucleophiles to the β-position of 8-alkenylBODIPYs. It was also anticipated that, upon addition, the initially non-emissive chromophores, would display high fluorescence.

Experimental

General Methods. 1H and 13C NMR spectra were recorded on a 200 or 500 MHz spectrometers in deuteriochloroform (CDCl3) or (CD3)2CO with either tetramethylysilane (TMS) (0.00 ppm 1H, 0.00 ppm 13C), chloroform (7.26 ppm 1H, 77.16 ppm 13C) or acetone (2.17 ppm 1H, 29.840 ppm or 206.260 ppm) as internal reference. Data are reported in the following order: chemical shift in ppm, multiplicities (br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), exch (exchangeable), app (apparent)), coupling constants, J (Hz), and integration. IR peaks are reported (cm–1) with the following relative intensities: s (strong, 67%), and w (weak 20–40%).

8-Methylthiobodipy, [6] and CuTC,[10] were prepared according to the literature procedures. The other reactants, ligands, and catalysts were commercially available.

Synthesis of S, S-didodecyl propanebis(thioate)

![Synthesis of S, S-didodecyl propanebis(thioate)](image)

By adaption of a procedure by Fukuyama et al.,[11] to a solution of malonic acid (120.7 mg, 1.1600 mmol, 1.00 equiv.) in CH2Cl2 (3.0 mL) was added oxalyl chloride (200 µL, 2.3319 mmol; 2.01 equiv.) and DMF (9 µL, 0.1160 mmol, 10 mol%). The solution was stirred for 30 min at r.t., and to this solution was added 1-dodecanethiol (556 µL, 3.2000 mmol, 2 equiv.). After stirring for 4 h at r.t., the reaction mixture was adsorbed on SiO2-gel. After flash-chromatography (SiO2-gel, 3:97 EtOAc/hexanes) purification, the thiol ester as a colorless oil (1.0786 mmol, 510 mg); yield = 93%; TLC (3:97 EtOAc/hexanes).

BODIPY 8. According to procedure reported in the literature,[9] an oven-dry Schlenk tube, equipped with a stir bar, was charged with trans-2-Phenylvinylboronic acid (1.2600 mmol, 186.5 mg, 3 equiv.), 8-Methylthiobodipy (0.4200 mmol, 100 mg, 1 equiv.) and dry THF (4.2 mL) under N2. The stirred solution was sparged with N2 for 10 min, whereupon Copper(I) thiophene-2-carboxylate (1.6600 mmol, 240.3 mg, 3 equiv), Pd2(dba)3 (0.0105 mmol, 9.6 mg, 2.5 mol%), and Tri(2-furyl)phosphine (0.0315 mmol, 7.3 mg, 7.5 mol%) were added under N2. The reaction mixture was immersed into a pre-heated oil bath at 55 °C. After 1 h, the reaction mixture was allowed to reach room temperature and was adsorbed on SiO2-gel. After flash-chromatography (SiO2-gel, 1:4 EtOAc/hexanes) purification, compound 1 was obtained as a cherry solid (0.3400 mmol, 100 mg); yield = 80%; 1H NMR (300 MHz, CDCl3): 3.85 (s, 2H), 7.61–7.75 (m, 2H), 7.44-7.41 (m, 5H), 7.32 (d, J = 4Hz, 2H), 6.52 (d, J = 3Hz, 2H); 13C NMR (75 MHz, CDCl3) δ 144.80, 143.84, 143.07, 135.66, 133.95, 130.63, 129.26, 128.39, 128.09, 121.24, 117.97.

General Procedure for Synthesis of Michael-adducts.

In a bottom flask, equipped with a stir bar, was charged with I (0.0680 mmol, 20 mg, 1 equiv.), the corresponding Michael donor (5 equiv.) and 2.3 mL of CH2CN. Next, Triethylamine (5 equiv., except for KCN) was added to the solution and the mixture was stirred to room temperature. After TLC showed that the reaction went to completion, 5 mL of H2O were added, the organic layer was extracted with EtOAc (3 x 10 mL), the organic phases were combined and washed with brine (2×10 mL). After, the organic phase was dried over MgSO4 anhydrous to be filtered and concentrated in vacuo. The residue was re-dissolved in EtOAc and was adsorbed on SiO2-gel. After flash-chromatography (SiO2-gel, EtOAc/hexanes gradient) purification, Michael adducts were obtained as colored solids. For purposes of characterization, the solid product was crystallized from CH2Cl2/petroleum ether.
Research Article 2018, 9(6), 426-431

Adapt 9. According to (GP): 1 (0.0680 mmol, 20 mg, 1 equiv.). Acetylacetone (0.3400 mmol, 35 µL, 5 equiv.) and 2.3 mL of CH3CN. Next, Triethylamine (0.3400 mmol, 47 µL, 5 equiv.). The product was isolated as an orange solid (0.0406 mmol, 16.0 mg); yield = 60%; TLC (1:1 EtOAc/Hexanes Rf = 0.4); mp = 203 - 205 °C; IR (KBr, cm⁻¹): 1699 (m), 1572 (m), 1413 (w), 1393 (m), 1359 (w), 1263 (m), 1193 (w), 1116 (m), 1083 (m), 950 (w); 1H NMR (200 MHz, CDCl3) δ 7.75 (s, 2H), 7.20 - 7.05 (m, 5H), 6.98 - 6.93 (m, 2H), 6.39 (dd, J = 4.1 Hz, J = 1.4 Hz, 2H), 4.44 (d, J = 11.6 Hz, 1H), 3.96 (td, J = 11.2 Hz, J = 3.5 Hz, 1H), 3.24 (dd, J = 12.0 Hz, J = 3.5 Hz, 1H), 2.72 (dd, J = 11.9 Hz, J = 11.0 Hz, 1H), 2.37 (s, 3H), 1.83 (s, 3H); 13C NMR (50 MHz, CDCl3) δ 203.20, 201.96, 146.27, 143.95, 138.53, 135.90, 129.29, 128.98, 128.19, 128.15, 118.31, 75.56, 48.42, 37.31, 31.34, 28.15; HRMS (ESI+): m/z calcd. for C29H23B3F2N2O4Na [M+Na]^+ 479.1534; found 479.1535.

Adapt 10. According to (GP): 1 (0.0680 mmol, 20 mg, 1 equiv.). Dimethyl malonate (0.3400 mmol, 47 µL, 5 equiv.) and 2.3 mL of CH3CN. Next, Triethylamine (0.3400 mmol, 48 µL, 5 equiv.). The product was isolated as an orange solid (0.0340 mmol, 14.5 mg); yield = 50%; TLC (1:2 EtOAc/Hexanes Rf = 0.3); mp = 195 - 196 °C; IR (KBr, cm⁻¹): 1752 (w), 1731 (m), 1566 (m), 1413 (w), 1413 (w), 1392 (m), 1262 (m), 1232 (m), 1114 (m), 1083 (m), 953 (w); 1H NMR (300 MHz, CDCl3) δ 7.74 (s, 2H), 7.19 - 7.10 (m, 5H), 7.03 - 7.00 (m, 2H), 6.39 (dd, J = 4.2 Hz, J = 1.6 Hz, 2H), 3.99 (d, J = 10.7 Hz, 1H), 3.91 - 3.81 (m, 4H), 3.52 (dd, J = 12.3 Hz, J = 3.7 Hz, 1H), 3.43 (s, 3H); 2.93 (dd, J = 12.2 Hz, J = 10.8 Hz, 1H); 13C NMR (50 MHz, CDCl3) δ 168.96, 167.59, 146.55, 143.71, 138.47, 135.72, 128.96, 128.75, 127.89, 127.83, 118.10, 118.07, 57.14, 53.22, 52.74, 48.95, 36.40; HRMS (ESI+): m/z calcd. for C29H23B3F2N2O4Na [M+Na]^+ 449.1459; found 449.1471.

Adduct 11. According to (GP): 1 (0.0680 mmol, 20 mg, 1 equiv.), 4-Hydroxycoumarin (0.1700 mmol, 27.6 mg, 2.5 equiv.) and 2.3 mL of CH3CN. Next, Triethylamine (0.1700 mmol, 24 µL, 2.5 equiv.). The product was isolated as an orange solid (0.0548 mmol, 25 mg); yield = 81%; TLC (2:1 EtOAc/Hexanes Rf = 0.7); mp = 213 - 215 °C; IR (KBr, cm⁻¹): 3306 (m), 2924 (m), 1681 47 (i), 1622 (i), 1568 (i), 1411 (m), 1394 (i), 1263 (i), 1215 (m), 1200 (m), 1116 (i), 1082 (i), 1069 (i), 955 (m), 754 (m); 1H NMR (500 MHz, Acetone) δ 7.94 (d, J = 8.0 Hz, 1H), 7.81 (s, 2H), 7.62 - 7.54 (m, 3H), 7.47 (d, J = 3.8 Hz, 2H), 7.34 - 7.18 (m, 5H), 6.52 (d, J = 4.1 Hz, 2H), 5.09 - 5.01 (m, 1H), 4.24 - 3.89 (m, 2H); 13C NMR (126 MHz, Acetone) δ 162.53, 161.60, 153.74, 150.82, 150.79, 143.47, 143.18, 136.71, 136.69, 132.94, 129.71, 129.01, 128.93, 127.47, 124.73, 123.80, 118.73, 118.71, 117.23, 116.66, 108.42, 108.40, 45.00, 33.40; HRMS (ESI+): m/z calcd. for C29H23B3F2N2O4Na [M+Na]^+ 479.1534; found 479.1535.

Adduct 12. According to (GP): 1 (0.0680 mmol, 20 mg, 1 equiv.), Potassium cyanide (0.1020 mmol, 6.7 mg, 1.5 equiv.). The product was isolated as an orange solid (0.0591 mmol, 19.0 mg); yield = 87%; 1H NMR (200 MHz, CDCl3): δ 7.88 (s, 2H), 7.42 - 7.27 (m, 5H), 7.09 (d, J = 4 Hz, 2H), 6.51 (d, J = 4Hz, 2H), 4.18 - 4.11 (m, 1H), 3.60 - 3.50 (m, 1H), 3.37 - 3.27 (m, 1H); 13C NMR (50 MHz, CDCl3) δ 145.39, 142.17, 135.51, 134.38, 129.80, 129.38, 128.60, 127.58, 119.57, 119.15, 40.30, 37.28.[12]

Adduct 13. According to (GP): 1 (0.0680 mmol, 20 mg, 1 equiv.), S.S-didodecyl propanebis(tio)ate (0.1700 mmol, 80.4 mg, 2.5 equiv.) and 2.3 mL of CH3CN. Next, Triethylamine (0.1700 mmol, 24 µL, 5 equiv.). The product was isolated as a red solid (0.0340 mmol, 14.5 mg); yield = 88%; TLC (1.2 EtOAc/Hexanes Rf = 0.3); mp = 190 - 191 °C; IR (KBr, cm⁻¹): 2922 (s), 2852 (s), 1684 (s), 1572 (s), 1485 (w), 1468 (w), 1455 (w), 1412 (m), 1398 (m), 1358 (w), 1266 (m), 1232 (w), 1197 (m), 1124 (s), 1090 (s), 1037 (m), 953 (m), 774 (w), 765 (w), 755 (w); HRMS (ESI+): m/z calcd. for C29H23B3F2N2O4Na [M+Na]^+ 449.1459; found 449.1471.
Results and discussion

The set of soft pro-nucleophiles chosen for this work are shown in Fig. 3.

![Chemical structures](image)

Fig. 3. Pro-nucleophiles studied

BODIPY 8 was prepared according to the literature procedure (eq. 2).[9]

![Chemical reaction](image)

With BODIPY 8 available, we proceeded to carry out the addition of nucleophiles 3-7. The results are illustrated in Table 1.

The conjugate-like nucleophilic addition took place smoothly at rt to yield the expected adducts 9-13. Our hypothesis borne out, in all the cases studied, the nucleophile added exclusively to the β-position of BODIPY 8. The chemical yields ranged from medium to good, with excellent reaction times. The regiochemistry of the addition can be explained in terms of the resonance stabilization by the BODIPY core, of the negative charge that develops on the α-C atom, after the addition takes place (Scheme 1).

Table 1. Conjugate-like addition of soft nucleophiles on 8-phenylethenyLBODIPY 8.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Nu-H</th>
<th>Product/ % yield</th>
<th>Reaction time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>1 h</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>1.5 h</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>15 min</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>1 h&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>30 min</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: BODIPY 8 (1 equiv.), Nu-H (5 equiv), Et₃N (5 equiv).

<sup>b</sup>In the case of the addition of KCN (1.5 equiv), no Et₃N was added.

Scheme 1. Resonance stabilization of the negative charge on the α-C atom upon nucleophilic addition.
The photophysical properties of the products are shown in Table 2.

Table 2. Photophysical Properties for all the Michael-adducts.\(^*\)

<table>
<thead>
<tr>
<th>Comp</th>
<th>(\lambda_{ab}) (nm)</th>
<th>(\lambda_{em}) (nm)</th>
<th>(\Phi_F)</th>
<th>Stokes shift/ (cm(^{-1}))</th>
<th>(\log \varepsilon_{max}) (M(^{-1})cm(^{1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>497</td>
<td>508</td>
<td>80.9</td>
<td>436</td>
<td>4.95</td>
</tr>
<tr>
<td>10</td>
<td>497</td>
<td>508</td>
<td>80.7</td>
<td>436</td>
<td>4.94</td>
</tr>
<tr>
<td>11</td>
<td>944(^{b})</td>
<td>503</td>
<td>1.6</td>
<td>362</td>
<td>4.93</td>
</tr>
<tr>
<td></td>
<td>494(^{b})</td>
<td>509</td>
<td>65.6</td>
<td>596</td>
<td>5.47</td>
</tr>
<tr>
<td>12</td>
<td>502</td>
<td>514</td>
<td>74.9</td>
<td>465</td>
<td>4.99</td>
</tr>
<tr>
<td>13</td>
<td>498</td>
<td>509</td>
<td>82.9</td>
<td>434</td>
<td>5.22</td>
</tr>
<tr>
<td>1</td>
<td>498</td>
<td>507</td>
<td>80.8(^{13})</td>
<td>356</td>
<td>5.02</td>
</tr>
<tr>
<td>8</td>
<td>410, 524</td>
<td>----</td>
<td>-----</td>
<td>5306</td>
<td>----</td>
</tr>
<tr>
<td></td>
<td>513</td>
<td></td>
<td></td>
<td></td>
<td>(\Phi_F)</td>
</tr>
</tbody>
</table>

\(^{a}\)Measured in MeOH at a concentration of 1x10\(^{-6}\) M. \(\lambda_{ab}\) = absorption maximum, \(\lambda_{em}\) = emission maximum, \(\Phi_F\) = fluorescence quantum yield estimated by using parent borondipyromethene 1 system (\(\Phi_F\) = 80.8\%) in EtOAc as the standard.[13]

\(^{b}\)Measured in EtOAc

Both the absorption and emission spectra of 8, show significant differences from those of the adducts 9-13. The UV-Vis spectrum of 8 shows two absorption bands at 410 and 513 nm, whereas that of the adducts show a main band at around 500 nm. However, the absorption spectra of products 9-13 do not display major differences among them (Figure S1). For example, adducts 9,10 and 13, having a 1,3-dicarbonyl substituent (diketone, diester, and dithioester, respectively) at the BODIPY 8-position, present optical properties practically identical (Table 2). This seems to indicate that none of the 1,3-dicarbonyl substituents affect the optical properties of the BODIPY core. The quantum yield (\(\Phi\)) of adducts 9, 10, and 13 is high and comparable to that of the parent BODIPY 1 (80.8\%).

To determine the influence of the different meso-substituents, the absorption and emission spectra of 10, 11 and 12 were compared to those of the parent BODIPY [13] (Figure S2). The absorption bands of adducts 10 and 11 present a hypsochromic shift of 1 and 3 nm, respectively, with respect to the parent BODIPY 1, whereas 12 presents a bathochromic shift of 4 nm.

The emission band of 10 presents a bathochromic shift of 1 nm. On the other hand, 11 presents a un hypsochromic shift of 4 nm when measured in MeOH, but, when measured in EtOAc, a bathochromic shift of 2 nm is observed. Finally, 12 shows a bathochromic shift of 7 nm with respect to the emission band of 1.

Noteworthy is the observation that the quantum yield of 11 in EtOAc is 41-fold larger than when measured in MeOH. The reduction in the fluorescence may occur via a photoinduced electron-transfer (PET) process. It is reported that in PET three-component systems (fluorophore-spacer-receptor), the receptor interaction with H\(^+\) inhibits the PET phenomenon (Figure S3).[14] In analogy, it proposed that the diminished fluorescent emission of 11 may occur via the mechanism shown in Fig. 4. In the present case, the PET may arise when the coumarin hydroxyl group forms a hydrogen bond with MeOH thereby developing a partial positive charge.

**Conclusion**

Nucceophilic addition of five soft nucceophiles was carried out on 8-phenylethenylBODIPY 8. This reaction took place smoothly at rt with medium to high chemical yields, and with complete regioselectivity for the β-alkenyl position. We have demonstrated that indeed, such position is electrophilic, similar to that of an α,β-unsaturated carbonyl compound. As expected, all the adducts, except for 11, were highly fluorescent in MeOH. However, when measured in EtOAc, the quantum yield of 11 increased 41-fold.

Finally, it was concluded that neither 1,3-dicarbonyl nor CN\(^{-}\) moieties perturb the optical properties of the BODIPY core.

**Acknowledgements**

This work was supported by CONACyT (grants 253623, 123732). E. A.-M. thanks CONACyT for graduate scholarship. We thank Cuantico de Mexico (www.cuantico.mx) for the kind donation of 8-methylthioBODIPY.

**Author’s contributions**

Conceived the plan: E. P.-C.; Performed the experiments: E. A.-M.; Data analysis: E. P.-C., E. A.-M; Wrote the paper: E. P.-C., E. A.-M.; Authors have no competing financial interests.

**Supporting information**

Supporting information are available from VBRI Press.
References

Microporous carbon spheres modified with EDA used as carbon dioxide sorbents

Daniel Sibera¹, Joanna Sreńsek-Nazzal¹, Waldemar A. Morawski¹, Beata Michalkiewicz¹, Jarosław Serafin¹, Rafal J. Wróbel¹, Urszula Narkiewicz¹

¹Institute of Chemical and Environment Engineering, Faculty of Chemical Engineering, West Pomeranian University of Technology, 70-322 Szczecin, Pułaskiego 10, Poland

DOI: 10.5185/amlett.2018.1872
www.vbripress.com/aml

Abstract

Carbon spheres for CO₂ adsorption were prepared using a modified Stöber method in a microwave assisted solvothermal reactor. For comparison purposes, the same preparation procedure was applied in an autoclave. A starting mixture composed of water-ethanol, ammonia water, EDA, resorcinol, potassium oxalate and formaldehyde, was stirred for 24 h at room temperature and then subjected to a pressure treatment in an autoclave (24 h at 100°C) or in a microwave solvothermal reactor (15 min under 2 MPa). The material with EDA prepared in the solvothermal reactor exhibited high CO₂ adsorption capacities, up to 5 mmol/g under ambient conditions and 6.6 mmol/g at 0°C. Copyright © 2018 VBRI Press.

Keywords: Carbon spheres, CO₂ capture, EDA

Introduction

Carbon is one of the most vital elements, both for life and for industry. A perfect carbon cycle occurring in nature has been recently interfered with intense industrial development, associated with an increase of carbon dioxide concentration in atmosphere, which has risen from 280 ppm before the industrial revolution to 390 ppm in 2010. The increase has contributed to the greenhouse effect and resulting climate changes [1]. Then, there is a challenge of a crucial importance to decrease the anthropogenic emissions of carbon dioxide and, if possible, to transform them into useful chemicals. The bottle-neck is the high thermodynamic stability of CO₂ molecule, then new processes are needed to resolve the problem. The processes intensively investigated are catalytic hydrogenation and methane dry reforming.

Polanski et al. [2] successfully performed a low temperature carbon dioxide methanation, using unalloyed nano-Ru/Ni catalyst supported on silica and reached an excellent efficiency at 200°C only with 100% conversion. Methane dry reforming can successfully occurs on nickel oxide nanoparticles supported on mesoporous silica [3]. Both catalytic processes are still at the laboratory scale due to the complexity of the reaction system and coking effect. The initial step before any carbon dioxide transformation or storage is its separation from exhaust gases. The existing processes used for PCCC (post combustion CO₂ capture) and based mainly on absorption in liquids (as amines, potassium carbonate or methanol) are costly, inefficient and may have inherent environmental problems. There is a need to develop new PCCC technologies, more cost and energy efficient, and friendly for environment. Solid sorbents can be used in such processes, instead of traditional liquids. Carbon spheres can be applied as such a solid sorbent, which was described for the first time by the team of Inagaki [4,5,6], and next by Liu [7] and Jaroniec [8,9,10]. To produce spherical carbon materials Liu et al. applied the method of Stöber, applying a treatment of resorcinol and formalin in an autoclave followed by carbonisation under nitrogen atmosphere. The research group of Jaroniec improved the method involving potassium oxalate as one of reactants and, in some cases, using ethylenediamine as an additional modifier [9].

All the produced materials were obtained in an autoclave using an one-stage process and had a high specific surface area (up to 2900 m²/g), as well as a high adsorption of CO₂ at 0°C (up to 6.6 mmol/g).

We have modified the preparation method of spherical carbon materials for the adsorption of CO₂ using a microwave assisted solvothermal reactor instead of an autoclave, which was patented [11] and described in our previous paper [12]. In the present paper a modification with ethylenediamine (also conducted in the microwave assisted solvothermal reactor) is presented.

Experimental

Materials/ chemicals details

The following reactants were applied to produce carbon spheres: resorcinol, ethanol, ammonium hydroxide, potassium oxalate, formaldehyde, ethylenediamine.
Material synthesis / reactions

Spherical carbon materials were prepared in a following way: 0.60 g of resorcinol was added to the mixture consisting of 60 ml of water, 24 ml of ethanol, and 0.30 ml of ammonium hydroxide under magnetic stirring for 10 min at room temperature. Next, 4.95 g of K$_2$C$_2$O$_4$·H$_2$O was added to the synthesis mixture under stirring for 30 min to achieve the potassium-carbon weight ratio equal to 7:1.

Next, ethylenediamine (0.2 ml or 1 ml) was added to the mixture. Afterwards, 0.9 ml of formaldehyde was added and the mixture was stirred for 24 h and then subjected to a treatment in the solvothermal microwave assisted reactor ERTEC MAGNUM II (pressure 1–3 MPa) for 15 min.

Subsequently, the solution was transferred to a Petri dish and dried at 80°C for 2 days. The dried materials were carbonised in argon atmosphere at 350°C for 2 h (1°C min$^{-1}$ heating rate); then, temperature was raised to 700°C, 750°C and 800°C (with a heating rate of 1°C min$^{-1}$) and kept at the highest temperature for 2 h. The carbonised materials were washed with deionised water until pH~7 was reached, to remove salt residues. Finally, the materials were dried at 80°C for 24 h.

Characterizations / device fabrications / response measurements

The helium density of the prepared samples was measured under helium using a Micro-Ultrapyc 1200e equipment at the pressure of 17 psi. The samples were purged with helium for 20 min.

The textural properties of the carbon spheres were determined by physical adsorption of N$_2$ at -196°C using a Quadrasorb apparatus (Quantachrome Instruments).

Specific surface area was assessed using multi-point BET (Brunauer–Emmet–Teller equation) [13] method using the N$_2$ adsorption isotherm over a relative pressure (P/P$_0$) in the range of 0.05–0.20. The total pore volume, V$_p$, including both the micropores and the mesopores, was estimated by converting the amount of N$_2$ gas adsorbed at a relative pressure of 0.99 to the liquid volume of the adsorbate (N$_2$). Micropore volume (< 2 nm), V$_\text{mic}$, was determined using the Density Functional Theory (DFT).

CO$_2$ adsorption isotherms were measured up to 1 bar at 0°C and 25°C using Quadrasorb volumetric apparatus. As in the previous case, samples before measurements were degassed under vacuum at 250°C for 16 h.

Carbon dioxide adsorption isotherms at 0°C and nitrogen adsorption isotherms at 0°C were determined using a Quadrasorb volumetric apparatus (Quantachrome Instruments).

Prior to each measurement all samples were degassed under vacuum at 250°C for 16 h.

Results and discussion

Fig. 1. shows low-temperature nitrogen adsorption–desorption isotherms for samples produced in the microwave assisted solvothermal reactor.

The two of adsorption isotherms in Fig. 1 (samples R+F600C and R+F600C_0,2mlEDA) are of Type I according to the IUPAC classification, which is characteristic for microporous materials. On the contrary, adsorption isotherm of the sample R+F600C_1ml EDA corresponds to Type IV, which according to the IUPAC classification is characteristic for mesoporous materials. Then, higher volume of EDA applied can block smaller pores.

![Fig. 2.](image)

Fig. 2. shows low-temperature nitrogen adsorption–desorption isotherms for samples produced in the autoclave.

![Table 1.](image)

Table 1. Structural parameters of the spherical carbon materials samples obtained in autoclave and in solvothermal reactor.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S$_\text{BET}$ [m$^2$/g]</th>
<th>Total Pore Vol. [cm$^3$/g]</th>
<th>Micro-pore Vol. [cm$^3$/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Autoclave</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R+F600C</td>
<td>594</td>
<td>0.330</td>
<td>0.276</td>
</tr>
<tr>
<td>R+F600C_0,2mlEDA</td>
<td>761</td>
<td>0.352</td>
<td>0.269</td>
</tr>
<tr>
<td>R+F600C_1mlEDA</td>
<td>957</td>
<td>0.684</td>
<td>0.326</td>
</tr>
<tr>
<td>Solvothermal reactor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R+F600C_0,2mlEDA_MW</td>
<td>954</td>
<td>0.431</td>
<td>0.339</td>
</tr>
<tr>
<td>R+F600C_1mlEDA_MW</td>
<td>1024</td>
<td>0.495</td>
<td>0.358</td>
</tr>
</tbody>
</table>
According to the results presented in Table 1, an addition of ethylenediamine resulted in an increase of the specific surface area and of the micropore volume. In the case of the sample with addition of 1 ml EDA obtained in the autoclave a significant increase of total pore volume can be observed, due to the presence of mesopores.

Spherical carbon materials produced in the solvothermal reactor have higher specific surface area than those produced in the autoclave. The specific surface area $S_BET$ of the sample produced with 1 ml of EDA in the solvothermal reactor (R+F600C_1mlEDA_MW) increased to 1024 m$^2$/g, although the total pore volume for the sample decreased (compared with the sample from the autoclave). Nevertheless, an increase of micropore volume can be observed for this sample, and these pores are essential for carbon dioxide adsorption.

The pore distribution determined using DFT method is shown in Fig.3.

It can be seen that the obtained spherical carbon materials contain both micropores (pores with diameter below 2 nm) and mesopores (pores with diameter in the range between 2 and 50 nm), which is in accordance with measured nitrogen isotherms.

The produced materials demonstrated a high adsorption capacity of carbon dioxide, due to the high specific surface area and high micropore volume.

The results of the measurements of carbon dioxide adsorption capacity are presented in Fig. 5, 6 and 7.
As it can be seen in Fig. 5, an addition of EDA does not affect the adsorption capacity on the samples produced in the autoclave, which at the level of 5 mmol/g. A significant increase can be observed for the samples produced in the microwave assisted solvothermal reactor. The best result of 6.6 mmol/g was obtained for the sample containing 0.2 ml of EDA. Although an increase of EDA content to 1 ml resulted in a drop of CO₂ adsorption capacity, it was still very high. Even the increase of adsorption temperature to 25 °C did not result in a significant adsorption capacity, which is very promising for future applications.

Conclusions
Application of the microwave assisted solvothermal reactor for preparation of spherical carbon materials delivered better results than the use of the autoclave. Modification of the material with ethylenediamine resulted in an improvement of CO₂ adsorption properties, up to 5 mmol/g under ambient conditions and 6.6 mmol/g at 0 °C.

Author’s contributions
Conceived the plan: AWM, DS, UN; Performed the experiments: DS, JSN, BM, JS, RJW; Data analysis: DS, JSN, UN; Wrote the paper: UN, DS. Authors have no competing financial interests.

References
8. Ludwinowicz J.; Jaroniec M.; Carbon, 2015, 82, 297.

Fig. 7. Carbon dioxide adsorption measured at 25 °C on the samples produced in the solvothermal reactor.
Synthesis of rGO via UV-assisted photocatalytic reduction of graphene oxide

Rui Liu1, Wein-Duo Yang2, Qiao Ying Jie3*, Ying Jin Song1, Yan-Ru Li2

1School of Science, Harbin University of Commerce, Harbin, 150076, China
2Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 807, Taiwan
3College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China

DOI: 10.5185/amlett.2018.1884
www.vbripress.com/aml

Abstract

We perform a novel strategy for the synthesis of reduced graphene oxide (rGO) with an 18 W UV-assisted photocatalytic reduction method. The surface morphology and internal structure of the obtained rGO were identified by Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). The rGO electrode materials have 2-6 layers graphene layers with a thickness of 1.1 nm to 2.2 nm after the photocatalytic reduction for 10 h. The rGO shows a superb capacitance of 250.41 F g⁻¹ with obvious triangles in the electrochemical charge-discharge analysis, which indicates good reversibility between the graphene oxide and reduced graphene oxide. This research may provide new insights that contribute to resolving the capacity issues of lithium batteries. Copyright © 2018 VBRI Press.

Keywords:

Introduction

Graphene has drawn significant attention due to its two-dimensional single crystal carbon atom layer composed of hybridized sp² orbitals. Graphene exhibits excellent electrical properties, good chemical stability and a high specific surface area. Recently, various methods to prepare reduced graphene oxide have been studied, such as the chemical reduction method, the high temperature reduction method, the solvothermal reduction route, and the electrochemical reduction method. However, graphene has an incomplete reduction due to defects and agglomerations using these synthetic methods. To overcome these disadvantages, many efforts have been undertaken to develop proper synthetic methods. Several works have used the photocatalytic reduction method to synthesize reduced graphene oxide. The photocatalytic reduction method is environmental friendly, has a high efficiency, low cost and tunable reduction degree. The photocatalytic methodology can avoid the re-aggregation of graphene to a certain extent, while producing a porous structure to obtain a high surface area and high energy density.

In this work, we use the photocatalytic reduction method to synthesize the rGO electrode material. The microstructure of the samples is investigated by Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). Furthermore, the electrochemical performance of the rGO electrode material, which shows a superb capacitance, is also investigated. Therefore, this study applied the photocatalytic reduction method for preparing graphene materials and explored its ultra-capacitance applications in lithium batteries.

Experimental

GO was synthesized by the improved Hummer’s method. Firstly, sulfuric acid and phosphoric acid in a volume ratio of 9:1 were mixed and 3 g of graphite was added to the mixture and stirred for 1 h. Secondly, 12 g of potassium permanganate (KMnO₄) was added with a stirring rate of 600 rpm for 2 h at 35°C. Thirdly, the reaction temperature was increased to 50°C with agitation for 12 h. Lastly, H₂O₂ was added to obtain a golden-colored solution. After centrifugation, acid washing, and water washing to neutral, the brownish-yellow GO was prepared with vacuum drying at 50°C for 24 h.

The synthesized GO was added into absolute ethyl alcohol. The solution was ultrasonicated for 30 min under a nitrogen atmosphere and then irradiated with UV-light (254 nm, 18 W, Philips) for different selected times. The temperature was controlled at 40°C and the suspended rGO black solution was washed with water and protected from light sources.

The as-prepared rGO was analyzed by TEM (JEOL, TEM-3010) at an acceleration voltage of 80 kV and by AFM (BRUKER, Dimension Icon).
The rGO, polytetrafluoroethylene as a binder, and a black carbon as a conductive additive at a weight ratio of 8:1:1 were dispersed in 2-propanol. The homogeneous mixture was obtained by stirring for 12 h. The slurry was coated onto graphite paper as a current collector, as previously reported[9].

The electrochemical properties were investigated with a three electrode cell system in a 1 M H₂SO₄ electrolyte by a cyclic voltammetry (CH Instruments, Model 400) method at scan rates of 10 and 75 mVs⁻¹ within the voltage range of -0.5 to 0.5 V.

Results and discussion

Fig. 1(a) shows the AFM images of the rGO electrode material after photocatalytic reduction for 10 h. In theory, the single layer thickness of graphene is approximately 0.35 nm. However, the actual thickness is higher than the theoretical thickness due to existence adsorbates on the surface. Fig 1(a) shows that the surface morphology of the as-prepared rGO has irregular flakes and distinct wrinkles. Moreover, disordered stacks occur on the surface of the samples during the reduction process.

The thickness of the rGO electrode material is between 1.3 nm and 2.0 nm, as shown in Fig. 1(b). Therefore, we can estimate that obtained rGO electrode material contains approximately 2-6 layers.

From the electron diffraction patterns, we can see an obvious halo around the electron diffraction patterns of the as-prepared rGO. However, with careful observation it is found that the tail of the light spots was missing. Upon further analysis, the intensity of the (1100) is stronger than the intensity of the (2110), which reveals that the spots are strong for the monolayer hexagonal structure.

We can observe an obvious halo around the electron diffraction patterns, which may be considered a result of the as-prepared rGO with several layers, and not a single layer. The results agree with the analysis of the AFM.

Fig. 1. AFM images (a) and thickness (b) of rGO electrode material after photocatalytic reduction for 10 h.

Fig. 2 shows TEM images of the as-prepared rGO electrode material after photocatalytic reduction for 10 h. As seen in Fig. 2 (a), the phenomena are likely to cause the graphene to gather and curl to produce folding. The electron diffraction pattern was used to observe the crystal structure and to determine the number of graphene layers. Fig. 2 (b) shows the electron diffraction patterns of the as-obtained rGO electrode material after photocatalytic reduction for 10 h. The spots from the hexagonal ring electron diffraction were observed in the electron diffraction maps of the rGO. However, with careful observation it is found that the tail of the light spots was missing. Upon further analysis, the intensity of the (1100) is stronger than the intensity of the (2110), which reveals that the spots are strong for the monolayer hexagonal structure.

From the electron diffraction patterns, we can see an obvious halo around it. It may be considered as the as-prepared rGO with several layers, not a single layer. The results agree with the analysis of the AFM.

The capacitance (Cᵥ) values of rGO electrode materials can be calculated from the C-V curves according to the following the equation[14]:

\[
cᵥ = \frac{\int \Delta I \, dv}{\nu m \Delta v}
\]

where \(m\) is the mass of the rGO electrode material (mg), \(\nu\) is the scan rate (Vs⁻¹), \(\Delta v\) is the potential window (V) and the integrated area under the C-V curve, and \(I\) is the current (A).

Fig. 2. TEM images (a) and electron diffraction patterns (b) of rGO electrode material after photocatalytic reduction for 10 h.

<table>
<thead>
<tr>
<th>Scan rate (0.01 V s⁻¹)</th>
<th>Capacitance (F g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td></td>
</tr>
<tr>
<td>1 h</td>
<td>74.69</td>
</tr>
<tr>
<td>5 h</td>
<td>221.21</td>
</tr>
<tr>
<td>10 h</td>
<td>189.26</td>
</tr>
<tr>
<td>250.41</td>
<td></td>
</tr>
</tbody>
</table>
Conclusions

In summary, rGO electrode materials have been synthesized by a photocatalytic reduction method. The surface morphology and internal structure were analyzed by TEM and AFM. A more complete reduction reaction was obtained by an increase in the photocatalytic reduction time, which is due to the removal of the oxygen functional groups at the surfaces and edges of the GO. Moreover, increasing the photocatalytic reduction time also increased the degree reduction of the graphene oxide for rGO, resulting in a higher capacitance value. The electron diffraction patterns of the rGO electrode material also revealed that the rGO electrode materials have between 2 and 6 layers of rGO and a thickness of between 1.3 nm and 2.0 nm.

Acknowledgments

The authors would like to express their gratitude to the Ministry of Science and Technology of Taiwan for supporting this research under the grant MOST 103-2221-E-151-055 and the Ph.D. program of Harbin University of Commerce of China (Grant No: 14LG13).

Reference

Synthesis and modelling of nanoparticles for chemical looping reforming

Stefan Andersson1, Paul Inge Dahl1, Stephen A. Shevlin2, Ingeborg-Helene Svenum1, Yngve Larring3, Julian R. Tolchard1, Zheng Xiao Guo2

1 SINTEF Materials and Chemistry, P.O. Box 4760 Torgarden, 7465 Trondheim, Norway
2 Department of Chemistry, University College London, Gower Street, London WC1E 6BT, United Kingdom
3 SINTEF Materials and Chemistry, P.O. Box 124 Blindern, 0134 Oslo, Norway

DOI: 10.5185/amlett.2018.1929
www.vbripress.com/aml

Abstract

Experimental and complementary modelling studies on the potential use of iron oxide nanoparticles in chemical looping reforming processes have been performed. In order to avoid coarsening of the nanoparticles, and thereby loss of reactivity, at relevant process temperatures (700-900°C), the active metal oxide was embedded in an inert support material of lanthanum silicate. Micro reactor tests indicate that partial combustion occurs in reactions of reduced iron oxide with methane instead of pure reforming. Density Functional Theory and kinetic Monte Carlo calculations have been used to support and complement the experiments. The modelling supports efficient reactivity towards exposure of hydrogen, which is also observed experimentally. Reactivity towards methane is only tested for the fully oxidised state, Fe3O4, and not for the reduced oxide, giving results that are complementary to the experiments. Copyright © 2018 VBRI Press.

Keywords: Chemical looping, nanoparticles, synthesis, modelling

Introduction

Chemical looping [1] is an emerging technology for producing electricity, fuels or chemicals with low CO2 emissions. In Chemical Looping Combustion (CLC), dual fluidized beds are often used to circulate the solid oxygen carrier particles, which provide the oxygen for combustion in the fuel reactor. The reduction of the particles in the fuel reactor makes it necessary to circulate oxygen carriers to the other fluidized bed, the air reactor, where the particles are oxidized. Subsequently, they are circulated back to the fuel reactor for another combustion cycle, and so on. The separation of fuel from air has several positive features: the combustion process becomes simpler, the combustion efficiency is in principle higher than for standard power plants, NOx emissions are significantly reduced since nitrogen is not present in the fuel reactor, and CLC generates a sequestration-ready CO2 stream, after condensation of water vapor [1]. However, to achieve the necessary efficiency gains of CLC in practice, efficient oxygen carriers are crucial.

Chemical Looping Reforming (CLR) [1, 2] techniques (see Fig. 1) follow the same basic outline as CLC, but here focus is on the catalytic production of CO and H2, for use in chemical industry, or, in the latter case, as a clean fuel. The CLR process uses less air than CLC, such that only partial oxidation of the oxygen carrier particles is achieved. In CLR, CH4 is reacted with a metal oxide in order to extract individual hydrogen atoms. Individual hydrogen atoms react together in order to form H2, which then desorbs from the surface. In the process the metal oxide is reduced by the extraction of oxygen by reaction with carbon from methane, forming CO. A reduction sequence Fe3O4→Fe2O3→FeO→Fe is then expected. This work concentrates on the Fe-oxides hematite, Fe2O3, and magnetite, Fe3O4, which forms naturally when Fe3O4 is reduced. At elevated temperatures Chemical Looping Combustion might occur instead, where hydrogen and carbon are completely oxidized to form H2O and CO2. The aim of our study is to evaluate the suitability of the different iron oxides for CLR.

Kinetic studies of unsupported iron nanoparticles have revealed improved reactivity, reduced mass resistance and enhanced heat transfer [3]. However, at temperatures above 450°C, particle sintering results in coarsening of the particles (up to µm scale), and the observed benefits disappear. In order to utilize the nanostructured materials it is therefore necessary to endow them with much greater thermal stability. This can be achieved by dispersing the active nano-catalyst within an inert support material, which suppresses coarsening and sintering via physical separation [4, 5]. In effect, a "mechanical caging" mechanism stabilizes the nanoparticles in the mesopores of the support material [6]. Such stabilized nano-composites have been successfully synthesised through reverse emulsion processes [7-8], but these routes are neither cost efficient, environmentally friendly, nor viable for large-scale production. More cost effective and "green" synthesis routes are therefore sought within this work.
In this paper we report on the synthesis, characterization and reactivity tests of nano-structured oxygen carrier particles as well as complementary modelling of the reactivity of iron oxide surfaces. In particular, we present kinetic Monte Carlo modelling results on the detailed kinetics of the CH$_4$ conversion to products as a function of temperature. This has to the best of our knowledge not been previously reported for chemical looping systems.

**Experimental**

*Material synthesis*

Active nanostructured particles embedded in an inert support were obtained by synthesis of a sol-gel of a composition which decomposes to two thermodynamically coexistent phases at high temperature. By forming the material as an atomically dispersed gel, the growth of the two phases can be controlled during gel heating/decomposition. Iron/iron oxide nanoparticles were embedded in a lanthanum silicate (La$_{0.33}$Si$_{6}$O$_{20}$) matrix in this fashion, via a modification of the method of Vojisavljević et al. [13]. Lanthanum acetate, iron nitrate, ethanol and nitric acid are mixed with tetraethyl orthosilicate and heated to form a gel. This was then dried at 60 °C and heated at 230 °C to decompose into an amorphous powder. Upon further heat treatment a composite of lanthanum silicate and iron/iron oxide nanoparticles with a well defined loading (e.g., ~20 wt%) is obtained.

*Characterization and reactivity tests*

The synthesized materials were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Furthermore, micro reactor tests were performed at 700-900°C using 10% CH$_4$ + 3% H$_2$O in argon as the feed gas. Mass spectroscopy was applied to determine the concentrations of the gasses out of the reactor.

*Computational details*

A Density Functional Theory (DFT) approach was taken to model chemistry on metal oxide surfaces. The VASP code was used in all calculations [15-18], with a plane wave cutoff of 520 eV. The projector augmented wave (PAW) method was used to treat the core electrons [19, 20]. All atoms were fully relaxed until the change in force upon ionic displacement was less than 0.01 eV/Å, with the change in energies no greater than 10$^{-5}$ eV. K-point meshes were chosen so that the difference in energies is less than 1 meV. The PBE+$U$ functional is used in all calculations, with the $U$ placed on the d-state of the Fe ions [21]. Literature studies of Fe-oxide materials use several different values for $U$, including 4.0 eV [22-24], 4.2 eV [25], and 5.0 eV [26]. We use a value of $U = 4.2$ eV as this gives a good match with experimental values. The Climbing Image Nudged Elastic Band method was used in order to determine the activation barriers for chemical reaction [27]. Four images were used in kinetics

---

**Fig. 1.** Idealized schematic representation of complete CLR process, involving reduction of the metal oxide under methane to a less oxygen-rich phase. Syngas is outputted from this reactor. Meanwhile, the reduced material is reoxidized in a separate air reactor before being fed back into the fuel reactor.

The available literature on nanostructured oxygen carrier materials mostly considers first-row transition metals, which are then dispersed onto a thermally stabilizing amorphous barium hexaaluminate (BHA) support [4, 5, 7, 9, 10]. BHA as the support material has a high sintering temperature and low reactivity towards metal oxides under employed operating conditions. However, substitution of BHA due to cost and in some cases toxicity of Ba-precursors, is desirable. The current paper reports results obtained with the lanthanum silicate La$_{0.33}$Si$_{6}$O$_{20}$ as an alternative matrix material.

Modelling studies can be a highly valuable complement to experimental studies. Three different studies have recently been published using Density Functional Theory (DFT) to characterize mechanisms and reaction barriers of CH$_4$ reacting with a Fe$_3$O$_3$ surface [11-13]. Although the calculation setups are quite similar, the studies disagree both regarding detailed mechanisms, as well as the energetics of the individual reactions. The mechanism of initial dissociation of CH$_4$ into CH$_3$ and H is in all studies found to be occurring on top of a surface Fe atom with the product H atom adsorbed at a surface O site. Still, the calculated reaction barrier height varies between 1 and 2 eV. For this work, DFT calculations for this reaction were performed in order to clarify the important mechanisms as well as to form a basis for modelling the reaction kinetics.
calculations unless otherwise stated. As both metal oxides studied are magnetic, Fe₂O₃ being antiferromagnetic and Fe₃O₄ being ferromagnetic, spin-polarisation was used in all calculations. In this paper we only report on calculated results for Fe₂O₃. The corresponding results for Fe₃O₄ will be published in a future study.

The kinetic Monte Carlo (kMC) method \cite{28, 29} was used to study the kinetics of the overall reactions occurring at the surface. For all calculations the kmos code was used \cite{30}. Barrier heights derived from DFT calculations were used to calculate rate constants using simple Transition State Theory calculations \cite{28}. The use of kMC allows for the kinetics of a system to be studied with greater accuracy than traditional microkinetic rate equation models. In particular, it allows for resolving a complex reactive system in molecular detail including individual sites and atoms and molecules. At the same time, there is no need to describe the system in atomistic detail, including molecular structures and interactions, such as for molecular dynamics or electronic structure calculations, allowing for fast simulations. In a lattice kMC model one only needs to specify a number of connected sites, populations of atoms and molecules at these sites, and the rates of reaction and transition (diffusion, adsorption, or desorption). Subsequently, a stochastic simulation of the motion and reaction of the species can be carried out, where one process at a time occurs.

Results and discussion

Characterization and reactivity tests

Electron microscopy characterization of the prepared materials is challenging due to the extremely small particle size, which limits the use of EDS elemental analysis. Fig. shows a sample which has been subjected to several reduction-oxidation cycles at 800 °C and 900 °C. The material shows quite unusual morphology, appearing “spotty”. These spots are interpreted to be iron oxide particles of ~10-15 nm. This is supported by Rietveld analysis of XRD data (not presented here) which indicates iron oxide (Fe₃O₄) crystallites in the region of 22 nm. A similar sample redox-cycled at only 700 °C demonstrates a smaller crystallite size of around 12 nm.

Micro reactor tests up to 700°C show very little reforming of methane. Applying a pre-conditioning step by reducing the sample in humid hydrogen (10% H₂ + 3% H₂O in N₂) at 900°C for 20 minutes and subsequent reforming tests (10% CH₄ + 3% H₂O in Ar) at 900°C for 90 minutes gave interesting results, see Fig. 1. About 30% conversion of methane was found. However, a significant amount of CO₂ was produced indicating partial combustion. Mass 28 will have some contribution from N₂ background (one decade lower) and splitting of CO₂ in the MS which should be less than 0.3% in this case. Further tests are planned in order to obtain a better understanding of the results.

Modelling

Fig. 4 shows the structures resulting from DFT calculations on CH₄ adsorption and dissociation on a Fe₂O₃ surface. The Fe-O₃-Fe surface termination was chosen since it has been found to be the most stable over a
wide range of oxygen pressures [23]. The CH$_4$ molecule is only weakly bound at a surface Fe site (Fig. 4a) with a binding energy of 0.16 eV. The barrier to dissociation of CH$_4$ into CH$_3$ and H, adsorbed at Fe and O sites (Fig. 4b), respectively, is 1.06 eV. As discussed earlier, literature values on this barrier height show a significant spread. In the DFT study by Huang et al. [11], whose results we have used for kinetic modelling (see below), this barrier is 1.76 eV. In addition, we find a reaction energy of 0.16 eV, whereas that of Huang et al. is 0.33 eV, but this is one of the smaller differences between this work and theirs. Another difference is that our calculations indicate that a solitary CH$_3$ species preferably binds to an O site (Fig. 4c), whereas Huang et al. conclude that CH$_3$ binds more strongly to a Fe site. The reasons for the above (and other) discrepancies between our work and the other DFT studies on this reaction [11-13] will need to be examined in more detail in the future.

In connection to the experiments on reduction of iron oxide by H$_2$ (Fig. 3), it is interesting to see that the DFT calculations predict a rather low barrier (0.4 eV) to H$_2$ dissociation at a surface Fe site. This barrier height is relative to H$_2$ in the gas phase, since H$_2$ adsorption to the Fe site is rather weak, with a binding energy of 0.18 eV. The coverage of adsorbed H$_2$ at 900°C is therefore expected to be extremely small. In contrast, the binding of a dissociated H$_2$ in the form of two H atoms at O sites is stable by 1.7 eV compared to gas-phase H$_2$. The reverse reaction has a barrier height of 2.1 eV to initiate H$_2$ formation from adsorbed H atoms. The energy required for two adsorbed H atoms to react with a surface O atom and desorb as a H$_2$O molecule is 1.8 eV, which effectively gives a lower activation energy than for H$_2$ formation. The conversion of H$_2$ into H$_2$O, and thereby reduction of the Fe$_2$O$_3$ surface, should therefore be a relatively efficient process, as the experimental results presented in Fig. 3 suggest.

Finally, we report on kinetic Monte Carlo simulations using the whole set of elementary reaction steps as determined by DFT to evaluate the overall kinetics of CH$_4$ reacting with Fe$_2$O$_3$. Since the calculations by Huang et al. [11] are more extensive than ours and give qualitatively similar results where comparable, although the exact energetics differ in many cases (see above), we used the model on their results. We exchanged the initial barrier to CH$_4$ dissociation to our value (i.e., 1.76 eV to 1.06 eV) and derived the H atom diffusion barrier height between O sites from our results (0.49 eV). This constitutes Model A as given in Table 1. To further examine the effects of changing the individual rates we exchanged the mechanisms involving only adsorbed H atoms (e.g., H$_2$ and H$_2$O formation), from that of Huang et al. to our values (called Model B in Table 1). The surface O atom concentration was assumed to remain constant, meaning that replenishing O from the bulk when a surface O atom has reacted to form CO, CO$_2$, or H$_2$O is effectively instantaneous compared to the time scale of the reactions. From Table 1 it can be seen that CO and H$_2$O should be the preferred products for the temperature range 700-1100°C, with only very minor production of CO$_2$. Experimentally, CO$_2$ production seemed to be comparable to and even exceeding CO production (Fig. 3). However, one should bear in mind that this was from a reduced iron oxide and simulations on Fe$_3$O$_4$ should therefore probably be better suited to compare to these experiments. This will form the topic of a future study.

Table 1. Branching fractions of CO and CO$_2$ products and H$_2$ and H$_2$O products from kMC simulations of CH$_4$ on Fe$_2$O$_3$.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>X$_{CO}$</th>
<th>X$_{CO_2}$</th>
<th>X$_{H_2}$</th>
<th>X$_{H_2O}$</th>
<th>X$_{H_2}$</th>
<th>X$_{H_2O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>0.999</td>
<td>0.001</td>
<td>0.116</td>
<td>0.884</td>
<td>0.002</td>
<td>0.998</td>
</tr>
<tr>
<td>800</td>
<td>0.999</td>
<td>0.001</td>
<td>0.150</td>
<td>0.850</td>
<td>0.004</td>
<td>0.996</td>
</tr>
<tr>
<td>900</td>
<td>0.998</td>
<td>0.002</td>
<td>0.183</td>
<td>0.817</td>
<td>0.006</td>
<td>0.994</td>
</tr>
<tr>
<td>1000</td>
<td>0.997</td>
<td>0.003</td>
<td>0.213</td>
<td>0.787</td>
<td>0.008</td>
<td>0.992</td>
</tr>
<tr>
<td>1100</td>
<td>0.994</td>
<td>0.006</td>
<td>0.241</td>
<td>0.759</td>
<td>0.011</td>
<td>0.989</td>
</tr>
</tbody>
</table>
Conclusion

We have reported results on both experimental (synthesis, characterization, and reactivity tests) and modelling studies of iron oxide nanoparticles for the potential use in chemical looping reforming processes. Nanoparticles of iron oxide of size <20 nm were successfully embedded in an inert support (lanthanum silicate) via a simple, scalable and relatively cheap synthesis route and shown to be stable to temperatures appropriate for chemical looping processes. Micro reactor tests on the reactivity were carried out. By exposure to humid hydrogen, the iron oxide nanoparticles were reduced. Further tests of the reactivity of reduced iron oxide with CH₄ indicated that both CO and CO₂ were formed as significant products at 900°C, meaning that partial combustion occurs, instead of pure reforming where mainly CO (and H₂) should be formed. Further tests are needed to investigate whether the capabilities for reforming can be enhanced. DFT calculations on the reaction mechanisms and energetics of H₂ reacting with a fully oxidized Fe₂O₃ surface confirm that H₂O formation, and thereby reduction of the oxide, should be efficient. Kinetic Monte Carlo simulations of CH₄ reacting with Fe₂O₃, based on DFT calculations, indicate that CO and H₂O should be the dominating products in this case. Simulations on a reduced oxide surface, Fe₃O₄, will be the topic of a future study. Then both the effects on reactivity of reducing the oxide as well as the predictive power of the modelling can be properly assessed in comparing to experiments.

Acknowledgements

We acknowledge funding by a European Union FP7 grant: NanoSim – A Multiscale Simulation-Based Design Platform for Cost-Effective CO₂ Capture Processes using Nano-Structured Materials (project number 604465).

Author’s contributions

Conceived the plan: PID, SA, SAS; Performed the experiments: JRT, PID, YL; Performed the modelling: SAS, IHS, SA; Wrote the paper: SA, PID, SAS, JRT, IHS, YL. Authors have no competing financial interests.

References

7. Solunke, R. D.; Vesper, G.; Energy Fuels, 2009, 23, 4787. DOI: 10.1021/ef900280m
28. Jansen, A. P. J.; An Introduction to Kinetic Monte Carlo Simulations of Surface Reactions; Springer, 2012. DOI: 10.1007/978-3-642-94988-4
Nanoparticles-enabled low temperature growth of carbon nanofibers and their properties for supercapacitors

Rickard Andersson\textsuperscript{1*}, Amin M. Saleem\textsuperscript{1}, Ioanna Savva\textsuperscript{2}, Theodora Krasia-Christoforou\textsuperscript{2}, Peter Enoksson\textsuperscript{3}, Vincent Desmaris\textsuperscript{1}

\textsuperscript{1}Smoltek AB, Regnbågsgatan 3, Gothenburg, SE-41755, Sweden
\textsuperscript{2}Department of Mechanical and Manufacturing Engineering, University of Cyprus, Nicosia, Cyprus
\textsuperscript{3}Microtechnology and Nanoscience, Electronics Materials and Systems Laboratory, Chalmers University of Technology, Gothenburg, SE-41296, Sweden

DOI: 10.5185/amlett.2018.1948
www.vbripress.com/aml

Abstract
Carbon nanostructures are of great interest for a variety of applications, but their current processing throughput limits their industrial full scale deployment. This paper presents a cost effective and simple fabrication process, where vertically aligned carbon nanofibers are grown using DC-PECVD at CMOS compatible temperatures from catalytic nanoparticles, spin-coated from stable polymer-nanoparticle colloidal suspensions. Two different catalysts, Co and Cu, are investigated by growing carbon nanofibers at temperatures ranging from 390 °C to 550 °C, using suspensions with various concentrations of nanoparticles. The length and morphology of the grown nanofibers are examined using SEM and the electrical properties are investigated using electrochemical measurements on samples arranged as supercapacitor devices. Vertically aligned CNFs are successfully grown from both types of catalyst. The Co-derived fibers are long and arranged in a denser carpet-like structure, while the Cu-derived fibers are shorter and in a sparser formation of free-standing individual fibers. All electrochemical measurements show typical supercapacitor behaviour even at high scan rates of 200 mVs\textsuperscript{-1}, with the fibers grown from Co showing great increase in capacitance over the bare chip reference device, including the samples grown at 390 °C. Copyright © 2018 VBRI Press.

Keywords: Nanoparticles, carbon, nanofibers, CNF, supercapacitor

Introduction
Carbon nanostructures are extensively researched for different applications in the microelectronics and semiconductor packaging industry, due to the natural abundance of carbon, along with extraordinary properties such as high thermal conductivity, good mechanical strength, and excellent electrical conductivity. For example, their electrical and mechanical properties make them interesting for interconnect applications, and the thermal properties of carbon nanostructures can be used for heat dissipation and heat transportation [1]. Furthermore, their high surface area to volume ratio makes carbon nanostructures a widely studied candidate for electrode materials in different capacitor applications, such as the electrical double layer capacitors (EDLCs) commonly referred to as supercapacitors [1-12].

In order to avoid expensive and time consuming transfer processing steps however, the nanostructures should be grown directly at the desired location on the substrate using a deposited catalyst to control the growth. Doing so creates a number of challenges, such as keeping the growth temperature low enough to leave the substrate and any other components present unharmed, and keeping the catalyst deposition process simple, thus ensuring high throughput.

One carbon nanostructure suitable for controlled growth at a desired location is the carbon nanofiber (CNF), consisting of cone shaped graphene sheets stacked inside each other to form a solid fiber [1]. CNFs have been proven to grow at temperatures below 400 °C, thus making the process temperature CMOS compatible, in a controlled pattern that is defined by for example a liftoff process [13-14]. CNFs have also been investigated in supercapacitor applications, grown either as a film such as for an electrode in a coin-cell device [6], or grown in a patterned structure to form interdigitated solid state gel electrolyte based supercapacitors [15].
In this work we compare the length, morphology, and electrical performance of vertically aligned carbon nanofibers (VACNFs) grown at CMOS compatible temperatures (< 400 °C), using colloidal suspensions of different polymer-stabilized nanoparticles (NPs) as the catalyst source for the CNF growth by means of direct current plasma enhanced chemical vapour deposition, DC-PECVD. The nanoparticle suspensions are simply spin-coated onto the samples [16], without the need for complicated and expensive equipment or processing for the catalyst deposition. Further advantages of using these catalytical colloidal suspensions are their non-toxicity and their low cost.

Experimental

Chemical reagents

Polyvinylpyrrolidone (PVP, 1300000 g/mol), copper(II) acetate monohydrate ((CO\textsubscript{2}CH\textsubscript{3})\textsubscript{2}Cu·H\textsubscript{2}O, 98%) hydrazine monohydrate (98%) and cobalt acetate ((CH\textsubscript{3}CO\textsubscript{2})\textsubscript{2}Co, 99.995%) were purchased from Sigma-Aldrich. Methanol (analytical grade, ACS reagent) was purchased from Scharlau. The above-mentioned reagents were used as provided by the manufacturer without further purification.

Synthesis of PVP-stabilized Cu nanoparticles

The PVP/Cu colloidal solution (mols vinyl pyrrolidone (VP) units/mols (CO\textsubscript{2}CH\textsubscript{3})\textsubscript{2}Cu·H\textsubscript{2}O = 300:1) were prepared as follows: In a vial equipped with a magnetic stirrer, PVP (2.0 g, 18 mmol of VP units) was dissolved in MeOH (20 mL). Subsequently, (CO\textsubscript{2}CH\textsubscript{3})\textsubscript{2}Cu·H\textsubscript{2}O (11.8 mg, 0.06 mmol) was added to the polymer solution and the mixture was left to stir under inert atmosphere (N\textsubscript{2}) for 30 minutes at room temperature until all components were completely dissolved. Afterwards, hydrazine monohydrate (14.7 µL, 0.3 mmol) was added and the colour of the solution became dark red/brown, indicating the formation of Cu NPs. The above-mentioned procedure was followed for the preparation of 2 more PVP/Cu systems with different Cu NP loading by varying the quantities of the reagents, as seen in Table 1.

Table 1: Quantities of the reagents used for the different PVP/Cu systems.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>PVP (mmol)</th>
<th>MeOH (mL)</th>
<th>Cu(II) salt (mmol)</th>
<th>Hydrazine (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300:1</td>
<td>18</td>
<td>20</td>
<td>0.060</td>
<td>0.3</td>
</tr>
<tr>
<td>150:1</td>
<td>18</td>
<td>20</td>
<td>0.120</td>
<td>0.6</td>
</tr>
<tr>
<td>75:1</td>
<td>18</td>
<td>20</td>
<td>0.240</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Synthesis of PVP/Co hybrid solution

The PVP/Co(II) solutions (mols (VP) units/mols (CH\textsubscript{3}CO\textsubscript{2})\textsubscript{2}Co = 300:1) were prepared as follows: In a round bottom flask equipped with a magnetic stirrer, PVP (2.0 g, 18 mmol of VP units) was dissolved in MeOH (20 mL). Subsequently, (CH\textsubscript{3}CO\textsubscript{2})\textsubscript{2}Co (10.6 mg, 0.06 mmol) was added to the polymer solution and the reaction mixture was left to stir for 2 hours at room temperature until all components completely dissolved. The above-mentioned procedure was followed for the preparation of 2 more PVP/Co(II) systems with different Co(II) loading, by varying the quantities of the reagents, as seen in Table 2.

Table 2: Quantities of the reagents used for the different PVP/Co systems

<table>
<thead>
<tr>
<th>Sample code</th>
<th>PVP (mmol)</th>
<th>MeOH (mL)</th>
<th>(CH\textsubscript{3}CO\textsubscript{2})\textsubscript{2}Co (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300:1</td>
<td>18</td>
<td>20</td>
<td>0.06</td>
</tr>
<tr>
<td>150:1</td>
<td>18</td>
<td>20</td>
<td>0.12</td>
</tr>
<tr>
<td>75:1</td>
<td>18</td>
<td>20</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Sample fabrication

An oxidized Si wafer was diced into square 14 mm by 14 mm samples. A metal stack of Ti/TiN was sputtered on each side of the individual samples to ensure a good electrical ohmic contact between the front and back since backside probing would be used during the electrochemical characterization.

The different colloidal solutions were spin-coated onto the samples using a standard resist spinner, followed by baking on a hotplate. VACNFs were then grown through DC-PECVD using a mixture of ammonia and acetylene as process gasses for 2 h at different temperatures. Before letting the gasses into the chamber the samples underwent a heating step in vacuum to remove the polymer through thermal decomposition, thus leaving the NPs deposited on the sample surface [18]. Each growth run contained two identical samples, forming the two electrodes of an EDLC in the ensuing electrochemical analysis setup. The samples coated with a PVP/Co(II) solution were also subjected to an in situ annealing step for 2 h at 325 °C in an N\textsubscript{2} environment in order for the Co(II) to form Co NPs. [17]

Two samples were also left without any CNF growth, i.e. only the TiN surface, to serve as reference.

Materials characterizations

The CNF length and fill-factor was characterized using a scanning electron microscope (SEM), taking images at normal incidence to the sample as well as at 40° tilt.

Cyclic voltammetry measurements were performed in a two electrode setup mimicking a supercapacitor device, where two identical CNF covered samples formed the two electrodes. Measurements were carried out using different scan rates ranging from 5 mVs\textsuperscript{-1} to 200 mVs\textsuperscript{-1}. The electrolyte used was 1 M KOH.
Results and discussion

Fig. 1(a) - (c) shows SEM images of the CNFs grown from the different PVP/Co systems at 390 °C both from a tilted view and from along the fiber axis (insets), while Fig. 1(d) shows the growth resulting from PVP/Co (75:1) at 550 °C. Similarly, Fig. 2(a) – (c) shows CNFs grown at 550 °C from the different PVP/Cu systems, while Fig. 2(d) shows the CNFs grown from PVP/Cu (75:1) at 390 °C. The different NP catalyst solutions yield CNFs with different length and fill-factors. The scale bars on the tilted images are the same for the two figures. Fig. 3 illustrates the measured length of the CNFs grown from different solutions.

As shown in Fig. 1 all fibers grown from the PVP/Co solutions are vertically aligned, and the images taken at zero tilt clearly demonstrate that a lowering of cobalt concentration leads to a lower CNF fill-factor when subjected to an identical growth environment. The top view images also illustrate the uniformity of the CNF film after spin-coating the samples, which is in line with previously published results for CNFs grown by spin-coating PVP/Pd solutions [16].

The length of the PVP/Co grown fibers increases with the growth temperature (Fig. 3), as suggested by [17]. This becomes most evident by studying the PVP/Co (75:1) solution.

The CNFs grown from the PVP/Cu solutions display a very different morphology compared to the PVP/Co ones. As seen in Fig. 2 they are much sparser and grow as individual free-standing fibers rather than as a CNF carpet. The NP concentration also has a dramatic impact on the fiber fill-factor as seen by comparing the insets of Fig. 2(a) – (c), the first of which showing fibers only growing in clusters around larger particles that are spread out over the sample.

Fig. 2(d) also shows that there is little to no CNF growth from the copper NPs at 390 °C, indicating either that 390 °C is not a suitable temperature for CNF growth using Cu as catalyst, or that altering the growth parameters is required.
Fig. 2. SEM images taken at 40° tilt and 0° tilt (insets) of CNFs grown from (a) PVP/Cu (300:1) at 550 °C. (b) PVP/Cu (150:1) at 550 °C. (c) PVP/Cu (75:1) at 550 °C. (d) PVP/Cu (75:1) at 390 °C.

The results of the electrochemical analysis are provided in Fig. 4, showing the CV curves at different scan rates for one device (PVP/Co (75:1) at 550 °C) in Fig. 4(a), and the capacitance per footprint area for all devices in Fig. 4(b). The near rectangular shape of the CV curves demonstrates the electrical double layer capacitor behavior of the grown CNFs, while the slight peaks at the ends indicate an influence of a pseudocapacitive charge storage. It is known that carbon EDLCs display part of their capacitance as pseudocapacitance caused by the Faradaic reactivity of surface oxygen-functionalities, which should be abundant along the edges of the cone shaped graphene layers that stack to form a CNF [20].

Another significant characteristic for electrode materials is the rate stability, which is demonstrated by the good shape retention of the CV curves even as the scan rate is increased to 200 mVs⁻¹.

From Fig. 4(b) it is evident that the capacitance for the CNFs grown from the PVP/Cu systems is approximately the same as for the bare-chip reference device. The implication is that the resulting CNFs are not long enough, and the CNF film is not dense enough, to create a 3D structure with a significant impact on the available surface area of the electrodes. An increase in capacitance for the PVP/Cu-grown CNF electrodes should follow if the parameters for the NP suspension and the growth are optimized to ensure longer fibers in a denser film.

Fig. 3. The measured CNF length for different solutions at different growth temperatures.
The supercapacitor devices derived from the PVP/Co catalysts, however, show significant improvement over the reference, as expected since the CNF structures are both longer and denser for these samples. The fill-factor of the CNF film seems to bear more significance to the capacitance, and by extension the available surface area, than the fiber length, as evidenced in Fig. 4 (b); the capacitance values for the CNFs grown at 390 °C using the Co-based samples drop significantly as the concentration of the NPs is lowered, even though it is seen in Fig. 3 that the fibers are longer for the PVP/Co (150:1) solution than for PVP/Co (75:1) at 390 °C.

Previously published studies of PVP/Pd catalytic suspensions also indicate that the fill-factor of the CNFs has the most significant impact on the capacitance, and that it can be controlled by changing the NP concentration [16]. In that case the specific capacitances per footprint area at 100 mVs\(^{-1}\) scan rate were found to be 0.6 mFcm\(^{-2}\) and 1.2 mFcm\(^{-2}\) for PVP/Pd (38:1) and PVP/Pd (18:1) respectively, which in combination with the results from this study further supports the claim that an increased NP loading leads to an increased capacitance.

The capacitance seems however to decrease with increasing CNF growth temperature for some devices. Since an increase in growth temperature results in longer CNFs (Fig. 3), the effect should be an increased surface area of the electrode, and thus an increase in capacitance, as seen for the PVP/Co (75:1) solution and in previous work [17]. One explanation for this could be an incomplete thermal decomposition of the PVP. The thermal decomposition of pure PVP starts at ca 380 °C [19], meaning that 390 °C is close to the limit where this occurs. It is possible that the heat pretreatments done at lower temperature growths did not fully remove all of the polymer, thus leaving residues that could possibly have reacted under the growth conditions to form a carbonaceous structure contributing to the capacitance via an increase in surface area compared to samples undergoing complete PVP burn-off. As seen in Fig. 3 the fiber length increases more dramatically for the PVP/Co (75:1) solution when the growth temperature is increased compared to the other NP concentrations. The large increase in surface area for this concentration of NPs due to fiber length could then be enough to negate the impact of PVP residues at lower temperatures. Another explanation is the tendency for the CNFs to bundle together as they grow longer to form straighter CNF pillars. This is somewhat visible in Fig. 1(d). The shorter CNFs (Fig. 1(a) – (c)) form a more porous structure of thinner, curlier, CNF strands. Thus, it can be the case that less surface area is available to the electrolyte for the higher temperature growths even though the fibers are longer, simply because a smaller percentage of each individual fiber is available to the electrolyte when they bundle together.

**Conclusion**

We successfully demonstrated a fast, simple, and cost effective method for growing vertically aligned CNFs at CMOS compatible temperatures by spin-coating different PVP-NP colloidal suspensions containing Cu or Co NPs. VACNFs were then grown from these nano-catalyst-particles using DC-PECVD at temperatures ranging from the CMOS compatible 390 °C up to 550 °C. SEM analysis has proven that the fill-factor of the CNF film can be controlled through the concentration of NPs in the suspension, and it is further shown through electrochemical measurements that the CNF films exhibit capacitive behavior typical for the electric double layer, making them feasible as electrode materials in a supercapacitor. Additionally, it is demonstrated that the fill-factor is of higher importance than fiber length for the capacitance in a supercapacitor application.

**Acknowledgements**

This work was supported by the grant “Postdoctoral Researchers” of the University of Cyprus supporting Dr. Ioanna Savva.
Author’s contributions

Authors have no competing financial interests.

References

   DOI: 10.1109/MNANO.2015.2409394
2. Kim, M. S.; Hsia, B.; Carraro, C.; Maboudian, R.; Carbon, 2014, 74, 163
   DOI: 10.1016/j.carbon.2014.03.019
3. Huang, P. et al.; Science, 2016, 351, 691
   DOI: 10.1126/science.aad3345
   DOI: 10.1002/smll.201600412
5. Yu, J. et al.; ACS Nano, 2016, 10, 5204
   DOI: 10.1021/acsnano.6b02226
   DOI: 10.20964/2017.07.46
   DOI: 10.1155/2016/1537269
   DOI: 10.1021/nl3034976
   DOI: 10.1126/science.1216744
    DOI: 10.1088/0957-4484/25/5/055401
    DOI: 10.1021/am509065d
    DOI: 10.1039/C3EE43526A
    DOI: 10.1109/ECTC.2014.6897421
    DOI: 10.1088/0957-4484/20/37/375302
    DOI: 10.1109/ECTC.2017.135
    DOI: 10.1088/1468-6996/16/1/015007
    DOI: 10.1016/j.sse.2015.01.022
    DOI: 10.1016/j.cap.2006.01.038
    DOI: 10.1002/app.21886
Mechanism of destruction of benzoyl peroxide on surface of sp$^2$-type carbon nanomaterials

Mykola Kar tel$^{1,2}$, Liudmyla Karachevtseva$^{2,3}$, Wang Bo$^2$, Daryna Haliarynk$^1$, Olga Bakalinska$^1$, Tetyana Kulyk$^1$, Borys Palyanytsya$^1$, Yevgen Demianenko$^1$, Anatoliy Grebenyuk$^1$, Volodymyr Kuts$^1$

$^1$Department of Nanoporous and Nanosized Carbon Materials, O. Chuiko Institute of Surface Chemistry, NAS of Ukraine, 17 General Naumov Street, Kyiv 03164 Ukraine;
$^2$China-Central and Eastern Europe International Science and Technology Achievement Transfer Center, Ningbo University of Technology, 201 Fenghua Road, Ningbo 315211, China;
$^3$Department of Photonic Crystals, V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, 41 Prospect Nauki, Kyiv 03028, Ukraine.

DOI: 10.5185/amlett.2018.1965
www.vbripress.com/aml

Abstract

The possible mechanisms of decomposition of benzoyl peroxide were investigated by the method of density functional theory with the exchange-correlation functionality of B3LYP, a basis set of 6-31G (d, p). It was carried out a comparative analysis of the quantum chemical calculations of the electronic structure of carbon nanoclusters simulating the active surface of sp$^2$ carbon materials, including their modifications by the heteroatoms N and O. The energy parameters of the benzoyl peroxide molecule and all possible products of its decomposition, as well as the interaction of the free radical Ph-COO• with model graphite-like nanoclusters were considered. The calculations are compared with the experimental results of the catalytic activity of the varieties of activated charcoal and the catalase enzyme in the reaction of the benzoyl peroxide decomposition in a non-aqueous medium. It has been established that in the benzoyl peroxide molecule, regardless of the polarity of the medium, the weakest is the bond (O-O). The greatest ability to decompose benzoyl peroxide, which is much larger than that of catalase, was detected on the N-containing carbonaceous materials. It is shown that the free radical Ph-COO• is lighter and kinetically, and thermodynamically interacted with the graphite-like plane of the model N-containing carbon nanoclusters. Copyright © 2018 VBRI Press.

Keywords: Carbon materials, benzoyl peroxide, catalytic activity, reaction mechanism, quantum chemistry, density function theory method, cluster approximation.

Introduction

It is known that nanoporous and nanodispersed carbon materials (CM) have the properties of catalysts in many chemical processes of red-ox and acid-base types (halogenation, dehydrogenation, decomposition, oxidation-reduction, etc.) [1]. Catalytic activity of the CM is dependent on both the structural and sorption characteristics (specific surface area, nature of porosity), and surface chemistry (the presence of heteroatoms in the structure of the carbonaceous matrix, surface functional groups of acid or basic nature) [2]. CM are able to influence on the variety of biologically important processes that make up the metabolic pathways of living organisms. The researches have established that the therapeutic action of the CM is related not only to its absorption properties, but also to the effect on the enzymatic processes (hydrolysis of proteins, fats and esters, sucrose inversions, decomposition of hydrogen peroxide, urea, etc.), that is, carbonaceous materials exhibit enzyme-like properties [3]. Several papers [4-7] showed that the decomposition of hydrogen peroxide on the surface of a sp$^2$-type carbon cluster (activated carbon surface, exfoliated graphite, fullerences, nanotubes, nanohorns, graphene, etc.) is carried out by transferring the electronic density from the cluster to peroxide molecule in the formed complexes "carbon cluster-H$_2$O$_2". Such a transfer leads to the collapse of the peroxide molecule, since the formation of anions OH$^-$ is more energetically efficient. The mechanism of the process is represented as the homolytic decay of the H$_2$O$_2$ molecule by the O-O bond onto two free radicals -OH, which are sufficiently strong electron acceptors (affinity energy 1.825 eV). Additional possibility for radicals -OH is an interaction with a free radical fragment of a carbon cluster with the formation of a chemical bond (the formation of phenolic groups on the surface of the CM). In such systems, the rate of decomposition reaction is determined by the ionization potential (or work of the electron output, or magnitude of the energy of the upper occupied molecular orbital) of the carbon cluster.
Recently, the attention of researchers attracts the use of enzymes in non-aqueous media, since a number of practically important organic peroxides and hydroperoxides are not water soluble [8-10]. Therefore, we consider interesting and relevant studies of the enzyme-like activity of CM in non-aqueous solutions.

The purpose of this work is to study the mechanism of decomposition of organic peroxide on the example of benzoyl peroxide (BP) on the basis of quantum chemical calculations of the molecular structure in different media, as well as to simulate the interaction of the benzoate-radical PhCOO• (product of PB decay) with model sp² carbon nanoclusters, which include N- and O-heteroatoms. Results of calculations are compared with experimental data of the BP decomposition in the presence of the samples of activated carbon KAU and its N- and O-modified forms [11].

**Experimental**

To establish the mechanism of the influence of the electronic structure of the CM on the BP decomposition, it is carried out the quantum-chemical calculations of the energy of the bonds in the molecule of the peroxide itself Ph-(CO)-O-O-(OC)-Ph, located in different media, and the interaction of the free radical PhCOO• formed during the homolytic breakdown of the BP peroxide group with graphite-like planes of model carbon nanoclusters, including ones with inclusion in the structure of a certain number of N- and O-heteroatoms. Calculations were made using the US GAMESS program [12] by the theory of function density with the exchange-correlation functional B3LYP [13, 14] with the use of the dispersion correction [15] and the base set 6-31G (d, p). The solvent medium was modeled in the approximation of the continuum solvent model (polarization continuum model, PCM) [16]. The free energy of physical adsorption (ΔG_{phys}) was calculated as the difference between the total energy of the physically adsorbed complexes [PhCOO•...CM] and the sum of the total energies of the individual radicals [PhCOO•] and graphite-like clusters [CM], taking into account the corresponding thermodynamic corrections:

\[ ΔG_{phys} = G^0_{298[PhCOO•...CM]} - G^0_{298[PhCOO•]} - G^0_{298[CM]} \]

The activation energy was defined by the formula:

\[ ΔG_{act} = G^0_{298} (\text{transition state}) - G^0_{298} (\text{reactants}) \]

and the energetic effect of the reaction (ΔG_{re}), respectively:

\[ ΔG_{re} = G^0_{298} (\text{reaction products}) - G^0_{298} (\text{reactants}) \]

where \( G^0_{298} = E_i + ZPE + G_{0→298K} \) in which \( E_i \) is the total energy of the corresponding optimized structure, and the energy of zero oscillations (ZPE) and the correction value \( G_{0→298K} \) were found by calculating the Hessian matrix of each of these states. For the reliability of the found energy minima and transition states on hypersurface of potential energy, a verification was carried out in accordance with the Merrell-Leydler theory with the additional calculation of the Hesse matrix [17], which allows to determine thermodynamic and kinetic characteristics (free energy of physical sorption \( ΔG_{phys} \), chemisorption \( ΔG_{ch} \), and Gibbs’ activation \( ΔG_{act} \)) for reaction of the interaction of the radical PhCOO• with graphite-like planes of model nanoclusters at 298 K.

For objective interpretation of the results of quantum-chemical calculations, they were compared with the data of experimental studies of BP decomposition on samples of activated carbon KAU and its two modifications - oxidized (O-KAU) and nitrogen-containing (N-KAU) ones obtained by treatment of 30% solution of nitric acid and by calcination of urea soaked oxidized carbon [11]. Characteristics of samples are presented in Table 1 [11, 18].

**Table 1.** Elemental composition, surface chemistry, structural-sorption and catalytic properties of carbon materials on the basis of activated carbon KAU.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Samples of CM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KAU</td>
</tr>
<tr>
<td>Elemental composition, wt. %</td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>99.4 (97.3)</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3.0 (2.4)</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.84</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.2</td>
</tr>
<tr>
<td>Functional surface groups, mg/g</td>
<td></td>
</tr>
<tr>
<td>Carboxylic</td>
<td>0.06</td>
</tr>
<tr>
<td>Lactonic</td>
<td>0.06</td>
</tr>
<tr>
<td>Phenolic</td>
<td>0.02</td>
</tr>
<tr>
<td>Total acidic</td>
<td>0.12</td>
</tr>
<tr>
<td>Total basic</td>
<td>0.12</td>
</tr>
<tr>
<td>Structural sorption characteristics:</td>
<td></td>
</tr>
<tr>
<td>Pore volume (V₂), cm³/g</td>
<td>0.50</td>
</tr>
<tr>
<td>BET surface area (Sₐ), m²/g</td>
<td>920</td>
</tr>
<tr>
<td>Average pore radius (rₗ), nm</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Catalytic activity on BP decomposition:

Michaelis' constant, mM/L        | 480           | 1120          | 30            |
Coefficient of affinity          | 2.1·10⁻³      | 8.9·10⁻³      | 3.3·10⁻²      |

*The catalytic ability of CM in relation to the decomposition of BP were determined and compared with the activity of catalase by the method of studying the kinetic regularities of the course of enzymatic reactions over the Michaelis’ constants (Kₐ) [18]. These constants were determined from the dependences of Laynäväär - Burk in the double inverse coordinates of the initial reaction rate and the concentration of the substrate (BP solutions in ethyl acetate) [19]. For catalase Kₐ in this reaction was 340 nmol/L (coefficient of affinity 2.9·10⁻⁹).*

The analysis of the reaction products of the BP decomposition was carried out by the method of TPD mass-spectrometry [20] in the range 1-210 a.m.u. The most probable products corresponding to certain masses are given in Table 2.

**Table 2.** Probable products of the catalytic benzoyl peroxide decomposition on the carbon materials (samples of activated carbons KAU) according to the temperature-programmable mass-spectrometry.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>17, 18</td>
<td>OH, H₂O</td>
</tr>
<tr>
<td>28</td>
<td>CO</td>
</tr>
<tr>
<td>44</td>
<td>CO₂</td>
</tr>
<tr>
<td>77</td>
<td>Ph</td>
</tr>
<tr>
<td>105</td>
<td>PhCOO⁻</td>
</tr>
<tr>
<td>121, 122</td>
<td>PhCOO⁻, PhCOOH</td>
</tr>
</tbody>
</table>
Results and discussion

The experimental data presented in the methodical part show that the catalytic activity of CM (activated carbon of KAU and its modifications) in the BP decomposition is significantly increased (KM decreases) with increasing volume of sorption pores (V3) and specific surface area of (Sp), and, vice versa, with a decrease in the average pore radius (r). But the greatest influence on catalytic activity is observed from the presence of N- and O-heteroatoms. Thus, the introduction of N-atoms into the carbon matrix increases, and O-atoms (in the form of surface groups of acidic nature) decreases the catalytic activity of CM in the BP decomposition. Similar patterns were observed in works [6, 7, 21] at study of H2O2 decomposition by different nitrogen and oxygen-containing CM. It should also be noted that the enzyme-like ability of N-containing carbon in a non-aqueous medium was on the order higher than activity of native catalase. This gives us reason to suppose that the activity of CM in the reactions of the BP decomposition in non-aqueous media will be equally determined by the electron-donor ability of a carbon catalyst, namely, its ionization potential fп (or the work of electron output Аe, or the energy level of upper occupied molecular orbital of the ЕHOMO, etc.).

Quantum-chemical study of homolytic degradation of benzoyl peroxide

The calculations for optimization of the structure and energy parameters of the BP molecule and all possible products obtained at breakage of bonds are made. In particular, it is considered the homolytic coupling of O–O (1) (Fig. 1a) with the formation of two free radicals PhCOO•, the relative molecular weight of which is 121 a.m.u. In turn (Fig. 1b), radical PhCOO• can homolytically decompose onto phenyl-radical Ph• (77 a.m.u.) with the release of CO2 molecule (44 a.m.u.).

The BP molecule can also decompose with coupling O–C (2) (Fig. 1a) onto two free radicals PhCOO• and PhCO• with respective molecular weight of 137 and 105 a.m.u. The first of these can be disintegrated with the formation of molecule O2 and a free radical PhCO•, which, in turn, can decompose with the breakdown of the C–C bond to the molecule CO (28 a.m.u.) and phenyl radical Ph•. It is also possible a breakage of the C–C bond (3) (Fig. 1a). In this case, the phenyl radical Ph• and the radical PhCOOOCO• with a weight of 165 a.m.u. can be formed. The last, like the preceding one, can decay with the break-up of the O–O bond (5) (Fig. 1c) and the formation of the PhCOO• radical and molecule CO2. Consequently, the absence in the experimental TPD of mass spectra of a fragment with a mass number of 165 a.m.u. is explained by the theoretically predicted thermodynamic instability of the mentioned radical (Fig. 1c).

The results of calculations on the values of the energy of bond breaks in the BP molecule are summarized in Table 3. As can be seen, regardless of the medium chosen for calculating, in the BP molecule the bond O–O is weakest (Fig. 1a), and this results to the formation of two radicals PhCOO•. Significantly stronger bond is between the carboxyl group and benzene ring C–C (3) (Fig. 1a). The strongest link is O–C (2) between the peroxide oxygen and carbon of the carboxyl group (Fig. 1a). The thermodynamic probability of its rupture is the lowest, which is confirmed by the absence in the experimental TPD of the mass spectrum of a fragment with a mass number of 137.

Table 3. The values of the energy of breaking of bonds in the molecule of benzoyl peroxide in different media (kJ/mol).

<table>
<thead>
<tr>
<th>Media (μ; ε)</th>
<th>Energy of breakage, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O-O</td>
</tr>
<tr>
<td>Ethyl acetate (6.1; 1.81)</td>
<td>92.55</td>
</tr>
<tr>
<td>Acetone (20.9; 2.84)</td>
<td>96.71</td>
</tr>
<tr>
<td>Carbon tetrachloride (2.2; 0)</td>
<td>101.3</td>
</tr>
<tr>
<td>Butanol (17.1; 1.66)</td>
<td>104.5</td>
</tr>
<tr>
<td>Acetic acid (6.19; 1.74)</td>
<td>114.9</td>
</tr>
<tr>
<td>Vacuum (1; 0)</td>
<td>105.5</td>
</tr>
</tbody>
</table>

Thus, with the breakdown of the bond C–C (3), four products of BP decomposition can be formed - stable molecules CO and CO2 (28 and 44 a.m.u.) and two free radicals PhCOO• and Ph• (105 and 77 a.m.u.), which can take part in interaction with CM.

The obtained results suggest that homolytic degradation of the BP molecule, irrespective of the medium, is most likely to be decomposed into two PhCOO• radicals, which subsequently interact with nanoclusters of CM surface or decompose on the phenyl radical Ph• and the molecule CO2.

Fig. 1. Possible ruptures of covalent bonds in the molecule BP (a) and products of its decomposing (b, c) by the homolytic mechanism.
Quantum-chemical study of the interaction of free radical PhCOO• with graphite-like nanocluster of CM

Coming from the elemental composition, structural-sorption characteristics and the nature of the surface functional groups of the studied CM (Table 1), it is practically impossible to uniquely propose universal structures that would simulate the reagent plots of the carbonaceous catalyst surface. The chemical composition of real catalysts involves the presence of four basic elements: C, H, O and N. Their ratio can vary widely, and this affects the identity and properties of the CM. Thus, a small percentage of H, O, and N in the material make it possible to consider as pure carbon. A significant percentage of H converge material to organic compounds of polyaromatic type. A high content of O in the material causes the presence of an independent class of substances called oxidized CM (oxidized carbon, oxidized graphite, oxidized graphene, oxidized nanotubes, etc.), and they are often considered as carbonaceous cation exchangers. Finally, CM with a high content of N (nitrogen-containing materials) are known as having an increased basicity and appear anion exchange and electron-donating properties.

It is known from experiment [11] that oxidation of CM leads to decrease, while nitrogenation of carbon matrix to increase of their catalytic activity in the reactions of decomposition of hydrogen peroxide, benzoyl and lauryl peroxides, etc. Typically, the value of the catalytic activity of the studied CM correlates with their electron donor capacity, which is quantified by physical parameters: ionization potential (I_p), work of electron output (A_e), energy level of upper occupied molecular orbitals (E_HOMO) for the corresponding model nanoclusters. It should be emphasized that the results of the calculation of I_p for model of carbon nanoclusters, which simultaneously contain N- and O-atoms, strongly depends on their number and location. The value of I_p can be either smaller or greater than the ionization potential of pure carbon nanoclusters [21]. For the pure carbon structure of planar (sp²) carbon nanoclusters the polyaromatic structure C_{10}H_{10} (calculated I_p = 5.246 eV) was used:

![Diagram of Carbon Nanoclusters](image)

Since oxidation and nitrogenation of the CM leads to the formation of O-, N-, and mixed O, N-containing products, their surface was modeled by appropriate O-, N-, and mixed N, O-containing nanoclusters. Selective structures are presented in Fig. 2. They are grouped so that the first group of them (1) - (6) has calculated values of I_p less, and the second group (7) - (12) more than for pure carbon nanoclusters C_{10}H_{10}. The results of calculations are presented in Table 4.
planes of pure carbon, nitrogen- and oxygen-containing materials we selected nanoclusters, accordingly, C_{16}H_{10}, C_{16}O_{2}H_{8} and C_{14}N_{2}H_{10}.

On the basis of quantum-chemical calculations it was established that the interaction of the graphite-like plane of the CM with the radical PhCOO• takes place in two stages:

1) Formation of a physically adsorbed complex [PhCOO•...CM]_{phys}.
2) Formation (after overcoming the energy barrier of the transition state [PhCOO•...CM]_{tr} chemical bond between the reactants [PhCOO•...CM]_{ads}.

The structure of corresponding nanocomplex (on example of O-containing carbon nanocluster C_{16}O_{2}H_{8} and radical PhCOO•) is shown in Fig. 4. For N-containing and pure carbon nanoclusters the structures of the complexes are similar. The resulting thermodynamic (ΔG_{phys}, ΔG_{chem}) and kinetic (ΔG_{act}) characteristics of the interaction radical PhCOO• and nanoclusters C_{16}H_{10}, C_{16}O_{2}H_{8} and C_{14}N_{2}H_{10} are presented in Table 5.

![Fig. 3. The dependence of the ionization potential (in eV) of nanoclusters from the content (in at. %) in them of N- and O-heteroatoms. The plane shows the potential value of polyaromatic structure C_{16}H_{10} that used as a model of pure carbon nanocluster (I_{p} = 5.246 eV).](image)

From Table 4 and Fig. 2 it can be seen that the structure (1) - (6) are N- and N, O-containing nanoclusters, which have higher electron-donor ability than pure carbon nanoclusters C_{16}H_{10}. Average value I_{p} for these structures is 3.08 ± 0.33 eV, which is very close to the magnitude of ionization potential of nanocluster (3) - C_{16}N_{2}H_{10} (3.108 eV). Structures (7) - (12) represent O- and O, N-containing nanoclusters that have lower electron-donor ability than pure carbon. The average value I_{p} for them is 6.42 ± 0.51 eV, which is close to the magnitude of the potential of the nanocluster (10) - C_{16}O_{2}H_{8} (6.370 eV). Therefore, for a detailed definition of the thermodynamic and kinetic characteristics of the interaction of free radicals PhCOO• with graphite-like nanoclusters of pure carbon, nitrogen- and oxygen-containing materials we selected nanoclusters, accordingly, C_{16}H_{10}, C_{16}O_{2}H_{8} and C_{14}N_{2}H_{10}.

![Fig. 4. Scheme of interaction of the radical PhCOO• with the nanocluster C_{16}O_{2}H_{8}.](image)

<table>
<thead>
<tr>
<th>Nanocluster</th>
<th>Ionization potential, eV</th>
<th>ΔG_{phys}, kJ/mol</th>
<th>ΔG_{act}, kJ/mol</th>
<th>ΔG_{chem}, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{16}H_{10}</td>
<td>3.108</td>
<td>-18.7</td>
<td>4.8</td>
<td>-5.30</td>
</tr>
<tr>
<td>C_{16}O_{2}H_{8}</td>
<td>5.246</td>
<td>-13.5</td>
<td>37.6</td>
<td>-6.60</td>
</tr>
<tr>
<td>C_{14}N_{2}H_{10}</td>
<td>6.370</td>
<td>-12.0</td>
<td>35.9</td>
<td>-6.67</td>
</tr>
</tbody>
</table>

As it can be seen from Table 5, the strongest physically adsorbed complex is [PhCOO•...C_{16}N_{2}H_{10}]_{phys}, since such system has most negative value of the energy of physical adsorption ΔG_{phys}. In such complexes the surface of radical PhCOO• is almost parallel to the graphite-like plane of the nanocluster (Fig. 4). The formation of the chemisorption complex [PhCOO•...C_{16}N_{2}H_{10}]_{chem} occurs through the formation of a transition state [PhCOO•...C_{16}N_{2}H_{10}]_{tr}, in which the radical is coordinated with the plane of the nanocluster by
one of the oxygen atoms of the group -COO•. The reliability of the existence of transition states is confirmed by the presence of one imaginary vibration mode (\(\nu_n\)) that corresponds to the transition vector, which characterizes the direction of the coordinate shifts of atomic nuclei at the transition from the starting materials to the reaction products.

According to the results of quantum chemical calculations, the chemisorption of radical PhCOO• is most easily carried out on the N-containing \(\text{C}_4\text{H}_8\text{N}_2\text{H}_{10}\) nanoclusters, since it requires the lowest activation energy \(\Delta G_{\text{act}}\) (4.8 kJ/mol), while for nanoclusters \(\text{C}_1\text{H}_{10}\) and \(\text{C}_1\text{O}_2\text{H}_8\) the activation energy \(\Delta G_{\text{act}}\) is much higher (37.6 and 35.9 kJ/mol, respectively). It is also clear from Table 5 that the highest value of the thermodynamic effect of PhCOO• chemisorption is observed on nanocluster \(\text{C}_4\text{H}_8\text{N}_2\text{H}_{10}\) with \(\Delta G_{\text{ads}} = -5.3\) kJ/mol, in comparison with similar values for \(\text{C}_1\text{H}_{10}\) and \(\text{C}_1\text{O}_2\text{H}_8\). This means that the surface of the N-containing carbon catalysts will be the easiest to regenerate for the next chemisorption acts of benzoyl decomposition products, first of all with PhCOO• radical.

Conclusion

In the benzoyl peroxide molecule, the weakest bond is \((O-O)\), due to the rupture of which the formation of two radicals \(\text{C}_6\text{H}_5\text{COO}\) is most likely to be. Radicals, in turn, are able to decompose with the formation of a phenyl radicals (\(\text{C}_6\text{H}_5\)) and \(\text{CO}_2\) molecules.

Thermodynamic \(\Delta G_{\text{pho}}, \Delta G_{\text{ads}}\) and kinetic \(\Delta G_{\text{act}}\) characteristics of the interaction of PhCOO• radical with carbon nanoclusters are determined by their electron-donor ability (ionization potential). In non-aqueous media (solutions) nitrogen-containing carbon materials have significantly higher catalytic activity compared to the enzyme catalase.

Acknowledgements

This work was supported by the Project of the Swedish Research Council (VR) under contract #348-2014-4250, Contract of Employment/Letter of Intent of 2014.12.01 of the Ningbo University of Technology (China) and Project of the National Academy of Sciences of Ukraine Program of Fundamental Research “New Functional Substances and Materials for Chemical Engineering”.

Author’s contributions

Conceived the plan: M. Kartel, D. Haliarnyk, V. Kuts; Performed the experiments: D. Haliarnyk, O. Bakalinska, Wang Bo, T. Kulyk, B. Palyanytsya; Data analysis: L. Karachevtseva, Ye. Demianenko, A. Grebenyuk, V. Kuts; Wrote the paper: M. Kartel, D. Haliarnyk, V. Kuts. Authors have no competing financial interests.

References

1. Fidalgo, B.; Menendez, J. A.; *Chinese J. Catal.*, 2011, 32, 207. DOI: https://doi.org/10.1016/S1872-2067(10)60166-0
2. Trogadas, P.; Fuller, T. F.; Strasser, P.; *Carbon*, 2014, 75, 5. DOI: 10.1016/j.carbon.2014.04.005
Plasmonic sensing through bioconjugation of Ag nanoparticles: Towards the development of immunoassays for ultralow quantification of antigens in colloidal dispersions

Pablo A. Mercadal¹, Juan C. Fraire¹, Rubén Motrich² and Eduardo A. Coronado¹

¹INFIQC-CONICET, Centro Láser de Ciencias Moleculares, Departamento de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba (5000). Argentina
²CIBICI-CONICET, Departamento de Bioquímica Clínica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba (5000). Argentina

DOI: 10.5185/amlett.2018.2001
www.vbripress.com/aml

Abstract

The combination of the optical properties of silver nanoparticles with some of the tool-kits of the widespread used ELISA method for antigen quantification immunoassays, give rise to an enzyme free, low cost, fast and more sensitive optical method denoted as Intensity Depletion Immuno-linked Assay (IDILA), that can be performed directly in colloidal dispersions without any immobilization of the capture antibody, antigen, secondary and primary antibodies on a substrate. The capabilities of the method for quantifying antigens at ultralow concentrations in colloidal dispersions as well as its performance are demonstrated for specific antigens of importance in medicine and in food science. Copyright © 2018 VBRI Press.

Keywords: Plasmonic nanoparticles, antigen quantification, bioconjugation, immunoassay.

Introduction

One of the most popular tools in biochemistry for antigen detection is the Enzyme-Linked Immuno-sorbent Assay (ELISA). It is used, for instance in the clinical analysis for the prognosis and diagnostics of several diseases [1-3], as well as in other areas such as the control of the quality of food[5-7], bio-technology[8,9], environmental monitoring of pollutants[10,11], defense and biotechnology.[12-14]

In the standard ELISA (see Fig.1), the antigen to be detected in a fluid phase is immobilized on a substrate, to a specific capture antibody, which is itself subsequently detected by a secondary, enzyme-coupled antibody that upon reacting with a substrate, yields a visible color change or fluorescence, indicating the presence of the antigen.[15]

Although this method has demonstrated to be robust and of easy implementation in laboratories, it has some shortcomings such as the several steps involved and the occasionally nonspecific binding of the antigen to the substrate that could lead to false positive results.

One of the most significant improvements of the ELISA assay performed in recent years is the so-called plasmonic ELISA (pELISA).[16] The basis of this method relies on the extraordinary signal amplification
generated by the enzyme using the unique optical properties of noble metal nanoparticles (NPs). These properties arise from the Localized Surface Plasmon Resonance (LSPR), a phenomenon generated by the collective excitation of the conduction electrons of noble metals induced upon illumination with light.[17] The frequency of the LSPR is highly dependent on NP size, shape, and composition as well as on the external dielectric environment and clusterization degree.[17-19] The absorption as well as the scattering cross section of Ag or Au NPs are highly enhanced at the LSPR frequency. The extinction cross section is the contribution from both scattering plus absorption cross sections. For relatively small NPs (around 15-20 nm diameter) absorption dominates the extinction spectra, while for NPs of large size (roughly above 100 nm) scattering is the main contribution.[17] For NPs of intermediate size both scattering and absorption processes are important. It should be noted that extinction spectra are the far field optical property measured in a conventional UV-Vis spectrophotometer. Using a dark field illumination and collecting the light using a high NA objective, the light scattered by individual nanoparticles can be detected as bright color points by the eye.[20] Furthermore, by collecting the scattering signal of a single NP and due to the extreme sensibility of the LSPR wavelength to the external dielectric environment, the binding of specific analytes to the NP surface can be monitored following the spectral shift of the LSPR. In this way, extremely sensitive LSPR sensors have been developed.[21-25]

Many different mechanisms for amplification of the signal in pELISA have been developed in recent years. All of them are based on inducing a change of color using the plasmonic properties of noble metal NPs. The product generated by the enzyme can produce, for instance, the agglomeration of a colloidal dispersion of Au/Ag NPs, the formation and growth of new NPs or the etching of noble metal NPs.[26-32] These different types of modulating the state of the plasmonic nanostructures, yields as a result a pronounced color change in colloidal solution as a function of the analyte concentration. In this way, the pELISA methods already mentioned are able to detect very low concentrations of antigens, offering relatively low cost, reliable and quick semi-quantitative determination. In spite of these significant improvements of the ELISA method by introducing plasmonic properties as signal traducers, its format is still the same, since in any case it involves detecting the antigen by its immobilization on a solid substrate (microplates) using the specific antibody, and the need to label it with a primary or secondary antibody with an enzyme. Therefore, the several time-consuming steps of incubation, washing and immobilization cannot be avoided together with the need to use an enzyme labelled antibody.

In order to surmount these shortcomings, we have developed a new method denoted as IDILA (Intensity Depletion Immunolinked Assay) that combines the plasmonic properties of silver nanoparticles with the biorecognition properties of the molecules used in the ELISA assay (biotinylated specific antibody and antigen) but with the important advantage that it can be performed totally in a colloidal dispersion, it does not require using an enzyme, and can be performed in almost one step.[33] This means that does not require high amounts of reagents to be immobilized, implying short experiment lengths and extremely low amounts of reagents, making it feasible for a fraction of the common price per experiment of ELISA (See table S1 in the Supporting Information).

**Basis of the IDILA methodology**

The IDILA method is based on the inhibition of the formation of nanoparticle dimers produced by linking two Ag NPs by a specific antibody in the presence of different concentration of the corresponding antigen to be detected. The formation of Ag dimers at a certain time, in the absence of antigen, produces a depletion of the extinction intensity (the degree of depletion depends on the fraction of dimers formed and therefore of the antibody concentration). In the presence of both the antigen and the antibody, the specific interaction between the antibody and the antigen, causes an inhibition of dimer formation. As a consequence, the fraction of dimers formed decreases as the antigen concentration increases (the comparison of the extinction intensities in the absence and in the presence of antigen is performed at the same reaction time, normally around 30 minutes, after which no change of the extinction intensity is observed).

The Ag NPs are functionalized, before adding the antigen, with biotin and streptavidin mixed in concentration ratio 1:1:1 between Ag NPs, biotin and streptavidin, in such a way to have on the average only one (or only a few) biotin-streptavidin complex per NP.

The first issue to be addressed is why the formation of silver NPs dimers causes a decrease of the extinction intensity. The answer to this issue is quite simple. Comparing the calculated extinction cross-section of 60 nm diameter Ag monomer and the corresponding dimer with a gap of around 20 nm (corresponding to the size of the molecules sandwiching the monomers, i.e. biotin-STV-antibody-STV-biotin, see figure 4) shows that although the average extinction cross section of a Ag dimer \( \sigma_{\text{Ext}} = \frac{1}{3}\sigma_x + \frac{1}{3}\sigma_y + \frac{1}{3}\sigma_z \) is larger by a factor of 1.5 with respect to the monomer, the quantity to be compared is the sum of the extinction cross-sections of two monomer with respect to one dimer, which is 0.75 times smaller. In addition, as the plasmon coupling in the Ag NP dimers is small due to the relatively large interparticle gap, the extinction spectra of the dimer have its peak intensity at almost the same wavelength. Considering these features, and the fact that as dimers are formed, the total number of particles (dimers plus monomers) decreases, it follows that the
The extinction intensity of the colloidal dispersion should also decrease.

![Image](extinction.png)

**Fig 2.** Comparison between the extinction cross-section corresponding to two monomers and the corresponding dimer with a gap of 20 nm for a) silver b) gold.

For the dimerization process:

\[ 2M \rightarrow D \]

where \( M \) stands for Ag monomers and \( D \) for Ag NPs dimers, the total concentration of particles at any time \( t \) \([\text{[NPs]}_t]\) as a function of the initial concentration of NPs \([\text{[NPs]}_i]\), and the fraction of dimers \( f_d = \frac{[D]_t}{[\text{NPs}]_t} \) is given by:

\[
\text{[NPs]}_t = \text{[NPs]}_i \left( \frac{1 - f_d}{1 + f_d} \right) + \text{[NPs]}_i \left( \frac{f_d}{1 + f_d} \right)
\]

The extinction intensity at any time \( E_t \) is obtained multiplying each term by the corresponding extinction cross-section.

\[
E_t = \text{[NPs]}_i \left( \frac{1 - f_d}{1 + f_d} \right) \sigma_m + \text{[NPs]}_i \left( \frac{f_d}{1 + f_d} \right) \sigma_d
\]

being \( \sigma_m \) and \( \sigma_d \) the extinction cross-section of the monomer and dimer respectively. Note that initially \( f_d = 0 \), and \( E_t = [\text{NPs}]_i \sigma_m \) as expected while as \( f_d \rightarrow 1 \), \( E_t = \frac{1}{2} [\text{NPs}]_i \sigma_d \), thus if \( \sigma_d = 1.5 \sigma_m \), then for a total conversion of monomer to dimers, the value of the extinction should be \( E_t = 0.75 [\text{NPs}]_i \sigma_m \), which corresponds to 25% of depletion with respect to the initial value. The addition of antigen produces a smaller fraction of dimers and as a consequence a less degree of depletion.

**Fig 3.** Degree of extinction depletion for two Ig-G antibodies as a function of their concentration.

**Dependence of the extinction depletion on the IgG antibody concentration**

Now we will illustrate the application of this principle to the quantification of antigens. **Fig. 3** illustrate the extinction depletion as a function of time after adding the specific capture biotinylated IgG antibodies for the detection of antigens of importance in clinical (i.e., interleukin 10 – IL-10) and food chemistry (i.e., gliadin) diagnosis.

It can be appreciated that the extinction intensity decreases with the addition of the different biotinylated IgG reaching a maximum depletion for a concentration around 1 ng/mL and then start to decrease again, until reaching almost the initial value. The initial intensity depletion implies that the formation of dimers is favored as IgG increases, the lower value corresponds to the antibody concentration where the maximum dimer fraction is produced. After this concentration value, the intensity starts to increase again, because the concentration of IgG is high enough that many of the available streptavidin sites at the surface of the Ag NPs are occupied by IgG and therefore are not able to form dimers.
The formation of dimers of Ag NPs structures is evidenced from the TEM images obtained after adding to the NPs dispersion a specific quantity of antibody at a given reaction time as shown in Fig. 4. Note also that the interparticle separation is around 20 nm in agreement with the molecular geometry.

Fig 4. (a) Scheme showing the dimensions of the molecular sandwich between two Ag NPs. (b) Representative TEM image of the dimers formed after 27 min of the addition of IgG-gliadin.

The regime for the applicability of the IDILA technique is the one that favor the dimer formation. In this regime, the presence of the antigen of interest according to the nature of the IgG used, will inhibit, according to its concentration the dimer formation.

On the general capabilities of the IDILA method for quantification of any type of antigen

One important question which arises is if once the intensity depletion in the presence of the biotinylated antibody, the capability biotin-STV functionalized Ag NPs is a general feature, independent of the antigen nature. In order to answer this issue, we have performed experiments using antigens of different composition and size. Fig. 5 depicts the significant change on the degree of depletion of the extinction intensity upon the addition of pico-molar concentrations of antigen to a colloidal dispersion of streptavidin-biotin functionalized Ag NPs at the same time (27 minutes) of reaction time. A comparison of the degree of depletion of the extinction spectra intensity with and without the antigen, show that the degree of depletion decreases as the antigen concentration increases, till reaching an asymptotic value where the formation of dimers is completely disfavored.

The reason of the behavior mentioned above can be explained in a simple way. At low antigen concentrations, a small quantity of Ag monomers can form dimers as a small fraction of monomers are bounded to the antibody and the remaining nanoparticles are functionalized with the antigen. This is translated in an increase of the intensity of the extinction as the antigen concentration increase (less formation of dimers). At high antigen concentrations dimer formation is completely inhibited because all antibodies are functionalized with antigens and therefore any is able to react with another nanoparticle to form a dimer or the biotinylated antibody hides their biotin groups (for instance by a conformational change when it is functionalized with the antigen), leading in any case to the same result. The underlying microscopic changes in antibody conformation or the specific changes induced by the molecular binding of the antibody to the antigen is a research topic under development.

The analytical performance of the IDILA methodology for the quantification of the two antigens discussed in the present article are shown in Table 1. The comparison of the detection sensitivity and limit of detection (LOD) between IDILA and ELISA revealed that the sensitivity is improved by IDILA by 1000-1000 folds over the traditional colorimetric assay.

Table 1. Comparison of the analytical parameters between IDILA and ELISA.

<table>
<thead>
<tr>
<th>Antigen</th>
<th>IDILA</th>
<th>ELISA</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL-10</td>
<td>0.06 ± 0.02 pg/mL</td>
<td>(1.5 ±0.1) x10² pg/mL</td>
</tr>
<tr>
<td>Gliadin</td>
<td>(1.6±0.1) x10² ng/mL</td>
<td>0.52 pg/mL</td>
</tr>
<tr>
<td>LOD</td>
<td>0.8 pg/mL</td>
<td>0.52 pg/mL</td>
</tr>
</tbody>
</table>

*data of commercially available ultra-sensitive ELISA kits from ThermoFisher.
Conclusions

In this perspective article, we have outlined the main principles underlying a new form of immunoassay that combines the unique optical properties of Ag plasmonic NPs, the strong streptavidin–biotin interactions and affinity between the antigen and its specific biotinylated antibody. This new method, denoted as intensity depletion immunolinked assay (IDILA), is based on the depletion of the intensity of extinction caused by the formation of silver nanoparticle dimers between biot-STV functionalized Ag NPs and the antibody. This depletion occurs because the extinction cross-section of two Ag NPs monomers is significantly greater than the corresponding Ag NP dimer. It was demonstrated that it is not expected to work with Au NPs since for this metal this condition is not fulfilled. The presence of different antigen concentrations, inhibits the process of dimer formation and therefore the extinction depletion varies with an upper bound equal to zero (when the antigen concentration is so high that dimers are not formed) and a lower bound that depends on the fraction of dimers formed (in the absence of the antigen).

This method proved to be robust, fast (< 2 hours), cheap, sensitive, accurate and potentially adaptable to any antigen (here we showed its performance for detection and quantification of IL-10 and Gliadin antigens, important for clinical and food chemistry diagnosis, respectively).

There are still many avenues that still need to be addressed in order to further prove/improve the capabilities of the IDILA method such as the role played by the initial concentration of the functionalized Ag NPs, the influence of the Ag NP size and shape, the dependence of its sensitivity upon the concentration of the antibody, for just mentioning the main issues under current study in our laboratories.

Acknowledgements

The authors acknowledge financial support from CONICET (PIP 112-201101-00430), FONCYT (PCT 2012-2286, PCT 2012-3094), SECYT-UNC and PME 1544 – 2006. P.A.M. acknowledges CONICET for being a recipient of a PhD fellowship.

Author’s contributions

Authors have no competing financial interests.

Supporting information

Materials and methods for the theoretical simulations, extinction depletion studies, TEM images, and fractional extinction depletion in the presence of a specific antigen. Table of comparative costs between IDILA and ELISA. Supporting informations are available from VBRI Press.

References

DOI: 10.1016/j.ab.2012.09.014

DOI: 10.1016/j.diagmicrobio.2014.02.006

DOI: 10.1016/j.autrev.2012.07.006

DOI: 10.1038/srep16092

DOI: 10.1016/j.foodchem.2014.12.017


DOI: 10.1016/j.foodchem.2012.07.053

DOI: 10.1016/j.talanta.2017.04.054

DOI: 10.1007/s10457-011-9745-8

DOI: 10.1016/j.chemosphere.2010.12.054

DOI: 10.1039/C3EM00296A

DOI: 10.1021/cr200061k

DOI: 10.1016/j.bios.2014.10.081

DOI: 10.1016/j.bios.2012.04.023

DOI: 10.1039/c3ana1835k

DOI: 10.1038/nano.2012.186

DOI: 10.1021/jp026731y

DOI: 10.1021/nn300474p

DOI: 10.1021/ip3123709

DOI: 10.1039/b711069c

DOI: 10.2217/nmn.11.117

DOI: 10.1021/nn500396

DOI: 10.1109/JPROC.2016.2624340

DOI: 10.1039/c4ra07119k
   DOI: 10.1039/c4an01070e
   DOI: 10.1021/nl2006092
   DOI: 10.1016/S1872-2040(13)60714
   DOI: 10.1038/srep32755
   DOI: 10.7150/thno.16129
   DOI: 10.1007/s00216-016-0028-5
   DOI: 10.1039/C6NR06079J
   DOI: 10.1039/C6RA16750K
   DOI: 10.1039/C6NR04897H
FIVE YEAR FREE MEMBERSHIP
ADVANCEMENT OF MATERIALS COMMUNITY
JOIN NOW

Benefits of IAAM

- You will get a five year IAAM membership complimentary.
- In conferences sponsored by IAAM, you will get discounted registration under IAAM member.
- FREE listing in, and access to, the online IAAM Member.
- First-to-know status for IAAM meeting programs and calls for papers.
- Regional forums for interaction through IAAM Sections.
- Regularly receive Advanced Materials Letters and Advanced Materials Proceedings.

Invite to Submit Symposia Proposals

Be a part of Advanced Materials series (www.iaamonline.org) in Asia (Spring, ASAMC, Singapore), Europe (Summer, EAMC, Sweden), and USA (Winter, AAMC, Miami).

International Association of Advanced Materials (IAAM, www.iaamonline.org) invite symposia proposals for our upcoming annual conferences. We welcome proposals that explore interdisciplinary connections with areas of advanced materials. The symposia can include about 8-10 sessions, each session running for 2 - 3 hours.

Symposia should cover the scientific subject area of congress and proposals are encouraged to address the theme. Symposia Proposals should be send via E-mail (with a short CV of the proposed organiser and co-organisers) to:

Prof. Ashutosh Tiwari, Secretary General
International Association of Advanced Materials
Teknikringen 4A, UCS, Mjardevi Science Park, Linköping, SE58330, Sweden
E-mail: secretarygeneral@iaamonline.org

Contact us:
Teknikringen 4A, Mjardevi Science Park 58330, Linköping, Sweden
www.iaamonline.org
contact@iaamonline.org
European Advanced Materials Congress

20 - 23 August 2018, Stockholm, Sweden

SESSIONS

- Nanomaterials and Nanotechnology (NMT)
- Thin film, Materials Surface & Interfaces (TMI)
- Composite and Ceramic Materials (CCM)
- Biomaterials and Biodevices (BB)
- Computational Materials and Modeling (CMM)
- Electronic, Magnetic and Optical Materials (EMOM)
- Functional Materials (FM)
- Energy Materials (EM)
- Structural and Engineering Materials (SEM)
- Science and Technology of Polymers (STP)
- Environmental and Green Materials (EGM)

SYMPOSIA

- Nanoenergy
- Global Graphene Forum
- Coating Materials Technology
- Graphene Interfacing Biological Systems
- Growth of Carbon Nanomaterials
- Advanced Materials Innovations