



Optochemical fiber sensor for Toluidine Blue detection in high turbidity media

Victoria Benavente Llorente*, Eustaquio M. Erro, Ana M. Baruzzi, Rodrigo A. Iglesias

INFIQC CONICET, Departamento de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba (UNC), Pabellón Argentina Ala 1 Piso 2, 5000 Córdoba, Argentina

ARTICLE INFO

Article history:

Received 21 November 2014
Received in revised form 25 February 2015
Accepted 26 March 2015
Available online 15 April 2015

Keywords:

Optical fiber sensor
Toluidine blue
Evanescent wave
Photo remediation

ABSTRACT

We report the analytical performance of an optochemical fiber optic sensor for the detection of dyes in aqueous media with high turbidity. Specifically, the analytical performance of this sensor was evaluated for the quantitative detection of Toluidine Blue (TB) in aqueous solution and also in turbid suspensions of TiO_2 anatase nanoparticles. The detection limit attained was 5×10^{-7} M with a linear sensitivity of $7 \times 10^4 \text{ M}^{-1}$ across a linear range from 5×10^{-7} to 5×10^{-6} M. We used the optochemical sensor for two main purposes: (1) *in situ* characterization of the adsorption isotherm of Toluidine Blue on TiO_2 nanoparticles; (2) *in situ* characterization of the photodegradation of Toluidine Blue mediated by UV irradiation of TiO_2 nanoparticles. The main aim of this report is to establish the construction and performance of a simple, cheap and small optochemical sensor with clear applications in the field of dye-polluted environmental monitoring.

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1. Introduction

Wastewaters containing dyes can be highly toxic considering that 20% of the total industrial dyes are lost during dying processes and are released as effluents [1,2]. The detection and quantification of colorants is of great interest; with this purpose evanescent field fiber-optic absorption sensors are extensively applied in continuous monitoring of concentrations of reactants in chemical processes [3–9]. The optical fibers are highly sensitive to external perturbation which makes them excellent candidates for the construction of optical sensors [10–12]. The evanescence wave spectroscopy applied to these sensors becomes then a really versatile, sensible, simple and low-cost experimental system. Khijwania et al. have reported a relative humidity sensor using an optic fiber coated with a CoCl_2 doped thin polymer film with fast response, full reversibility and large dynamic range [13]; Miled et al. have presented an optic pH sensor based on a dye activated mesostructured silica coated optical fiber, achieving excellent reversibility [14].

Elimination of a pollutant from a contaminated site is an important phase of the process known as remediation. The removal of colored pollutants can be done by physical techniques like adsorption on activated carbon, ultrafiltration, reverse osmosis,

coagulation by chemical agents, ion exchange on synthetic adsorbent resins [15–19]. Nevertheless, as these strategies do not destroy the pollutants, different alternatives like chlorination and ozone treatment were evaluated, but the results have shown slow degradation rates and high operation costs [18,20–23].

Heterogeneous photocatalysis has attracted increasing attention in order to eliminate undesirable organic pollutants in aqueous phase [1,24,25]. When a semiconductor metal oxide absorbs a photon of energy equal to or greater than its band gap width, an electron may be promoted from the valence band to the conduction band resulting in an electron–hole pair that can move through the semiconductor and reach the catalyst surface participating in redox reactions with adsorbed species [24,25]. $\text{TiO}_{2(s)}$ has been proved to be an excellent catalyst in the photocatalytic degradation of organic pollutants, because it is an effective, photostable, reusable, inexpensive, and non-toxic material [24–30].

There are few reports of techniques allowing the continuous and *in situ* monitoring of the concentration of dyes in turbid aqueous solutions for photodegradation tests [1,24,25]. This kind of characterizations are normally performed by exposing a solution of dyes containing nanosized TiO_2 to UV light, then centrifuging or filtrating the samples in order to measure the dye's concentration through spectrophotometry after sample concentration conditioning [1,24,25]. These drawbacks can be overcome by an optochemical sensor based on a fiber optic able to quantify the dye concentration without any sample pretreatment and continuously in real time. As far as we know, optical fiber sensor reports

* Corresponding author. Tel.: +54 351 5353866x53487; fax: +54 351 4334188.

E-mail addresses: vbenavente@fcq.unc.edu.ar, benaventevictoria@gmail.com, infiqc@fcq.unc.edu.ar (V.B. Llorente).

are mostly made of glass optical fibers. Plastic optical fibers are barely found in recent reports for dye detection. In addition there are also few reports for dye detection in high turbidity media based on plastic optical fiber.

In this paper, a plastic optical fiber sensor based on the interaction of the evanescent wave with Toluidine Blue adsorbed on the decladded and unfunctionalized fiber is presented. As a new analytical approach, we have used the optochemical sensor for two main purposes: (1) *in situ* characterization of the adsorption isotherm of Toluidine Blue on TiO₂ nanoparticles; (2) *in situ* characterization of the photodegradation of Toluidine Blue mediated by UV irradiation of TiO₂ nanoparticles.

2. Materials and methods

Toluidine Blue (TB) was obtained from ALDRICH. Mono- and di-basic potassium phosphate (Ciccarelli) for buffer solutions were used as received. PH value was adjusted with hydrochloric acid or potassium hydroxide. Titanium (IV) oxides, anatase (25 nm particle size) and rutile nanopowders (100 nm particle size) were obtained from ALDRICH. Ultrapure water (18 MΩ cm) was obtained using a Milli-Q water purification system (Millipore).

To fabricate the sensor, plastic optical fibers were used. This kind of fiber is commercially available as standardized optical fiber connection systems (Toslink). The fiber is composed by a 920 μm OD polymethylmethacrylate (PMMA) core, a fluorinated polymer clad with a thickness of 20 μm and a black polyethylene jacket. The core and clad refraction indexes are 1.49 and 1.46, respectively.

A 10 cm piece of plastic fiber was cut and the black jacket was completely removed, the middle region of the fiber was carefully decladded to partially expose the core. The entire piece was bent slowly until it became U-shape with the decladded zone in the curved area, and immobilized on a polyamide plug by introducing the extremes in two positioned holes performed for this purpose. A white LED acts as light source at one end of the fiber while the output signal is directed to an optical fiber (Ocean Optics Inc.) coupled to a HR2000 Ocean Optics Spectrometer (Ocean Optics Inc.) connected to a laptop. A quartz beaker compatible in size with the fabricated polyamide plug was used to put the sensor in contact with 10 mM pH: 7.0 phosphate buffer solution. Several aliquots of 2.5×10^{-3} M TB standard solution were added to the buffer medium and the optical fiber attenuation was registered (computed as an absorbance change). The measured signal is produced by the interaction between adsorbed Toluidine Blue on the fiber surface and the evanescent wave in the interface fiber/solution. All the experimental work has been done with magnetic stirring at room temperature.

Adsorption of Toluidine Blue on Titanium IV oxide was used to evaluate the sensor performance in a high turbidity medium. A known quantity of TiO₂ was dispersed in a small volume of phosphate buffer or Toluidine Blue solutions taken from the experimental system using a Pasteur pipette and then the dispersion was returned immediately to the system. A Shimatzu P600 UV-visible spectrophotometer was used to contrast the obtained results.

Photodegradation of Toluidine Blue adsorbed on TiO₂ with different crystal phases was tested using the same optochemical sensor. For this purpose, TB adsorbed on TiO₂ was irradiated with a 300 W Osram Ultra Vitalux mercury tungsten blended UV reflector.

The sensor was cleaned and reused after every experiment. The cleaning process consists of a washing step with buffer solution during 20–30 min under convection, and then the fiber is gently cleaned with a wet tissue paper. The fiber was always stored into 10 mM pH 7.0 phosphate buffer solution.

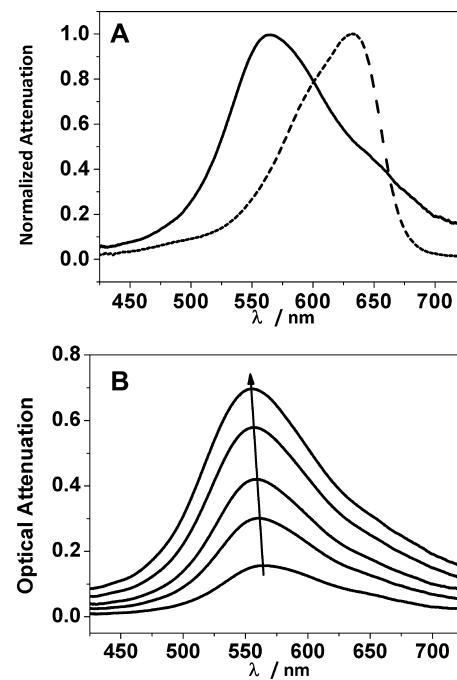


Fig. 1. (A) Normalized TB spectra obtained from optical attenuation of the fiber probe immersed in a TB solution (solid line) and visible spectrum of TB solution taken with a spectrophotometer (dash line). (B) Optical attenuation of fiber probe for increasing TB concentration: 2.5, 5.0, 19.0, 30.0 and 90.0 μ M.

3. Results and discussion

3.1. Analytical performance

[Fig. 1A](#) shows the visible absorption spectra for two molecular states of Toluidine Blue (TB) adsorbed on the optical fiber (solid line) and TB in solution (dash line), respectively. The spectral change, the shifting of the maximum wavelength locus from 632 to 555 nm, evidences that the analytical response of the optical fiber is produced by the interaction between the evanescent wave and TB adsorbed on the fiber probe resulting in a hypsochromic shift of the spectrum. Ionic strength, pH value and temperature were carefully controlled, monitored and kept constant during the experiments. Spectral changes observed cannot be explained in terms of acid–base equilibrium, neither changes given by coupled reactions; in fact, the change must be given by the immobilization of the dye molecules on the fiber surface where the environment has different electrical properties.

[Fig. 1B](#) shows the sensor performance detecting different TB concentration levels (2.5, 5.0, 19.0, 30.0 and 90.0 μ M). All these spectra were obtained in a single step experiment successively adding known volumes of TB standard solution. Clearly, the increase of the optical signal is given by the detection of the added dye, evidenced by a spectral profile characteristic of TB adsorbed on the fiber ([Fig. 1A](#), solid line). Changes of the spectral baseline or in different wavelength regions were not observed. [Fig. 2A](#) shows the continuous change of the optical fiber signal, at the wavelength of maxima (555 nm), with sequential additions of TB solution. The signal was registered as a function of time reaching an absorbance steady value after ten minutes for each standard addition. This experiment was performed by addition of 5 μ L aliquots of a 2.5×10^{-3} M TB standard solution to a stirred 10 mM pH 7.0 phosphate buffer solution. These values, for each TB concentration, are shown in [Fig. 2B](#). This profile, an isotherm-like shape, is also a clear indication that the adsorbed TB is being tested by the evanescent wave of the optical fiber. Considering the adsorption of TB on

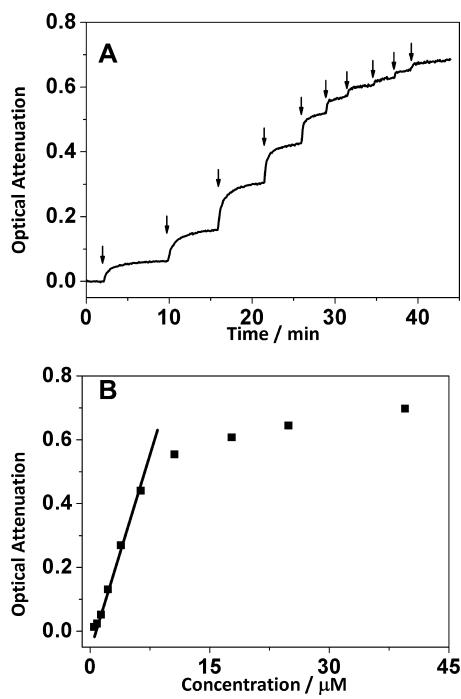


Fig. 2. (A) Fiber probe response as a function of time at 565 nm, arrows indicates the addition of TB solution. (B) Signal change at 565 nm for increasing TB concentration.

the optical fiber, the analytical performance of the sensor has a linear response (see straight line in Fig. 2B) ranging from 5.0×10^{-7} to 5.0×10^{-6} M, with a sensitivity of $7.0 \times 10^4 \text{ M}^{-1}$, a detection limit of 5.0×10^{-7} M ($r^2 = 0.995$; variation coefficient = 3.7%; for four consecutive experiments).

3.2. Toluidine Blue adsorption on nanoparticulated titanium dioxide $\text{NPTiO}_{2(s)}$

The aim of the optical sensor studied is the detection of dyes in high turbidity media. With this purpose the detection of TB was followed after the addition of $\text{NPTiO}_{2(s)}$. Once a steady optical signal was reached at a TB concentration of $10 \mu\text{M}$, 20 mg of anatase $\text{NPTiO}_{2(s)}$ nanoparticles were added to the solution; a clear decrease in the signal was observed (see supp. info Figure S1) due to a decrease of TB concentration in solution after the adsorption of the dye on TiO_2 . Noticeably the spectral shape did not change (see supp. info Figure S2) after the addition of nanoparticles, indicating the capability of the sensor of detecting TB even in a medium with high turbidity. Considering these two evidences, it can be concluded that the optical sensor output is correlated with the amount of dye in solution and it is not affected by the presence of TiO_2 nanoparticles. Furthermore, the signal change can be used to quantify the amount of dye adsorbed on TiO_2 ; consequently the optical sensor was used to characterize the adsorption of TB on TiO_2 nanoparticles. Fig. 3A shows the analytical responses of the sensor towards TB in presence and absence of 100 mg of $\text{TiO}_{2(s)}$ dispersed in the buffer solution.

In order to obtain the adsorption isotherm for TB on NPTiO_2 several experiments like the presented in Fig. 3A were done, with different NPTiO_2 masses. A summary of these results is plotted in Fig. 3B. It should be noted that this figure plots the mole amount of adsorbed dye per gram of TiO_2 added into the solution; i.e. the adsorption isotherm of the dye on TiO_2 . The amount of dye adsorbed was quantified with the information given by Fig. 3A and the linear response region of the sensor indicated in Fig. 2B. For comparison, the same

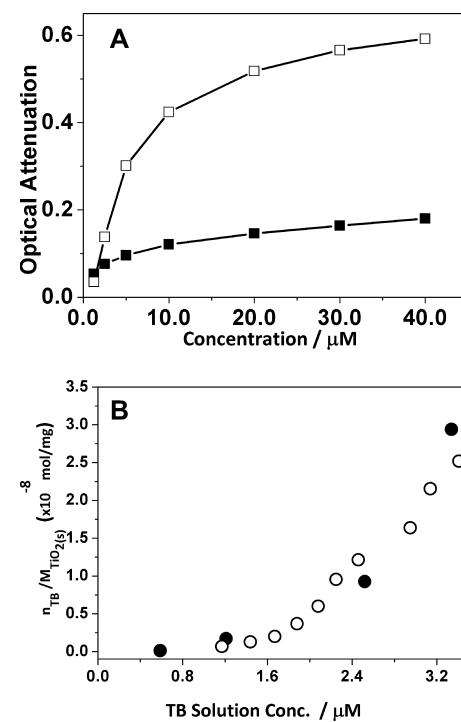


Fig. 3. (A) Fiber signal at $\lambda: 565 \text{ nm}$ for different TB concentration values in presence of 100 mg of NPTiO_2 (■) and absence of NPTiO_2 (□). (B) Comparison of TB adsorption isotherm on NPTiO_2 obtained with the optical fiber sensor at $\lambda: 565 \text{ nm}$ (○) and UV-vis spectrophotometer at $\lambda: 632 \text{ nm}$ (●).

adsorption isotherm was quantified by spectrophotometric measurements (only four points involving several chemical steps: aliquot extraction–centrifugation–filtration–dilution). A reasonable good coincidence of curves is obtained for the interval of concentration ranging from 1 to $3.4 \mu\text{M}$.

3.3. Photoinduced degradation of Toluidine Blue assisted by NPTiO_2

As we mentioned before, TB as other dyes can be destroyed under ambient conditions if they are adsorbed on TiO_2 and irradiated with UV light, being this attribute an interesting way for remediation of polluted aquatic environment. Following in situ this process allows for a quantitative characterization of the remediation action. With this purpose the optical fiber sensor was tested for an in situ monitoring of heterogeneous photodegradation of TB over TiO_2 particles. Fig. 4 shows the sensor response at $\lambda = 565 \text{ nm}$

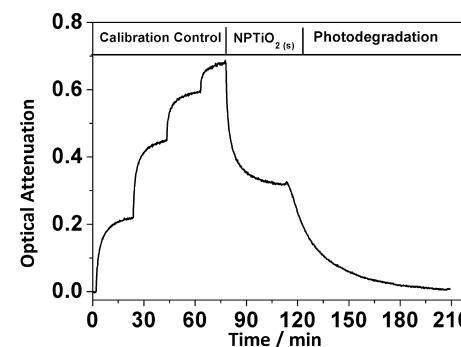


Fig. 4. Optical fiber sensor performance for an in situ three steps experiment; first stage is a four point calibration control, second stage is the NPTiO_2 addition, and the third stage shows TB photodegradation.

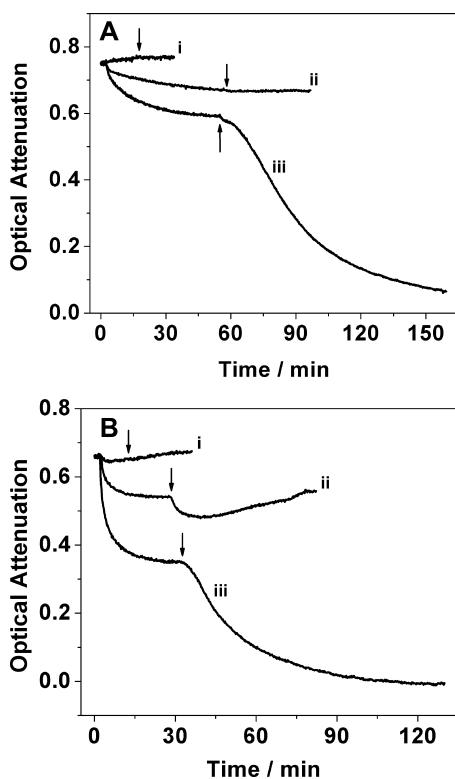


Fig. 5. Optical sensor responses at λ : 565 nm for adsorption and photodegradation of TB by four different TiO_2 substrates. Arrows indicates the beginning of UV irradiation. (A) Nanotubular TiO_2 substrate. (i) Control experiment (0 mg), (ii) 7 mg amorphous TiO_2 nanotubes, (iii) 7 mg anatase TiO_2 nanotubes. (B) Nanospherical TiO_2 substrate, (i) 10 mg rutile TiO_2 , (ii) 100 mg rutile TiO_2 and (iii) 10 mg anatase TiO_2 .

in a three steps experiment to monitor the photodegradation of TB adsorbed on TiO_2 nanoparticles.

In the first step, sensor calibration control was performed before every experiment adding four aliquots of 20 μL of TB 2.5×10^{-3} M standard solution to cover the sensor dynamic range. This can be observed in Fig. 4 as four absorbance increasing steps. After that 100 mg of NPTiO₂ were added to the system and the absorbance decreases as previously described. Finally, the third step initiates when the system is irradiated with UV light. At this point, the absorbance signal decreases with a simultaneous TB solution bleaching. This evidence suggests that the colorant molecules have suffered a photodegradation process and the absorbance change curve can be used to describe the kinetic behavior of this photodegradation. The curve can be fitted by a simple exponential suggesting a pseudo-first-order kinetics. Control experiments were carried out in the absence of NPTiO₂ under UV-irradiation, where no signal change was observed. The three steps experiment was performed without any centrifugation, filtration or dilution steps.

3.4. Sensor response for TB adsorption and photodegradation on different photocatalysts

In order to describe the photocatalytic activity of different substrates, several experiments were carried out using commercial anatase and rutile nanoparticles, and lab-made anatase and amorphous TiO_2 nanotubes. Fig. 5 shows the TB photodegradation of every TiO_2 substrate.

It is very well recognized that the photocatalytic activity of anatase TiO_2 is very efficient and much better (thermodynamically and kinetically) than other crystal structures of TiO_2 [1,17–22]. Fig. 5A shows a control experiment without TiO_2 (curve i) where

no TB photolysis was observed. Curves (ii) and (iii) indicate that TB adsorbs more strongly on anatase than on amorphous nanotubes. The same trend can be inferred from the photodegradation step; it is faster and almost complete for anatase TiO_2 nanotubes than for amorphous nanotubes (same size, same amount). Two nanospherical TiO_2 substrates were also tested; the obtained responses are plotted in Fig. 5B. Curves (i) and (ii) correspond to 10 and 100 mg of rutile TiO_2 nanospheres (mean size: 100 nm) and curve (iii) corresponds to 10 mg of anatase TiO_2 nanospheres (mean size: 25 nm). Clear differences are observed in the amount of dye adsorbed. Adsorption over anatase nanoparticles is higher than on rutile nanoparticles, even when the amount of the last one is one order of magnitude larger. Under UV irradiation, anatase nanospheres catalyze the total degradation of TB in approximately 2 h while rutile nanoparticles induces a small and slow photodegradation.

One aspect to be noted is that anatase TiO_2 has a similar photocatalytic activity towards TB independently of the nanogeometry used. Low and none photocatalytic activity were exhibit by the rutile and amorphous TiO_2 nanoparticles.

4. Conclusions

The plastic optical fiber sensor presented in this paper is able to quantify TB in aqueous medium with a high level of turbidity. The interaction between the evanescent wave and the dye adsorbed on the fiber has been evidenced and plays a central role in the sensor operation. The sensor presented can be used as a tool to construct the TB on $\text{TiO}_{2(s)}$ adsorption isotherm in its dynamic range of concentration. The experimental data evidence the analytical system capacity to provide direct measure for concentration changes of TB in a turbid suspension without any centrifugation or filtration steps. The TB photodegradative TiO_2 mediated process was clearly evidenced and kinetic information can be easily accessed.

Acknowledgment

V. Benavente Llorente thanks CONICET by the doctoral fellowship granted. E.M. Erro thanks CONICET by the postdoctoral fellowship granted. Authors want to acknowledge the supporting agencies: SeCYT-UNC, FONCYT-ANPCyT and CONICET.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2015.03.085>

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Biographies

Victoria Benavente Llorente received his B.S. degree in 2005 in chemistry at the National University of Córdoba. During her BS's thesis, she worked on photoelectrochemistry of nanostructured semiconductors and its applications on photoremediation and photovoltaics. She started a Ph.D. thesis on chemistry on the National University of Córdoba in 2014 granted by the National Council of Scientific and Technical Research (CONICET). Currently, she is working on her Ph.D. thesis on the area of photoelectrochemistry of nanostructured semiconductors under the supervision of Prof. Rodrigo Iglesias in the Institute of Physicochemical Research in the National University of Córdoba.

Eustaquio M. Erro received his B.S. degree in 2003 in chemistry and Ph.D. degree in 2011 in chemistry from the National University of Córdoba. During the period of 2012–2014, he worked in Prof. Ana Baruzzi's group as a postdoctoral research associate in the Institute of Physicochemical Research in the National University of Córdoba.

Ana M. Baruzzi is currently head professor of the Faculty of Chemistry, National University of Córdoba, and Principal Researcher of the National Council of Scientific and Technical Research, Argentina. She got her diploma in physical chemistry in 1978 and the Ph.D. degree in 1982 at the same university in the area of electrocatalytic processes on Pt electrodes. She has been supervisor of seven doctoral theses and of three researchers of the CONICET. She has 53 publications in International journals. Her current area of research is focused on optical and electrochemical studies of processes at different interfaces and physicochemical properties of polymeric matrices used for biomolecules immobilization, especially for biosensors based on enzymatic amperometric electrodes.

Rodrigo A. Iglesias received his B.S. degree in 1998 in chemistry and Ph.D. degree in 2003 in physical chemistry from National University of Córdoba. During the period of 2004–2006, he worked in Prof. Ezequiel Leiva's group as a postdoctoral research associate in National University of Córdoba performing multiscale atomistic simulations; later he moved for a period of two years to The Biodesign Institute at Arizona State University under the supervision of Prof. Nongjian Tao. During this postdoctoral stay R.A.I. developed several platforms for breath and environmental analysis of trace compounds. Now he is an adjunct research professor in National University of Córdoba and his current research is focused on the synthesis, fabrication and characterization of nanostructured wide band gap semiconductors modified with semiconducting nanocrystals for the fabrication of liquid junction hybrid solar cells.