Preparation, Characterization and Application of Modified Surfaces with 3,5-Bis(3,5-dinitrobenzoyl-amino) benzoic acid

Julieta I. Paez,[1] *Ariel L. Cappelletti,*[1] *Ana M. Baruzzi,*[2] *Verónica Brunetti,*[2] *Miriam C. Strumia**[1]

Summary: The spontaneous adsorption of the dendron 3,5-Bis (3,5-dinitrobenzoylamino) benzoic acid (D-NO_2) onto gold and carbon electrodes produced conductive surfaces with electroactive chemical functions. A comparative electrochemical behavior of both electrodes after dendron immobilization led us to conclude that the self-assembly of D-NO_2 on carbon is faster and stronger. Considering this advantage, the surface of magnetic maghemite nanoparticles (MNPs) was modified using D-NO_2. Firstly, MNPs were modified with APS as silane coupling agent and afterwards, D-NO_2 was covalently attached to the surface, achieving nitro-functionalized MNPs. Subsequently, the immobilization of these modified MNPs onto glassy carbon surfaces was explored to generate a novel platform promising for biosensors development.

Keywords: dendritic molecules; electrochemistry; maghemite; magnetic nanoparticles; self-assembly

Introduction

Research on functionalized surfaces is of growing interest nowadays and has attracted interdisciplinary attention.[1–2] The efficiency of any immobilization process relies on the careful balance of intermolecular forces that promotes the interaction between the solid surface and the molecule to be grafted.[3] In this context, surface chemistry is a powerful tool to tailor surface properties.

More specifically, thin films and self-assembled monolayers (SAMs) have potential applications in materials science and biological sensors.[4] Interest in thin films lies in their potential as inexpensive, versatile surface coatings for applications including the control of wetting and adhesion, chemical and microbial resistance, biocompatibility and molecular recognition for sensors, especially those related to biology.[5] The attachment of thiol compounds to a gold surface to form an ordered structure is used in most SAMs. Other approaches include attaching terminal alkenes to silica or attaching chlorosilanes, phosphonic acids, carboxylic acids and alcohols to non-metals and metals with a native oxide layer.[4]

Magnetic nanoparticles (MNPs) possess high surface area and unique magnetic properties with a broad range of potential biomedical applications[6–9] (e.g., diagnostic medicine, hyperthermia, cell labeling and sorting, separation o cells), and other nonbiomedical uses[10] (e.g. high-density memory devices, magnetic sensors, imaging reagents, ferrofluids). In all cases the magnetic nanoparticles must remain non-aggregated, be stable against oxidation, and

[1] Departamento de Química Orgánica (IMBIV-CONICET), Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Argentina
E-mail: mcs@fcq.unc.edu.ar
[2] Departamento de Fisicoquímica (INFIQC-CONICET), Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Medina Allende y Haya de la Torre, Ciudad Universitaria, Córdoba (5016), Argentina

display high magnetization.[11] In recent years there has been a significant progress in the application of these novel nanomaterials in biosensors.[12] One of the main issues in this field is the surface modification of nanoparticles using various useful materials. This produces desirable surface functionalities that can be tailored to specific applications. Zhang et al[13] have presented a novel method for the preparation of hydrogen peroxide biosensor using carbon-coated iron nanoparticle as a novel kind of magnetic nanomaterials, obtained by coating a layer of carbon uniformly on the surface of the nanoscale iron. The coated nanoparticles exhibited resistance to corrosion and oxidation, and a small average size, which make them highly promising for applications.[14] Recently, Lee et al. have reported useful magnetic carriers prepared by coating a layer of polymer onto magnetic nanoparticles.[15] They have been successfully applied in enzyme immobilization because of its abundant functional groups and magnetic character, which is also useful in the separation of them from the reaction medium by using a magnetic field.[16]

In addition, several specific dendrimers and dendrons have been studied using self-assembled monolayers (SAMs) to give organic thin films.[17–19] They are of particular interest to nano and polymer research as building blocks due to their unique, architecturally driven, macromolecular properties.[20–24] By using dendritic molecules, the selectivity of the material can be increased.[25] Examples like Newkome-type dendrons that terminate with carboxylates have been used to attach a ferrocene in close proximity to a gold electrode that is coated with ammonio-terminated thiols.[26] They are also used to impart water solubility on highly hydrophobic aromatic groups.[27] In previous works,[25,28,29] we demonstrated the benefits of the use of dendrons with specific functionality as structure modifiers in the synthesis of hybrid and amphiphilic structural polymers.

Lately, we have studied the use of one specific dendron (3,5-bis(3,5 dinitrobenzoylamino)benzoic acid) or (D-NO_2) to modify gold and carbon surfaces[30,31] showing an optimal molecular structure and wide versatility to self assemble onto different surfaces. The dendritic molecule contains three aromatic rings in its body, four nitro groups as peripheral-ends, and a carboxylic acid group at the focal point. The presence of the three aromatic rings contributed as a rigid fragment, which appears to be responsible for the readiness of the dendrons for self-assembly and for their rapid interaction with some surfaces.[31]

We report here a comparative analysis of the behavior of D-NO_2 self-assembled onto gold and carbon surfaces and the application of this dendron to chemically modified magnetic nanomaterials. A synthetic pathway was developed to prepare the D-NO_2-coated magnetic maghemite (γ-Fe_2O_3) nanoparticles. Subsequently, the immobilization of these modified magnetic nanoparticles onto glassy carbon surfaces was explored to generate a novel platform promising for the development of biosensors.

Experimental Part

Materials and Equipment

3,5-Dinitrobenzoyl chloride (Fluka, 98%), 3-(aminopropyl)trimethoxysilane (APS, Sigma Aldrich, 99%), and tionylchloride (SO_2Cl, Sigma Aldrich) were used as received; N,N-Dimethyladetamide (DMAc, Tedia) and toluene (Ciccarelli) were dried over 4 Å molecular sieves; 3,5-Diaminobenzoic acid (Aldrich, 98%) and ninhydrine (Anedra, p.a) were purified by recristallization from water. Maghemite (Fe_2O_3) iron oxide magnetic nanoparticles (MNPs), with a nominal size of 9 nm, were kindly provided by Prof Iñaki Mondragón (Universidad del País Vasco, Spain) and were used as received. The rest of commercially available chemicals were reagent grade and used without further purification. All solutions were prepared immediately prior to their use. Phosphate buffer solutions (PBS) used in this work contain 0.1 M Na_2HPO_4/NaH_2PO_4. Water was purified with a Millipore Milli-Q system.

Infrared spectroscopy (FT-IR) was carried out on a Nicolet-5SXC, using KBr or AgBr pellets; thermogravimetric analyses (TGA) were performed on a 2950 TGA HR thermogravimetric analyzer, TA Instruments, between 20 and 500 °C, and at heating rate of 10 °C/min under nitrogen flow.

Dendronization of MNPs with DNO_2

The dendron (3,5-Bis (3,5-dinitrobenzoylamino) benzoic acid) or D-NO_2 was obtained following Kakimoto's procedure[32,33] by using 3,5-Diaminobenzoic acid and 3,5-dinitrobenzoyl chloride in DMAc.

a) Synthesis of MNPs-APS: the functionalization of MNPs with APS was achieved following similar procedures to those previously reported.[34,35] In a dry three-necked flask and under a nitrogen atmosphere, MNPs (50 mg, 0.087 mmol, 1 eq) were dispersed in dry toluene (6 mL). Then, APS (0.065 mL, 0.277 mmol, 3.2 eq) was then added with a syringe under sonication. The dispersion was sonicated for 3 h at room temperature. The MNPs were subsequently washed with tetrahydrofuran (THF) six times and centrifuged in order to remove the remaining APS. The modified MNPs were dried under vacuum at 45 °C until constant weight. Using the ninhydrin method,[36] which allows the determination of primary amino groups, the efficiency of this first step was quantified.

FT-IR (cm^{-1}): 3419, 2961, 2930, 1561, 1408, 1100, 1035, 673, 637, 586.

b) Synthesis of MNPs-APS-D-NO_2: as was previously reported,[28] in a dry three-necked flask and under a nitrogen atmosphere, D-NO_2 (10 mg, 0.0185 mmol) was exposed to thionylchloride (SO_2Cl, 3 mL) and 3 drops of DMF were used as a catalyst; after that, the mixture was refluxed for 5 h. Then, the excess of SO_2Cl was removed under vacuum, and MNPs-APS (20 mg) were added as a solid. The mixture obtained was dispersed in dry DMAc (5 mL), cooled at 0 °C and stirred for 6 h. The temperature was subsequently allowed to rise at room temperature, and the dispersion was stirred for 18 h. In order to remove the remaining D-NO_2, the resulting mixture was washed and centrifuged twice with HCl 1.5 M, milli-Q water, saturated $NaHCO_3$ solution, and four times with THF. The product was dried under vacuum at 45 °C until constant weight.

FT-IR (cm^{-1}): 3442, 2924, 1570, 1543, 1345, 1020, 689, 635, 584.

Electrochemical Measurements

Electrochemical measurements were perfomed with an Autolab electrochemical analyzer and a conventional three-electrode system, comprising a carbon (or gold) working electrode, a platinum foil as counter-electrode, and an Ag/AgCl 3.0 M NaCl electrode (from BAS) as reference. All potentials were reported versus the Ag/AgCl reference electrode at room temperature. Nitrogen gas was used to deaerate all aqueous solutions before use.

a) Preparation of working electrode: 1.6 mm-polycrystalline gold (Bioanalytical System Inc. (BAS), Lafayette, IL) or 3.0 mm- glassy carbon electrodes (GCE from CH Instruments, Inc. Austin, TX) were polished with 1.0, 0.3 and 0.005 mm alumina slurry on a microcloth pad, rinsed with water and ethanol and sonicated (10 min) in distilled water. The gold electrodes were subsequently activated by repeatedly scanning the potential between the hydrogen evolution and the oxygen evolution regions in 1 M H_2SO_4, rinsed with water and dried in N_2 flux.

b) Attachment of D-NO_2 onto carbon and gold electrodes by self-assembly technique: The cleaned working electrode was incubated in a Dimethylsulfoxide (DMSO) solution containing 10 mM of D-NO_2 at intervals ranging from 5 seconds up to overnight. Following the modification, the derivatized surface was subsequently rinsed with copious volumes of ethanol and water, and used following its preparation.

c) Attachment of MNPs-APS-D-NO_2 onto GCE: The cleaned glassy carbon electrode was incubated in a DMSO suspension containing1 mg/mL of dendronized-maghemite

(MNPs-APS-D-NO_2) at intervals ranging from 15 min up to overnight. Following the modification, the derivatized surface was subsequently rinsed with copious volumes of ethanol and water, and was employed immediately after its preparation.

Results and Discussion

Comparative Behavior of D-NO_2 Immobilized onto Gold and Carbon Electrodes

The attachment of D-NO_2 onto the electrode was monitored through the observation of the electrochemical signal of reporting groups, such as the nitro group. The voltammetry of nitrobenzene and nitrosobenzene physisorbed onto different substrates[37–39] reveals that the voltammetric response observed was indeed characteristic of the electrochemical reduction of an aromatic nitro compound and consistent with the general mechanism shown elsewhere.[40] The cathodic wave at −0.50 V during the first scan corresponded to the four-electron reduction of each nitro moiety to the corresponding aryl hydroxylamine onto gold electrodes (see Figure 1a). On the subsequent sweep, the pair of anodic and cathodic peaks could be attributed to the two-electron oxidation/reduction of the aryl-hydroxylamine/aryl-nitroso moieties onto gold (see Figure 1b). In addition, the properties of D-NO_2 modifying carbon surfaces enable the proposal of a more detailed mechanism than adsorbing onto gold electrodes. Figure 1c shows the electrochemical profile obtained for the reduction of D-NO_2 attached onto GCE during the first scan exhibiting two waves instead of one. This behavior could be explained considering the differences in energy for the reduction of the two NO_2 substituents in each aromatic ring of D-NO_2.[31]

Assuming that the cathodic peak at −0.48 V (A) is associated with the reduction of one NO_2 substituent, the reduction of the second NO_2 substituent (the cathodic peak (B) at −0.60 V) occurs at more negative potentials due to the disappearance of the negative inductive effect of an electron acceptor like NO_2 in the meta position.[31] On the subsequent positive-going sweep, the anodic peak at −0.03 V (C) is related to the oxidation of one NHOH substituent, while the anodic peak at 0.04 V (D) is associated with the oxidation of the other NHOH substituent, which now has a NO substituent in the meta position (see Figure 1d).

The presence of functional groups could significantly alter the nature and the magnitude of the interactions between aromatic molecules and the electrode surface. Although the electrochemical behavior of D-NO_2 adsorbed onto GCE is qualitatively similar to that observed for gold, we found that DNO_2 exhibits a greater affinity to form spontaneous layers on carbon than on gold. Immersing the glassy carbon electrode in 10 mM D-NO_2 solutions for only 5 seconds allowed us to obtain the electrochemical signal of an aromatic nitro compound instead of the approximately 8-12 hours needed with gold electrodes. In our opinion, the cooperative effect of phenyl rings and the multifunctionality of D-NO_2 (containing carboxyl and nitro groups) allowed a direct and rapid adsorption onto carbon surfaces favored by π-π interactions. Taking into account the strong affinity between D-NO_2 and carbon surfaces, the subsequent step, in our case, was the incorporation of this dendron onto the surface of magnetic maghemite nanoparticles. The idea was to use the dendron as a linker for the immobilization of dendron-coated magnetic nanoparticles onto GCE.

Synthesis and Characterization of MNPs-APS-D-NO_2

The modification of MNPs with D-NO_2 involved a two-step synthetic strategy shown in Scheme 1. First, MNPs were modified with APS as silane coupling agent. Afterwards, D-NO_2 was covalently attached to modified MNPs, achieving nitro-functionalized magnetic nanoparticles. In

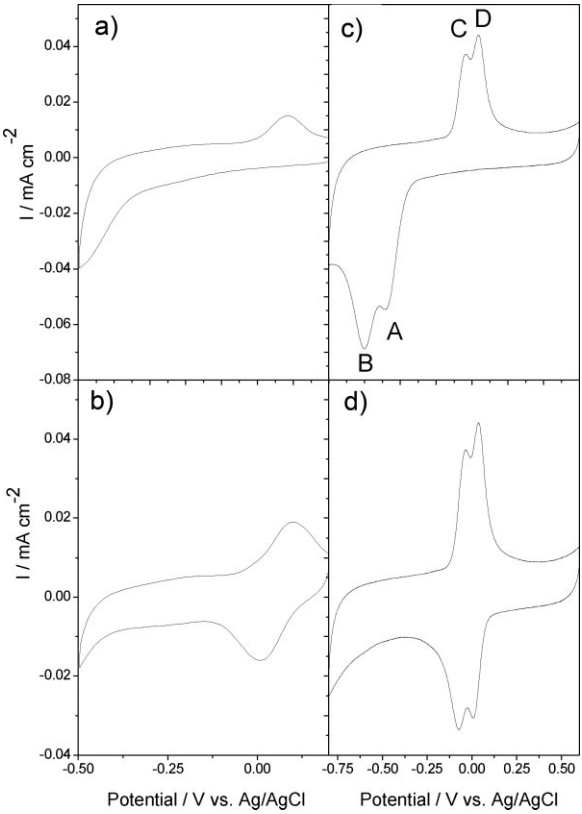
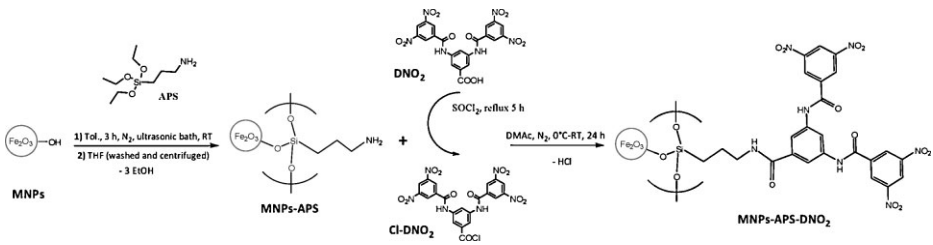


Figure 1.
Cyclic voltammograms at 0.1 Vs for D-NO_2 modified surfaces in 0.1 M PBS (pH 7). Gold electrode, first (a) and second (b) scan. Glassy carbon electrode, first (c) and second (d) scan.

the first step, the conversion degree of superficial OH groups into NH_2 groups was estimated to be of 15%, using the ninhydrin method. After each step, modified MNPs were characterized by FTIR and TGA. It is important to notice that an increase in the solubility in organic solvents was observed after the organic derivatization.

Figure 2 and 3 show the spectra of MNPs, MNPs-APS and MNPs-APS-D-NO_2. The comparative analysis of them and the appearance of new bands confirmed the synthetic modification achieved. Spectra of MNPs-APS shows the incorporation of new peaks corresponding into APS, as an aliphatic C-H stretching between 3000-



Scheme 1.
Synthetic pathway used in order to obtain dendron-coated magnetic nanoparticles.

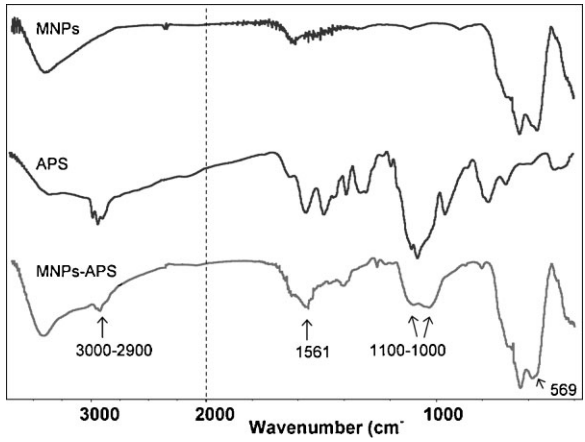


Figure 2.
FTIR spectra for unmodified MNPs, APS, MNPs-APS.

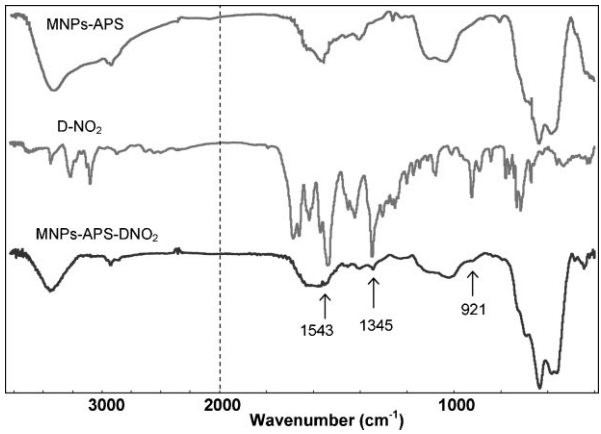


Figure 3.
FTIR spectra for MNPs-APS, D-NO2 and MNPs-APS-D-NO2.

2900 cm^{-1}, N-H bending at 1561 cm^{-1}, Si-O-Si and Fe-O-Si between 1000-1100 cm^{-1}, and a variation in the relative intensities of other two peaks due to Fe-O stretching bond between 560-640 cm^{-1}. The peak at 569 cm^{-1} exhibits an intensity decrease, while the peak at 630 cm^{-1} remains constant. The spectrum of MNPs-APS-D-NO_2 shows bands which confirmed that D-NO_2 was attached to MNPs-APS, as an incorporation of asymmetric and symmetric stretching of nitro group at 1543 and 1345 cm^{-1}, respectively. Another peak at 921 cm^{-1}, due to C-H out-of-plane deformation of trisubstitued aromatic ring can be observed as well. Other characteristic bands of the dendron are overlapped with the bands of MNPs-APS. The spectra show a low degree of derivatization, mainly after the second synthetic step.

In addition, TGA experiments were carried out. Figure 4 shows the weight loss for modified and unmodified MNPs for the heating process from 20-500°C. Grafting is proved by the weight loss and by the degradation of the organic part in the

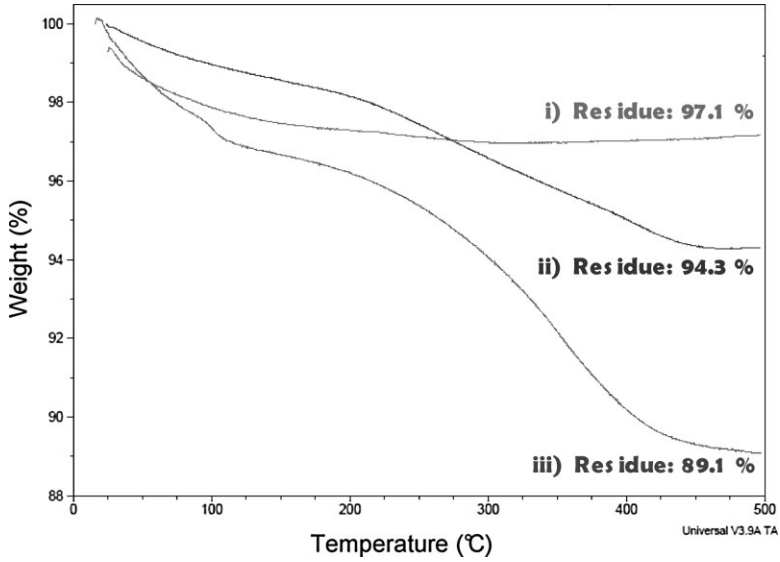


Figure 4.
TGA thermogram of (i) unmodified MNPs; (ii) MNPs-APS; (iii) MNPs-APS-D-NO_2.

modified nanoparticles, as previously reported.[41] In all cases, the thermograms exhibit one first step of weight loss of 3% before 100 °C, attributed to water loss. MNPs-APS thermogram shows a weight loss of 3% between 225 - 420 °C corresponding to APS organic modification, and MNPs-APS-D-NO_2 displays a weight loss of 8% between 120 - 420 °C corresponding to dendron and APS chemical modification.

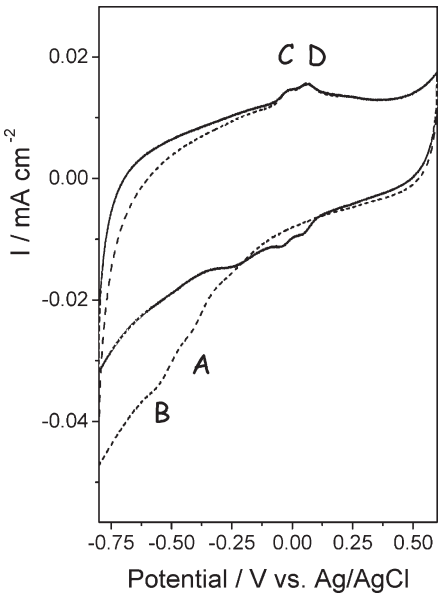


Figure 5.
Cyclic voltammograms at 0.1 Vs for MNPs-APS-D-NO_2 modified glassy carbon electrode in 0.1 M PBS (pH 7). First scan (dashed line) and second scan (solid line).

Self-Assembly of MNPs-APS-D-NO_2 onto GCE

From Figure 5 it is clearly seen that the spontaneous self-assembly of MNPs-APS-D-NO_2 onto GCE was achieved because the electrochemical signal of nitro moieties were observed. The voltammetric feature is similar to that observed for D-NO_2 attached directly onto carbon surface. The main difference, however, lies in the total amount of the charge related to nitro moiety which, in this case, is considerably smaller. These results are in a good agreement with the low degree of MNPs functionalization achieved.

Conclusion

The spontaneous adsorption of 3,5-Bis (3,5-dinitrobenzoylamino) benzoic acid (D-NO_2) onto gold and carbon surfaces results

in a simple and rapid way to produce conductive surfaces with electroactive chemical functions. A comparative electrochemical behavior of both metals after dendron immobilization was presented. The glassy carbon electrode shows better results (shorter adsorption times for self-assembly) and allows the advancement of a more detailed mechanism.

With the aim of investigating new routes to produce sensor platforms and taking into account the strong affinity between D-NO_2 molecules and carbon, a synthetic pathway was developed to obtain D-NO_2-coated magnetic nanoparticles. Maghemite magnetic iron oxide nanoparticles were modified with 3-(aminopropyl)trimethoxysilane as silane coupling agent. Afterwards, D-NO_2 was covalently attached to the modified MNPs, achieving nitro-functionalized magnetic nanoparticles. The immobilization of the novel dendritic molecule-coated MNPs onto carbon surfaces was subsequently achieved. The attachment of the dendron was monitored through the observation of the electrochemical signal of the nitro group. These results point out a simple method to add magnetic material in carbon electrodes and thus generate promising surfaces for the development of biosensors.

The dendron covalently bounded to nanoparticles plays an essential role in the immobilization of the functionalized nanoparticles onto the electrode surface. We believe that the novel strategy for the synthesis presented in this work can be generalized and adapted to synthesize other dendronized surfaces. The novel and versatile hybrid nanostructured material obtained will promote the exploration, design, fabrication, and search for new applications in biosensor developments and pave the way for many applications such as biocompatible delivery systems and electronic and photonic devices. We are currently actively exploring this area of research.

Acknowledgements: The authors gratefully acknowledge financial support from CONICET, ANPCyT, and SECYT of Universidad Nacional de Córdoba. J.I.P. wishes to thank CONICET for the fellowship provided.

[1] A. A. Williams, B. S. Day, B. L. Kite, M. K. McPherson, C. Slebodnick, J. R. Morris, R. D. Gandour, *Chem. Commun.* **2005**, *40*, 5053.
[2] S. Mohapatra, P. Panchanan, *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2009**, *339*, 35.
[3] I. J. Bruce, T. Sen, *Langmuir* **2005**, *21*, 7029.
[4] A. Ullman, *Chem. Rev.* **1996**, *96*, 1533.
[5] M. Mrksich, *Chem. Soc. Rev.* **2000**, *29*, 267.
[6] Y. Boguslavsky, S. J. Margel, *Colloid Interf. Sci.* **2008**, *317*, 101.
[7] S. A. Gomez-Lopera, R. C. Plaza, A. V. Delgado, *J. Colloid Interf. Sci.* **2001**, *240*, 40.
[8] M. Arruebo, R. Fernández-Pacheco, M. R. Ibarra, J. Santamaría, *Nanotoday* **2007**, *2*, 22.
[9] C. C. Berry, *J. Mater. Chem.* **2005**, *15*, 543.
[10] M. Takafuji, S. Ide, H. Ihara, Z. Xu, *Chem. Mater.* **2004**, *16*, 1977.
[11] Y. Boguslavsky, S. Margel, *J. Colloid and Interface Sci.* **2008**, *317*, 101.
[12] X. Zhang, Q. Guo, D. Cui, *Sensors* **2009**, *9*, 1033.
[13] H.-L. Zhang, X.-Z. Zou, G.-S. Lai, D.-Y. Han, F. Wang, *Electroanalysis* **2007**, *19*, 1869.
[14] L. Paz, M. Santos, C. Ballesteros, M. M. Koc, *J. Mater. Chem.* **2005**, *15*, 4311.
[15] T. H. Chung, H. C. Pan, W. C. Lee, *J. Magn. Magn. Mater.* **2007**, *311*, 36.
[16] G.-S. Lai, H.-L. Zhang, D.-Y. Han, *Sensors and actuators B* **2008**, *129*, 497.
[17] V. V. Tsukruk, *Adv. Mater.* **1999**, *10*, 253.
[18] G. H. Degenhart, B. Dordi, H. Schonherr, G. J. Vancso, *Langmuir* **2004**, *2*, 6216.
[19] G. Cooke, J. Couet, J. F. Garety, C. Q. Ma, S. Mabruk, G. Rabani, V. M. Rotello, V. Sindelar, P. Woisel, *Tetrahedron Lett.* **2006**, *47*, 3763.
[20] B. Huang, D. A. Tomalia, *J. Luminisc.* **2005**, *111*, 215.
[21] M. Mackay, C.R. *Chimie* **2003**, *6*, 747.
[22] Z. Bo, L. Zhang, Z. Wang, X. Zhang, J. Shen, *Mater. Sci. Eng. C* **1999**, *10*, 165.
[23] F. Zeng, S. Zimmerman, S. Kolatuchin, D. Reichert, *Tetrahedron* **2002**, *58*, 825.
[24] D. Smith, A. Hist, C. Love, J. Hardy, S. Brignell, *B. Huang, Prog. Polym. Sci.* **2005**, *30*, 220.
[25] M. Martinelli, M. Calderón, M. C. Strumia, *Reactive Funct. Polym.* **2007**, *67*, 1018.
[26] Y. Wang, C. M. Cardona, A. E. Kaifer, *J. Am. Chem. Soc.* **1999**, *121*, 9756.
[27] W. Ong, M. Gomez-Kaifer, A. E. Kaifer, *Chem. Commun.* **2004**, *10*, 1677.
[28] P. Froimowicz, J. Paez, A. Gandini, N. Belgacem, M. Strumia, *Macromol. Symp.* **2006**, *245–246*, 51.
[29] M. Martinelli, M. Calderón, E. Rodríguez, J. Freire, M. Strumia, *Eur. Polym. J.* **2007**, *43*, 1978.

[30] J. Paez, P. Froimowicz, A. Baruzzi, M. Strumia, V. Brunetti, *Electrochem. Comm.* **2008**, *10*, 541.
[31] J. Paez, M. Strumia, M. Passeggi, Jr., J. Ferrón, A. Baruzzi, V. Brunetti, *Electrochem. Acta* **2009**, *54*, 4192.
[32] P. Froimowicz, *Ph. D. Diss., Universidad Nacional de Córdoba*, Argentina, **2005**.
[33] Y. Ishida, M. Jikei, M. Kakimoto, *Macromolecules* **2000**, *33*, 3202.
[34] E. Marutani, S. Yamamoto, T. Ninjbadgar, Y. Tsujii, T. Fukuda, M. Takano, *Polimer* **2004**, *45*, 2231.
[35] I. Garcia, N. Zafeiropoulos, A. Janke, A. Terajak, A. Eceiza, M. Stamm, I. Mondragon, *J. Polym. Sci.: Part A: Chemistry* **2007**, *45*, 4744.
[36] S. W. Sun, Y. C. Lin, Y. M. Weng, M. J. Chen, *Journal of Food Composition and Analysis* **2006**, *19*, 112.
[37] E. Casero, M. Darder, K. Takada, H. D. Abruña, F. Pariente, E. Lorenzo, *Langmuir* **1999**, *15*, 127.
[38] X. Y. Xiao, S. G. Sun, *Electrochim. Acta* **2000**, *45*, 2897.
[39] A. T. Masheter, L. Xiao, G. G. Wildgoose, A. Crossley, J. H. Jones, R. G. Compton, *J. Mater. Chem.* **2007**, *17*, 3515.
[40] G. G. Wildgoose, S. J. Wilkins, G. R. Williams, R. R. France, D. L. Carnahan, L. Jiang, T. G. J. Jones, R. G. Compton, *Chem. Phys. Chem.* **2005**, *6*, 352.
[41] M. Sangermano, A. Priola, G. Kortaberria, A. Jimeno, I. Garcia, I. Mondragon, G. Rizza, *Macromol. Mater. Eng.* **2007**, *292*, 956.

