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Polymeric nanowires directly electrosynthesized on the working electrode

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ABSTRACT

Poly(1-amino-9,10-anthraquinone) (P1AAQ) nanowires have been directly electro-synthesized on a steel electrode, previously modified with a thin film of poly(P1AAQ-co-o-phenylenediamine), *via* a SiO_2 mesoporous template. Nanostructures obtainment was verified by electrochemical techniques and TEM. After template removal, it was corroborated that the nanowires, about 30 nm in diameter and 200 nm in length, were attached to the P1AAQ surface. The reproducibility of the method exhibited a standard deviation $3.357 \cdot 10^{-6}$ for $P_{ox(0.8\,V)}$ and $3.901 \cdot 10^{-6}$ for $P_{red(0.003\,V)}$ and, in addition, the response remains stable over ten successive voltammetric cycles. Characterization was conducted utilizing electrochemical techniques and visualized by SEM micrographs. Thus, to the pioneering methodology for obtaining polymeric nanowires utilizing just electrochemical techniques, this modification is now added in order to assure the adhesion of the polymeric nanostructures to the electrode surface; the feasibility of use of the device in the varied applications that these materials hold, is therefore envisaged.

1. Introduction

Since its accidental discovery by iodine-doping of polyacetylene, an intrinsically insulating organic conjugated polymer (Heeger, MacDiarmid and Shirakawa, 1977) [1], the field of electrically conducting polymers or synthetic metals, have grown very rapidly and have aroused great scientific interest because the doped polymer underwent a conductivity increase of more than 10 orders magnitude. The unusual property observed in these organic materials broadened their field of study. The result is that at present many novel conducting systems are known, among which polypyrrole (PPy), polythiophene (PTH), polyaniline (PANI), poly(1-amino-9,10-anthraquinone) and its derivatives, etc. [2–4] stand out.

Other outstanding properties of conductive polymers over other materials are, for example, flexibility, strength, elasticity and ease of production, qualities that have turned them into subject of interest for research in nanotechnology [5].

By definition, a compound with "*nano*" characteristics, either in one (1-D), two (2-D) or three-dimensional (3-D) [5,6], must contain in one of their directional axes one size measuring less than 100 nm. The findings in this area have revolutionized science, enabling for the first time to understand the large difference when the scale involves several zeros of difference. It has been found that the mechanical, physical and chemical properties of these compounds change, magnifying some and appearing other non-existing in macroscale [7].

Production methods of nanoscale compounds are varied. In the literature two widespread techniques for producing nanostructures in 1-D are found. For example, Samitier et al. [8,9] have reported a technique called Nanoimprint (Fig. 3a) [10–12]. However, this technique, despite being the domain of the authors, has not yet been widely mass produced since it has not been able to offset results with costs. Other reported technique is the use of a *template* or mold, as a basis for obtaining nanomaterials [5,13,14]. According to their chemical stability, templates can be classified into two groups namely, *hard-templates* [15–18] and *soft-templates* [19,20]. *Hard-templates* were used to obtain various types of one-dimensional (1-D) nanostructures. Usually consist of zinc oxide or silica mesoporous materials, reporting obtaining nanowires and nanorods PPy [21], PANI [22], PEDOT [23–25], etc. Hard-templates are not easy to remove, requiring very aggressive conditions for removal. One of the most widely used chemicals for this purpose is hydrofluoric acid (HF), owing to its well-known ability for attacking silicon compounds without damaging the polymeric structure, or the supports surrounding the electrodes.

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Soft-templates are prepared from a surfactant that serves to guide the polymer growth, within or around micelles assembled over a related surface. Its removal after polymerization, involves mild washing conditions with either ethanol or methanol, etc., otherwise by total decomposition of the material used as a template, using heat.

If it were possible to join the amazing results exhibited by the nano-technology with the properties presented by conducting polymers (CP), besides the speed and low cost of using electrochemical techniques, simple and inexpensive devices such as sensors [26,27], solar cells [28,29], electrocatalysts [30,31], electrochromic systems [32,33], etc., with great projection in the field of intelligent systems, could be obtained.

Nanostructured CPs exhibit improved properties that are explained by the increase in the effective surface area [5,34–37]. In this sense, nanostructured polythiophene has been already electro-synthesized by our group [38], using a thin SiO_2 mesoporous film [39,40]. This research work allowed demonstrating for the first time the feasibility of obtaining polymer nanowires directly on the electrode, using only electrochemical techniques. Later, it was corroborated that the methodology could be extended to other polymers and electrodes, being able, for example, to selectively sense dopamine employing poly(3,4-ethylenedioxythiophene) (PEDOT) nanowires [34,41]. Besides, nanostructured materials prepared in this way showed substantial properties enhancement, as compared with the respective bulk electrodes, showing an increase in current response of up to 2 orders of magnitude [42,43]. However, despite the great projections that signified the attainment of CP nanowires directly on an electrode, the difficult of template removal, that also had a bearing on the poor adhesion of the nanowires to the working electrode, hindered its handling. To overcome this drawback, a previous electro-coating of a thin layer of a chemically analogous deposit on the bare SS electrode was proposed; subsequently, on this modified electrode, the template was deposited and the previously described methodology followed. Thus, the adhesion of the nanowires covalently bound to the substrate would be warranted.

In the current paper, preparation of poly(1-amino-9,10-anthraquinone) (P1AAQ) nanowires is reported. To this purpose, a thin layer of poly(P1AAQ-co-o-phenylenediamine) (P(1AAQ-co-OPD)), whose electrosynthesis had been previously reported [34], was deposited. This copolymer was selected because its matrix possesses the monomer that ensures chemical bonding between them. Upon the copolymer, the template that subsequently will allow the electro-synthesis of the nanostructured P1AAQ, is deposited.

These results show the successful obtainment, employing just electrochemical techniques, of P1AAQ nanowires on stainless steel electrodes (SS) previously modified with P(1AAQ-co-OPD). To do this, a SiO_2 *template* is still used, but now it has been successfully removed, yielding thus an electrode whose surface presents highly ordered and adhered nanostructures, evidencing great projections for the preparation of devices that have, at present, a wide range of recognized uses.

2. Experimental

All solutions were prepared with fresh Milli-Q grade water obtained from a Heal Force (Smart Series) deionizer. All experiments were conducted at room temperature (20 °C) under a high purity argon atmosphere in a three-compartment, three-electrode anchor-type electrochemical cell. A 0.07 cm^2 geometric area steel (AISI 316) disc (SS) was used as working electrode, and a platinum wire coil of large geometric area, was the counter electrode. Ag|AgCl in a solution of tetramethylammonium chloride, whose potential matched that of a saturated calomel electrode (SCE) [44], was the reference electrode. The monomers used in the electrosynthesis were 1AAQ (98%, Aldrich), OPD (99.5%, Aldrich), obtained following the protocols reported elsewhere [34]. The template was prepared in an ethanol (98%): milli-Q water (50% v/v) mixture containing 0.05 mol L^{-1} of potassium nitrate (KNO_3, Aldrich) as supporting electrolyte, 0.0034 mol L^{-1} tetraethyl orthosilicate (Aldrich) as precursor of silicon oxide (SiO_2) and 0.115 mol L^{-1} hexadecyltrimethylammonium bromide, (CTAB, Aldrich) as surfactant, by applying a fixed potential of -1400 mV for 5 s, and then dried for 12 h at 130 °C. Surfactant extraction was accomplished by using a 0.1 mol L^{-1} hydrochloric acid (HCl 37%, Aldrich) solution in an ethanol/milli-Q water mixture (1:1% v/v). For the evaluation of silica film permeability, voltammograms between -500 and 1000 mV at 100 mV s^{-1} of a 0.01 mol L^{-1} ferrocene (98%, Aldrich) and 0.1 mol L^{-1} $TBAPF_6$ solution in CH_3CN were recorded. Finally, template extraction was performed using 0.5 mol L^{-1} NaOH (Aldrich) solution and then washing with $NaHCO_3$ (Merck, 99.0%) and finally with plenty of water.

Electrode stability was measured in a 0.1 mol L^{-1} NaCl (99.5%, Merck), 2.6 mmol L^{-1} KCl (99.5%, Merck), pH 7.35 phosphate buffer, PBS, (0.04 mol L^{-1} Na_2HPO4 (99%, Merck), 0.01 mol L^{-1} KH_2PO_4 (99.5%, Merck)) aqueous solution. In addition to analyzing its likely use as sensor, a dsDNA solution extracted from fish sperm (0.088 g L^{-1}, Aldrich, stock solution) was utilized. From this solution, aliquots were taken to prepare 25.0 mL of $1.46 \cdot 10^{-4}$ and $5.67 \cdot 10^{-5}$ mol L^{-1} solutions.

All electrochemical measurements were carried out on a CH Intruments Electrochemical Workstation. Images from the electrode surface were obtained at Bristol University on an IT300 Scanning Electron Microscope (SEM) from JEOL Ltd. and on a Hitachi HF2000-FEG transmission electron microscope (TEM), using carbon-coated nickel grids.

3. Results and discussion

3.1. Electro-obtention, optimization and characterization of P1AAQ nanowires

Steel electrodes have been modified, using methods previously developed by our group, by electro-depositing a P(1AAQ-co-o-PDA) conductive copolymer [34]. Onto this modified electrode, a thin layer of SiO_2 was electro-synthesized by applying a fixed potential of -1400 mV for 5 s. The permeability of the template on the copolymer was evaluated against a ferrocene/ferrocenium redox couple, obtaining voltammograms as those seen in Fig. 1a-b; it can be observed that applying a suitable potential for no longer than 5 seconds, a mesoporous film, with pores perpendicular to the surface of the modified electrodes, was obtained.

The comparison of the electrochemical responses of the ferrocene redox couple on the copolymer and on the template revealed its permeability, with a slight increase of 0.27 V in the $E_{pa}-E_{pc}$ difference, decreasing the reversibility of the redox process when the mesoporous film is on the copolymer. Furthermore, a decrease of the SS electrode area, evidenced as a current decrease of the redox process, was observed. Complementary rate studies allowed verifying that the effective area decreases to nearly half (2.83×10^{-2} cm^2).

In addition, TEM images of a cross section of the template on the copolymer are exhibited in Fig. 1c.

The characterization of the template on the copolymer shows its arrangement as nano-channels, normal to the surface; this is also reflected in its redox response, assessed by the ferrocene couple that showed the permeability of the silica thin film. It was thus verified that the *template* is obtained on the copolymer in much the same way as on a metallic electrode [38].