Electrochemical preparation of distinct polyaniline nanostructures by surface charge control of polystyrene nanoparticle templates†

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Received (in Cambridge, UK) 15th February 2007, Accepted 5th June 2007
First published as an Advance Article on the web 15th June 2007
DOI: 10.1039/b702488f

A family of nanostructured polyaniline (PANI) materials including polystyrene (PS)/PANI core/shell particles, PANI hollow spheres, PANI/PS nanocomposite and nanoporous PANI, were conveniently prepared by surface charge control of PS nanoparticle templates which resulted in different polymer growth mechanisms when PANI was electropolymerized around the templates.

In recent years, considerable interest has focused on the template-assisted synthesis of nanostructured materials,[1] as it offers an effective approach for the fabrication of novel materials with well-designed structures and unique properties. The templates extensively used nowadays include three main categories, *i.e.*, diblock copolymers,[2] anodized alumina layers[3] and organic or inorganic colloidal particles.[4] Among these, polystyrene (PS) particles are ideal template materials as they can be easily obtained with desired sizes and can be simply removed by dissolution in common solvents such as toluene,[5] chloroform[6] and tetrahydrofuran.[7] Recently, various nanostructured materials have been prepared by templating PS particles; for instance, metals,[8] inorganic oxides[9] and conducting polymers.[10] Among these materials, conducting polymers, especially polyaniline (PANI), have received great attention, as they possess tunable redox properties, are environmentally stable, and have many potential applications.[11] Moreover, PANI can be synthesized through electropolymerization, which allows for greater control over the quality of the prepared PANI materials by either adjusting the electrochemical polymerization time, the applied potential or current.[12]

For the PS template-assisted electrochemical preparation of PANI nanomaterials, the general procedure is firstly to form the PS template on a conducting substrate, then carry out electropolymerization of aniline, followed finally by the removal of the PS template.[13] Bartlett *et al.*[14] demonstrated an approach for synthesizing highly ordered macroporous PANI films using a self-assembled PS particle template. Following this work, Knoll and co-workers[15] reported the fabrication of ordered three-dimensional (3-D) macroporous PANI and its copolymers *via* an electrochemical method. They argued that the PANI grew firstly from the surface of the conducting substrate, and then gradually covered the 3-D templates from bottom to top. A similar growth mechanism was also suggested for the fabrication of 2-D PANI honeycomb films by Zhou *et al.*[16] In the present work, we investigated the electropolymerization of aniline using oppositely charged PS nanoparticles as templates, which resulted in the fabrication of distinct PANI nanostructured materials due to the different growth mechanisms involved.

The general strategy for the synthesis of different nanostructured PANI is illustrated in Scheme 1. Oppositely charged PS nanoparticles were self-assembled onto the surfaces of glassy carbon electrodes (GCEs) with the addition of different polyelectrolytes: negatively charged poly(sodium 4-styrenesulfonate) (PSS) and positively charged poly(diallyldimethylammonium chloride) (PDDA). As can be seen from Fig. 1a and Fig. 2a, sub-monolayers of sulfate-PS and amine-PS were formed on the GCE surfaces, respectively, which could then act as templates for the electropolymerization of aniline and the fabrication of different nanostructured PANI materials according to Scheme 1. The electropolymerization of aniline was carried out at a constant potential of +0.9 V in the solution containing 1.0 M HCl, 2.0 mM PSS and 0.05 M aniline, and prior to electropolymerization, the electrodes were kept in the solution for two minutes.

For the sulfate-PS-modified GCE, it was found that the PANI preferred to grow around the PS nanoparticles, and PS/PANI core/shell particles were formed. As the sulfate-PS nanoparticles are negatively charged, they can adsorb the positively charged aniline monomers, which results in the electropolymerization of aniline around the PS nanoparticles, similar to our previous report on the formation of silica/PANI core/shell particles.[17] Different PS/PANI core/shell particles resulted from the electropolymerization of aniline for 200, 400 and 600 s, as shown in Figs. 1b, 1c and 1d, respectively. It was apparent that the PS nanoparticles were wrapped by a layer of PANI, and the thickness of the PANI layer gradually increased with the extension of the electropolymerization time. For example, the size of the PS/PANI core/shell particles corresponding to 400 s was about 140–190 nm. Considering that the size of the original sulfate-PS nanoparticles was 100 nm, the thickness of the PANI shell was calculated to be 20–45 nm. If the electropolymerization time was too long, the PANI shell would become thick enough to make the core/shell particles connect to each other, as shown in Fig. 1d.

It can be supposed that after the removal of the PS nanoparticles from the PS/PANI core/shell particles, PANI hollow spheres could be obtained. Fig. 2 shows the scanning electron microscopy (SEM) images of the PANI hollow spheres with different shell thicknesses resulting from different electropolymerization times. Obviously, at the time of 200 s, many of the obtained PANI hollow spheres appear to be broken (Fig. 2a), which may be ascribed to the fact that at this time the PANI shells of the

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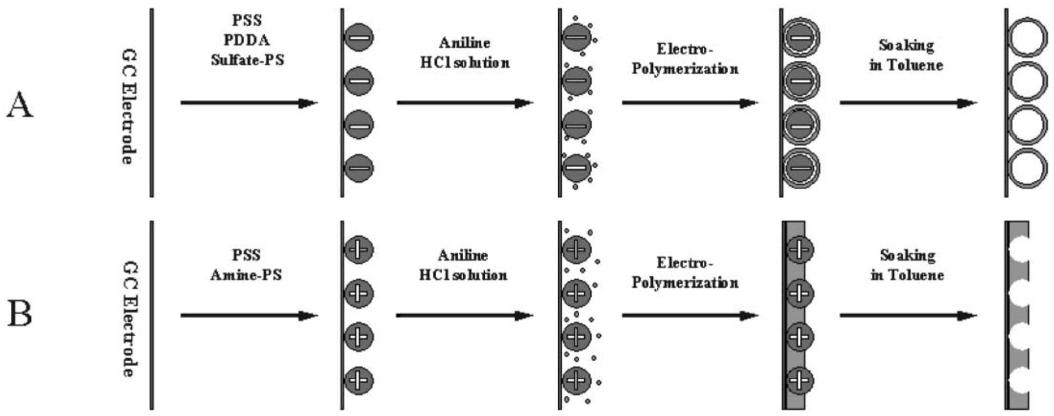
† Electronic supplementary information (ESI) available: Experimental details and SEM images verifying the hollow structure of the PANI hollow spheres. See DOI: 10.1039/b702488f



Scheme 1 Schematic representation of the formation of different nanostructured PANI materials.

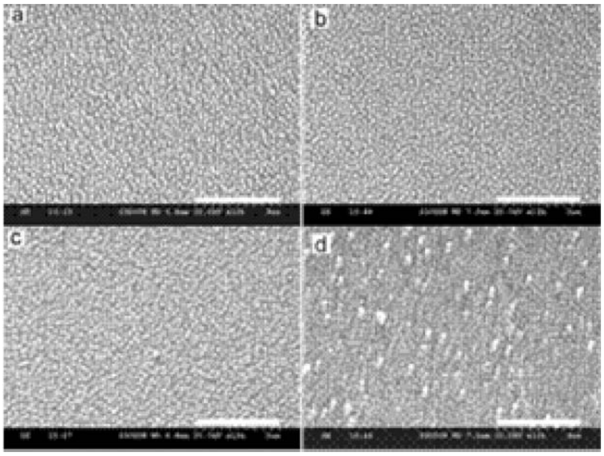


Fig. 1 SEM images of the sulfate-PS template electropolymerized with aniline for (a) 0, (b) 200, (c) 400 and (d) 600 s. Scale bars represent 3 μm. Mag. 12k.

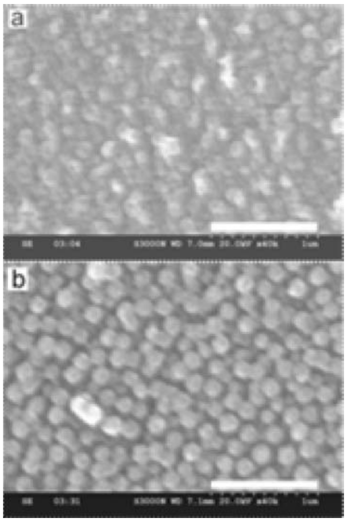


Fig. 2 SEM images of the PANI hollow spheres. The hollow spheres were prepared through the removal of the sulfate-PS nanoparticles from the PS/PANI core/shell particles electropolymerized for (a) 200 and (b) 400 s. Scale bars represent 1 μm. Mag. 40k.

PS/PANI core/shell particles are very thin, and after the dissolution of the PS nanoparticles, the thin PANI shells cannot sustain their structure without the support of the PS nanoparticle and so collapse. At the time of 400 s, well-formed PANI hollow spheres are observed (Fig. 2b). This is because the electropolymerized PANI shells at this time were thick enough to sustain their structure even without the support of the PS nanoparticles. The hollow spheres could also be compressed, whereas the core/shell particles could not (see ESI†).

For the amine-PS-modified GCE, the growth of PANI was quite different from that at the GCE modified with sulfate-PS template. As can be seen from Fig. 3, the electropolymerized PANI preferred to grow from the electrode surface and it gradually embedded the amine-PS nanoparticles as electropolymerization time increased. As a result, a PANI/PS nanocomposite, and not a PS/PANI core/shell structure, was formed. Since the amine-modified PS nanoparticles were positively charged, they should repel the positively charged aniline monomers, which appears to prevent the electropolymerization of aniline around the amine-PS nanoparticles, and therefore the PANI can only grow from the GCE surface. In this case, by adjusting the electropolymerization time, the degree of embedding of the PS nanoparticles could be easily controlled.

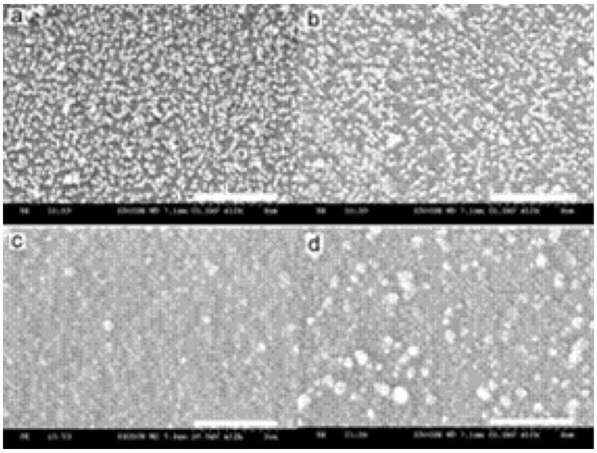


Fig. 3 SEM images of the amine-PS template electropolymerized with aniline for (a) 0, (b) 200, (c) 300 and (d) 400 s. Scale bars represent 3 μm. Mag. 12k.

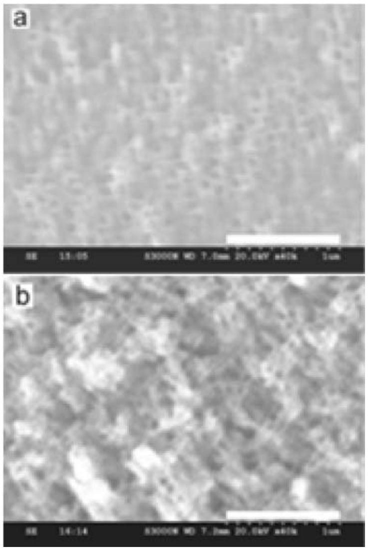


Fig. 4 SEM images of the porous PANI films prepared through the removal of the amine-PS nanoparticles from the PANI/PS nanocomposite electropolymerized for (a) 200 and (b) 300 s. Scale bars represent 1 μm. Mag. 40k.

Following the removal of the PS nanoparticles, nanoporous PANI films were obtained. Fig. 4 presents the SEM images of different nanoporous PANI films resulting from different electropolymerization times. At a time of 200 s, the electropolymerized PANI embedded only a small part of each of the PS nanoparticles, and shallow nanoholes were left after the removal of the PS nanoparticles (Fig. 4a). At a time of 300 s, a greater part of each of the PS nanoparticles was embedded by the electropolymerized PANI, and thus considerably deeper nanoholes were obtained after the dissolution of the PS nanoparticles (Fig. 4b). However, at a time of 400 s, the PS nanoparticles were totally embedded, and the nanoholes left after the removal of the PS nanoparticles were covered by the PANI layer. Therefore, different nanoporous PANI films could be obtained by controlling the electropolymerization time.

It has been reported that PANI is able to electrocatalyze the oxidation of reduced β-nicotinamide adenine dinucleotide (NADH).[18] The preliminary results of the application of the prepared PANI nanostructures for the electrocatalytic oxidation of NADH showed that all the nanomaterials synthesized exhibited enhanced catalysis over that of bulk PANI, as shown in Fig. 5. It is conceivable that these materials could be applied to biosensing systems which employ NADH with further optimization of the PANI nanostructures. Further efforts to implement these nanostructures in biosensing are underway.

In conclusion, four different nanostructured PANI materials could be electrochemically fabricated using oppositely charged PS templates. When electropolymerization of aniline was performed in the presence of negatively charged sulfate-PS templates and positively charged amine-PS templates, PS/PANI core/shell particles and PANI/PS nanocomposites could be prepared, respectively, due to different growth mechanisms of PANI. Following the removal of the PS nanoparticles, PANI hollow spheres and nanoporous PANI films could be obtained, respectively. Moreover, by the simple control of electropolymerization time, the characteristics of these PANI nanomaterials such as size and shape could be adjusted. These PANI nanostructures may find novel application in sensing systems.

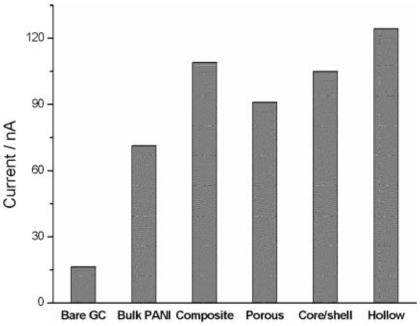


Fig. 5 Comparison of the electrocatalytic efficiency of different PANI materials. Electropolymerization time is 300 s, and the NADH concentration is 0.2 mM.

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