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Nanocomposite and Nanoporous Polyaniline Conducting Polymers Exhibit Enhanced Catalysis of Nitrite Reduction

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Abstract: Nanostructured polyaniline (PANI) conducting polymer films were prepared on electrochemically pretreated glassy carbon electrodes, which were previously modified with multilayers of polystyrene (PS) nanoparticles with a diameter of 100 nm. PANI was electropolymerised and grown through the interstitial spaces between the PS nanoparticles, which formed a nanocomposite film of PANI and PS nanoparticles on the electrode surface. Furthermore, a nanoporous PANI film was fabricated through the removal of the PS nanoparticles by dissolution in toluene. As a result of their nanostructure, both of the PANI films (before and after removal of the PS nanoparticles) exhibited enhanced electrocatalytic behaviour towards the reduction of nitrite relative to bulk-PANI films; however, partial collapse or shrinkage may have occurred with the removal of the nanoparticles and could have resulted in a less enhanced response. Under optimised conditions, the nanocomposite-film-modified electrode exhibited a fast response time of 5 s and a linear range from 5.0×10^{-7} to 1.4×10^{-3} M for the detection of nitrite; the detection limit was 2.4×10^{-7} M at a signal-to-noise ratio of 3.

Keywords: electropolymerization · nanostructures · nitrite · polyaniline · sensors

Introduction

Recently, there has been much interest in the preparation of macroporous/mesoporous materials owing to their wide range of applications in catalysis, separation systems, sensors, photonic-crystal devices and so forth.[1] A variety of macroporous/mesoporous materials, such as metals,[2] inorganic oxides[3] and polymers,[4] have been prepared. Among these materials, macroporous/mesoporous conducting polymers have received great attention because they possess tuneable redox properties, are environmentally stable and have many potential applications. Moreover, these conducting polymers can be electrochemically synthesised through electropolymerisation, which allows for greater control over the quality of the nanostructured materials obtained compared with chemical synthesis, by adjusting either the electropolymerisation time, the applied potential or the applied current.

The most popular approach towards the electrochemical synthesis of macroporous/mesoporous conducting polymers involves carrying out electropolymerisation of monomers that are within the interstitial spaces between closely packed colloidal templates, followed by removal of the templates by using appropriate solvents. Sumida et al.[5] first reported the preparation of macroporous polypyrrole films by means of an electrochemical method. Pyrrole was potentiostatically electropolymerised in the presence of an ordered silica sphere template, and following the dissolution of the silica spheres with an aqueous HF solution, a macroporous polypyrrole film with regular arrays of interconnected spherical voids was obtained. Shortly afterwards, Bartlett et al.[6] described a general approach for synthesising highly ordered macroporous conducting films of polypyrrole, polyaniline (PANI) and poly(bithiophene) by using a self-assembled colloidal template composed of polystyrene (PS) latex spheres. In their work, conducting polymers were electrochemically grown through the interstitial spaces between self-assembled PS spheres on gold substrates. The PS spheres were subsequently removed by dissolution in toluene and macroporous conducting polymers were thus fabricated. Shrinkage of the structures was found for some polymers. Other related reports on the electrochemical preparation of macroporous/mesoporous conducting polymers, such as PANI honeycomb films,[7] polypyrrole/nanoparticle composite inverse opals,[8]

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truncated eggshell structures of polyelectrolyte/PANI composites,[9] porous poly(3,4-ethylenedioxythiophene) and polypyrrole films on microelectrode arrays,[10] have also been published in recent years.

Although a large number of studies on macroporous/mesoporous conducting polymers have been reported, most of these reports were focused on the preparation and morphological characterisation of these materials. Few studies to date have addressed possible applications for these macroporous/mesoporous conducting polymers. For example, Cassagneau and Caruso reported the use of conducting polymer inverse opals for biosensor applications. Poly[thiophene-*co*-(3-thiophenemethanol)] copolymer inverse opals were used for optical-affinity biosensing,[11] and creatinine deiminase-doped polypyrrole inverse opals were used for potentiometric biosensing.[12] Moreover, little attention has been paid to the precursors of these macroporous/mesoporous conducting polymers, that is, composites composed of the colloidal particles and conducting polymers prior to removal of the colloidal templates. In theory, the structures of the conducting polymers before and after the removal of the templates should share several similar properties, if there is no shrinkage or collapse during the removal of the templates. Therefore, the composites, as well as the macroporous/mesoporous conducting polymers, may also possess interesting properties.

In this work, a polyaniline/polystyrene (PANI/PS) nanocomposite film was prepared by means of the electrochemical polymerisation of aniline within the interstitial spaces of a PS nanoparticle (100 nm diameter) template on an electrochemically pretreated glassy carbon (GC) electrode. A nanoporous PANI film was also fabricated by removing the PS template. Both of these nanostructured materials exhibited clear electrocatalytic properties towards the reduction of nitrite compared with bulk-PANI films. In addition, the PANI/PS nanocomposite film was more stable and reproducible than the nanoporous PANI film. A highly stable and sensitive nitrite sensor based on the nanostructured PANI-modified pretreated GC electrode was thus developed, and its analytical performance characteristics were investigated.

Results and Discussion

For the preparation of porous materials by using templating methods, the most important procedure is to form well-ordered templates. Although many studies into the formation of colloidal templates on different surfaces have been reported, the formation of PS templates on GC electrode surfaces has not yet been investigated. By using a solution evaporation method reported previously,[6] we tried to form PS templates on GC electrode surfaces but we found that after the evaporation of water, the PS nanoparticles usually formed aggregates or clusters rather than ordered multilayers on the electrode surface. This effect may be attributed to the poor hydrophilicity of the GC electrode surface. The GC electrode was electrochemically pretreated because this should introduce many oxygen-containing functional groups, such as hydroxyl, carbonyl, carboxyl and quinone moieties,[13] onto the surface and therefore make the electrode surface more hydrophilic,[14] and may help to form ordered PS templates. Figure 1a and b show scanning electron microscopy (SEM) images of the PS template that formed on the pretreated GC electrode surface. The images show that the PS template layer consisted of close-packed PS nanoparticles and was evenly distributed across the electrode surface. The thickness of the PS template layer was calculated to be 3.5 μm according to the GC electrode surface area, and the amount and size of the PS nanoparticles deposited. The PS template-modified GC electrode was used for the electropolymerisation of aniline at 0.9 V (vs. Ag/AgCl). PANI was grown between the interstitial spaces of the PS template and a nanocomposite of PANI and PS nanoparticles was thus formed, as shown in Figure 1c and d. Nanoporous PANI films were obtained after the removal of the PS template with toluene, as shown in Figure 1e and f. As the thickness of the PANI film is dependent upon the electropolymerisation time, film thickness could be easily controlled. Figure 1e and f show the SEM images of nanoporous PANI films that were electropolymerised for 100 and 200 s, respectively. After 100 s, the PANI film that formed was below the top layer of the PS template, and after the removal of the PS

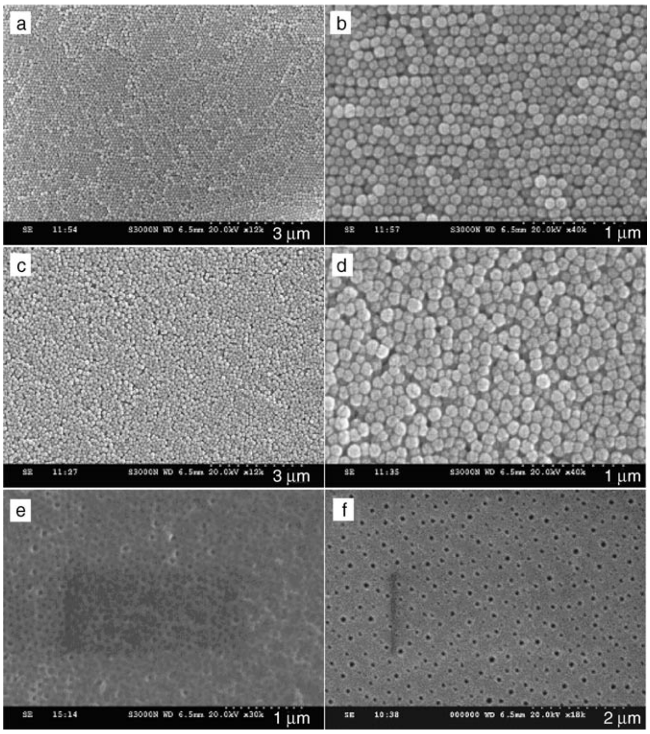

Figure 1. SEM images of the PS template (a and b), PANI/PS nanocomposite films prepared through electropolymerisation for 200 s (c and d), and the nanoporous PANI film formed by dissolution of PS from PANI/PS nanocomposite films prepared through electropolymerisation for e) 100 s and f) 200 s. Magnifications: ×12k (a, c), ×18k (f), ×30k (e), and ×40k (b, d).

template an open three-dimensional nanoporous structure was obtained (Figure 1e). After an electropolymerisation time of 200 s, the PANI film that formed appeared to have almost reached the top layer of the PS template, and after the removal of the PS template, a nanoporous structure with some open pores at the top of the polymer layer was obtained (Figure 1f). If the electropolymerisation time is further increased, then the PANI film will cover the whole PS template, and no open pores in the top layer would be apparent. A similar result was also reported by Knoll and coworkers for the preparation of inverse opals of PANI and its copolymers.[15]

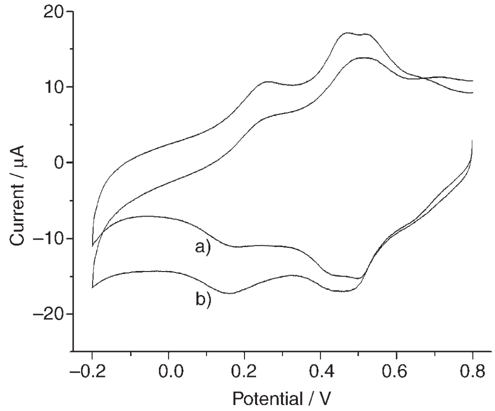

Figure 2. Cyclic voltammograms of the PANI/PS/GC electrode in an aqueous HCl solution (0.1 M) a) without and b) with $NaNO_2$ (0.5 mM) at a scan rate of 50 mV s^{-1} (vs. Ag/AgCl).

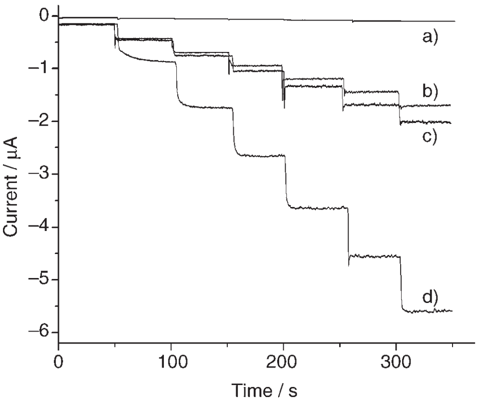

Figure 3. Amperometric response of different electrodes to successive additions of $NaNO_2$ (0.05 mM) in an aqueous HCl solution (0.1 M) at +0.05 V (vs. Ag/AgCl). a) Un-pretreated GC electrode, b) pretreated GC electrode, c) bulk-PANI-film-modified pretreated GC electrode and d) PANI/PS-nanocomposite-film-modified electrode.

The electrochemical behaviour of the PANI/PS nanocomposite film was studied in an aqueous HCl solution (0.1 M), and typical redox peaks corresponding to different PANI states were observed[16] as shown in Figure 2a. It has been reported that species can be thermodynamically oxidised or reduced by using PANI if their redox potentials are within the potential range in which PANI is electroactive,[17] which implies that for some electrochemical reactions PANI can be used as a mediator. In a previous report,[18] Huang and Yang unexpectedly observed the reduction of nitrite at a PANI/PS-composite-modified GC electrode during the analysis of Cr^{VI} content in seawater samples. Therefore, PANI may be used as a mediator for the electroreduction of nitrite, and the modified electrode may be developed for use as a sensitive nitrite sensor. Upon the addition of nitrite, the oxidation peak currents decreased and the reduction peak currents increased (Figure 2b), which indicated that the PANI/PS nanocomposite film could catalyse the electrochemical reduction of nitrite over a wide potential range. To clearly define the reason for this catalytic effect, the reduction of nitrite using different electrodes was investigated, and the results are shown in Figure 3. Almost no reduction occurred on the un-pretreated GC electrode with the addition of $NaNO_2$ (0.05 mM) (Figure 3a), whereas reduction clearly occurred on the pretreated GC electrode (Figure 3b), which indicated that the pretreated GC electrode was able to catalyse the reduction of nitrite. As previously mentioned, pretreatment of the GC electrode should introduce functional groups onto the electrode surface, and these functional groups may also act as catalysts for the reduction of nitrite because the catalytic effect of pretreated GC electrodes towards other substances has been reported.[19] As for the bulk-PANI-film-modified electrode, its response to nitrite was slightly greater than that of the pretreated GC electrode (Figure 3c). However, by disregarding the response caused by the pretreated GC electrode, the net response originating from the bulk-PANI film was insignificant, which was in accordance with a previous report.[20] Interestingly, the response of nitrite to the PANI/PS-nanocomposite-modified GC (PANI/PS/GC) electrode was much greater than the response of nitrite to the other electrodes, and by disregarding the response resulting from the pretreated GC electrode, the net response corresponding to the PANI/PS composite film was more than ten times greater than that corresponding to the bulk-PANI film. As the PS nanoparticles are electrochemically inert, the large difference in response to nitrite should only be a result of the difference in structure between PANI in the PANI/PS composite film and the bulk-PANI film. In the PANI/PS composite film, the PANI was grown between the interstitial spaces of the close-packed PS nanoparticles and thus the PANI that formed was nanostructured. Compared with the bulk PANI, the nanostructured PANI had a larger surface area and higher surface energy, which are desirable properties for catalysts. Therefore, it is conceivable that the enhancement in response of the PANI/PS nanocomposite film to nitrite originated from the nanostructured PANI.

After the removal of PS from the PANI/PS nanocomposite film, the nanostructure of PANI was maintained, and a nanoporous PANI film was obtained. As it was found that the nanostructured PANI in the PANI/PS nanocomposite film could catalyse the electrochemical reduction of nitrite, it was supposed that the nanoporous PANI film should also be able to do the same. The response of nitrite on the nanoporous PANI film-modified electrode was studied, and the results are shown in Figure 4. As can be seen, the response of nitrite on the nanoporous PANI/GC electrodes was equal to, or less than that on the PANI/PS/GC electrode and was also very variable. As the nanoporous PANI film results from the removal of the PS nanoparticles in the PANI/PS nanocomposite film, the PANI structures of these two kinds of materials should be theoretically the same, and they should have similar catalytic properties toward the reduction of nitrite. The reason that the nanoporous PANI-modified electrodes exhibited poorer electrode-to-electrode reproducibility, and in most cases smaller responses than the PANI/PS/GC electrode, can be attributed to the collapse or shrinkage of the nanoporous PANI structure during the dissolution of the PS template, which is a common phenomenon when preparing macroporous/mesoporous materials with sacrificial templating methods,[21] and the SEM investigation did reveal film collapse in some cases (data not shown). Therefore, the nanocomposite-modified electrode was more sensitive and reproducible than the nanoporous PANI-modified electrode, and was used further for the study of the catalytic reduction of nitrite.

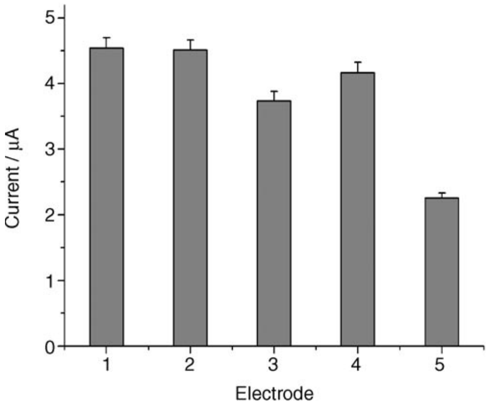

Figure 4. Response currents of PANI/PS-nanocomposite-modified electrode (1) and independently prepared nanoporous PANI-film-modified electrodes (2–5) for the detection of $NaNO_2$ (0.25 mM) in an aqueous HCl solution (0.1 M) at +0.05 V (vs. Ag/AgCl) (n=3).

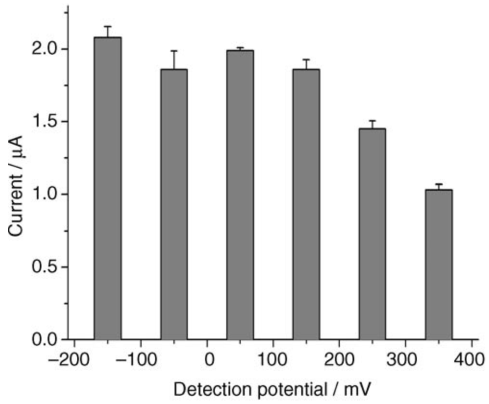

Figure 5. Influence of applied potential (vs. Ag/AgCl) on the response of the PANI/PS/GC electrode to $NaNO_2$ (0.1 mM) in an aqueous HCl solution (0.1 M) ($n=3$).

Figure 2 shows that the nanocomposite-modified electrode could catalyse the reduction of nitrite within a wide potential range, so it was necessary to optimise the potential for the detection of nitrite. Figure 5 shows the response of the nanocomposite-modified electrode to $NaNO_2$ (0.1 mM) at different applied potentials. By decreasing the applied potential from +350 to +150 mV, the response of the electrode increased gradually, whereas over the potential range from +150 to −150 mV, there was no great difference in the electrode response. At negative potentials, oxygen dissolved in the solution may be electrochemically reduced and result in a high background current, and thus interfere with the detection of nitrite. Therefore, an applied potential of +50 mV was selected to eliminate this influence, and at the same time maintain a high signal from the electrode.

In this work, the PANI/PS/GC electrodes were prepared through the electropolymerisation of aniline on the PS-template-modified electrode at a constant potential of 0.9 V, and the thickness of the formed PANI/PS nanocomposite film was dependent upon the electropolymerisation time. Therefore, by adjusting the electropolymerisation time, the thickness of the PANI/PS nanocomposite film could be easily controlled, and thus affect the response of the PANI/PS/GC electrode. Figure 6 shows the effect of the electropolymerisation time on the responses of the corresponding PANI/PS/GC electrodes. For comparison, the effect of the electropolymerisation time on the responses of the bulk-PANI-modified electrodes was also studied. The responses of the PANI/PS/GC electrodes increased with the increase in the electropolymerisation time, and the response was found to plateau at 200 s. This result was in accordance with the SEM characterisation, which showed that at 200 s PANI

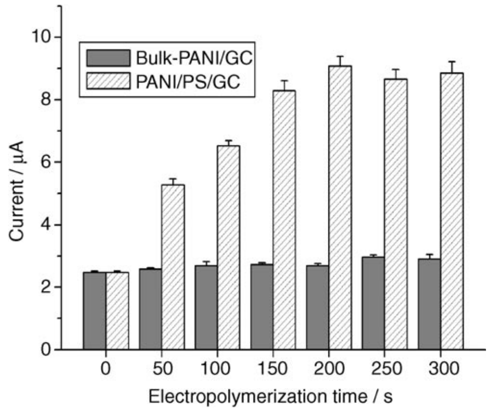

Figure 6. Influence of electropolymerisation time on the response currents of bulk-PANI-film-modified GC electrode and PANI/PS-nanocomposite-film-modified electrode. The currents were obtained by measuring $NaNO_2$ (0.5 mM) in an aqueous HCl solution (0.1 M) at +0.05 V (vs. Ag/AgCl) ($n=3$).

had just grown above the top of the PS template. That is, at 200 s the thickness of the PANI/PS composite film reached its greatest value. Increasing the electropolymerisation time further did not increase the response because under these conditions the PANI layer had grown above the PS template. Therefore, only a bulk-PANI film was formed, which is not catalytically active towards the reduction of nitrite. As for the bulk-PANI-modified electrodes, owing to their poor catalytic properties, no obvious increase in response was found by increasing the electropolymerisation time.

The steady-state current response of the optimised nanocomposite-modified electrode to nitrite standards was investigated, and the corresponding calibration curve is shown in Figure 7. A linear range from 5.0×10^{-7} to 1.4×10^{-3} M (r = 0.999, n = 12), with a sensitivity of 18.4 μA mM^{-1} was observed. The response time of the nanocomposite-modified electrode was within 5 s, and the detection limit was estimated to be 2.4×10^{-7} M based on a signal-to-noise ratio of 3, which was significantly lower than that previously reported for an electrode modified by a PANI/multiwalled-carbon-nanotube composite that had a detection limit of about 1.0×10^{-6} M.[20]

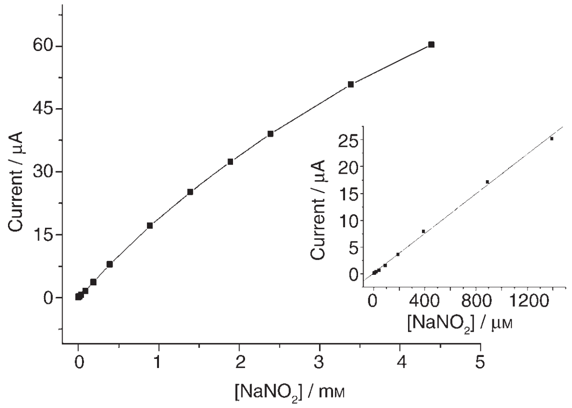

Figure 7. Calibration curve of the PANI/PS/GC electrode for the detection of $NaNO_2$ in an aqueous HCl solution (0.1 M) at +0.05 V (vs. Ag/AgCl). Inset: linear range of the calibration curve.

The stability and reproducibility of the nanocomposite-modified electrode were also studied. The electrodes were stored at 4 °C in an aqueous HCl solution (0.1 M) and in air, and their stabilities were investigated by measuring the current response at intervals of about one week, and the results are shown in Figure 8. After being stored for 50 days, the response of the electrode in an aqueous HCl solution (0.1 M) decreased gradually to about 87 % of its initial value, whereas for the electrode stored in air, no obvious decrease in response was observed. The stability of the nanocomposite-modified electrode for the detection of nitrite was much better than that of the nitrite sensor based on the PANI/multiwalled-carbon-nanotube composite, which retained 82 % initial response after 30 days,[20] and than that of the nitrite biosensor based on nitrite reductase mediator-coupled amperometric detection, which retained about 85 % activity after 8 days.[22] The excellent stability of the PANI/PS/GC electrode may be attributed to the stability of PANI itself and the enhancement effect of the PANI/PS nanocomposite, in which PANI can prevent the detachment of the PS nanoparticles from the electrode surface, and the PS nanoparticles can adsorb PANI and strengthen its mechanical properties. In terms of reproducibility, it was found that the relative standard deviation (RSD) of the nanocomposite-modified electrode was 3.7 % for nine successive measurements of $NaNO_2$ (0.05 mM). Three PANI/PS-nanocomposite-film-modified electrodes, fabricated independently, showed good reproducibility with an RSD of 2.4 % for the detection of $NaNO_2$ (0.25 mM). The satisfactory reproducibility and long-term stability of the nanocomposite-modified electrode make it attractive and suitable for the development of a chemical nitrite sensor.

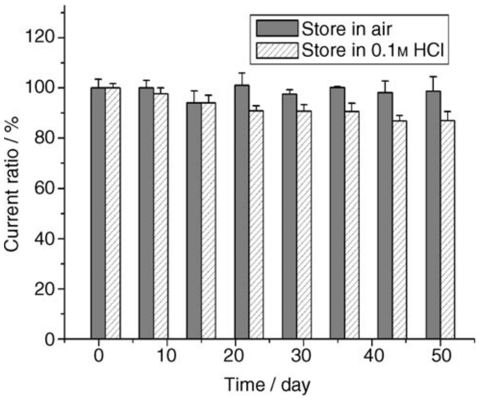

Figure 8. Stabilities of the PANI/PS/GC electrodes stored in an aqueous HCl solution (0.1 M) and in air. Measurements were carried out in an aqueous HCl solution (0.1 M) for $NaNO_2$ (0.25 mM) at +0.05 V (vs. Ag/AgCl). The initial responses of the electrodes were taken as 100 %.

Conclusion

Nanostructured films created from PANI and PS nanoparticles were electrochemically prepared through the electropolymerisation of aniline onto PS-template-modified GC electrodes. Nanocomposite and nanoporous films could be created with and without the removal of the PS template. Both of these materials were able to effectively catalyse the electroreduction of nitrite owing to nanostructured PANI. The catalytic response of the PANI/PS nanocomposite film to nitrite was more than tenfold greater than that of an equivalent bulk-PANI film. Furthermore, the nanocomposite film exhibited better stability and reproducibility than the nanoporous PANI film because the PS nanoparticles could maintain the structural properties of the PANI/PS film, whereas the nanoporous PANI film may have suffered from collapse or shrinkage. The electrode modified with the PANI/PS nanocomposite film was regarded as promising for the fabrication of a nitrite sensor owing to its excellent reproducibility, long-term stability and high sensitivity.

Experimental Section

Chemicals and instrumentation: Aniline (99%) and poly(sodium 4-styrene sulfonate) (PSS, $M_r \approx 70\,000$) were purchased from Aldrich; aniline was vacuum distilled and stored frozen under nitrogen prior to use. PS nanoparticles (0.1 μm mean particle size, 10% (w/v) aqueous suspension) were obtained from Sigma. All other chemicals were of analytical grade, and Milli-Q water (resistivity over 18 MΩ cm) from a Millipore Q water purification system was used throughout.

Electrochemical experiments were performed on a CHI 1000 electrochemical workstation (CH Instruments, USA) by using a conventional three-electrode system with the modified or unmodified GC electrode as the working electrode, a platinum mesh as the counter electrode and a Ag/AgCl reference electrode (Bioanalytical Systems, UK).

SEM was performed by using a Hitachi S3000N scanning electron microscope (Hitachi, UK). An acceleration voltage of 20 kV was employed. The samples for SEM were prepared on a GC electrode with a removable tip.

Preparation of nanostructured PANI film-modified electrodes: GC electrodes (3 mm in diameter) were polished by sequentially using 1.0, 0.3 and 0.05 μm alumina slurries and were then ultrasonically washed in water and in ethanol for about 5 min each, respectively. The cleaned electrodes were then electrochemically pretreated in pH 5.0 phosphate buffer solution (PBS) according to the literature.[23] In brief, the GC electrodes were held at a potential of +1.80 V in a stirred solution of pH 5.0 PBS for 300 s, and then the electrodes were scanned between +0.3 and +1.25 V with a scan rate of 50 mV s^{-1} until steady-state cyclic voltammograms were obtained. After the pretreatment process, the GC electrode surfaces became more hydrophilic and were suitable for the self-assembly of PS nanoparticles. The PS templates were prepared by dropping 1.0 μL of a 2.0% (w/v) PS nanoparticle suspension (diluted from 10% (w/v) suspension with water) onto the pretreated GC electrode surfaces with a micropipette. As the electrode surfaces were very hydrophilic, the deposited suspension spread throughout the whole electrode surface and formed a very thin liquid layer. The electrodes were then placed vertically and covered with a beaker, and the water was allowed to evaporate slowly over 5 to 7 h.

Electropolymerisation of aniline: GC electrodes coated with the PS templates were immersed into an aqueous solution containing HCl (1.0 M), PSS (2.0 mM) and aniline (0.05 M), and remained there for several minutes to allow the solution to penetrate into the templates before electropolymerisation was conducted. The electropolymerisation of aniline was then carried out at a constant potential of +0.9 V for 200 s (unless otherwise stated), and PANI was formed within the interstitial spaces between the closely packed PS nanoparticles. After electropolymerisation, the electrodes were rinsed with water, immersed in an aqueous HCl solution (1.0 M), and subsequently cycled at a scan rate of 50 mV s^{-1} from −0.2 to +0.8 V for 5 min to remove residual monomers and oxidation products.

When the electropolymerisation was complete, electrodes modified with a nanocomposite film of PANI and PS nanoparticles were obtained. To prepare the nanoporous PANI-modified electrodes, the PS templates were removed by soaking the nanocomposites in toluene for 12 h. Then the electrodes were thoroughly rinsed with ethanol and with water.

Electrochemical experiments: The electrochemical behaviour of the nanostructured PANI-modified electrode in an aqueous HCl (0.1 M) solution was investigated by means of cyclic voltammetry in the potential range between −0.2 and +0.8 V. Amperometric determination of nitrite was carried out at an applied potential of +50 mV (unless otherwise stated) under magnetic stirring in aqueous HCl solution (0.1 M). After the background current reached a relatively steady value, standard nitrite solutions were injected into the detection solution, and the steady-state currents produced were recorded as the response. All experiments were carried out at room temperature.

Acknowledgements

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