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Inverse Opals of Polyaniline and Its Copolymers Prepared by Electrochemical Techniques

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Ordered 3D arrays of polyaniline (PANI) inverse opals were fabricated via electrochemical methods by using colloidal crystals of polystyrene beads as sacrificial templates. Compared with films obtained by chemical synthesis, the inverse opaline samples obtained by electrochemistry had a much higher structural quality. To explore potential biosensing applications, PANI composite inverse opals were fabricated for the first time by modifying the structure with different dopants, such as poly(acrylic acid) (PAA) and poly(styrene sulfonate) (PSS). It was found that these dopants had a major effect on the structure of the obtained opaline films. With selection of suitable dopants, PANI composite inverse opals could be fabricated with very high quality. The obtained films remained electroactive in buffer solutions of neutral pH. Owing to their huge surface area, they should be ideal candidates for biosensing applications, e.g., as electrocatalysts or bioreactors. Our first effort to use such macroporous structures as electrocatalysts for the oxidation of reduced β-nicotinamide adenine dinucleotide (NADH) showed that the electrocatalytic efficiency of the inverse opline film was much higher compared with that of an unpatterned film.

Introduction

Recently, sacrificial template methods[1−7] have been shown to offer an effective approach for the fabrication of structured materials with unique properties that are difficult to produce by traditional patterning procedures (such as photolithography,[8] soft lithography,[9,10] and dip-pen nanolithography,[11] holographic patterning[12]). The templates normally used include diblock copolymers,[13−16] anodized alumina layers,[17−20] organic or inorganic colloidal crystals,[21−23] and others.[24,25] Among these, self-assembled colloidal crystals (synthetic opals) stand out as ideal templates for creating highly ordered three-dimensional (3D) structures with interconnected macropores (the so-called "inverted opals" or "inverse opals"), which show potential applications ranging from photonic crystals to catalysts and bioreactors.[26−35] To date, inverse opals from numerous materials, such as metals,[36,37] inorganic oxides,[21−23] or polymers,[31−32,35,38−42] have been fabricated by using a variety of colloidal crystal templates.

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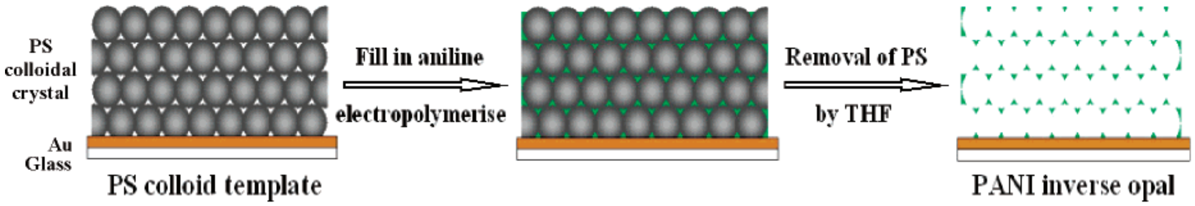

Figure 1. Schematic illustration of the procedure used for fabricating PANI inverse opals.

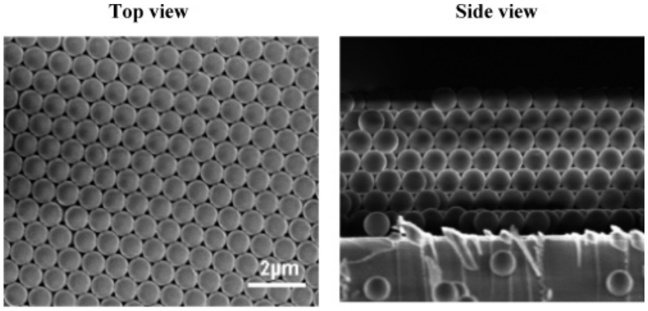

Figure 2. Typical SEM images of a 3D PS colloidal crystal template prepared by vertical lifting deposition.

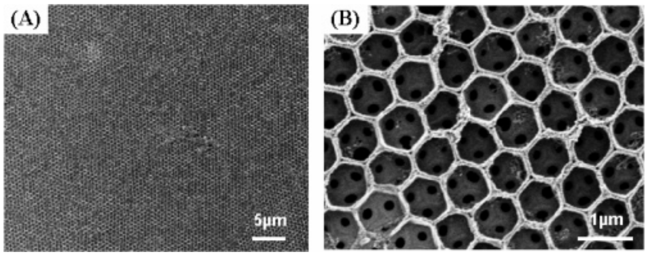

Figure 3. SEM images of PANI inverse opals prepared via cyclic voltammetry, at low (A) and higher (B) magnification. CV scan rate 20 mV s^{-1}, 10 scan cycles.

The original interest for preparing inverse opals with conjugated polymers originated from the motivation to obtain photonic band gap crystals with enhanced interaction with light. The ease of tuning the refractive index of the conjugated polymers[38,39] suggested they be used as model systems to investigate how the periodic structure of the crystal enhances the optoelectronic properties of the polymer and how the polymer enhances the properties of the photonic crystal. Recently, considerable research interest also focused on their potential applications for biosensing purposes, by exploiting the advantages provided by the highly ordered porous structure and the huge surface area they posses.[31−35]

Until now, inverse opals based on different conjugated polymers, such as polypyrrole,[32,40,43] polythiophene,[31,43] polyphenylenevinylene,[38,39] and polyaniline,[44] have been prepared by polymerizing the corresponding monomers in the interstitial voids of the colloidal crystal template, either chemically or electrochemically. Compared to the chemical synthesis, electrochemical polymerization allows for a much better control of the structural quality of the inverse opal (e.g., uniformity of the film thickness and size of interconnected pores) by either controlling the polymerization time or the applied potential or both.[31−35,38−44]

Here, we apply electropolymerization methods to prepare polyaniline (PANI) inverse opals by using polystyrene (PS) colloidal assemblies as sacrificial templates. A chemical polymerization method for the preparation of inverse PANI opal was reported previously by Caruso and co-workers.[44] However, the quality in terms of defect density and detailed structural integrity of the obtained PANI inverse opals was somewhat poor, due to the inherent drawbacks of the method used (vide post). Moreover, the loss of redox activity of PANI in neutral solutions[45,46] also precludes the use of such pure PANI inverse opaline structures for biosensing applications. It has been demonstrated, however, that the redox activity of PANI can be sustained in neutral pH solutions by doping it with different polyanions (such as poly(styrene sulfonate), PSS),[47−52] modified gold nanoparticles,[53,54] or modified carbon nanotubes.[55] By using electropolymerization, we demonstrate that PANI inverse opals can be obtained with much higher quality. Furthermore, by controlling the polymerization time, we can exactly control whether the topmost layer of the inverse opal is open or closed. Finally, efforts are also directed toward fabricating inverse opals of PANI composites by electro-copolymerizing aniline in the presence of different dopants, to explore their potential for biosensing applications.

Experimental Section

Materials. Aniline (99%), poly(styrene sulfonate) (PSS, Mw ca. 70000 g mol^{-1}), poly(acrylic acid) (PAA, sodium salt, 45 wt % solution in water, Mw ca. 8000 g mol^{-1}), 2-aminobenzoic acid (2-ABA), and 3-mercapto-1-propanesulfonic acid (sodium salt, MPS) were obtained from Aldrich. β-Nicotinamide adenine dinucleotide (NADH, reduced form, disodium salt, approximately 98%) was obtained from Sigma. All these materials were used as received. Other materials used were of analytical grade. Millipore water (18 MΩ cm) was used throughout the experiments.

Fabrication of PS Colloidal Templates. Negatively charged colloidal PS particles were synthesized by surfactant-free emulsion

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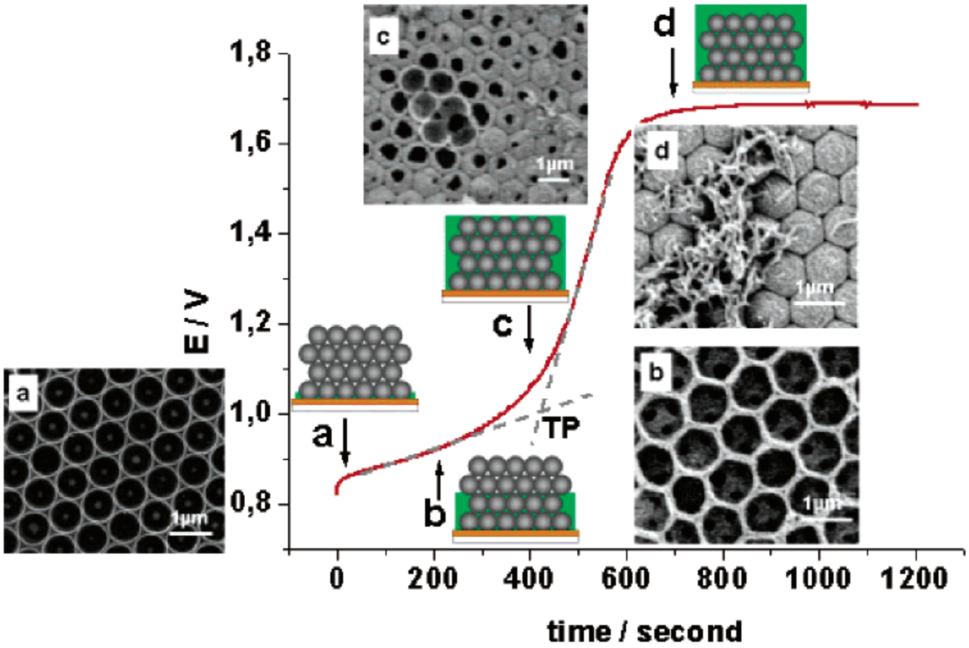

Figure 4. Voltage changes during the electropolymerization process for preparing PANI inverse opals by a galvanostatic method at a current density of 0.05 mA cm^{-2}. The inset sketches show the stage of the formed PANI inside the PS template at each point as indicated by the arrows. SEM images of the corresponding PANI inverse films obtained by stopping the polymerization at these points are also shown.

polymerization.[56] In brief, an aqueous styrene emulsion was polymerized with potassium peroxodisulfate for 24 h at 75 °C under a nitrogen atmosphere. Then sodium chloride, styrene sulfonic acid sodium salt, and acrylic acid were added in appropriate amounts to adjust the particle size and to obtain carboxylated polystyrene particles. After completion of the polymerization the latex particles were purified by filtration and centrifugation. The colloidal crystal templates were fabricated on Au substrates (50 nm Au evaporated onto LaSFN9 glass slides with a 2 nm Cr adhesion layer between) by a vertical lifting deposition from the colloidal suspension (0.5−2.5 wt %) on a homemade dipping device.[57,58] The withdrawing speed ranges from 1 μm s^{-1} to several cm s^{-1}. To increase the wettability of the Au substrate, it was pre-functionalized with a layer of hydrophilic thiol (normally MPS).

Fabrication of the PANI Inverse Opals. The fabrication procedure of the PANI inverse opals by electropolymerization using the PS colloidal templates is shown in Figure 1. After infiltration of aniline solution (0.02 M aniline in 0.5 M H_2SO_4, in the case for PANI composite inverse opals, 0.02 M dopants were also added) into the interstices of the PS colloidal template, electropolymerization was carried out either by a galvanostatic method or by cyclic voltammetry. After polymerization, the resulting polymer film was thoroughly rinsed with 0.5 M H_2SO_4, and then exposed to a tetrahydrofuran (THF) solution for ∼10 h in order to remove the PS template and to obtain the well-structured PANI inverse opals. The above whole preparation process was carried out in an electrochemical cell.

Apparatus and Measurements. The electropolymerization and electrochemical measurements were performed with an EG&G 273A potentiostat, with the PS colloidal assembly loaded Au substrate as the working electrode, a coiled platinum wire being used as the counter electrode, and an Ag/AgCl (3 M NaCl) electrode as the reference electrode. All potentials reported here are with respect to this reference electrode. The morphologies of the colloidal crystals and inverse opals were imaged with a low-voltage scanning electron microscope (LVSEM, LEO 1530 Gemini), operated normally at 1 kV.

Results and Discussion

PS Colloidal Templates. With use of the vertical deposition method at the proper conditions (e.g., solvent evaporation rate, substrate withdrawal rate, and colloidal concentration), well-ordered 2D or 3D PS colloidal assemblies can be formed on the modified Au substrate. Figure 2 shows one example of the prepared 3D colloidal PS latex arrays (PS opals). It can be seen that the colloidal crystals display a highly ordered fcc (face-centered cubic) packing, with the [111] plane being parallel to the substrate surface. The average particle size is around 839 nm. After the PS colloidal assembly was dried, the PS spheres adhered well enough to each other and to the Au substrate without detaching or disintegrating, even upon re-immersing the sample into the aqueous aniline solution and applying a potential. This good adhesion allows for their direct use as templates for the preparation of PANI inverse opals by electropolymerization without any further modifications, as shown below.

Fabrication of PANI Inverse Opals. Shown in Figure 3 are SEM images of one sample of the PANI inverse opals fabricated by cyclic voltammetry at a scan rate of 20 mV s^{-1} for 10 cycles. A well-ordered 3D network of PANI was obtained covering a very large area (∼0.7 cm^2, limited by the electrochemical cell). This PANI inverse opaline structure was believed to be held together by physical cross-linking and weak interactions such as hydrogen bonding and van der Waals forces between PANI chains.[44] The enlarged image in Figure 3B shows that the pores are assembled in a hexagonal array and are connected to each other via similarly

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symmetrical smaller pores, indicating a continuous macroporous 3D structure typical for an inverse fcc lattice. Compared with the chemical polymerization method,[44] the quality of the PANI inverse opals prepared by this electropolymerization method was greatly enhanced in terms of defect density and structural fidelity of the walls and holes. Furthermore, the shrinkage in our case (<5%) is reduced to only one-third of that in the former case (~15%), retaining almost the original geometry of the used PS template, which may also explain the low defect density over a very large area in the prepared inverse opaline films. The improved quality in our case may arise from the well-controlled polymerization process by using a slow potential scan rate, which allows the in situ formation of PANI chains starting from the gold electrode at the base of the colloid crystal template to fill the interstices by a layer-type growth mechanism in a highly ordered way and leading to a much more compact structure without blocking the pores above the PANI growth front. In contrast, the polymerization rate in the chemical polymerization approach via infiltration is more difficult to control, and isotropic polymerization and precipitation may result in the aggregation of the formed PANI chains within all pores and packing into a relatively loose and disordered structure. Thus, further infiltration of monomer and oxidizer to increase the PANI loading is impeded. Actually, in our experiments, we found that the quality of the obtained PANI inverse opals decreased with increasing potential scan rate, possibly due to a very loose packing of the rapidly forming PANI chains. If the scan rate was too high, this could even lead to the collapse of the 3D structures after the removal of the PS colloidal template.

In a second route, the PANI inverse opals were prepared by a galvanostatic method. By adjusting the polymerization time and applied current, this method allows for the exact control over the structure formation and film thickness of the obtained PANI inverse opaline films. Figure 4 shows the voltage changes during the electropolymerization process along with the resulting film morphologies. The curve exhibits a transition point (TP), after which the voltage increases very sharply. A similar phenomenon was also found in the current changes seen during a potentiostatic preparation.[40,59] This TP was ascribed to a rapid increase of the electrochemical reaction area once the growth front of the deposited material reached the template/bulk solution interface. This was confirmed in our experiments by stopping the polymerization process at different stages as indicated by the arrows and taking SEM images of the obtained PANI inverse opaline films at each stage (also shown in Figure 4). If the polymerization process was stopped at a very early stage ((a), after 10 s), a bowl-shaped PANI array was obtained. At this stage, the thickness of the formed PANI layer is thinner than that of a monolayer of PS particles (cf. inset sketches for references). If the polymerization process was stopped at a later stage ((b), after 200 s, but before the TP), an open 3D macroporous structure was obtained, with smaller channels connecting each cavity with its neighbors. The image (c) corresponded to the termination of the polymerization process near the TP. It is clear that, right at the TP, some of the pores at the top layer begin to close. If the polymerization process is continued further, then all the pores of the topmost layer are closed. Beyond this point, hyperbranched PANI fibrils start to form on top of the closed pores ((d)). For practical purposes, an opened 3D structure like (b) is preferred to allow access of dissolved species to the interior of the macroporous PANI inverse opal, so care must be taken to stop the polymerization process before the TP.

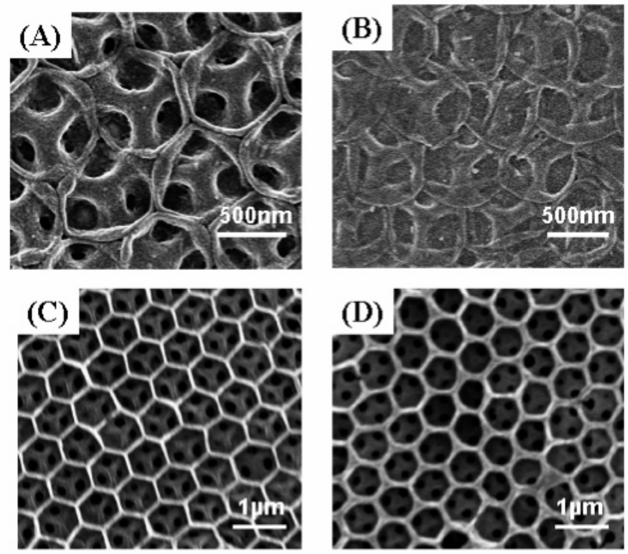

Figure 5. SEM images of PANI composite inverse opaline films by copolymerizing aniline with PAA (A), 2-ABA (B), or PSS (C) and (D). (A), (B), and (C) were prepared via cyclic voltammetry at a scan rate of 20 mV s^{-1} for 10 cycles, while (D) was obtained by a galvanostatic method at a current density of 0.05 mA for 10 min. The concentration of PAA, PSS, and 2-ABA is 0.02 M each, based on the molecular weight of the corresponding monomers.

Preparation of PANI Composite Inverse Opals. To explore their applications for biosensing purposes, we also tried to fabricate PANI composite inverse opals either by doping with negatively charged polyelectrolytes[47−52] or by copolymerizing aniline monomers with aniline derivatives containing acidic groups, like 2-aminobenzoic acid (2-ABA). In this way, an inverse opaline film that remains electroactive at neutral pH is expected to be formed. Shown in Figures 5A and 5B are the SEM images of PANI composite inverse opaline films prepared by copolymerization of aniline with either PAA or 2-ABA, respectively, using the same growth conditions as those for pure PANI. It is clear that, in both cases, the obtained structures collapsed to some extent, especially the one of the copolymer with 2-ABA. The main reason may be the poor mechanical properties of the used dopants or some phase separation occurring during the polymerization process.

However, if we use a dopant with a higher internal mechanical strength, like PSS, high-quality 3D structures can be obtained by either cyclic voltammetry or by galvanostatic preparation, as shown in Figures 5C and 5D, respectively. Very nice interconnected hexagonal arrays were obtained in both cases, just like those of the pure PANI inverse opaline films. A most important finding is that the PANI/PSS inverse

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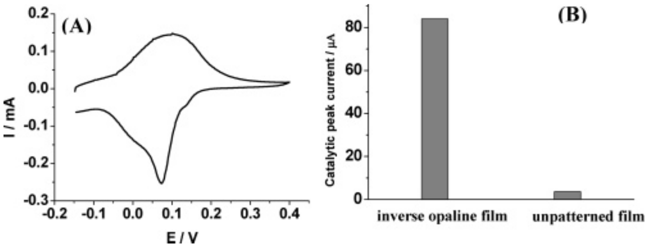

Figure 6. (A) Cyclic voltammogram of PANI/PSS inverse opaline films as shown in Figure 5C, measured in 0.1 M PBS buffer, pH 7.1. (B) Comparison of the electrocatalytic activity of a PANI/PSS inverse opaline film toward the oxidation of NADH and that of the unpatterned PANI/PSS film with the same film thickness. NADH concentration was 10 mM, CV scan rate was 5 mV s^{-1}.

opaline films still retain a good redox activity at neutral pH, after removal of the PS template by THF, as shown in Figure 6A. A broad redox peak is observed between −0.15 and +0.4 V, with the redox potential at around +0.083 V, similar to that found for the unpatterned PANI/PSS system.[49,51] Considering the huge surface area of the obtained PANI/PSS films and their capability of being redox-active at neutral pH, they should be very promising candidates either for electrocatalysis or as a support for biomolecules, like enzymes or other proteins. It has been reported previously[48−52] that the doped PANI can electrocatalyze the oxidation of reduced β-nicotinamide adenine dinucleotide (NADH). Our preliminary efforts to use PANI/PSS inverse opaline films as electrocatalytic supports for the oxidation of NADH showed that the electrocatalytic ability of these inverse opaline films is more than 1 order of magnitude higher than that for unpatterned PANI/PSS film (Figure 6B). With optimization of the fabrication procedures used above and with selection of a more suitable system, the sensitivity of the PANI composite inverse opal films may be further enhanced and extended to other biological systems. Further efforts to implement these structures in biosensors are currently underway.

Conclusion

High-quality inverse opals of pure PANI and its copolymers (like PANI/PSS) were fabricated via electrochemical methods based on PS colloidal crystal templates. The incorporated dopants had a significant effect on the structure and the mechanical stabilities of the prepared opaline films. The obtained PANI composite films remained electroactive at neutral pH. Together with their huge surface area, they would be ideal candidates for biosensing applications, e.g., as electrocatalysts or bioreactors.

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