

Supplementary information for

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

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Experimental details:

Chemicals and instrumentations: Aniline (99%) was purchased from Aldrich, vacuum distilled and stored frozen under nitrogen. Poly(sodium 4-styrene-sulfonate) (PSS, M_w ca. 70,000) and poly(diallyldimethylammonium chloride) (PDDA, low molecular weight, 20 wt. % in water) were purchased from Aldrich. Normal PS nanoparticles (sulfate-modified, 0.1 μm mean particle size, aqueous suspension, 10% solids) and amine-modified PS nanoparticles (fluorescent orange, 0.1 μm mean particle size, aqueous suspension, 2.5% solids) were obtained from Sigma. β -nicotinamide adenine dinucleotide (NADH) was purchased from Sigma. All other chemicals were of analytical grade, and Milli-Q water (resistivity over 18 $\text{M}\Omega$ cm) from a Millipore Q water purification system was used throughout.

Electrochemical experiments were performed on a CHI 1000 electrochemical workstation (CH Instruments, USA) using a conventional three-electrode system with the glassy carbon electrode (GCE) as the working electrode, a platinum mesh as the counter electrode, and a silver/silver chloride (Ag/AgCl) reference electrode (Bioanalytical Systems Ltd., UK). SEM was performed with a Hitachi S3000N

scanning electron microscope (Hitachi, UK). An acceleration voltage of 20 KV was employed. The samples for SEM were prepared on a GCE with a removable tip.

Preparation of nanostructured PANI materials: GCEs (3 mm in diameter) were polished with 1.0, 0.3 and 0.05 μm alumina slurries in sequence and then ultrasonically washed in water and ethanol for about 5 min, respectively. The cleaned electrodes were then electrochemically pretreated in pH 5.0 phosphate buffer solution (PBS, 0.1 M). In brief, the GCEs were held at a potential of +1.80 V under stirring in pH 5.0 PBS for 300s, 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. The PS templates were prepared by self-assembling PS nanoparticles on the GCE surfaces with the help of the negatively charged PSS and the positively charged PDDA. For the formation of the sulphate-PS template, the GCE was firstly soaked in 5.0 mg mL^{-1} PSS and 5.0 mg mL^{-1} PDDA for 30 min, respectively. Then it was soaked in 0.1% (w/v) sulfate-PS nanoparticle suspension for about 2 hours, and the negatively charged sulfate-PS nanoparticles were self-assembled on the GCE surface. For the formation of the amine-PS template, the GCE was firstly soaked in 5.0 mg mL^{-1} PSS for 30 min, then it was soaked in 0.1% (w/v) amine-PS nanoparticle suspension (pH 2.0, adjusted with HCl) for about 2 hours, and the positively charged amine-PS nanoparticles were self-assembled on the GCE surface.

For the aniline electropolymerization, GCEs modified with the PS templates were immersed into the solution containing 1.0 M HCl, 2.0 mM PSS and 0.05 M aniline, and before electropolymerization, the electrodes were kept in the solution for two minutes. The electropolymerization of aniline was then carried out at a constant potential of +0.9 V for a period of time, and PANI materials were thus formed on the electrode surfaces. To remove the PS nanoparticles, the GCEs were soaked in toluene for 12 hours.

NADH detection: Amperometric detection of NADH was carried out at an applied potential of 150 mV under magnetic stirring in pH 7.0 PBS. After the background

current reached a considerably steady value, standard NADH solutions were injected into the detection solution, and the steady state currents produced were recorded as response. All experiments were carried out at room temperature.

SEM images of PS/PANI core/shell particles and hollow PANI spheres after compression:

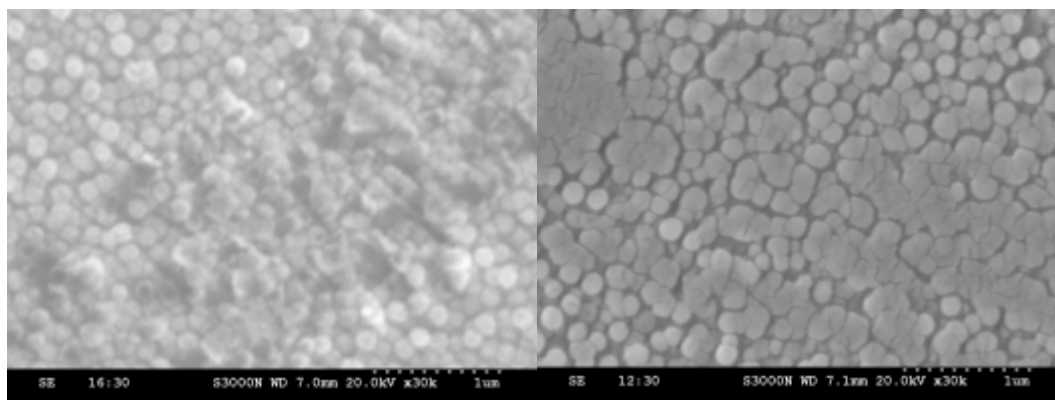


Figure 1 SEM images of the PS/PANI core/shell particles (left) and hollow PANI spheres (right) after compression. As can be seen, the core/shell particles were broken when compressed. As the PS nanoparticles are quite hard and PANI is soft, the hard PS core is squeezed out and the PANI shell is left, while for the hollow PANI spheres, they were easily squashed into flat forms, as the PANI is soft and there is no hard PS particle left in the core. The electropolymerization time was 400 s. Magnification: $\times 30k$. The morphologies of both the core/shell structures and the hollow spheres after compression can be compared with the structures prior to compression in Figs 1f and 2d, respectively. The clear morphological changes following compression appear to indicate that a distinct difference exists between the core/shells and the hollow spheres and that this difference is due to the efficient dissolution of the latex particles.