Supplementary information

Nanostructured conducting polymer for dopamine detection

Mireia Martí, a Georgina Fabregat, a,b Francesc Estrany, b,c Carlos Alemán, a,b* and Elaine Armelin, a,b*
Supplementary information

**Preparation of polystyrene microspheres.** PS microspheres were prepared following the procedure described by Lascelles et. al. In a three-necked round flask provided with magnetic stirring and a condenser, poly(N-vinylpyrrolidone) (PVP) stabilizer (3.8 g) dissolved in isopropyl alcohol (180 mL) was heated until 70°C for 1h under nitrogen atmosphere. Then, a solution of α-azoisobutyronitrile (AIBN, 0.25 g) and styrene monomer (25 g) was added dropwise to the reaction vessel. The mixture was vigorously stirred at 70°C for 24h, and after this it was left to cooling at room temperature. The very fine white resulting emulsion was centrifuged several times, and washed repeatedly with deionized water to remove the PVP stabilizer excess. The chemical composition of the polystyrene (PS) samples was evaluated with FTIR spectroscopy, while the size of the latex particles was determined by SEM and TEM.

**Preparation of polystyrene sulfonated microspheres.** Concentrated sulphuric acid (98%, 11 ml) was introduced in a 30 ml centrifuge tube. PS microparticles (10% in deionized water, 3 ml) were added dropwise under magnetic stirring. The sulfonation reaction was allowed to take place at 40°C during 24h under reflux. When the vessel cooled to the room temperature, the solution was centrifuged and the solid was washed several times with an excess of ethanol. A white fine powder, made of PS sulfonated (PSS) core/shell particles, was obtained after drying under vacuum for 48h.

**Preparation of PNMPy/PSS and PPy/PSS microspheres.** PSS microparticles (0.06 g) were dispersed in 3.5 ml of deionized water in a 30ml centrifuge tube. A solution of 0.02 ml of N-methypyrrole (NMPy) and 1.5 ml of ethanol was introduced into the PSS suspension under magnetic stirring. After 15 min, 0.1 g of FeCl₃·6H₂O and 2 ml of deionized water were added. The polymerization process took place at room temperature during 24h. The resulting powder was washed by centrifugation, with an
excess of deionized water and with ethanol. Finally the sample was dried under vacuum for 48h. In order to reach a suitable poly(N-methylpyrrole) (PNMPy) thickness in PNMPy/PSS microspheres, this polymerization step was repeated 3 times. The same procedure was used to obtain PPy/PSS core-shell systems, where PPy refers to polypyrrole. The complete synthesis procedure, including the doping of the PNMPy/PSS and PPy/PSS microspheres and the extraction of the PSS core to obtain hollow spheres (see below), is displayed in Figure 1.

**Doping process of PNMPy/PSS and PPy/PSS core-shell microspheres.** PNMPy/PSS core-shell microspheres (0.02 g) were mixed with 0.05 ml of dodecylbenzenesulphonic acid (DBSA) and 0.5 ml of ethanol, the mixture being stirred at 40 °C under nitrogen atmosphere for 2h. After this, it was washed by centrifugation with an excess of deionized water, and dried under vacuum for 48h.

Another portion of PNMPy/PSS core-shell microspheres (0.015 g) was mixed with 0.5 ml of FeCl$_3$·6H$_2$O at room temperature under magnetic stirring and nitrogen atmosphere for 20h. The mixture was washed by centrifugation with an excess of ethanol and with deionized water (several times), and dried under vacuum for 48h. The same process was followed for the doping of the PPy/PSS core-shell systems.

**Preparation of PNMPy hollow microspheres.** The PNMPy/PSS core-shell microspheres were dispersed into tetrahydrofuran (THF) under magnetic stirring for 48h at room temperature. The resulting mixture was washed by centrifugation, and the final product was dried in vacuum at 40 °C for 24h. The chemical composition and the morphology of the polymer microspheres were characterized by spectroscopic techniques.

**Preparation of Au colloidal nanoparticles.** In order to remove any adsorbed substance on the glassy carbon electrode (GCE) surface, prior to the conducting
polymer deposition, it was polished repeatedly with alumina slurry, followed by successive sonication in ethanol and doubly distilled water for 5 min, and dried under a nitrogen flow.

Preparation of the Au colloidal nanoparticles (AuNPs) for deposition onto GCEs, which were used to fabricate the nanomembranes of conducting polymer, was performed following the standard procedure described in the literature.\textsuperscript{2-4} All glassware used in such preparation was thoroughly cleaned in aqua regia (3:1 HCl:HNO\textsubscript{3}), rinsed in doubly distilled water, and oven-dried prior to use. In a 1 L round-bottom flask equipped with a condenser, 500 mL of 1 mM HAuCl\textsubscript{4} was brought to a rolling boil with vigorous stirring. Rapid addition of 50 mL of 38.8 mM sodium citrate to the vortex of the solution produced a colour change from pale yellow to burgundy. Boiling was continued for 15 min. After this, the heating mantle was removed while the stirring was continued for 30 min. When the solution reached the room temperature, it was filtered through a 0.2 \textmu m membrane filter. The resulting solution of colloidal particles showed an absorption maximum at 520 nm indicating that the particle size ranged from 9 to 22 nm. A spherical model for a particle size of 13 nm was used to determine approximately the concentration of mother solution from UV-vis absorption, which was estimated to be 7.4 nM.\textsuperscript{5} The AuNPs concentration in the modified electrode surface was determined to be 22.6·10\textsuperscript{9} nanoparticles/mm\textsuperscript{2}, assuming that all the AuNPs were well adhered to the PNMPy-modified GCE, since no absorption band at 520 nm was identified in the electrochemical solution after tests.

References


Figure S1. Scheme of Poly(N-methylpyrrole) backbone overoxidated.
**Figure S2.** UV-vis reflectance spectra obtained for uncoated PS microspheres and for PNMPy/PS core-shell particles. The lower reflectance of the latter reflects an increase of the light absorption by the PNMPy-coated PS core-shell particles.
**Figure S3.** XPS survey spectra of: (a) PNMPy/PSS core-shell microspheres prepared by LbL self-assembly deposition and with a core thickness of about 30nm; and (b) PS uncoated microspheres used as template.
Figure S4. Scheme showing the oxidation of dopamine to dopaminequinone molecules.
**Figure S5.** Cyclic voltammograms of PNMPy/AuNPs-modified GCE without dopamine and with 1.5 µM (6, 7, 8 and 9 cycles).