Electronic supplementary information for

Highly conductive free standing polypyrrole films prepared by freezing interfacial polymerization

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Experimental

Materials

Pyrrole monomer (Acros Organics) was purfied by distillation under reduced pressure and then was stored at -20°C after being purged with nitrogen. Cyclohexane, *p*-toluenesulfonic acid (PTS), ammonium persulfate(APS) and anhydrous ferric chloride (FeCl₃) are analytical grade reagents, they were purchased from Aladdin Reagent Co, Shanghai, China, and were used without further purification as received. Distilled water was used throughout.

Preparation of PPy films

In a typical procedure, a solution of pyrrole dissolved in cyclohexane (4 mL) and an aqueous solution containing the oxidant and the dopant (4 mL) were precooled at 4-5°C firstly, and then they were added into a glass vial. Due to the difference in density and polarity, the solutions separated into two phases after mixing, with the organic phase on the top. The test tube was kept in a freezer at -20°C for 4 days to complete the polymerization of pyrrole. Finally, after being thawed at room temperature, the PPy film was filtered and washed with distilled water and ethanol for several times to remove residual ions and unreacted monomers thoroughly, and then was vacuum dried at 60°C for 24 h.

Characterizations

The morphologies of the PPy films were investigated with a Hitachi S-4800 scanning electron microscope (SEM) (Tokyo, Japan). Due to their high conductivities, the samples were investigated directly, without the treatment of sputtering a thin layer of gold. The thickness of the films was measured from the cross-sectional images taken by SEM. Fourier-transform infrared (FTIR) spectra of the samples were recorded on a Nicolet-380 FTIR spectrometer (USA) using the KBr method in the range of 400-3600 cm⁻¹. Raman spectra were measured from 800 to 1800 cm⁻¹ on a microscopic confocal Raman spectrometer (LavRAM Aramis, Horiba Jobin Yvon, France), using a 633 nm He-Ne laser. X-ray diffraction (XRD) analyses were performed on pristine films rather than grounded powder by using a D8 Advance X-ray diffractometer (PANalytical, Netherland) with Cu K α radiation in the 2 θ range

5-60°. The conductivities of the PPy films were measured on pristine films by using the four-point probe method.

Results and discussion

Supporting Figures



Fig. S1 SEM images of the PPy film prepared with $FeCl_3$ as the oxidant and PTS as the dopant. (a) Low magnification; (b) high magnification. Synthetic conditions: $[FeCl_3]=[PTS]=0.36 \text{ M}, [Py]=0.18 \text{ M}.$



Fig. S2 XRD patterns of the PPy films prepared with different n(PTS)/n(Py). The synthetic conditions are: [Py]=0.18 M, $[FeCl_3]=0.36$ M, and the n(PTS)/n(Py) for the samples are 0/1(A), 4/1 (B) and 2/1 (C).