Photoluminescent Properties of PB Shells and PPy/PB Core/Shell Nanoparticles Prepared via Miniemulsion Periphery Polymerization (MEPP)

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Experimental.

Materials: Poly(ethylene glycol)-b-poly(propylene glycol)-b-poly(ethylene glycol) triblock copolymers (Mn = 14,000g/mol, PDI = 1.10), 4-(dimethylamino)-pyridine, sodium pentacyanoaminoferrate, triethylenamine, bromoacetyl chloride were purchased from Aldrich (United Kingdom). Pyrrole was purchased from Aldrich (China). All other chemicals (analytical grade) were obtained from Shanghai Chem. Co. The materials were all used without further purification.

Synthesis of PPy/PB core/shell nanoparticles: To prepare miniemulsion system, toluene (0.5 g) was first mixed with hexadecane (HD) (20 mg). This organic phase was then added to the aqueous phase consisting of distilled water (27.2 g), 0.4 g organometallic surfactant of poly(ethylene glycol)-b-poly(propyleneglycol)-b-poly(ethylene glycol) terminated with pentacyano (4-(dimethylamino)pyridine)ferrate (EPE-Fe). The solution was stirred vigorously for 45 min, the resulting mixture was subsequently sonicated for a period of 15 mins. After 175 μL Py were added and mixed with the miniemulsion, 0.163 g $FeCl_3$ were subsequently added to induce the metal coordination polymerization at the periphery of the miniemulsion and oxidative polymerization of Py inside the miniemulsion. The polymerization was allowed to proceed for 72 h at room temperature under agitating. The resulting suspension was then precipitated by adding dropwise to methanol. After centrifugation and filtration, the resultant solid was washed in sequence with distilled water and ethanol several times, and finally dried under vacuum for 24 h, yielding dark blue powdery PPy/PB core/shell nanoparticles.

Synthesis of PB nanoshells: The process for the synthesis and purification of the PPy/PB core/shell nanoparticles was adopted, but no Py was added and only 0.059g $FeCl_3$ were used to induce metal coordination polymerization. The obtained PB nanoshells are dark blue powders.

Synthesis of PPy nanoparticles: The process for the synthesis of the PPy/PB core/shell nanoparticles was adopted, but 0.57g oxidant $(NH_4)_2S_2O_8$ (APS) instead of $FeCl_3$ was used to induce the oxidative polymerization of Py. The polymerization led to black colloids. Upon centrifugation and filtration, the solid product was washed with distilled water several times, and finally dried under vacuum for 24 h, yielding black powders of PPy.

Characterization: Powders of the prepared nanoparticles were used directly for Fourier-transform infrared (FTIR) and Raman measurements. FTIR spectra of the samples in solid state (KBr matrix) were recorded using a Bruker VECTOR22 spectrometer with $1 cm^{-1}$ resolution. Raman measurements were made on a Renishaw Raman spectrometer with 514.5 nm line of an argon ion laser as the excitation source.

Dispersions of the nanoparticles were prepared by dispersing the as-prepared powders in distilled water by sonication. The dispersions were used for UV-Vis and fluorescence measurements. The UV-Vis spectra were recorded on Perkin Elmer Lambda35 instrument with 1 nm resolution. The emission spectra excited at 488 nm were obtained on F-4600 Flspectorohotomet (HITACHI, Japan) with 1 nm resolution.

The relative fluorescence quantum yield of the dispersion was measured according to the following equation: [1]

$$\psi_f = \psi_s \frac{F_f}{F_s} \cdot \frac{A_s}{A_f}$$

where F is the measured fluorescence integral area (under the fluorescence spectra), A is the UV-Vis absorbance at 488 nm and ψ is the quantum yield. Fluorescein in 0.1 M NaOH was used as a standard; Quantum yield of the standard (ψ_S = 0.95) was adopted from literature. The subscripts f and s correspond to the sample and the fluorescein reference, respectively.

Transmission electron microscopy (TEM, JEOL 2000FX) was used for TEM measurements. The samples were prepared by placing a drop of ethanol solution onto a carbon-coated copper grid, after about two minutes the excess solvent was removed using a filter paper and the grid was dried under ambient conditions. Elemental mapping and EDX analysis were performed on an FEI Tecnai-F30 high-resolution electron microscope equipped with EDX apparatus. The accelerating voltage for EDX analysis was 300 kV.

Cell studies.

The human liver cancer Bel-7402 cells were seeded onto coverslips in 6-well plate at a density of 1×10^5 cells per well and incubated at 37 ºC in a humidified atmosphere of 5% CO_2. The culture medium was a DMEM (High Glucose) supplemented with 10% fetal calf serum, 100 µg/mL streptomycin, 100 U/mL penicillin and 4 mM L-glutamine and changed every other day until 80% confluence had been reached. Thereafter, the cells were incubated with PPy/PB core/shell nanoparticles at 37 ºC with a final particle concentration of 10 µg/mL. After 2 h incubation, the cell monolayer on the coverslip was taken out of the medium from the incubator, fixed with 4% paraformaldehyde solution for 15mins, repeatedly rinsed with PBS (Phosphate Buffered Saline) after removal of the fixing solution, then sealed with a microscope glass slide and observed with laser scanning confocal microscopy (LSCM) LSM-710 (Zeiss Inc., Germany) at an excitation wavelength of 488 nm.

CV measurements.

CV measurements of the samples were performed on a CHI 660C Electrochemical Workstation (CH Instruments, USA) with 0.02g KNO_3 powder added as electrolyte and a scan rate of 20 mVs^{-1} from −1.5 to 1.5 V(Vs. Ag/AgCl). A conventional three-electrode system (a glass carbon electrode, a platinum counter electrode, an Ag/AgCl electrode) was used throughout the experiments.

175 μL Py, 350 μL Py, 525 μL Py were respectively added into the as-prepared miniemulsion (27.2 g water, 0.4 g EPE-Fe, 0.5 g toluene, and 0.02 g hexadecane) in three glass cells. CV experiments on the three Py containing miniemulsion systems (A, B and C) with increased amount of Py were performed. In the system A, the Py concentration is same as that used for the synthesis of PPy/PB core/shell nanoparticles. As a control, CV experiment on 100μL Py in 28mL pure water was also performed (system D).

The CV profile of system D (100μL Py in water) shows a remarkable peak at 1.26V, which is a signal for eletropolymerization of Py. The similar peak can also be observed in the CV profile for system C (525 μL Py in miniemulsion), suggesting that there are a noticeable amount of Py monomer existing in the water phase of system C. Whereas for system A (175 μL Py) and system B (350 μL Py), only a pair of peaks at 0.22 V and -0.05 V appeared, which can be attributed to the oxidation and reduction processes of the Fe irons in the surfactant. No eletropolymerization signal was observed in these two systems. Considering the amount of Py in both system A and B are larger than that in system D, the absence of electropolymerization signal suggesting Py was incorporated into the electrolyte-free oil phase of the miniemulsion and their contact with the electrodes was avoided. As a similar amount of Py was used for PPy/PB core/shell nanoparticle synthesis, it is reasonable to believe that the oxidative polymerization occurred in the core of the miniemulsion.

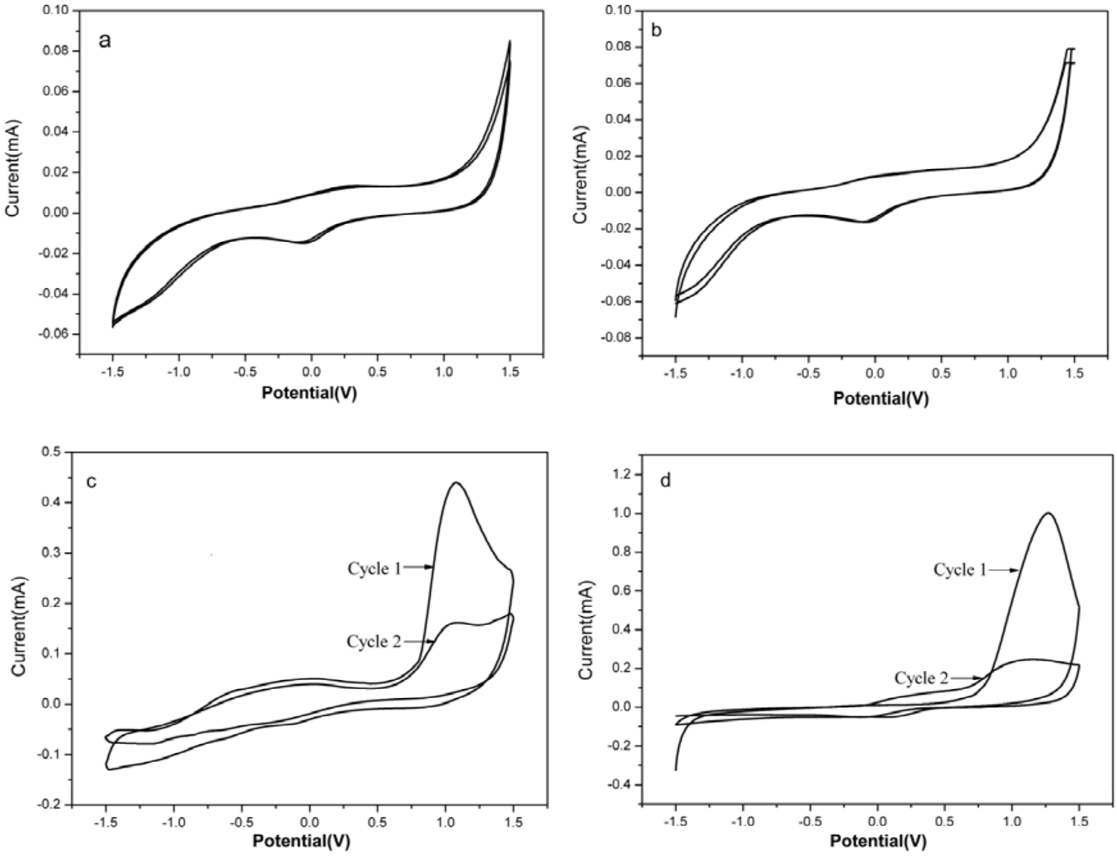

Fig. S1 CV curves of miniemulsion system A (a), B (b), C(c) and water system D (d).

UV-vis spectra and IR spectra

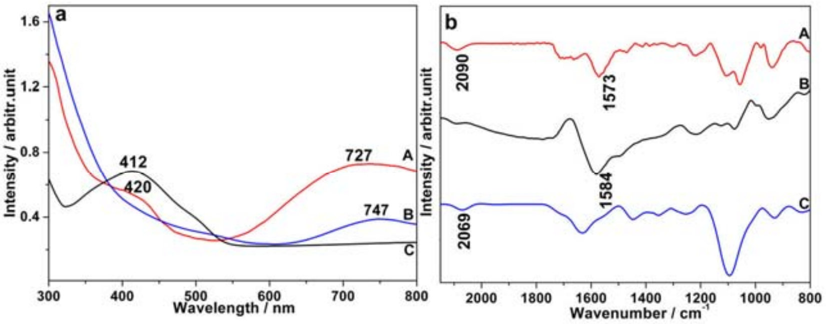

Fig. S2 (a) UV-vis spectra for PPy/PB core/shell nanoparticles (A), PB nanoshells (B) and PPy nanoparticles (C). (b) FT-IR spectra for PPy/PB core/shell nanoparticles (A), PPy nanoparticles (B) and PB nanoshells (C).

Raman spectra.

The Raman spectrum (Fig. S2A) for PPy/PB core/shell nanoparticles exhibits characteristic bands for PPy at 1627cm^{-1} (C=C stretching), 1349 cm^{-1} (pyrrole ring), 1092cm^{-1} (-C-H in-plane deformation), 966 cm^{-1} (pyrrole ring in-plane deformation), and bands for PB at 2028, 2150 cm^{-1} (-C≡N stretching), 558cm^{-1} (Fe-CN stretching)

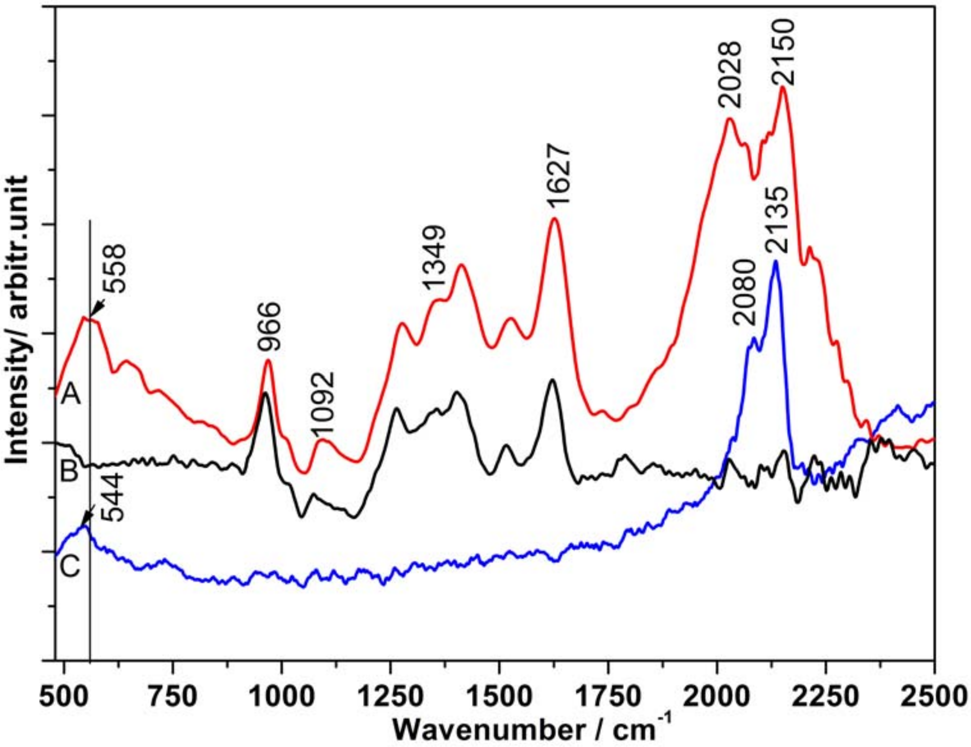

Fig. S3 Raman spectra for PPy/PB core/shell nanoparticles (A), PPy nanoparticles (B) and PB nanoshells (C).

Note and Reference:

1 J. R.Lakowicz, Principles of Fluorescence Spectroscopy, 2nd ed.; Kluwer Academic /Plenum, New York, **1999**.