Versatile method for the synthesis of porous nanostructured thin films of conducting polymers and their composites

LingFeng Dai,[a] Yuan He,[a] Xiang Huang,[a] Xin Cui,[a] Shihui Wang,[a] Dongtao Ge,*[a] Nifang Zhao,[b] Yue Li,[b] Yanan Sun[a] and Wei Shi*[a]

[a]Department of Biomaterials, College of Materials, Xiamen University, Xiamen, 361005, China.
[b]Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen, 361005, China.
E-mail: gedt@xmu.edu.cn; shiwei@xmu.edu.cn

Experimental section

Reagents: Pyrrole, aniline and EDOT were purchased from Sinopharm Chemical Reagent Co., Ltd (China) and were distilled before use under reduced pressure. All other chemicals were of analytical grade and were used as received.

Preparation of porous nanostructured thin film of $FeCl_3$: Fixed amounts of $FeCl_3 \cdot 6H_2O$ were dissolved in 10 ml ethanol to form ethanol solutions of $FeCl_3$ with different concentrations. Then 125 μl ethanol solution of $FeCl_3$ was dropped onto a rectangular titanium (or glass and PET) substrate that had been washed with ethanol then deionized water prior to use. The solution-coated substrate was placed in a temperature controlled oven and dried under a pre-set temperature.

Polymerization of porous nanostructured thin film of CPs by CVD: The obtained $FeCl_3$ film was placed into a chamber, which was then vacuumized immediately at room temperature until the internal pressure reduced to 10^{-2} Torr. For the preparation of porous nanostructures of PPy, the pyrrole monomer was injected into the chamber by a micro-syringe, and the chamber was heated to 60 °C for 1 h. For the preparation of porous nanostructures of PANI and PEDOT, the reaction procedures were the same as described above, except that the pyrrole monomer was replaced by aniline and EDOT monomers. Finally, the obtained CP products were washed thoroughly with ethanol and dried in an oven at 60 °C for 30 min. The preparation procedure for the transparent PPy film was the same as that described above, except that the amount of the $FeCl_3$ solution and the polymerization time were reduced to 30 μL (0.1 M) and 10 min, respectively.

Preparation of porous nanostructured thin film of CP/polymer composite on the glass coverlip: For preparing PPy/PEDOT film, the porous PPy thin film was produced at first by the same procedure as above except that the polymerization time was reduced to 30 min. Then the PPy film was placed into another chamber, followed the same route for preparing thinner PEDOT film except that the reaction time was reduced to 30 min. For preparing PPy/PDA film, the porous PPy thin film was produced at first by the same procedure as above except that the polymerization time was reduced to 30 min. Then the PPy film was immersed into a dopamine solution (0.013 M dopamine in 10 mM Tris, PH 8.5) for 24 h.

Preparation of porous nanostructure of $FeCl_3/CaCl_2$ and PPy/$CaCl_2$: Fixed amounts of $CaCl_2$ were added to 0.1 M $FeCl_3$ solution to form a $FeCl_3/CaCl_2$ solution. The remaining preparation steps for $FeCl_3/CaCl_2$ of porous nanostructure was the same as that for $FeCl_3$ porous nanostructure (Fig. 1b), and the preparation for porous PPy/$CaCl_2$ nanostructure was the same as that for PPy porous nanostructure (Fig. 1c).

Formation of apatite particles on the porous PPy/$CaCl_2$ nanostructure surface: After being washed with deionized water several times, the obtained porous nanostructure of PPy/$CaCl_2$ was soaked in 5 ml SBF at 36.5 °C for a fixed

time period. The samples were removed from the solution, washed with de-ionized water, and dried at room temperature.

Characterization: Morphologies of the products were examined by SEM (LEO 1530, Germany). EDS analysis was carried out on a Oxford Link ISIS 300 instrument. FTIR spectroscopy and UV/Vis spectroscopy were recorded on an Avatar 360 spectrophotometer (Nicolet, USA) and lambda750 (Perkin Elmer, USA) respectively. Contact angle was tested by FM40MK2 (KRUSS, Germany). The characterization of electric conductivity of Polymers were carried out by four point probe instrument SX1934 (Baishen, China).

Data Section

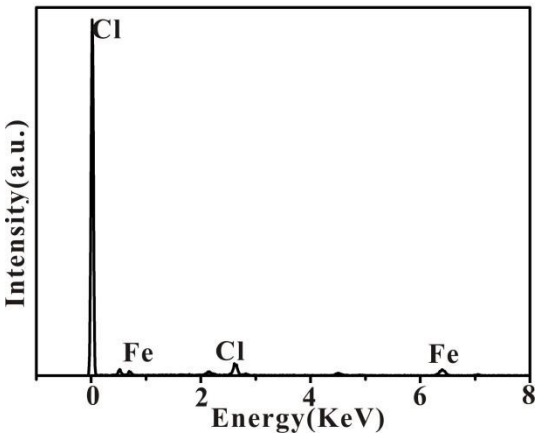

Fig. S1 EDS spectrum of the porous nanostructures of $FeCl_3$ obtained by evaporating ethanol from 0.05 M ethanol solution of $FeCl_3$ at 45 ^oC.

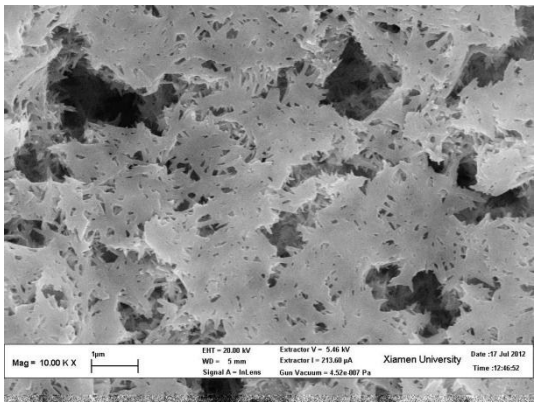

Fig. S2 SEM image of $FeCl_3$ film obtained by evaporating ethanol from 0.1 M ethanol solution of $FeCl_3$ at 25 ^oC

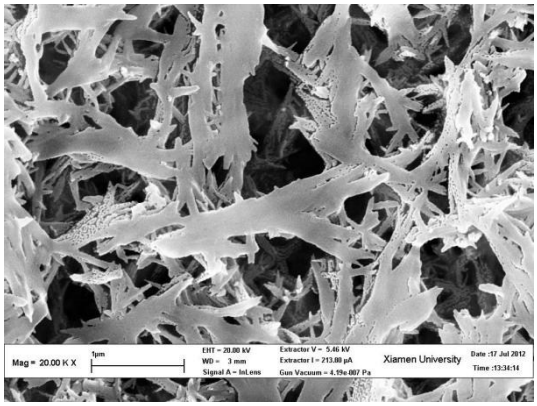

Fig. S3 SEM image of $FeCl_3$ film obtained by evaporating ethanol from 0.1 M ethanol solution of $FeCl_3$ at 60 ^oC.

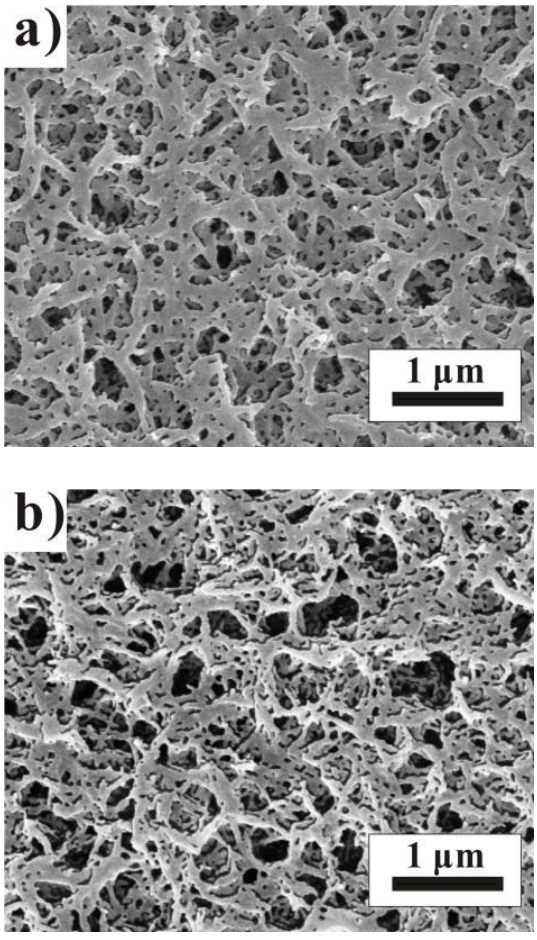

Fig. S4 SEM image of the $FeCl_3$ porous nanostructure obtained by evaporating ethanol from 0.1 M ethanol solution of $FeCl_3$ at 40 (a) and 50 ^oC (b) respectively.

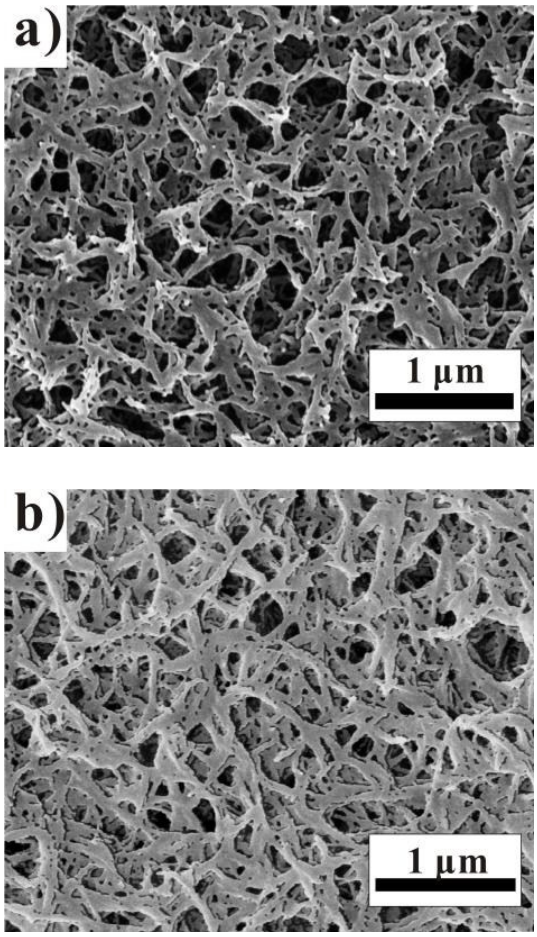

Fig. S5 SEM images of the $FeCl_3$ porous nanostructure obtained by evaporating ethanol from 0.05 M (a) and 0.1 M ethanol solution of $FeCl_3$ at 45 ^oC respectively.

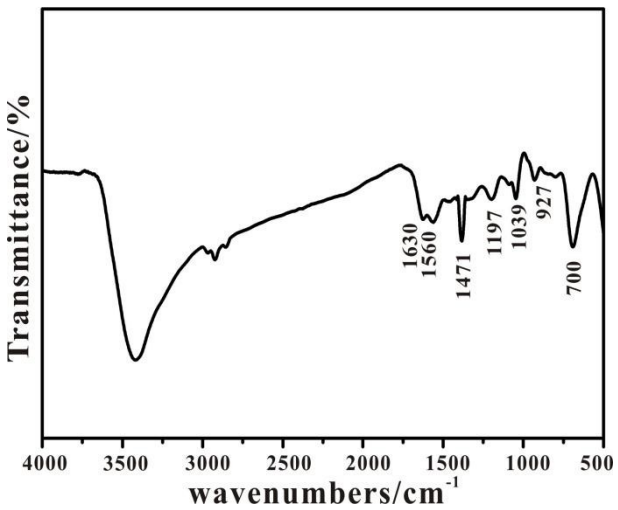

Fig. S6 FTIR spectrum of PPy.

Fig. S7 The contact angle of water on the porous PPy nanostructure surface.

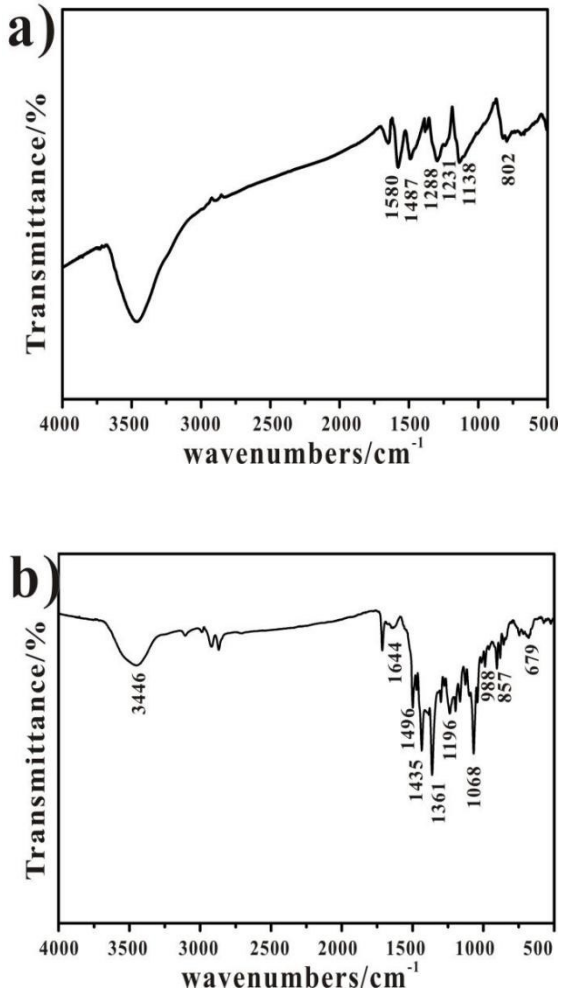

Fig. S8 FTIR spectra of PANI (a, 1580 cm^{-1}: C=C stretching of the quinoid rings; 1487 cm^{-1}: C=C stretching of the benzeniod rings; 1288 and 1231 cm^{-1}: C-N stretching modes of the benzenoid ring; 1138 cm^{-1}: C-H in-plane bending modes; 802 cm^{-1}: C-H out-of-plane bending modes) and PEDOT (b, 3446 cm^{-1}: O-H stretching; 1644 and 1496 cm^{-1}: C=C stretching; 1435 and 1361 cm^{-1}:C-C stretching; 1196 and 1068 cm^{-1}: C-O-C stretching; 679, 857 and 988 cm^{-1}: C-S stretching).

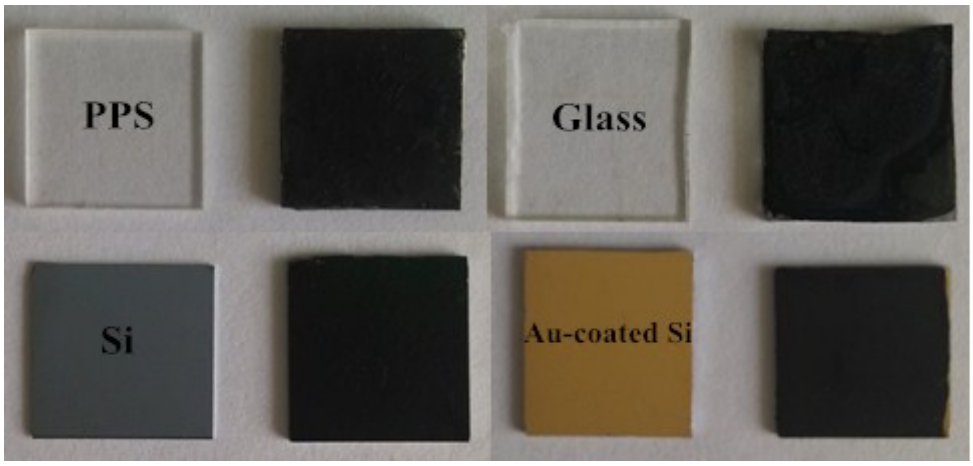

Fig. S9 Digital photos of porous nanostructured PPy thin films that were formed on PPS , glass, Si wafer, and Au-coated Si wafer.

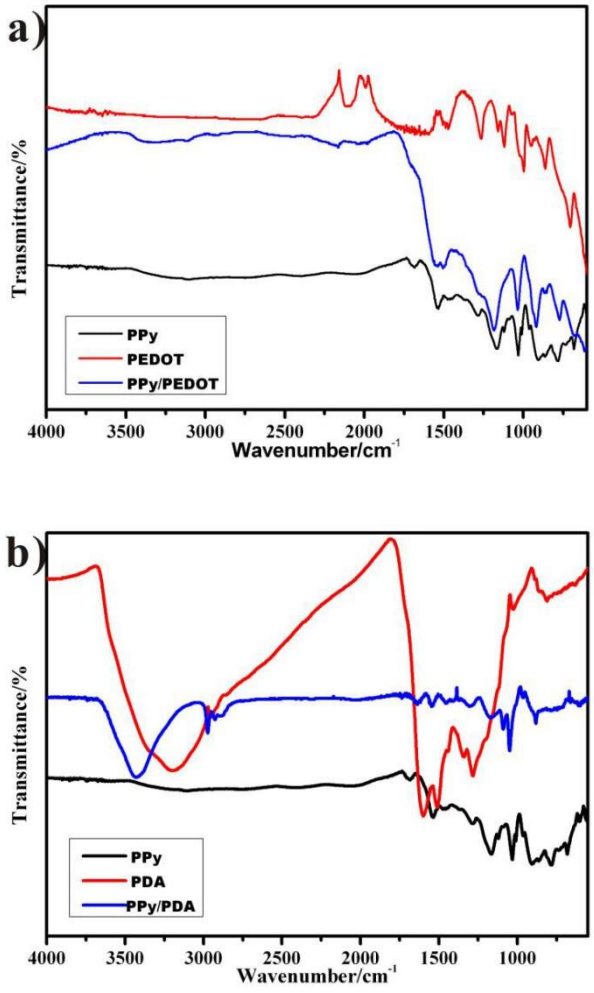

Fig. S10 FTIR spectra of a) PPy/PEDOTI nanocomposite (1031 and 1505 cm^{-1} are the characteristic peaks of PPy, 984 and 1184cm^{-1} are the characteristic peaks of PEDOT, which collectively confirm the formation of PPy/PEDOT) and b) PPy/PDA nanocomposite (1048, 1545 and 1639 cm^{-1} are the characteristic peaks of PPy, 1304, 1454 and 3430 cm^{-1}, are the characteristic peaks of PDA, which collectively confirm the formation of PPy/PDA).