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

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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 FeCl₂: Fixed amounts of FeCl₂·6H₂O were dissolved in 10 ml ethanol to form ethanol solutions of FeCl₂ with different concentrations. Then 125 µl ethanol solution of FeCl₂ 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 FeCl₂ 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 FeCl₂ 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 FeCl₂/CaCl₂ and PPy/CaCl₂: Fixed amounts of CaCl₂ were added to 0.1 M FeCl₂ solution to form a FeCl₂/CaCl₂ solution. The remaining preparation steps for FeCl₂/CaCl₂ of porous nanostructure was the same as that for FeCl₂ porous nanostructure (Fig. 1b), and the preparation for porous PPy/CaCl₂ nanostructure was the same as that for PPy porous nanostructure (Fig. 1c).

Formation of apatite particles on the porous PPy/CaCl₂ nanostructure surface: After being washed with deionized water several times, the obtained porous nanostructure of PPy/CaCl₂ 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 an 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

![EDS spectrum of the porous nanostructures of FeCl₃ obtained by evaporating ethanol from 0.05 M ethanol solution of FeCl₃ at 45 °C.](image)

**Fig. S1** EDS spectrum of the porous nanostructures of FeCl₃ obtained by evaporating ethanol from 0.05 M ethanol solution of FeCl₃ at 45 °C.

![SEM image of FeCl₃ film obtained by evaporating ethanol from 0.1 M ethanol solution of FeCl₃ at 25 °C.](image)

**Fig. S2** SEM image of FeCl₃ film obtained by evaporating ethanol from 0.1 M ethanol solution of FeCl₃ at 25 °C.
Fig. S3  SEM image of FeCl$_3$ film obtained by evaporating ethanol from 0.1 M ethanol solution of FeCl$_3$ at 60 °C.

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 °C (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 °C 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, $1580 \text{ cm}^{-1}$: C=C stretching of the quinoid rings; $1487 \text{ cm}^{-1}$: C=C stretching of the benzenoid rings; $1288$ and $1231 \text{ cm}^{-1}$: C-N stretching modes of the benzenoid ring; $1138 \text{ cm}^{-1}$: C-H in-plane bending modes; $802 \text{ cm}^{-1}$: C-H out-of-plane bending modes) and PEDOT (b, $3446 \text{ cm}^{-1}$: O-H stretching; $1644$ and $1496 \text{ cm}^{-1}$: C=C stretching; $1435$ and $1361 \text{ cm}^{-1}$: C-C stretching; $1196$ and $1068 \text{ cm}^{-1}$: C-O-C stretching; $679$, $857$ and $988 \text{ cm}^{-1}$: 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/PEDOT nanocomposite (1031 and 1505 cm$^{-1}$ are the characteristic peaks of PPy, 984 and 1184 cm$^{-1}$ 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).