Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Fabrication of a flexible porous polypyrrole film with 3D micro-nanostructure and its electrochemical properties

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1. Morphology and microstructure of PPy NTs

Figure S1 shows the morphology and microstructure of PPy NTs that were prepared by template-free synthesis. The SEM result in figure S1 (a) indicates that PPy NTs have a high aspect ratio. Figure S1 (b) shows a hollow structure of PPy NTs and the diameter of PPy NTs is 100-120 nm. The hollow structure provides more channels for ions insertion and extraction. In addition, the hollow structure can reduce internal stress during the oxidation/reduction process of PPy.

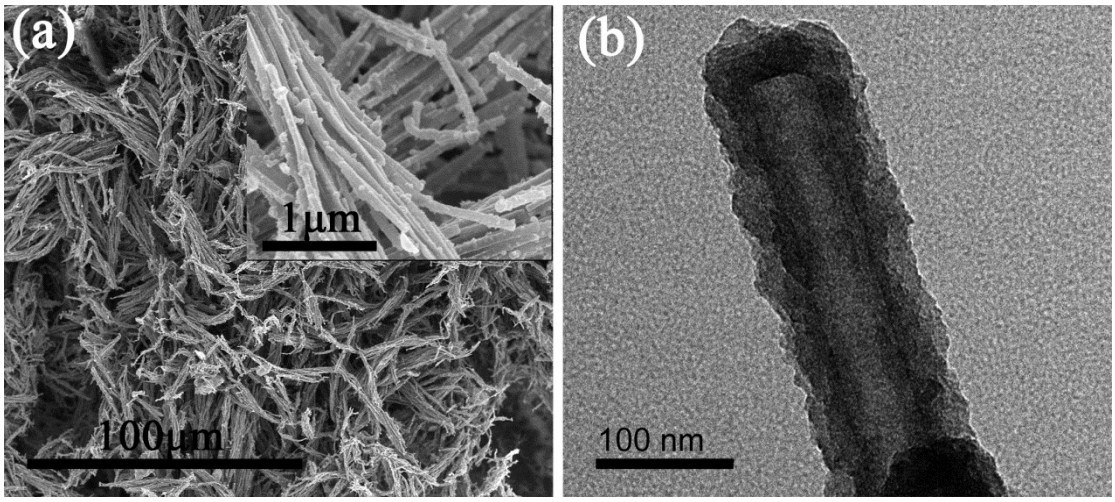

Figure S1 Morphology and microstructure of PPy NTs

2. X-ray diffraction patterns of PPy NTs

Figure S2 shows the X-ray diffraction patterns of PPy NTs. The diffraction pattern clearly indicates that PPy NTs are mainly amorphous structure. The peak at 26° is thought to arise from PPy chains close to the interplanar Van der Waals distance for aromatic groups.

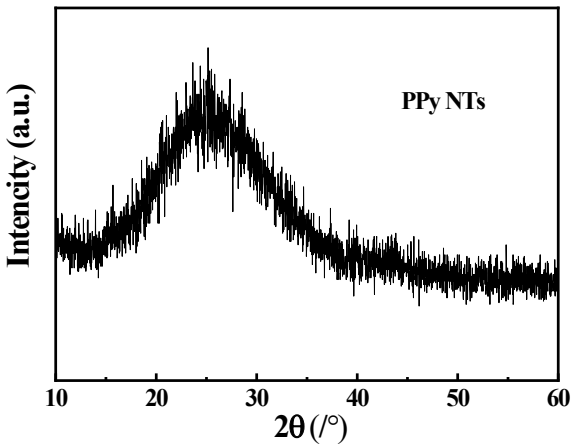

Figure S2 X-ray diffraction patterns of PPy NTs

3. Fabrication of flexible porous PPy film

The preparation process of the flexible porous PPy film is shown in figure S3. Firstly, the as-prepared PPy NTs of 20 mg were dispersed in alcohol of 200 ml by the ultrasound to form a homogeneous mixture. The mixture was filtered through a porous titanium plate with a surface morphology shown in figure S4. Then the porous

titanium plate containing PPy NTs was then immersed for 30 minutes in an aqueous electrolyte and used as the working electrode for galvanostatic polymerization. The aqueous electrolyte for polymerization contained 0.3M sodium ptoluenesulfonate and 0.1 M pyrrole (Py) monomer. Finally, the flexible porous PPy films were prepared on the porous titanium plate.

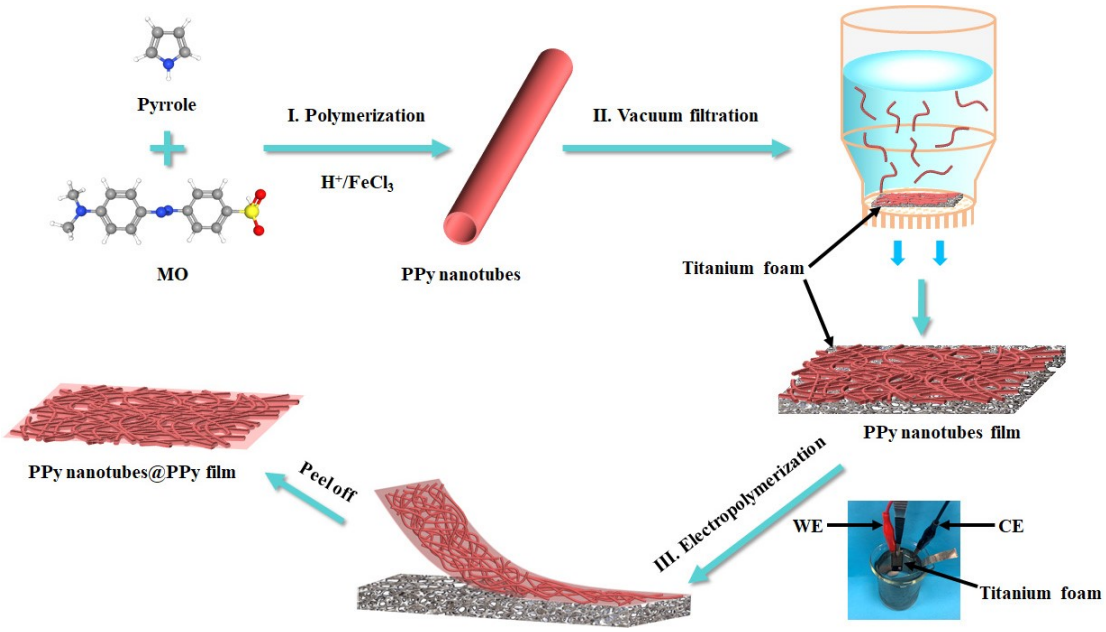

Figure S3 Schematic for preparation of flexible porous PPy film

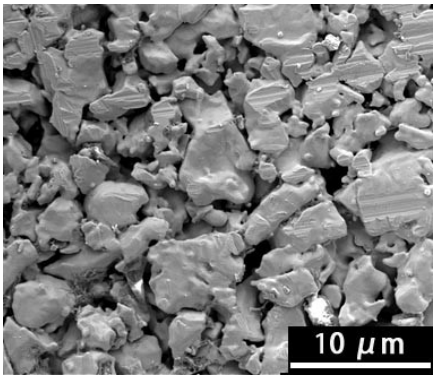

Figure S4 Morphology of porous titanium plate

4. Preparation of compact PPy film

The compact PPy films were prepared by a galvanostatic polymerization using a two-electrode system, as shown in figure S5. A smooth titanium plate (1×3 cm^2) used as the working electrode and a Pt plate (2×2 cm^2) was used as the counter electrode. The area of the working electrode for electropolymerization was 1×1 cm^2 or 1×2 cm^2.

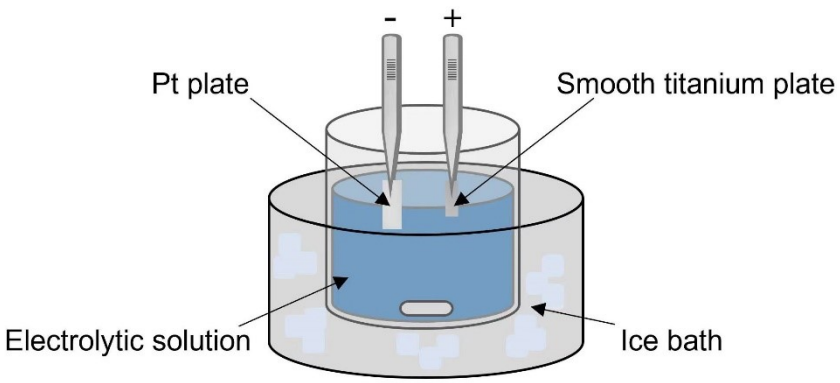

Figure S5 Schematic for preparation of compact PPy film

5. Fabrication of flexible supercapacitors

Gel electrolyte composed of polyvinyl alcohol (PVA) and H_2SO_4 was coated on the surface of PPy films. Then the two coated PPy films were pressed together by a sheeting presser. As shown in figure S6, the bonded PPy film was encapsulated by polydimethylsiloxane.

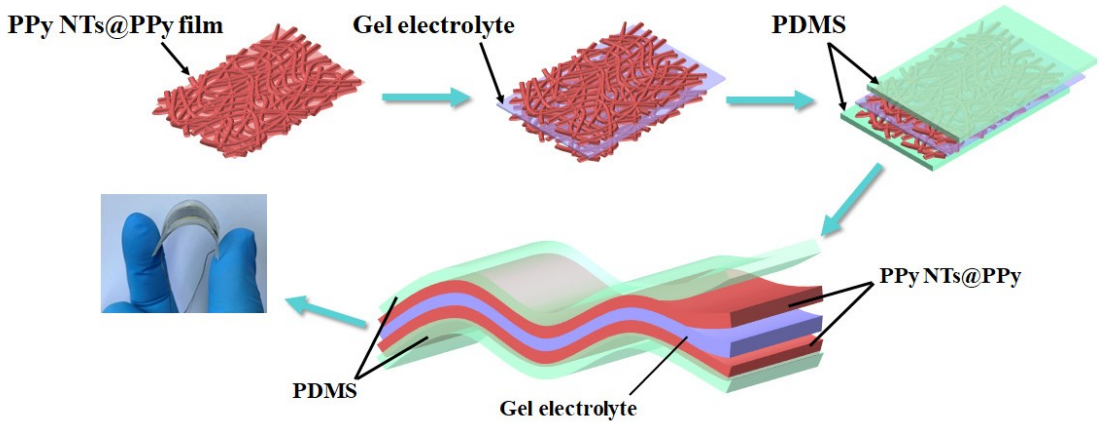

Figure S6 Schematic for fabrication of flexible supercapacitors

6. Surface and Cross-section of compact PPy film

The surface of compact PPy film is in figure S7. The surface morphology of compact PPy film is characteristic of cauliflower. The cross-section morphology of compact PPy film is shown in figure S8. There do not appear to be any pores on the surface and cross-section of PPy film. During the oxidation/reduction process, the ions in the electrolyte cannot reach the inner layer of PPy film.

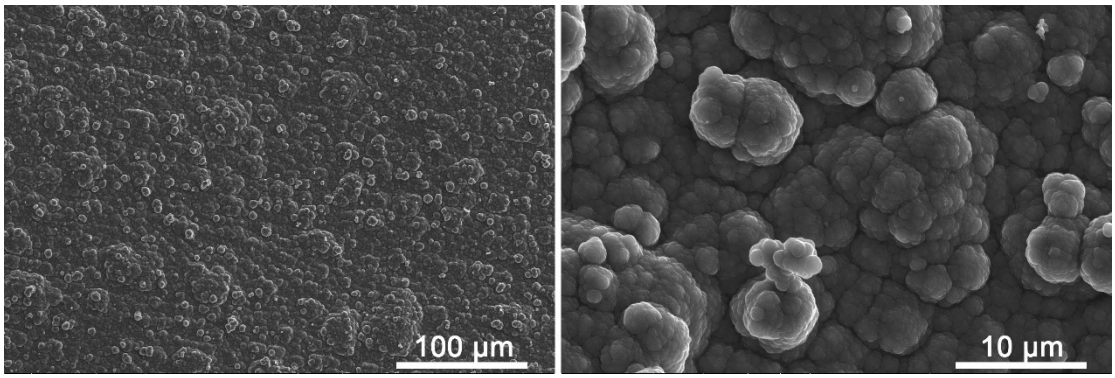

Figure S7 Surface morphology of compact PPy film

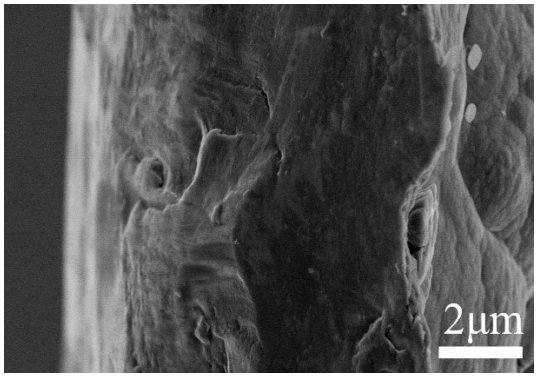

Figure S8 Cross-section morphology of compact PPy film

7. Cross-section of flexible porous PPy films after cycle measurement

The cross-section morphology of flexible porous PPy films after cycle measurement is shown in figure S9. Noting that after cycle measurement, all PPy NTs display disordered arraying, which can result from the repeated volume change of PPy films during the oxidation/reduction process. The PPy film@N1.5/E1.5 became loose and the crosslinking network between different PPy NTs was obviously damaged, which should be one of main reasons for the capacitance fading of PPy film. The PPy film@N1.5/E3 appears to have a compact structure, and their capacitance retention was relatively high. There is some electro-polymerization PPy disconnecting with PPy NTs during oxidation/reduction process of PPy film@N1.5/E6，which can result in its capacitance fading.

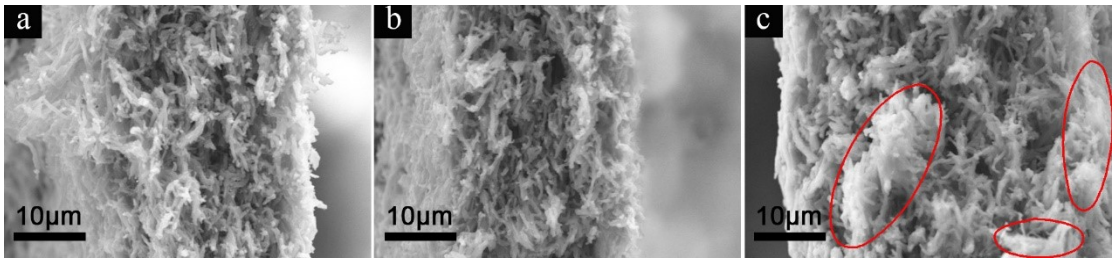

Figure S9 Cross-section of flexible porous PPy films after cycle measurement, PPy film@N1.5/E1.5 (a), PPy film@N1.5/E3 (b), PPy film@N1.5/E6 (c)