

## Polypyrrole capacitance characteristics with different doping ions

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### **1. Electrochemical properties of PPy films with polymerization charge of 4 C·cm<sup>-2</sup>**

Figure S1 shows electrochemical properties of PPy films with a low polymerization charge of 4 C·cm<sup>-2</sup>. There is a greater gap between ion/Ts<sup>-</sup> films and two other films. Noting that the CV charge didn't increase when polymerization charge of ion/Ts<sup>-</sup> film increased from 2 C·cm<sup>-2</sup> to 4 C·cm<sup>-2</sup>. In other words, all increment of ion/Ts<sup>-</sup> films from 2 C·cm<sup>-2</sup> to 4 C·cm<sup>-2</sup> became "inactive areas". Therefore, as electrode material for various devices, ion/Ts<sup>-</sup> films is not suited for the applications with a thick-layer structure.

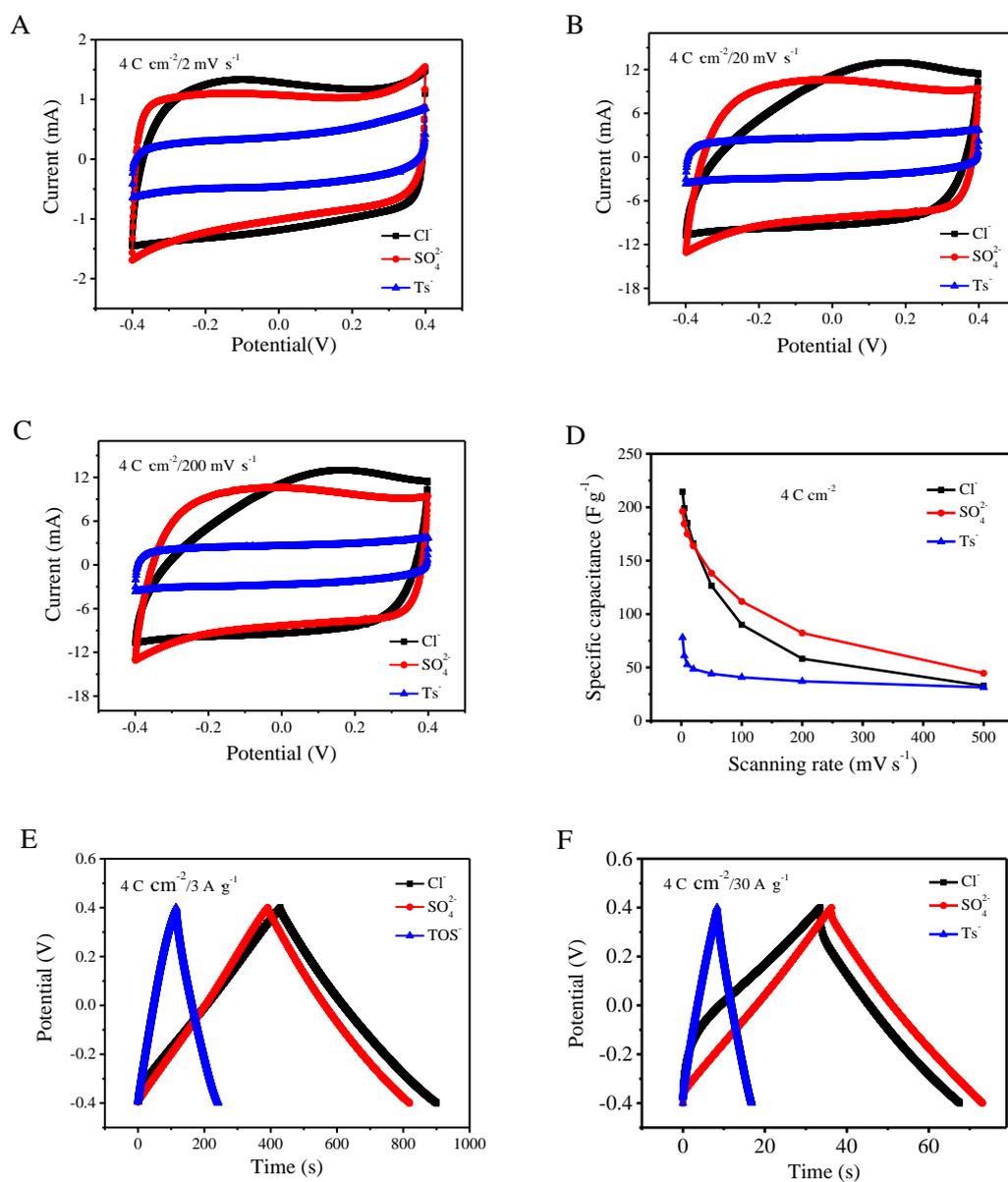


Figure S1 Cyclic voltammetry and constant current charging/discharging curves of PPy films with a polymerization charge of  $4 \text{ C cm}^{-2}$ , (A)  $2 \text{ mV s}^{-1}$ , (B)  $20 \text{ mV s}^{-1}$ , (C)  $200 \text{ mV s}^{-1}$ , (D) specific capacitance change with CV scan rate, (E) galvanostatic charging/discharging curves of  $3 \text{ A g}^{-1}$ , (F) galvanostatic charging/discharging curves of  $30 \text{ A g}^{-1}$

## 2. Surface morphology of PPy films with different thickness

Figure S2 shows the surface morphology of PPy films with different thickness. All PPy

films exhibit 'cauliflower' structures, which is the typical structure of PPy films prepared by electrochemical method. However, it is obvious that the fluctuations on PPy surface became greater when polymerization charges increased. Silk et al.<sup>1,2</sup> also found the same phenomenon in the course of PPy growth, which can be related to PPy unbalance growth on roughened surface<sup>3</sup>. In addition, the surface of PPy/Ts<sup>-</sup> films has more spherical structures than that of PPy/Cl<sup>-</sup> and PPy/SO<sub>4</sub><sup>2-</sup> films. The different mobility of Ts<sup>-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> can result in the different-sized spherical structures<sup>2</sup>.

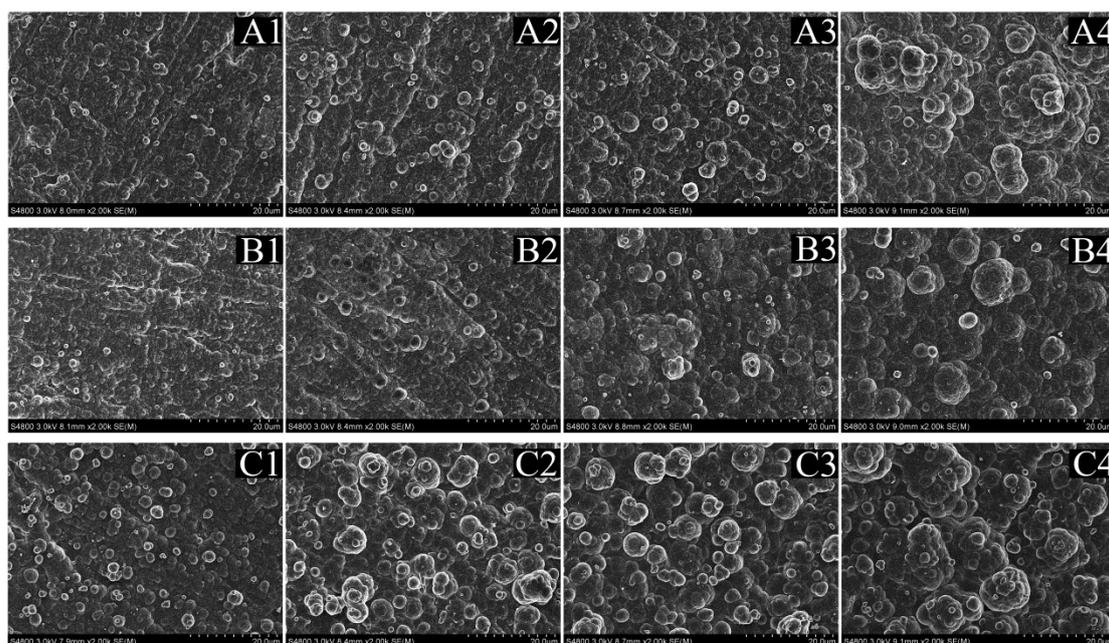


Figure S2 Surface morphology of PPy/Cl<sup>-</sup> films (A1-A4) of 0.5 C·cm<sup>-2</sup>, 1 C·cm<sup>-2</sup>, 2 C·cm<sup>-2</sup> and 4 C·cm<sup>-2</sup>, PPy/SO<sub>4</sub><sup>2-</sup> films (B1-B4) of 0.5 C·cm<sup>-2</sup>, 1 C·cm<sup>-2</sup>, 2 C·cm<sup>-2</sup> and 4 C·cm<sup>-2</sup>, PPy/Ts<sup>-</sup> films (C1-C4) of 0.5 C·cm<sup>-2</sup>, 1 C·cm<sup>-2</sup>, 2 C·cm<sup>-2</sup> and 4 C·cm<sup>-2</sup>

### 3. X-ray diffraction (XRD) patterns of PPy films

Figure S3 shows XRD patterns of PPy/Cl<sup>-</sup>, PPy/SO<sub>4</sub><sup>2-</sup> and PPy/Ts<sup>-</sup> films with a polymerization charge of 2 C·cm<sup>-2</sup>. The front of PPy film is the side which directly

contact with working electrolyte. The back of PPy film is the side which directly contact with tantalum sheet. The XRD patterns of all film fronts show relatively sharper peaks. In the initial stage of PPy growth, the roughened surface of tantalum sheet can result in the unbalance growth of PPy films<sup>3</sup>, which reduced the crystallinity of PPy back.

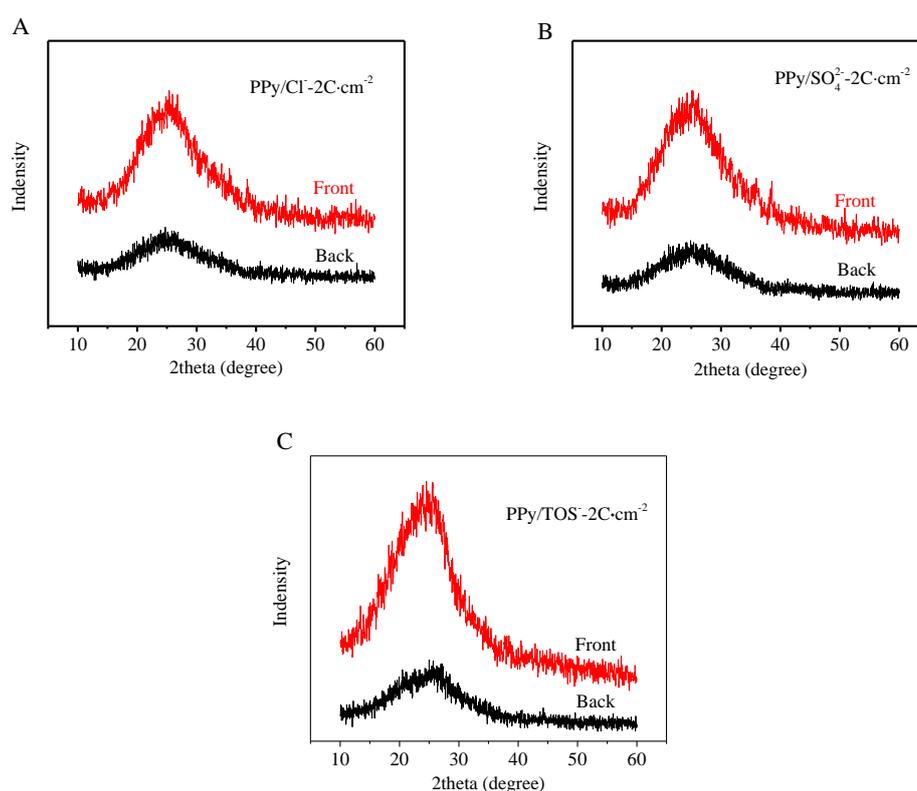


Figure S3 X-ray diffraction patterns of PPy films doped by different anions with polymerization charge of  $2\text{ C}\cdot\text{cm}^{-2}$ , (A) PPy/Cl<sup>-</sup>, (B) PPy/SO<sub>4</sub><sup>2-</sup> and (C) PPy/Ts<sup>-</sup>

#### 4. Electronic conductivity of PPy films

The electronic conductivities of PPy films were measured by four point probe resistivity meter (Guangzhou 4probes Tect, RTS-9) at  $23\pm 1^\circ\text{C}$ . As shown in table S1, the electronic conductivities of PPy/Ts<sup>-</sup> films ( $2\text{ C}\cdot\text{cm}^{-2}$ ) is greatest, which can result from the relatively high crystallinity.

Table S1 Electronic conductivities of PPy films with polymerization charge of 2 C·cm<sup>-2</sup>

PPy/Cl <sup>-</sup> (S·cm <sup>-1</sup> )	PPy/SO <sub>4</sub> <sup>2-</sup> ( S·cm <sup>-1</sup> )	PPy/Ts <sup>-</sup> ( S·cm <sup>-1</sup> )
4.61	2.44	43.7

#### 5. Test of tensile breaking strength for PPy films

The tensile breaking strength can be calculated according to the following equation,

$$\sigma = \frac{P}{a \times b},$$

Where  $\sigma$  is the tensile breaking strength,  $P$  is the maximum load,  $a$  is the width of cross section and  $b$  is the length of cross section. The value  $a$  and  $b$  can be obtained by SEM results. The value of  $\sigma$  in table 1 was the average of five samples. The sample area was 1×2 cm<sup>2</sup> and the polymerization charge was 2 C·cm<sup>-2</sup>. Figure S4 shows the broken sample of PPy film.



Figure S4 Broken sample of PPy film with a polymerization charge of 2 C·cm<sup>-2</sup>

#### 6. Change of PPy crystallinity after swelling

As shown in Figure S5, The crystallinity of PPy/Ts<sup>-</sup> film decreased obviously after the

swelling. The ions from working electrolyte enter into PPy matrix and produce force to PPy molecular chain. The long-term and repeated force to PPy molecular chain can change PPy original structure.

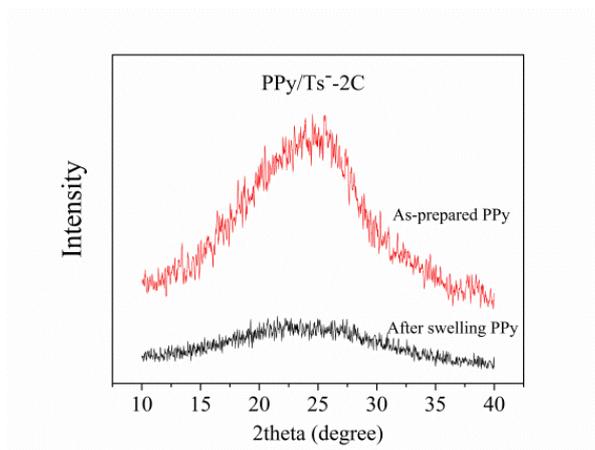


Figure S5 Change of PPy crystallinity after swelling

#### Reference

1. T. Silk, Q. Hong, J. Tamm and R. G. Compton, *Synthetic Metals*, 1998, 93, 59-64.
2. T. Silk, Q. Hong, J. Tamm and R. G. Compton, *Synthetic Metals*, 1998, 93, 65-71.
3. C. O. Yoon, H. K. Sung, J. H. Kim, E. Barsoukov, J. H. Kim and H. Lee, *Synthetic Metals*, 1999, 99, 201-212.