Supplementary Materials

Preparation of TiO₂/PEDOT nanorods film with enhanced electrochromic property

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1. FTIR spectra of EDOT monomer and bare PEDOT

As shown in Figure S1a and b, the main functional groups of EDOT monomer are the same as the bare PEDOT. The stretching vibration of the EDOT monomer is very close to the PEDOT molecule. The purity of the EDOT monomer is higher than the PEDOT film and the signal of the FTIR is stronger. Compared with the EDOT monomer, the absorption frequency is slightly altered. Because PEDOT forms longer conjugated chain molecules and larger conjugated system, which can create π - π * inducing effects on the intramolecular chemical bonds. Figure 1c is the FTIR spectra of TiO₂/PEDOT film and the main functional groups of TiO₂/PEDOT film are the same as EDOT monomer and bare PEDOT. The above results confirmed the formation of electrochromic PEDOT on the TiO₂ nanorod arrays.



Figure S1. FTIR spectra of (a) EDOT monomer and (b) bare PEDOT film.

2. The morphology of bare PEDOT and TiO₂/PEDOT nanorod arrays films

The pare PEDOT on FTO prepared by electropolymerization exhibits dense morphology (Figure S2).



Figure S2. Top-view scanning electron microscope (SEM) images of bare PEDOT on FTO.

All three composites (180, 240 and 300 mC films) have a nanorod array structure. However, there are still differences in the diameter and morphological structure of the composite nanorods for the 180 and 300 mC films compared to the 240 mC film (Figure S3). This is due to the difference in electrodeposition time, resulting in difference of PEDOT content present on the nanorods and in their gap. This ultimately resulted in a thinner nanorod for the 180 mC film and a thicker diameter for the 300 mC film (Figure S3a and c). In addition, the PEDOT of the 300 mC film had been deposited onto the surface, making it too dense between the nanorods. A sparse active layer is not conducive to the increase of active sites, while a dense active layer is an obstacle to the deeper transport of ions. The 240 mC film morphology is optimized in terms of the structure of the active layer (Figure S3b), resulting in relatively good electrochromic properties.



Figure S3. Top-view scanning electron microscope (SEM) images of (a) 180 mC, (b) 240 mC and (c) 300 mC TiO₂/PEDOT nanorod arrays films.

3. Electrochemistry performance of bare PEDOT

The CV curves of bare PEDOT (240 mC) performed at different potential scan rates range from 10 to 100 mV s⁻¹ is shown in Figure S4. Compared with the $TiO_2/PEDOT$ (240 mC) film (Figure 3b), the redox peaks of bare PEDOT film had a larger deviation, which indicated that the electrochemical reversibility was poor. At a sweep rate of 100 mV s⁻¹, there is only one pair of redox peaks.



Figure S4. CV curves of the PEDOT (240 mC) at different scan rates.

4. Electrochemistry performance of TiO₂, PEDOT and TiO₂/PEDOT

The chronoamperometry (CA) curves at the potential step from -1 to 1 V for 10 s were showed in Figure S5. It could be seen from the CA curves that the $TiO_2/PEDOT$ (240 mC) exhibited a higher transient current density than that of the pure TiO_2 and PEDOT films, also demonstrating that there were more active sites in $TiO_2/PEDOT$ film for ion insertion/extraction.^{1,2}



Figure S5. CA curves of TiO₂, PEDOT and TiO₂/PEDOT (240 mC).

5. Electrochemistry performance of TiO₂/PEDOT electrode and TiO₂/PEDOTbased device

We have calculated the specific capacitances of electrode and device by referring to electrochemical characterization methods in other literatures.^{3,4} The galvanostatic charge/discharge (GCD) tests were carried out on a CHI 760E electrochemical workstation (Chenhua, Shanghai). Based on the follow equation (1), the specific capacitance of TiO₂/PEDOT (prepared at 240 mC) film could be calculated:^{3,4}

$$C = \frac{I \times \Delta t}{\Delta V \times S} \tag{1}$$

where, *C* is the areal specific capacitance, *I* is the applied current, Δt is the time of discharge process, ΔV is the potential window, *S* represents the active surface area of the electrode. The charge/discharge curves of the electrode exhibited typical pseudocapacitive characteristic (Figure S6). The calculated area specific capacitance of the TiO₂/PEDOT (prepared at 240 mC) film is ~27 mF cm⁻² at 0.4 mA cm⁻², which indicates that the electrode has electrochemical energy storage capacity. The specific capacitances of the electrode decreases with the increase of current density. It shows that the stability of electrochemical energy storage still needs to be improved.



Figure S6. Galvanostatic charge/discharge profiles of TiO₂/PEDOT (prepared at 240 mC) film.

We tested the GCD in the same environment (Figure S7). The calculated area specific

capacitance of the device is ~ 3.18 mF cm⁻² at 0.4 mA cm⁻², which also indicates that the electrode has electrochemical energy storage capacity.



Figure S7. Galvanostatic charge/discharge profiles of a symmetrical supercapacitor assembled with TiO₂/PEDOT (prepared at 240 mC) film as the electrode.

We used cyclic voltammetry (CV) to study the electrochemical properties of the symmetrical supercapacitor assembled with $TiO_2/PEDOT$ (prepared at 240 mC) as the electrode (Figure S8). It is obvious that the CV curves show a typical capacitive characteristic. In addition, the redox peaks remain with increasing sweep speed, indicating that the $TiO_2/PEDOT$ electrode has a stable redox reversibility.



Figure S8. CV curves of a symmetrical supercapacitor assembled with TiO₂/PEDOT (prepared at 240 mC) as the electrode.

References

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