Pseudocapacitive-Dye-Molecule-Based High-Performance Flexible Supercapacitors

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1. Experimental Section

1.1 Preparation of the dye-based electrodes: The PPy/MB, PPy/ARS and PPy/MB/ARS electrodes deposited on carbon cloth (Gashub, Singapore) were prepared by a galvanostatic polymerization process reported previously.¹ Typically, 190 mg p-toluene sulfonic acid and 70 mg pyrrole were dissolved in 20 mL distilled water with dye molecules (0.1-0.5 mM) and then the mixture was stirred, cooled on ice, deoxygenized with nitrogen gas. Afterward, the carbon fabric (total area was 3.5 cm×1 cm, 1.8 cm×1 cm was immersed in the reaction solution for deposition) was controlled by a CHI 660D electrochemical workstation at a galvanostatic current density of 1 mA cm⁻² for different time (20 min, 30 min, 40 min, 50 min). After electrodeposition, the carbon cloth was washed with deionized water and dried in air, and then a single carbon fiber was teared off the carbon cloth as the resultant electrode (active length was 1.8 cm). The pure PPy electrode was prepared with similar procedures, without addition of dye molecules. For the evaluation of dye removal efficiency, the initial concentration of dye is 0.1 mM for MB and 0.2 mM for ARS, the active area of carbon cloth is 10 cm² and the galvanostatic current density is 1 mA cm⁻².

1.2 Fabrication of the symmetrical supercapacitor devices: The PPy/MB/ARS fibers were placed closely and in parallel on a piece of glass sheet, and then coated with polyvinyl alcohol (PVA)-H₂SO₄ gel electrolyte. The PVA-H₂SO₄ gel electrolyte was prepared by dissolving 10 mL H₂SO₄ and PVA powder (10 g) in 100 mL distilled water, which was heated at 80 °C with vigorous stirring to obtain a homogeneous gel-like suspension. Polyethylene terephthalate (PET, 0.3 mm thick) film was used as alternative substrate to test the flexibility of the asymmetric supercapacitors, and the capacitive performance was tested in two-electrode configuration.

1.3 Characterizations and electrochemical tests: The surface morphologies of as-prepared electrodes were tested by the scanning electron microscope (JSM-250 from JEOL, 10 KV). Fourier transform infrared spectroscopy (FTIR) spectra of the electrodes were tested on a NicoletiN10 spectrophotometer in the attenuated total reflection (ATR) mode. UV-vis absorption spectra of dye solution during electropolymerization process were recorded at 300 to 800 nm using a Hitachi U-3010 spectrometer. The electrochemical properties of electrodes were investigated with CV and GCD measurements in a conventional three-electrode cell in 0.5 M H₂SO₄ aqueous electrolyte, with a saturated Ag/AgCl electrode as the reference electrode and a platinum sheet as the counter electrode, employing a CHI 660D electrochemical workstation (Chenhua, Shanghai). For PPy, PPy/MB and PPy/ARS electrodes, the parameters of DPV test were pulse width 250 ms, pulse height 50 mV, step height 5 mV, step time 10 ms, scan rate 5 mV s⁻¹. The EIS was tested over the frequency range of 10^{-1} to 10^{5} Hz with a 10 mV amplitude at open circuit potential.



Fig. S1. Electrochemical redox reaction mechanism of MB (a) and ARS (b) dyes.



Fig. S2. SEM images of a) single device scan and b) section details of PPy/MB composite. The diameter of single device is 0.02 cm. The volume of the as-prepared supercapacitor cell was determined to be about 1.13×10^{-3} cm³.



Fig. S3. FTIR of MB and ARS standard sample, respectively.



Fig. S4. CV curves (a) and length capacitances (b) of PPy/MB electrodes prepared with different mole concentration of MB at a scan rate of 100 mV s⁻¹. c) Capacitance retention of the PPy/MB electrodes prepared with different electropolymerization time after 2000 cycles at a scan rate of 200 mV s⁻¹.

The experimental condition was optimized by adjusting the concentration of added ARS and the electropolymerization deposition time, and the result showed that the concentration of ARS aqueous solution at 4×10^{-4} mol L⁻¹ and the deposition time of 40 min are most favorable to high capacitance and stability of PPy/MB electrodes.



Fig. S5. CV curves (a) of bare PPy and PPy/MB (b) electrodes at different scan rates in the potential range of -0.2 to 0.6 V (*vs.* Ag/AgCl). c) The specific capacitance of PPy and PPy/MB electrodes as a function of scan rate, respectively. d) Nyquist plots of bare PPy and PPy/MB electrodes.



Fig. S6. CV curves of bare PPy (a) and PPy/MB (b) electrodes collected in the first 10 cycles at a scan rate of 100

mV s⁻¹.



Fig. S7. CV curves (a) and length capacitances (b) of PPy/ARS electrodes prepared with different mole concentration of ARS at a scan rate of 100 mV s⁻¹. c) Capacitance retention of the PPy/ARS electrodes prepared with different electropolymerization time after 2000 cycles at a scan rate of 200 mV s⁻¹.

The experimental condition was optimized by adjusting the concentration of added ARS and the electropolymerization deposition time, and the result showed that the concentration of ARS aqueous solution at 4×10^{-4} mol L⁻¹ and the deposition time of 40 min are most favorable to high capacitance and stability of PPy/ARS electrodes.



Fig. S8. CV curves and bare PPy (a) and PPy/ARS (b) electrodes at different scan rates in the potential range of -0.4 to 0.4 V (*vs.* Ag/AgCl). c) The length capacitance of bare PPy and PPy/ARS electrodes as a function of scan rates, respectively. GCD curves (d) and rate capability (e) of PPy/ARS electrodes at different current densities. f) Capacitance retention of the PPy/ARS electrodes prepared with different electropolymerization time after 2000 cycles at a scan rate of 200 mV s⁻¹.



Fig. S9. CV curves of PPy/MB/ARS (a) and bare PPy (b) electrodes in the potential range of -0.4-0.6 V (*vs.* Ag/AgCl) at different scan rates. c) The specific capacitance of PPy and PPy/MB/ARS electrodes as a function of scan rate, respectively. d) GCD curves of PPy/MB/ARS electrodes at different current densities.



Fig. S10. a) GCD curves at different current densities of PPy/MB/ARS-electrodes-based flexible symmetric supercapacitor within a voltage range of $0 \sim 1$ V using H₂SO₄–PVA as gel electrolyte. The volumetric energy density of a symmetric supercapacitor was derived using the GCD data and by dividing the overall capacitance to its volume according to reference 53. b) Capacity retention of the symmetrical flexible supercapacitor based on as-prepared PPy/MB/ARS electrodes after 1000 cycles at a scan rate of 200 mV s⁻¹. CV curves of one, two, three and four symmetrical supercapacitors connected in serial (c) and parallel (d) at a scan rate of 100 mV s⁻¹.

References

1. Y. Yang, H. Wang, R. Hao and L. Guo, *Small*, 2016, **12**, 4683-4689.