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Supporting Information

High-capacity aqueous Zn-ion hybrid energy storage device

using poly(4,4'-thiodiphenol)-modified activated carbon as a

cathode material

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1. Method

Materials characterization

The electrode morphology was characterized by employing a scanning electron microscope (SEM, Zeiss Supra55). The nitrogen adsorption-desorption isotherms were collected by using an automatic volumetric sorption analyzer (ASAP 2460, Micromeritics, USA). The pore size distributions were obtained using the Barrett-Joyner-Halenda (BJH) method. The X-ray energy disperse spectra (EDS, TecnaiG2 20ST (T20)) elemental mappings were collected at an electron acceleration voltage of 100 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific ESCALAB 250Xi instrument with monochromatic Al K α radiation (hv = 1486.6 eV) at ultrahigh vacuum (below 10⁻⁸ Pa). Raman spectra were measured on a Raman spectroscopy (Thermo Nicolet iS10) was used to collect the FTIR spectra of samples with reflection mode.

2. Brunauer-Emmett-Teller Analysis

In order to investigate the change of specific surface area of AC coating after the electrodeposition of poly(4,4'-TDP), three samples were used to perform the BET measurements, i.e, the pure AC powder, the AC coating, and the poly(4,4'-TDP)/AC coating. Note that the coatings were scratched off the carbon fabric substrate for BET measurement. Figs. S1a, b, and c show nitrogen adsorption and desorption isotherms of pure AC powder, AC coating, and poly(4,4'-TDP)/AC coating, respectively. The pure AC product has a high specific surface area of 2282 m² g⁻¹. However, the AC coating containing small portions of PVDF binder and black carbon has a reduced specific surface area, as $1820 \text{ m}^2 \text{ g}^{-1}$. After the electrodeposition of poly(4,4'-TDP), ths

value was further decreased to $1030 \text{ m}^2 \text{ g}^{-1}$. The pore size distributions of AC powder, AC and poly(4,4'-TDP)/AC coatings are shown in Figs. S1d, e, and f, respectively. Interestingly, their pore size distributions are almost identical except the pore volume. A majority of nanopores have sizes in the range of 1 - 3 nm.



Fig. S1 (a, b, and c) N_2 adsorption and desorption isotherms of pure AC powder, AC coating, and poly(4,4'-TDP)/AC coating, respectively. (d, e, and f) Pore size distributions of the three samples, respectively.

3. Electrochemical Behaviors of a Zn//AC Hybrid Supercapacitor

Without the presence of poly(4,4'-TDP), a bare AC coating on carbon fabric was used as the cathode to match with the Zn anode. CV loops of this sandwich-structured cell using ZnSO₄ electrolyte are shown in Fig. S2a. The CV loops within the voltage range of 0.2 - 1.8 V are in quasi-rectangular shape, indicating the non-Faradaic process. Fig. S2b shows a typical GCD curve of this cell. Using the discharge curve, the areal specific capacity is deduced to be 0.38 mAh cm⁻². Using the AC mass loading of 3.7 mg cm⁻², the gravimetric specific capacity at 0.3 A g^{-1} is calculated to be 102 mAh g^{-1} .



Fig. S2 (a) CV loops of a Zn//AC cell at different voltage scan rates. (b) GCD curve of the cell at 1 mA cm⁻².

4. Electrochemical Behaviors of the Poly(4,4'-TDP)/AC Electrode

The poly(4,4'-TDP) was electropolymerized in a three-electrode cell filled with an aqueous solution containing 1 M H₂SO₄ and 0.03 M 4,4'-TDP monomers. The Carbon-fabric-supported AC coating was used as work electrode. With using a Pt foil counter electrode and an Ag/AgCl reference electrode, the electrodeposition of poly(4,4'-TDP) was conducted by running CV cycles at 20 mV s⁻¹. As shown in Fig. S3a, the area of CV loop kept enlarging with cycling the CV test, indicating that the capacity was enhanced by depositing poly(4,4'-TDP) onto the AC coating. However, the area of CV loop reached a saturation level when the cycle number is beyond 80. Therefore, the optimal number of CV cycles for electrodeposition is determined to be 80. To understand the influence of poly(4,4'-TDP) amount on the charge storage capacity of a Zn-ion cell, we prepared two cathodes with poly(4,4'-TDP) electrodeposited for 20 and 80 cycles, respectively, and used them to make Zn-ion cells with using 2 M ZnSO₄ electrolyte. CV loops at 5 mV s⁻¹ from the two cells are shown in Fig. S3b. Apparently,

the device with more poly(4,4'-TDP) in the cathode exhibits higher capacity, according to the area of CV loop.



Fig. S3 (a) Evolution of the CV loop at 20 mV s⁻¹ with cycling during the electrodeposition process. (b) CV loops at 5 mV s⁻¹ collected from two Zn//poly(4,4'-TDP)/AC cells with poly(4,4'-TDP) electrodeposited for 20 and 80 cycles, respectively.

The Zn//poly(4,4'-TDP)/AC cell can be operated within a voltage range of 0.1 - 1.9 V, while the maximum voltgage range of a Zn//AC cell is 0.2 - 1.8 V. In order to investigate the mechanism behind the widened voltage window of Zn-ion cell by introducing poly(4,4'-TDP), we studied AC and poly(4,4'-TDP)/AC coatings in a three-electrode cell filled with 1 M H₂SO₄ electrolyte, and their CV loops are shown in Figs. S4a and b, respectively. With using a Pt foil counter electrode and an Ag/AgCl reference electrode, the suitable voltage window for AC electrode is -0.2 - 0.8 V. beyond this range the CV curve exhibits polarization behavior due to water splitting. However, the poly(4,4'-TDP)-modified AC coating shows a maximum voltage window of -0.6 - 1.1 V, as shown in Fig. S4b. For comparison, the suitable voltage window of the well-known PANI in H₂SO₄ is -0.2 - 0.9 V. Hence, we believe that the effect

of poly(4,4'-TDP) on broadening the voltage window in H_2SO_4 electrolyte can be used to account for the wide voltage window, as 0.1 - 1.9 V, of the Zn//poly(4,4'-TDP)/AC cell using ZnSO₄ aqueous electrolyte. As discussed in the context of this paper, we attribute the widened voltage range to the intercalation and deintercalation of H⁺ in poly(4,4'-TDP).



Fig. S4 CV loops within different voltage windows collected from (a) a bare AC coating and (b) a poly(4,4'-TDP)/AC coating, respectively, in a three-electrode cell filled with $1 \text{ M H}_2\text{SO}_4$.

To check whether the SO_4^{2-} ions have contribution in charge storage, CV curves of a beaker-based Zn//poly(4,4'-TDP)/AC cell using ZnCl₂ and ZnSO₄ electrolytes, respectively, are compared in Fig. S5. It can be seen that both CV loops have two oxidation peaks and two reduction peaks, suggesting a similar redox behavior. When using ZnCl₂ electrolyte, although the 1.9 V limit is too high, the overal shape of CV loop is similar to that with using ZnSO₄ electrolyte. Considering that the oxidation capability of Cl⁻ is weak, the redox reaction between SO_4^{2-} and poly(4,4'-TDP) molecules is ruled out. In the charging process, the first oxidation peak, O1, could be related to the extraction of Zn²⁺ from poly(4,4'-TDP). The second peak named O2, can be resulted from the extraction of H^+ from poly(4,4'-TDP).



Fig. S5 CV loops at 5 mV s⁻¹ from a beaker-based Zn//poly(4,4'-TDP)/AC cell using ZnCl₂ and ZnSO₄ electrolytes, respectively.

5. XPS, Raman, and FTIR Measurements

Fig. S6a shows two XPS survey spectra from a bare AC coating and a poly(4,4'-TDP)/AC cathode, respectively. The emerged S signal, together with enhanced O signal, confirm the presence of electrodeposited poly(4,4'-TDP). Fig. S2b shows Raman spectra of the two samples. Both contain D (disorder-induced) and G (sp²– related) bands contributed by the graphitic carbon. With the presence of poly(4,4'-TDP) over AC granules, the G band was enhanced, probably due to the cross-linked aromatic molecules in the polymer. Fourier transform infrared (FTIR) spectra collected from purer AC powder, 4,4'-TDP powder, and poly(4,4'-TDP)/AC coating are compared in Fig. S6c. Because the reflection mode was used for measuring the black-color cathode, FTIR signals from poly(4,4'-TDP) are too weak to be discernible.



Fig. S6 (a) XPS survey spectra and (b) Raman spectra collected from a poly(4,4'-TP)/AC cathode and a bare AC coating, respectively.(c) FTIR spectra of poly(4,4'-TP)/AC cathode, 4,4'-TDP monomer powder, and bare AC coating, respectively.



Fig. S7 (a) Ex situ Raman and (b) ex situ FTIR spectra of the poly(4,4'-TDP)/AC cathode at different charge states.

Ex situ Raman and FTIR spectra were collected from poly(4,4'-TDP)/AC samples at different charge states, as shown in Figs. S7a and b, respectively. In Fig. S7a, the weak signal at ~ 460 cm⁻¹ is related to the v₂ bending mode of SO_{4}^{2-} .¹ Hence, the freshly prepared cathode is free of SO_{4}^{2-} , while the SO_{4}^{2-} Raman signal is emerged in the cathode at fully charged or discharged states. As shown in the inset in Fig. S7a, the SO_{4}^{2-} signal from the discharged cathode is stronger. In Fig. S7b, FTIR spectra of SO_{5}^{2-}

the cathode at charged and discharged states, respectively, show a stricking contrast. A discharged cathode means cations (Zn²⁺ and H⁺) are extracted and Zn₄SO₄(OH)₆•5H₂O flakes tend to grow out over the surface. The broad band at 3278 cm⁻¹ is contributed by the O–H stretching vibrations of water molecules. The two peaks between 1050 – 1200 cm⁻¹ and a peak at 592 cm⁻¹ can be assigned to the O–H bending modes and SO_4^{2-} bending vibration, respectively, implying the presence of Zn₄SO₄(OH)₆•5H₂O.

6. 3D Molecular geometry of poly(4,4'-TDP) Chain

Fig. S8 shows the 3D molecular structure of a section of poly(4,4'-TDP) chain at relaxation. A pair of neighboring =O groups, as marked by the dashed-line rectangle, are believed to have the most possibility to bond a Zn^{2+} . Other =O groups may bind the intercalated H⁺ ions.



Fig. S8. 3D geometry of the poly(4,4'-TDP) molecule. A pair of =O marked by the rectangle could be bond to one inserted Zn^{2+} .

6. Morphologies of Cathode and Anode after Cycling Test

Fig. S9a and b show low- and high-magnification SEM images of the poly(4,4'-TDP)/AC cathode after 2000 cycles, respectively. In the close-view image, inorganic flakes identified as $Zn_4SO_4(OH)_6 \cdot 5H_2O$ can be found. The other two SEM images in Fig. S9c and d depict the morphology of the Zn foil anode after 2000 cycles. $Zn_4SO_4(OH)_6 \cdot 5H_2O$ flakes over the Zn surface are thin and flexible, and densely packed to form micro particles. Also, Zn dendrites sparsely distributed in the surface are observed.



Fig. S9 SEM images of (a, b) poly(4,4'-TDP)/AC cathode and (c, d) Zn foil anode after being charged and discharged for 2000 cycles.

Reference

S1. R. L. Frost, S. Bahfenne, J. Raman Spectroscopy 2011, 42, 219-223.