Supplemental Information

Aqueous asymmetric supercapacitors based on electrodeposited

poly(1,5-naphthalenediamine) and poly(4,4'-oxydianiline)

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1. Calculation

In a three-electrode cell, the areal capacitances (C_A) of an electrode material was calculated using galvanostatic CD curves, according to $C_A = (I \int dt)/(\Delta V) = (I \Delta t)/(\Delta V)$, where *I* is the current density (A cm⁻²), Δt is the time for a full discharge, ΔV is the potential window. The gravimetric specific capacitance C_g can be deduced using C_g = C_A/ ρ , where ρ is the areal mass loading (mg cm⁻²) of the electrode material.

Using CV curves measured from an two-electrode cell, the specific capacitance of the cell, C_{cell} , can be calculated according to $C_{cell} = \oint I dV / (v\Delta V)$. Here, *I* is the areal current density, $\oint I dV$ is the area of a CV loop, *v* is the potential scan rate, and ΔV is the voltage window.

Though the GCD curves of our device are not linear and the capacitance calculation using the slope of discharge curve might be an approximate estimation, we found that, the calculated capacitance from the GCD curve at 1 A g⁻¹ is equivalent to that from the CV loos at 5 mV s⁻¹, indicating the validity of the capacitance calculation using the slope of a GCD curve. The energy density E was estimated by using the equation $E = C_{cell}\Delta V^2/[2(m_1 + m_2) \times 3.6]$, Where m₁ and m₂ are areal mass loadings of positive and negative electrodes, respectively. For a symmetric cell, m₁ = m₂. The average power density P is calculated as P = E/t, where t is the time for a full discharge.

2. BET Measurement

The carbon cloth, as depicted in Fig.S1a, was used as the base to coat AC through a slurrycoating process. A SEM image of the AC coating is shown in Fig. S1b, revealing that the granules of nanoporous AC are about several micrometers in size. Fig. S1c shows an optical photograph of the AC-coated carbon cloth. For BET measurement, the AC coating was scratched off the carbon cloth.



Fig. S1. SEM images of (a) a carbon cloth and an (b) activated carbon coating on carbon cloth.(c) Photograph of the AC coating on carbon cloth.

Figs. S2a, b, and c show N₂ adsorption/desorption isotherms of an AC powder, an AC coating, and a poly(1,5-NAPD)/AC coating, respectively. The pure AC powder has a high specific surface area of 2280 m² g⁻¹. The AC coating was scratched off the carbon cloth for BET measurement, and its specific surface area was 1820 m² g⁻¹. This value is resonable because the AC coating contains 10 wt% of carbon black and 10 wt% of polymer binder. The specific surface area of the poly(1,5-NAPD)/AC coating was much lower, as 141 m² g⁻¹. Pore size distributions of the three samples are shown in Figs. S2d, e, and f., respectively. The BET adsorption average pore sizes of pure AC powder, AC coating, and poly(1,5-NAPD)/AC coating are 2.1, 2.4, and 4.3 nm, respectively. Hence we conclude that the electrodeposited polymer was not only coated onto the outer surface, but also filled into the nanopores of AC granules.



Fig. S2. N₂ adsorption/desorption isotherms of (a) pure AC powder, (b) AC coating, and (c) poly(1,5-NAPD)/AC coating. Pore size distributions of the three samples are shown in (d), (e), and (f), respectively.

3. Characterizations of the Electrodeposited Polymers

Fig. S3a shows a SEM image of the poly(1,5-NAPD)/AC sample. Corresponding to this area, C and N mappings are shown in Figs. S3b and c, respectively. The flower-shaped structure in Fig. S3d was formed during the electrodeposition process of poly(4,4'-ODA) onto the AC coating. C and N mappings for this sample are shown in Figs. S3e and f, respectively. The emerged N signals from the two samples confirm the presence of amino-containing polymers over AC surface.

X-ray photoelectron spectroscopy (XPS) survey spectra of the mesoporous carbon base, the poly(1,5-NAPD)/AC, and the poly(4,4'-ODA)/AC samples are displayed in Fig. S3g. The carbon base is nearly free of N. The introduction of amino-containing polymer to the AC base leads to enhanced N 1s signal. Figs. S3h and i show the high-resolution XPS N1s peaks of poly(1,5-NAPD) and poly(4,4'-ODA), respectively. Deconvolution of the N 1s XPS peak reveals –NH and $-NH^{+}_{2}$ bonds for both samples.



Fig. S3. (a) SEM image of the poly(1,5-NAPD)/AC sample, of which the C and N mappings are shown in (b) and (c), respectively. (d) SEM image of the poly(4,4'-ODA)/AC sample. C and N mappings from the same area as in (a) are shown in (e) and (f), respectively. (g) Survey XPS spectra of AC powder, poly(1,5-NAPD)/AC and poly(4,4'-ODA)/AC samples. (h) and (i) High-resolution N 1s XPS spectra of poly(1,5-NAPD) and poly(4,4'-ODA), respectively.

4. Electrochemical Test of an As-Prepared ASC Button-Cell

The carbon-cloth-based electrodes were punched to make disk-shaped electrodes, which were assembled into 316 stainless steel button cells filled with H_2SO_4 electrolyte. A typical cell with AC mass loading of 1.5 mg cm⁻² on the carbon cloth was tested, and the results are shown in S5

Fig. S4. CV loops at 20 mV s⁻¹ but within different voltage windows ranging from 1.0 to 1.6 V are shown in Fig. S4a. Correspondingly, CD curves at 10 mA cm⁻² but within different voltage windows are shown in Fig. S4b.Winthin the voltage window of 1.6 V, CV loops of the cell at different voltage scan rates are shown in Fig. S4c. This cell was further tested by continuously running CD for 10000 cycles. Two CV loops collected at the beginning and after the stability test are shown in Fig. S4d.



Fig. S4. (a) CV loops at 20 mV s⁻¹ and (b) CD curves at 10 mA cm⁻² measured within different voltage windows. (c) CV loops at different voltage scan rates. (d) Two CV loops collected before and after the long-term stability test.

5. DFT Calculation for Molecular Orbital Energy Levels of Poly(1,5-NAPD) and Poly(4,4'-ODA)

The organic molecules with optimized structures were computed by using the Gaussian 09 software package. There are several possible molecular structures for the polymer formation, but the polymerization of monomers of the same kind obeys the principle of minimum energy. Therefore, through quantum chemistry calculation we determined the molecular structures of poly(1,4-NAPD) and poly (4,4'-ODA). In Fig. S5, the variations of HOMO and LUMO levels of the two polymers with polymerization degrees from low to high are given. For high degree of polymerization, the computation is lengthy and the results are absent. However, the trend of energy gap narrowing with adding the polymerization degree is revealed. It can be concluded that poly(1,5-NAPD) and poly(4,4'-ODA) are conducting polymers and their energy levels in eV are close.



Fig. S5. Energy level diagrams of poly(1,5-NAPD) and poly(4,4'-ODA) with different polymerization degrees.

6. Comparison of Electrochemical Behaviors Between Poly(4,4'-ODA) and Small 4,4'-ODA Molecules

Fig. S6 shows CV loops at 20 mV s⁻¹ measured with using a three-electrode setup. The CV loop of poly(4,4'-ODA)/AC electrode in 2 M KOH electrolyte shows redox humps and a broad voltage window from -1.2 V to 0.2 V versus the Hg/HgO reference electrode, as seen in Fig. S6a. For the small 4,4'-ODA molecules adsorbed onto an AC coating, their CV loops in H₂SO₄ and KOH electrolytes are shown in Fig. S6b. When exposed to the acidic electrolyte, the redox reactions of $-NH_2$ in the molecule give rise to redox peaks over the CV loop within the voltage window from -0.2 V to 0.8 V, versus Ag/AgCl reference electrode. However, when in KOH electrolyte, these small molecules have no redox reaction, as can be seen from the quasi-rectangular shaped CV loop in Fig.S6b. By comparing Figs. S6a and b, we conclude that the poly(4,4'-ODA) has a different charge storage mechanism from that of small 4,4'-(ODA) molecules. That is, ions can be intercalated into the polymer to react with internal molecular chains, irrespective of the electrolyte pH value.



Fig. S6. (a) CV loop of the poly(4,4'-ODA)/AC electrode in KOH solution. (b) CV loops of small 4,4'-ODA molecules adsorbed onto AC, measured in H_2SO_4 and KOH electrolytes, respectively.

7. Calculation of the b-value

For an ASC, the CV loops at different potential sweep rates are shown in Figure S7a. The peak current of the hump over CV loop, I, is a function of the potential sweep rate v. In theory, log(v) is proportional to log(I), as log(v) = blog(I) + k, where b is the slope, k is the intercept, a shown in Fig. S7b. The two parameters can be obtained by linear fitting of the data.



Fig. S7. (a) CV loops of a typical ASC. The peak current value of humps and the potential scan rates are used to determine the b-value, as demonstrated in (b).

8. Frontier Molecular Orbital Diagrams of Trimers of Poly(1,5-NAPD) and

Poly(4,4'-ODA)

In Fig. S8, calculations of MO diagrams are based on the two trimers of NAPD and ODA, and their molecular structures are shown as well. Both $-NH_2$ and -NH- have redox activities that can be utilized to store charges.



Fig. S8. Frontier MO diagrams for two pentamers of poly(1,5-NAPD) and poly(4,4'-ODA), respectively.

8. Comparison of the Energy Storage Performance Between Our Device

and Other ASCs

PE	SC (F g ⁻¹)	NE	SC (F g ⁻¹)	Electrol.	WV (V)	Cell SC	SED (Wh kg ⁻¹)	Cycles Retention	Ref.
Poly(1,5- NAPD)/AC	570	Poly(4,4'- ODA)/AC	610	1 M H ₂ SO ₄	1.6	1.65 F cm ⁻² ; 165 F g ⁻¹	58	10000/91%	This work
MnO ₂ /Ni	214	PPy/Ni	754	0.5 M Na ₂ SO ₄	1.6	135 mF cm ⁻²	48.9	20000/106%	1
MnO ₂ @CNTs	—	PPy@CNTs	—	KCl- silica	2.0	281 mF cm ⁻²	40	5000/85%	2
PANI NTs	414	AQ@PNCNT s	448	1 M H ₂ SO ₄	1.4	120 F g ⁻¹	32.7	1000/80%	3
PANI NTs	541	WO ₃ NRs	573	1 M H ₂ SO ₄	1.5	151F g ⁻¹	42	10000/71%	4
PANI	176	V_2O_5	213	3 M KCl	2.0	41 F g ⁻¹	26.7	2000/73%	5
Na _{0.5} MnO ₂	366	Fe ₃ O ₄ @C	344	1 M Na ₂ SO ₄	2.6	200 mF cm ⁻² ; 88 F g ⁻¹	81	10000/93%	6
3D MnO ₂ /rGO	382	3D Fe ₂ O ₃ /rGO	260	2 M LiCl	1.8	74	41.7	5000/89	7
VO2@Ni NWs	100	MoO3@Ni NWs	277	1 M Li ₂ SO ₄	1.6	307 mF cm ⁻² ; 47 F g ⁻¹	27.3	20000/106%	8
Co ₂ AlO ₄ @MnO 2	915	Fe ₃ O ₄	380	PVA- KOH	1.6	99 F g ⁻¹	35	5000/92%	9
MnO ₂	110	Bi ₂ O ₃	51	1 M Na ₂ SO ₄	1.8	97 mF cm ⁻² ; 25.2 F g ⁻¹	11.3	4000/85%	10
CuCo ₂ O ₄ /CuO	642	rGO/Fe ₂ O ₃	470	2 M KOH	1.6	93 F g ⁻¹	33	5000/83%	11
Mn ₃ (Fe(CN) ₆) ₂	238	Fe ₃ O ₄ /rGO	230	0.5 M Na ₂ SO ₄	1.8	96 F g ⁻¹	43.2	1000/82%	12

Table 1. Comparison of the energy storage performances of ASCs.

PE : Positive electrode; SC: specific capacitance; Electrol.: electrolyte; WV: working voltage; SED: specific energy density.

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