Electronic Supplementary Information

One-pot solvothermal incorporation of graphene into chainengineered polyquinones for metal-free supercapacitors

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Experimental Section

Materials

GO was synthesized by the Hummers' method as described in our previous work.^[1] 2,6-diaminoanthraquinone (DAQ, 97%), *p*-phthalaldehyde (PPD, 98%), and 2,5-dihydroxy-1,4-benzenedicarboxaldehyde (DBD, 97%) were purchased from Tokyo Chemical Industry Co. Ltd., Aladdin Industrial Co. LTD., and Leyan Industry Co. Ltd., respectively. Dimethyl sulfoxide (DMSO), N, N'-dimethylacetamide (DMAC), and ethanol were supplied by Sinopharm Group Chemical Reagent Co. Ltd., China. All chemicals were used without further purification.

Synthesis of AQP and AQPOH

AQP was synthesized by a Schiff-base condensation between DAQ and PPD. In a typical procedure, DAQ and PPD with an equimolar amount of 2 mmol were dispersed into 40 mL DMSO under an Ar atmosphere, and the reaction mixture was heated to 180°C and kept stirring for 24 h. After reaction, the final mixture was cooled down to room temperature, followed by centrifugation and washing with DMAC and ethanol repeatedly. The yellow power product was obtained by drying at 120°C overnight under vacuum. Similarly, AQPOH was also achieved by a Schiff-base condensation between DAQ and DBD under the same experimental conditions mentioned above. Yields: AQP, 87%; AQPOH: 79%.

Synthesis of Gr/AQP and Gr/AQPOH composites

GO sheets were ultrasonically dispersed into DMSO. To this stable suspension was added an equimolar amount of DAQ and PPD monomers. Afterwards, the reaction mixture was finally subjected to the same procedures as described in the synthesis of AQP. Furthermore, the loading level of graphene was tailored by changing the mass feed ratio of GO to two monomers (where keeping DAQ and PPD equimolar) in 1:9, and 1:4 to afford two graphene/AQP (Gr/AQP) composites, designated as Gr/AQP-1 and Gr/AQP-2, respectively. Similarly, the graphene/AQPOH (Gr/AQPOH) composite was also fabricated by using the feed ratio of GO to two monomers (where keeping DAQ and DBD equimolar) in 1:4 in weight. Yields: Gr/AQP-1, 86%; Gr/AQP-2, 89%; Gr/AQPOH: 83%.

Materials characterization

Fourier transform infrared spectroscopy (FT-IR) was recorded using a Thermo Nicolet NEXUS 470 in the wavenumber range of 4000-500 cm⁻¹. Scanning electron microscope (SEM, Hitachi SU 8010) and transmission electron microscopy (TEM, Tecnai G20) were conducted to determine microstructures. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI Multi Pak system with the Mg K α radiation. X-Ray diffraction (XRD) patterns were implemented on a Rigaku D/Max2400 system in the range of 2 θ = 5~60°. Thermogravimetric analysis (TGA) was performed on a TG209 F3 instrument under N₂ at 10°C min⁻¹. Raman spectra were collected on a Thermo Scientific DXR spectrometer with an excitation laser λ =532 nm.

Electrochemical measurements

Electrochemical properties of the as-prepared electrodes were investigated using a CHI 660E electrochemical workstation (CH Instruments, Inc.) at room temperature. For the three-electrode system, the working electrode was prepared by mixing active materials, super P, and polyvinylidene fluoride (PVDF) with the mass ratio of 6:3:1, and the Pt foil and Ag/AgCl were used as the counter and reference electrodes, respectively. The as-fabricated working electrodes were also assembled into two-electrode coin-type symmetrical supercapacitors by using the filter paper as separator and 1 M H₂SO₄ as the electrolyte. Cyclic voltammetry (CV) was performed in the potential range of -0.4~0.4 V. Galvanostatic charge-discharge (GCD) was carried out at different current densities from 0.5 to 10 A g⁻¹. Electrochemical impedance spectroscopy (EIS) was performed in the frequency range of $0.01~10^5$ Hz.

Calculation of performance parameters

Under a three-electrode configuration, the specific capacitance (C, F g⁻¹) is calculated from the CV curves using the following equation.²

$$C = \frac{1}{m\nu \times \Delta V} \int I dV$$

where *I* (A) is the voltammetry current, v (V s⁻¹) is the scanning rate, ΔV (V) is the

potential window, and *m* (g) is the mass of active materials, respectively.

Under a two-electrode configuration, the specific capacitance (C_s , F g⁻¹) is calculated based on the GCD curves using the following equation.

$$Cs = \frac{2 \times I \times \Delta t}{m \times \Delta V}$$

where *I* (A), *m* (g), ΔV (V), and Δt (s) are the discharge current, mass of active materials in the single electrode, operating potential window, and discharge time, respectively.

The energy density (*E*, Wh kg⁻¹) and power density (*P*, W kg⁻¹) are calculated based on the flowing equations.

$$E = \frac{Cs \times (\Delta V)^2}{8 \times 3.6}$$
$$P = \frac{3600 \times E}{t}$$

Supplementary Figures



Fig. S1 TGA curves of GO, graphene, polymers and their composites.



Fig. S2 Typical TEM images of GO, AQP and AQPOH.



Fig. S3 Optical pictures of DAC monomer, AQP, AQPOH, and their composites in (a) ethanol, (b) 1 M H₂SO₄ aqueous solution, and (c) the Gr/AQPOH electrode slice in 1 M H₂SO₄ after running 10,000 charge/discharge cycles.



Fig. S4 FT-IR spectra of (a) monomers and polymers, and (b) graphene and polymer composites; (c) Raman shifts and (d) XRD patterns of GO, graphene, polymer and their composites.

In the Fourier transform infrared (FT-IR) spectra, several absorption bands of DAQ (v_{as} =3423 and v_{s} =3330 cm⁻¹ for –NH₂) and PPD or DBD ($v_{C=0}\approx1688$, $v_{C-H}\approx1385$ cm⁻¹ for –CH=O) are clearly observed, and all disappear entirely after Schiff-base condensation (**Fig. S4a**). New characteristic peaks appear at 1666 cm⁻¹, corresponding to the C=N stretching vibration of imine-linked polymers while quinone groups at 1581 cm⁻¹ are still present in AQP and AQPOH. The newly-generated C=N bands and remained C=O of DAQ are well preserved in Gr/AQP-1, Gr/AQP-2, and Gr/AQPOH (**Fig. S4b**).

Raman spectra of GO, graphene and composites exhibit well-referred *D* (*ca.* 1340 cm⁻¹) and *G* (*ca.* 1580 cm⁻¹) bands (**Fig. S4c**). The calculated intensity ratio (I_D/I_G) of the *D* to *G* band is 1.25 for GO, which is increased to 1.84 for graphene and its composites. The enhanced I_D/I_G values are indicative of the decreased average size of sp²-hybridized regions in graphene *via* creating a great number of graphitic domains, in combination with abundant conjugated units and topological defects in AQP and AQPOH.²¹ X-ray diffraction (XRD) spectra also verify that the (002) sharp peak of GO at 20=10.3° is developed into a broad band at 20=25.6° for the (002) plane of graphene due to the solvothermal reduction (**Fig. S4d**). The characteristic diffraction profiles of Gr/AQP and Gr/AQPOH nearly resemble those of AQP and AQPOH counterparts (**Fig. S4d**), due to the complete coating of AQP and AQPOH onto graphene.



Fig. S5 (a) XPS survey spectra of graphene, polymer and their composites, core-level high-resolution C 1s spectra of (b) graphene, and (c) polymer and their composites, and (d) N 1s spectra of polymer and their composites.

Further insight into chemical components was also examined by X-ray photoelectron spectroscopy (XPS). All specimens display two distinct peaks of C 1s (285 eV) and O 1s (532 eV) (**Fig. S5a**). Except for graphene, new N 1s signals at 400 eV are clearly present in the polymers and their composites, corresponding to the C=N bonds. The C/O atomic ratio (2.1) of GO is raised to 5.7 after effective reduction, and the C=C configuration dominates the core-level C 1s spectrum of graphene (**Fig. S5b**). For AQP and AQPOH and their composites, the C 1s spectra can be deconvoluted into four bands cantered at 284.6, 285.7, 286.6, and 289.1 eV (**Fig. S5c**), corresponding to sp² C=C, sp³ C-C, C=N/C-N, and C=O, respectively. Furthermore, the high-resolution scan of N 1s also reveals the presence of C=N (398.8 eV) and C-N (400.2 eV) signals (**Fig. S5d**).



Fig. S6 Proposed redox mechanisms of (a) AQP, and (b) AQPOH through the reversible proton-coupled electron switching between quinone and hydroquinone.



Fig. S7 AQP electrode: (a) CV curves at scan rates from 5 to 10 mV s⁻¹, (b) the absolute peak current density and sweep rate obeying the power law relationship $(i=av \ ^b)$ during the charge/discharge processes, (c) decoupling of the capacitance contributed by the fast-kinetic (green shadow) and slow-kinetic (blank) processes at 10 mV s⁻¹, and (d) the histograms of capacitance contributions from the fast-kinetic (green) and slow-kinetic intercalation (grey) processes at different rates.



Fig. S8 AQPOH electrode: (a) CV curves at scan rates from 5 to 10 mV s⁻¹, (b) the absolute peak current density and sweep rate obeying the power law relationship (*i=av* ^{*b*}) during the charge/discharge processes, (c) decoupling of the capacitance contributed by the fast-kinetic (pink shadow) and slow-kinetic (blank) processes at 10 mV s⁻¹, and (d) the histograms of capacitance contributions from the fast-kinetic (pink) and slow-kinetic intercalation (grey) processes at different rates.



Fig. S9 Gr/AQP electrode: (a) CV curves at scan rates from 5 to 10 mV s⁻¹, (b) the absolute peak current density and sweep rate obeying the power law relationship (*i=av* ^{*b*}) during the charge/discharge processes, (c) decoupling of the capacitance contributed by the fast-kinetic (blue shadow) and slow-kinetic (blank) processes at 10 mV s⁻¹, and (d) the histograms of capacitance contributions from the fast-kinetic (blue) and slow-kinetic intercalation (grey) processes at different rates.



Fig. S10 Gr/AQPOH electrode: (a) CV curves at scan rates from 5 to 10 mV s⁻¹, (b) the absolute peak current density and sweep rate obeying the power law relationship $(i=av \ ^b)$ during the charge/discharge processes, (c) decoupling of the capacitance contributed by the fast-kinetic (red shadow) and slow-kinetic (blank) processes at 10 mV s⁻¹, and (d) the histograms of capacitance contributions from the fast-kinetic (red) and slow-kinetic intercalation (grey) processes at different rates.



Fig. S11 GCD profiles of coin-type symmetrical supercapacitors fabricated by graphene, polymers, and their composites in the current density of 0.5 to 20 A g⁻¹.



Fig. S12 Hydrogen ion transmission coefficients (D_{H^+} , cm² s⁻¹) of symmetrical supercapacitors fabricated by graphene, polymers and their composites. The inset shows a Gr/AQPOH-based coin-type supercapacitor powering LED lamps.

Table S1. A cost comparison of conventional metal oxides used for supercapacitorelectrodes and key chemicals and materials used in this work

| Items | Chemicals or Materials | Products No. | Purity | CAS No. | Price # (USD/g) |
|--|---|-----------------|--------|------------|--------------------|
| Conventional metal oxides used for supercapacitor electrode materials | Ruthenium dioxide (RuO ₂) | 238058-5G | 99.9% | 12036-10-1 | 49.2 |
| | Ruthenium (IV) oxide hydrate RuO ₂ •xH ₂ O | 463760-5G | 99.9% | 32740-79-7 | 63.4 |
| | Manganese (IV) oxide (MnO2) | 243442-100G | ≥99% | 1313-13-9 | 0.6 |
| | Manganese (II, III) oxide (Mn ₃ O ₄) | 377473-100G 97% | | 1317-35-7 | 0.4 |
| | Vanadium(V) oxide (V ₂ O ₅) | 204854-25G | 99.95% | 1314-62-1 | 15.8 |
| | Iron (II, III) oxide (Fe ₃ O ₄) | 518158-50G | 99.99% | 1317-61-9 | 11.9 |
| | Iridium dioxide (IrO ₂) | 206237-5G | 99.9% | 12030-49-8 | 172.6 |
| | Molybdenum trioxide (MoO ₃) | 203815-25G | 99.97% | 1313-27-5 | 10.2 |
| | Niobium(V) oxide (Nb ₂ O ₅) | 203920-250G | 99.99% | 1313-96-8 | 2.0 |
| Key chemicals used in this work | Diaminoanthraquinone | D12007- 100G | 97% | 131-14-6 | 1.5 |
| | Terephthalaldehyde | T2207-500G | 99% | 623-27-8 | 0.4 |
| | Graphite (flakes) | 332461- 12KG | 95% | 7782-42-5 | 0.02 |

The price of chemicals and materials is online collected from the Sigma-Aldrich, Inc. and fixed in USD per gramme. **Table S2.** A comparison of specific capacitance between Gr/AQPOH and metal-free polymer-based supercapacitors reported previously

| Electrode materials | Electrolytes | Capacitance (F g ⁻¹) | Current density /Scan rate | Cell configuration | Ref. |
|---|---------------------------------|-------------------------------------|-------------------------------|-----------------------|------|
| Polybromopyrrole-grafted graphene | H ₂ SO ₄ | 68 | 5 A g ⁻¹ | two-electrode | [3] |
| 1, 4, 5, 8-tetrahydroxy anthraquinone/graphene on nylon 66 filter paper | H ₂ SO ₄ | 245.4 | 0.1 mA cm ⁻¹ | two-electrode | [4] |
| Poly(3,4- ethylenedioxythiophene)/p oly(aminoanthraquinon) | HClO ₄ | 74 | 1 A g ⁻¹ | two-electrode | [5] |
| Redox-active ferrocene moieties on graphene | H_2SO_4 | 231 | 0.5 A g ⁻¹ | two-electrode | [6] |
| Graphene/poly(1,5- diaminoanthraquinone) composites | Et4NBF4-AN | 80.8 | 0.5 A g ⁻¹ | two-electrode | [7] |
| Graphene/polypyrrole composites | Li ₂ SO ₄ | 114 | 5 mV s ⁻¹ | two-electrode | [8] |
| Graphene/poly(<i>p</i> - phenylenediamine) composites | H ₂ SO ₄ | 248 | 2 A g ⁻¹ | two-electrode | [9] |
| 2,5-dimethoxy-1,4- benzoquinone on graphene | H ₂ SO ₄ | 650 | 5 mV s ⁻¹ | three-electrode | [10] |
| Graphene/poly(imine- | H ₂ SO ₄ | 347 | 0.5 A g ⁻¹ | two-electrode | This |
| composites | | 1204 | 10 mV s ⁻¹ | three-electrode | work |

Table S3. A comparison of specific capacitance between Gr/AQPOH and metal oxide containing electrodes reported previously

| Electrode materials | Electrolytes | Capacitance (F g ⁻¹) | Current density /Scan rate | Cell configuration | Ref. | |
|-------------------------------------|---------------------------------|-------------------------------------|-------------------------------|-----------------------|------|--|
| TiO ₂ /C | H ₂ SO ₄ | 137 | 0.25 A g ⁻¹ | two-electrode | [11] | |
| TiO2/CNTs | КОН | 130 | $1~{ m A~g^{-1}}$ | two-electrode | [12] | |
| TiO2/CNTs | KCl | 282 | 10 mV s ⁻¹ | two-electrode | [13] | |
| MnO ₂ /CNTs | Na2SO4 | 85.8 | 0.2 A g ⁻¹ | two-electrode | [14] | |
| SnO ₂ /Graphene | КОН | 195 | 20 mV s ⁻¹ | two-electrode | [15] | |
| MnO ₂ /CNTs/PPy | Na ₂ SO ₄ | 365 | 5 mV s ⁻¹ | three-electrode | [16] | |
| N-Doped TiO2 | Na2SO4 | 216 | $1 \mathrm{A g^{-1}}$ | three-electrode | [17] | |
| RuO ₂ /carbon nanofibers | КОН | 225 | 10 mV s ⁻¹ | three-electrode | [18] | |
| Graphene/poly(imine- | H2SO4 | 347 | 0.5 A g ⁻¹ | two-electrode | This | |
| composites | | 1204 | 10 mV s ⁻¹ | three- electrode | work | |

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