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Supporting Information

Achieving Ultrahigh Volumetric Performance of Graphene

Composite Films by an Outer-Inner Dual Space Utilizing Strategy

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1. Experimental Section

Synthesis of GO film and DA/GO film: GO suspension was synthesized by modified Hummer's method as we reported previously.^[S1] The DA/GO film was fabricated by an interface self-assembly approach. In detail, 10 ml GO suspension ($\sim 5 \text{ mg ml}^{-1}$) was firstly mixed with DA in suitable weight ratios (GO/DA=10:4 unless otherwise noted) and stirred vigorously for 1 h at room temperature. After that, the as-obtained solution was poured into a petri dish and placed horizontally at 70°C in an oven for 12 h to evaporate water. After being dried, the as-prepared DA/GO film was carefully peeled off petri dish. The pure GO film was fabricated using the above-mentioned experimental step without adding DA.

Synthesis of DA/rGO@PDA film: The obtained DA/GO film was directly sealed in a 100 ml Teflon-lined autoclave filled with 40 ml DA solution (10 mg ml^{-1}) and then reduced at 180°C in an oven for 3 h. After hydrothermal process, the PDA coated DA/rGO film (DA/rGO@PDA) with a mass loading of 2 mg cm^{-2} was successfully obtained and then washed with deionized water several times to remove any impurities and finally dried at 70°C for 12 h.

Synthesis of DA/rGO film and rGO film: For comparison, DA/rGO film without PDA layer and rGO film without PDA layer were also prepared, which was denoted as DA/rGO and rGO, respectively. In detail, the obtained DA/GO film or GO film was directly sealed in a 100 ml Teflon-lined autoclave filled with 40 ml deionized water and then reduced at 180°C in an oven for 3 h. After hydrothermal process, the DA/rGO film or rGO film was successfully obtained and then washed with deionized water several times to remove any impurities and finally dried at 70°C for 12 h.

Characterization: The morphology characterization was performed by field-emission scanning electron microscopy (FESEM, Hitachi S-4800). The surface chemical composition of samples was investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) using Al K α X-ray source operating at 12 kV and 6 mA. The X-ray diffractions (XRD) results of samples were measured by a Bruker D8 Advance X-ray diffractometer (Cu-K α , $\lambda = 1.5418 \text{ \AA}$). The Raman spectra were recorded by a WITec Alpha 300R with a 532 nm laser. The UV-vis adsorption spectra were collected by SHIMADZU UV 2600. The FTIR results were collected by Bruker Vertex 70 FTIR spectrophotometer.

Electrochemical measurements: All electrochemical measurements were performed by CHI660E electrochemical workstation. The electrochemical performance of as-prepared films was firstly investigated in the three-electrode system using 1M H₂SO₄ aqueous solution as electrolyte. The working electrode ($0.4\sim 0.5 \text{ cm}^2$) was simply fabricated by directly pressing

the sample onto the stainless steel mesh under the pressure of 20 MP for 30 second, and then immersed into electrolyte for 12 hour before electrochemical test. Platinum plate and Ag/AgCl were adopted as a counter electrode, reference electrode, respectively. For coin-like symmetric supercapacitor, two similar working electrodes were symmetrically assembled into a 2032 coin cell with a glassy fibrous as separator, 1M H₂SO₄ as electrolyte.

The gravimetric capacitance was calculated by GCD curves using the following equations:

$$C_g = \frac{It}{m\Delta V} \quad (2)$$

(For three electrode system)

$$C_g = \frac{2It}{m\Delta V} \quad (3)$$

(For two electrode system)

Where C_g (F g⁻¹) is the gravimetric capacitance, m (g) is the mass of a single electrode material, ΔV (V) is the potential window of GCD curves (exclude IR drop), I (A) is the discharge current and t is the discharge time (s).

The volumetric capacitance was calculated using the following equation:

$$C_v = C_g \times \rho \quad (4)$$

Where C_v (F cm⁻³) is the volumetric capacitance, C_g (F g⁻¹) is the gravimetric capacitance and ρ (g cm⁻³) is the density of electrode.

$$\rho = \frac{m}{s \times l} \quad (5)$$

Where ρ (g cm⁻³) is the density of electrode, m (g) is the mass of electrode, s (cm²) is the area of electrode and l (cm) is the thickness of electrode.

The volumetric energy density and power density was calculated using the following equation:

$$E_v = \frac{1}{3.6 \times 8} C_v \Delta V^2 \quad (6)$$

$$P_v = \frac{3600 E_v}{t} \quad (7)$$

Where E_v (Wh L⁻¹) is the volumetric energy density, C_v (F cm⁻³) is the volumetric capacitance, ΔV (V) is the potential window, P_v (W L⁻¹) is the the volumetric power density and t (s) is the discharge time.

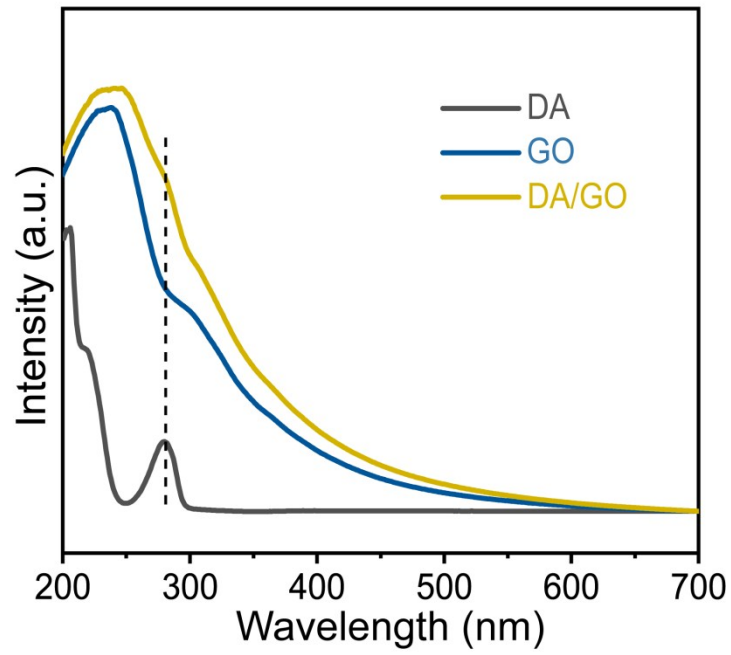


Fig. S1. The UV-vis absorption spectroscopies of pure DA, pure GO, and DA/GO solution

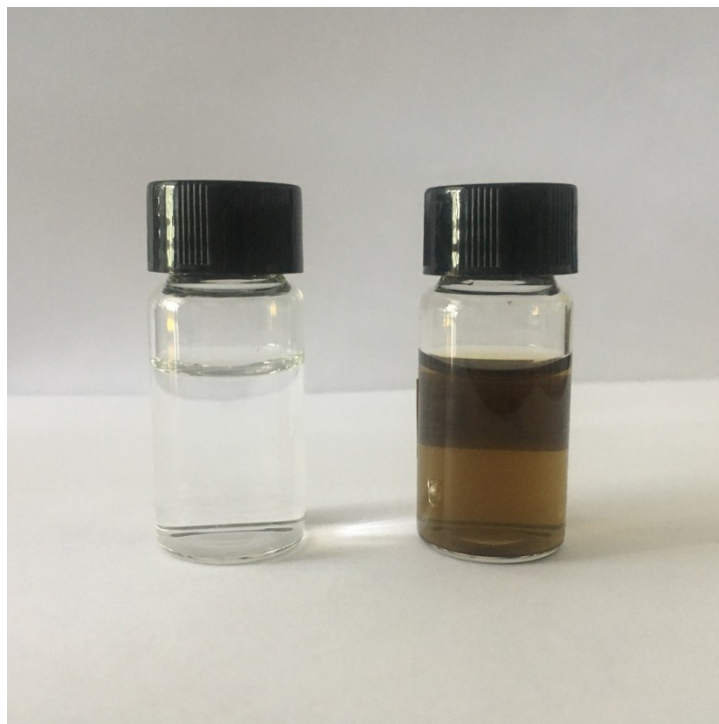


Fig. S2. The optical image of DA solution before (left) and after (right) hydrothermal reaction.

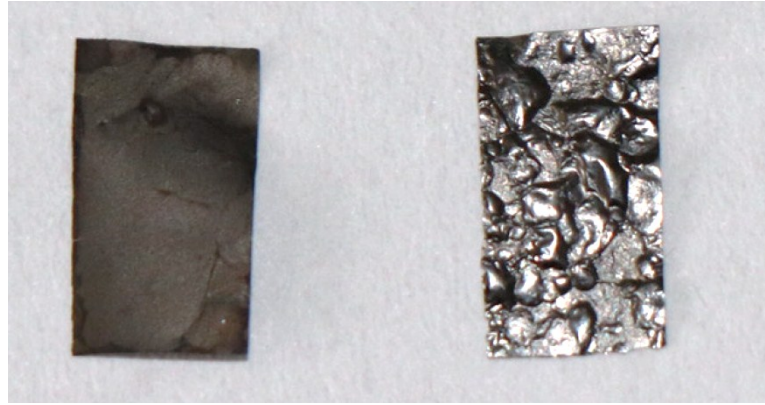


Fig. S3. The optical photo of DA/rGO@PDA(left) and DA/rGO (right).

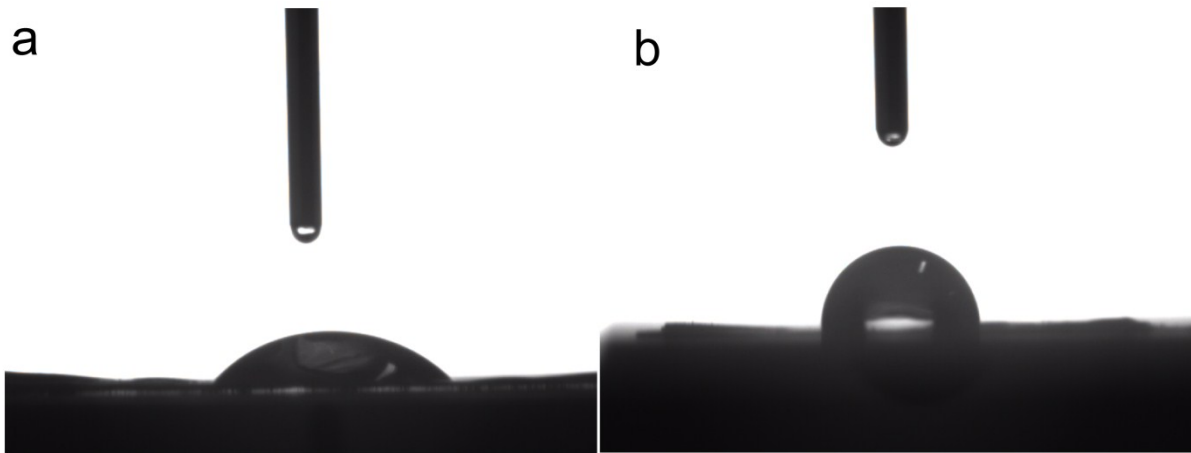


Fig. S4. The water contact angle of a) DA/rGO@PDA, and b) DA/rGO.

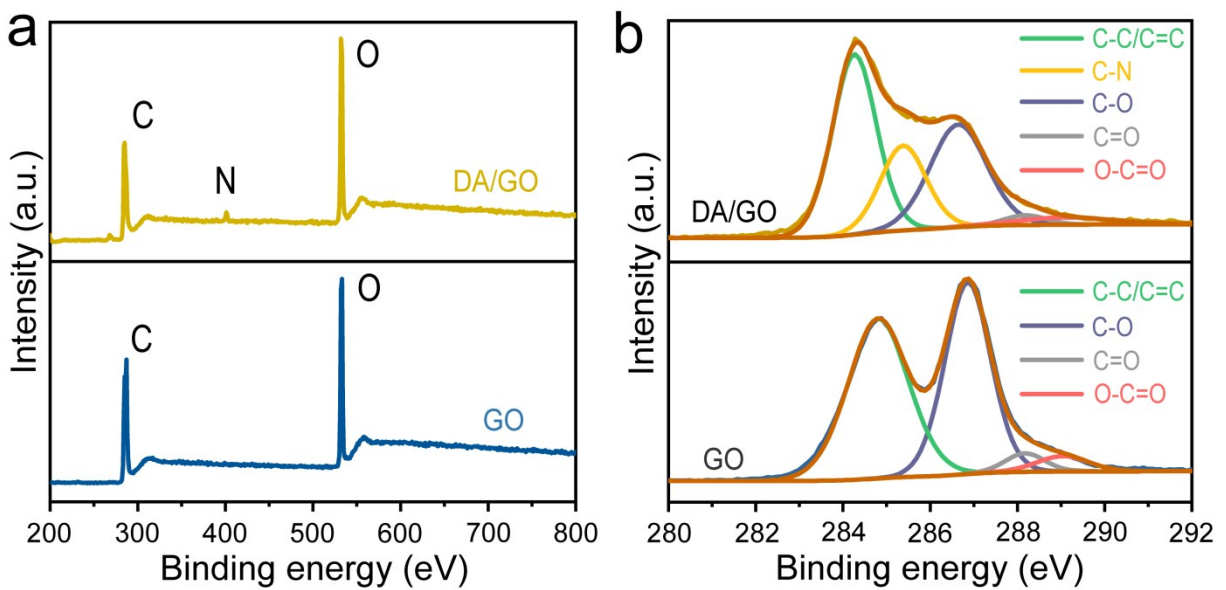
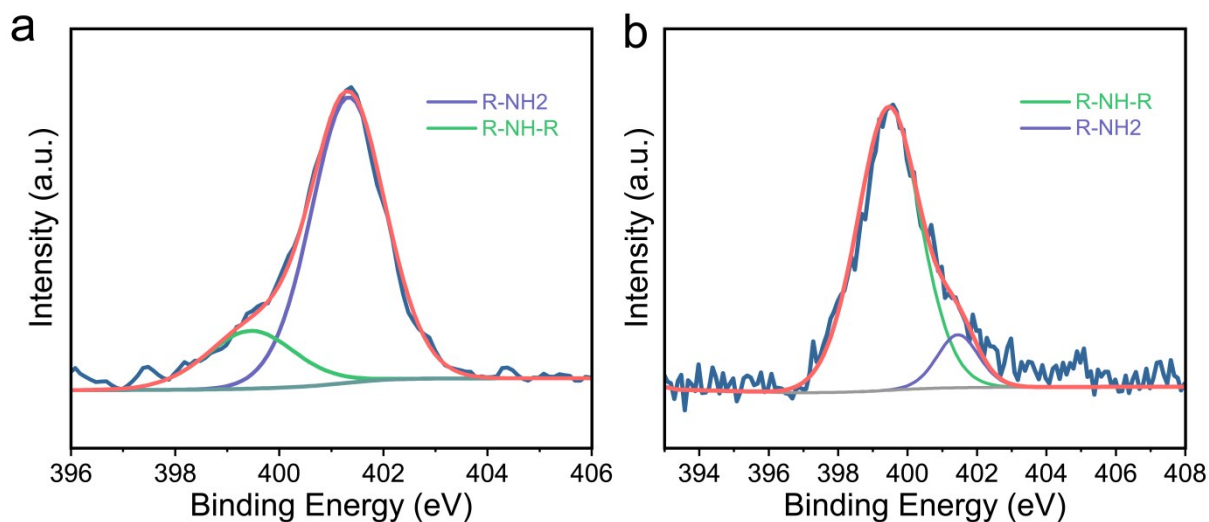
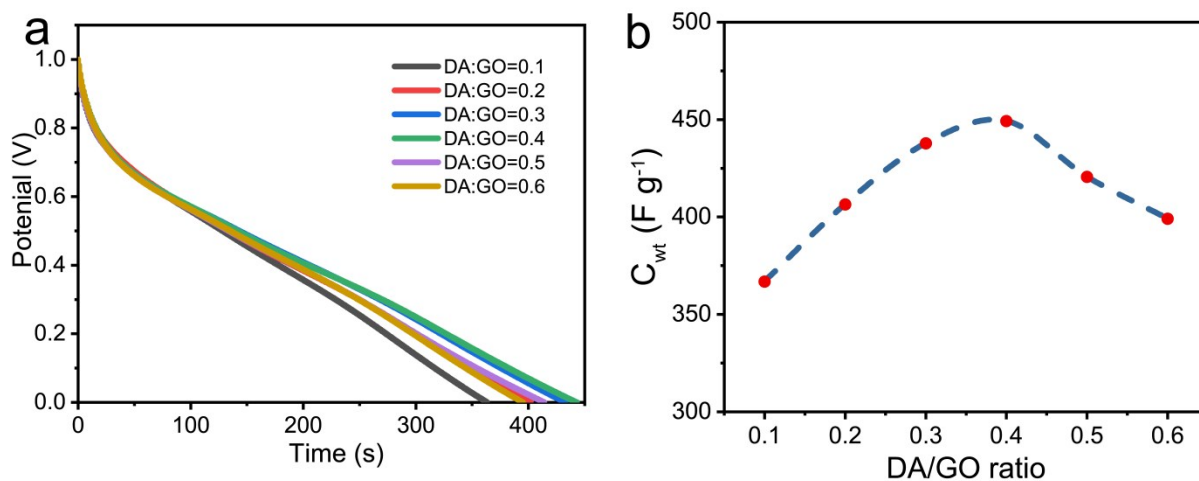


Fig. S5. a) The XPS spectra of GO and DA/GO. b) High-resolution C1s spectra of GO and DA/GO.

Table S1. The element content of all samples

Materials	GO	DA/GO	rGO	DA/rGO	DA/rGO@PDA
C (at%)	67.53	62.06	86.35	82.68	76.39
O (at%)	32.47	34.74	13.65	14.32	17.94
N (at%)		3.2		3	5.67

**Fig. S6.** The high resolution N 1s spectra of a) DA/GO and b) DA/rGO.**Fig. S7.** a) Galvanostatic charge-discharge profiles of samples with different mass ratio of DA. b) The gravimetric capacitance of samples with different mass ratio of DA

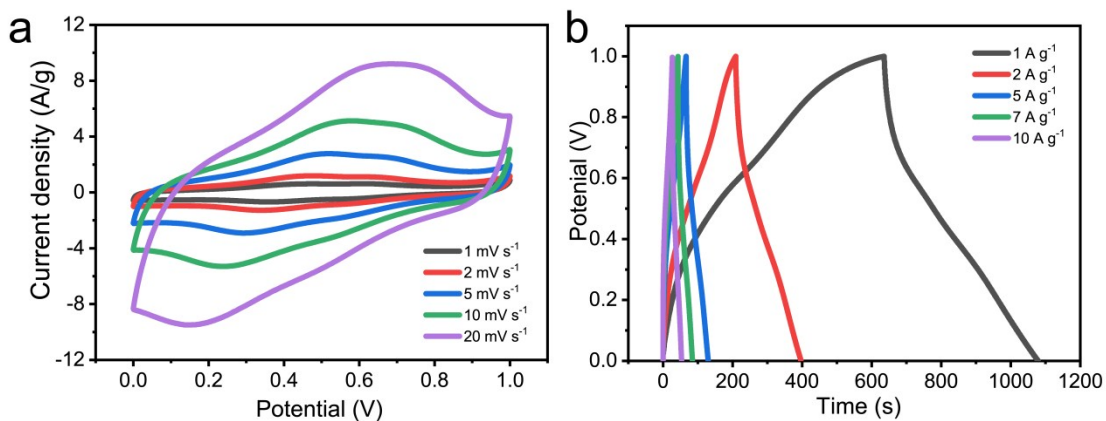


Fig. S8. a) Cyclic voltammogram curves of DA/rGO@PDA at different scan rate. b) Galvanostatic charge-discharge profiles of DA/rGO@PDA at different current density.

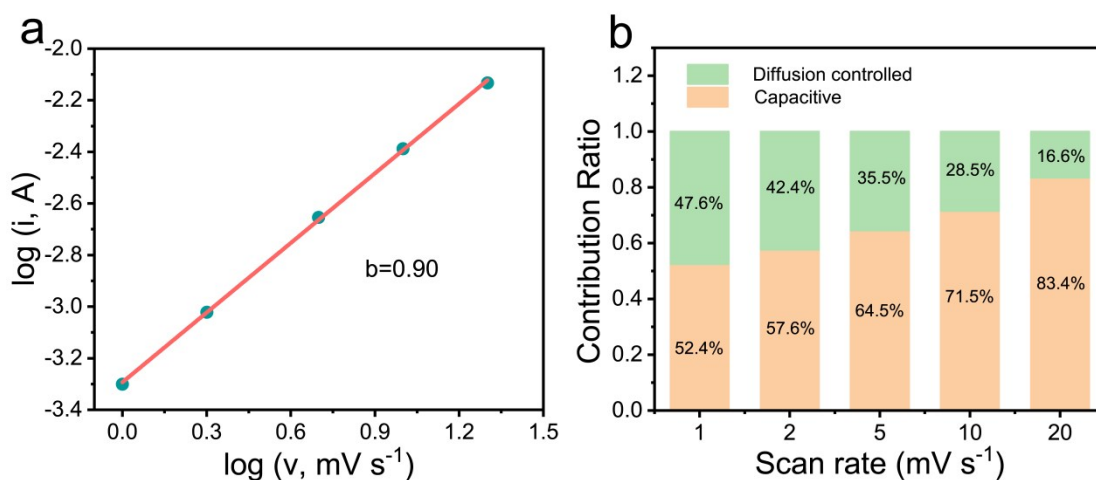


Fig. S9. a) The log i versus log v plot of the peak currents. b) The Capacitance contribution differentiation at the different scan rate from 1 mV s⁻¹ to 20 mV s⁻¹.

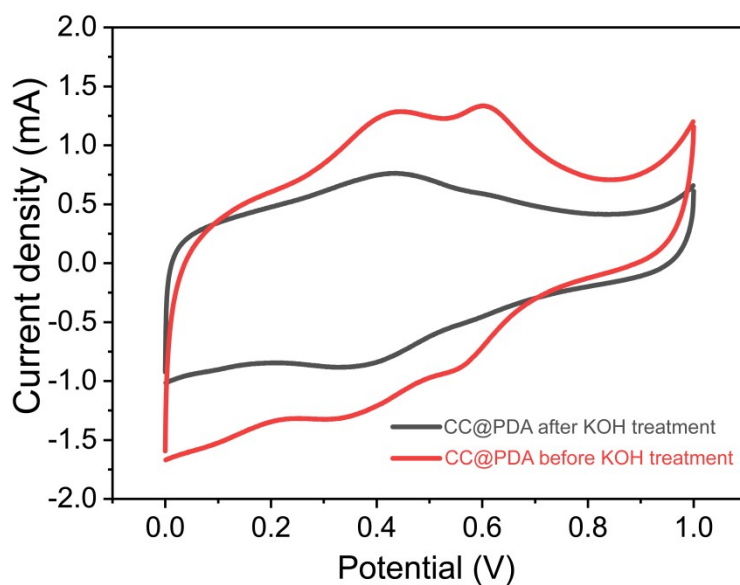


Fig. S10. The CV curves of CC@PDA before and after KOH treatment.

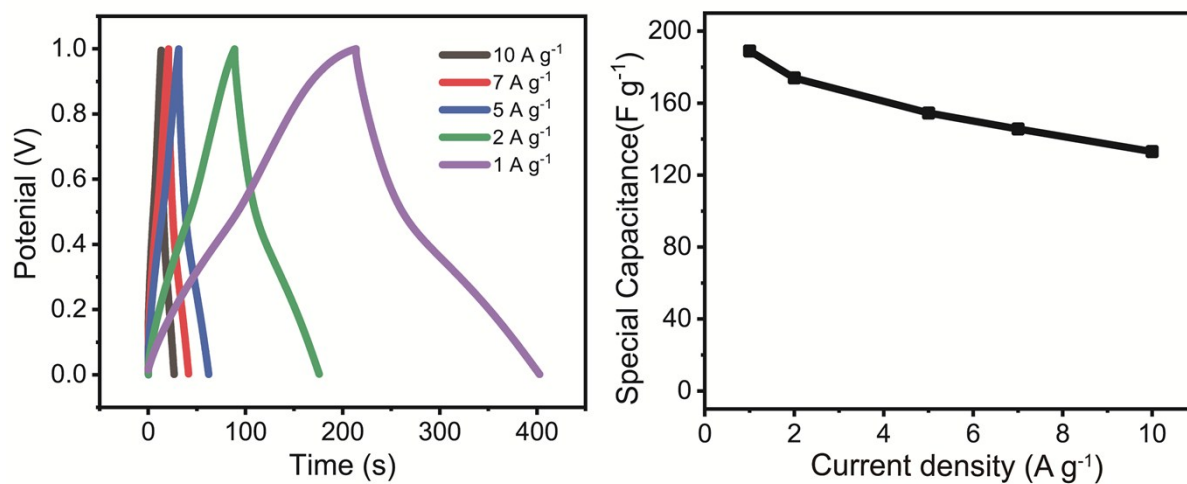


Fig. S11. a) The GCD curves of rGO@PDA at different current density. b) the gravimetric capacitance of rGO@PDA at different current density

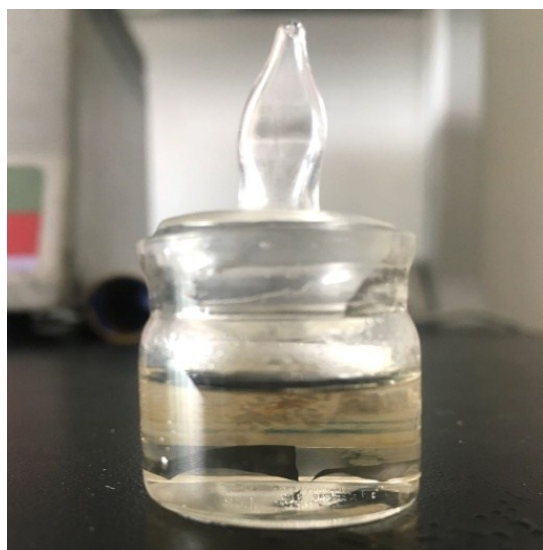


Fig. S12. The optical photo of DA/rGO@PDA immersed in 85 wt% H₃PO₄

Table S2. Comparison of electrochemical performances of graphene based materials

Materials	Density (g cm ⁻³)	Electrolyte	Test	C _g (F g ⁻¹)	C _v (F cm ⁻³)
Activated carbon-graphene ^[S2]	0.76	6.0 M KOH	1 A g ⁻¹		120♦
Ternary-doped holey graphene hydrogel ^[S3]	0.67	1.0 M H ₂ SO ₄	1 A g ⁻¹	350	234★
Graphene-carbon nanosphere films ^[S4]	1.4	6.0 M KOH	1 A g ⁻¹		252♦
Graphene-CNT films ^[S5]	1.5	6.0 M KOH	1 A g ⁻¹		250♦
The reduced holey graphene films ^[S6]	1.14	1.0 M H ₂ SO ₄	1 A g ⁻¹	260	297★
Halloysite-polyaniline-graphene oxide films ^[S7]		1.0 M H ₂ SO ₄	0.5 A g ⁻¹	291.2★	
Lignosulfonate functionalized graphene hydrogels ^[S8]		1.0 M H ₂ SO ₄	1 A g ⁻¹	432★	
Folded Graphene Ribbon Film ^[S9]	0.92	6.0 M KOH	2 mV s ⁻¹	318	293★
Nitrogen-doped graphene film ^[S10]	1.64	1.0 M H ₂ SO ₄	1 A g ⁻¹	252	413♦
Carbon nanofiber graphene ^[S11]	0.00075	1.0 M H ₂ SO ₄	1 A g ⁻¹	215	0.161★
Defect-enriched graphene block ^[S12]	0.917	6.0 M KOH	1 A g ⁻¹	235	215★
3D porous RGO film ^[S13]	0.95	1.0 M H ₂ SO ₄	1 A g ⁻¹	181.3	172.3♦
			1 A g⁻¹	449.3	772.8★
This work	1.72	1.0 M H₂SO₄	0.5 A g⁻¹	277	476.4♦

★ represents the three electrode system ♦ represents the two electrode system

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