Electronic Supplementary Information (ESI)

Conformation-driven percolative interface architecting in phaseengineered 3D Printed graphene/PEDOT:PSS supercapacitors enabling ultra-high energy density and superior ion transport

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1. Experimental Section

Preparation of the printable ink.

First, GO was dispersed in deionized water at a concentration of 50 mg/mL, after which PEDOT:PSS was added to the GO dispersion at a predetermined ratio to prepare a composite dispersion (in a typical ink formulation, the GO content is 80 wt.%). The ink was then stirred using a high-speed homogenizer (IKA T10 ULTRA-TURRAX) for 30 minutes to achieve a stable dispersion. Subsequently, diethylene glycol (DEG) was added at a concentration of 37.2 mg/mL, and the mixture was further stirred until a well-dispersed ink was obtained.

3D Printing Process and post-processing.

For direct ink writing, the prepared ink was loaded into a syringe and extruded through a tapered nozzle with a diameter of 700 μ m using an air-powered fluid dispenser (Electron Fusion Devices, Inc.), which maintained an applied pressure of approximately 15 psi. The printing speed was set at 5 mm/s to pattern electrodes into a woodpile structure, where the rod center-to-center distance was fixed at 700 μ m. Following printing, the 3D-printed structure was frozen for 12 hours and subsequently freeze-dried for 48 hours to remove the solvent. The resulting aerogel was then immersed in 5 wt.% HPA and heated at 60 °C for 24 hours to facilitate the reduction of graphene oxide. After thorough rinsing with water, the material was soaked in 5 M H₂SO₄ for 6 hours. Finally, the treated printed electrode was rinsed with water and dried at room temperature. *Material characterizations*.

The rheological properties of the ink were evaluated using a rheometer (TA Instruments AR2000EX) at room temperature. The apparent viscosity as a function of shear rate was measured in dynamic frequency sweep mode, while the storage modulus and loss modulus were analyzed in dynamic stress sweep mode at a frequency of 1 Hz. X-ray diffraction (XRD) analysis was performed using an X'Pert PRO diffractometer (Panalytical, Eindhoven, Netherlands) with Cu K α radiation ($\lambda = 1.5418$ Å) over a 2 θ range of 5–80° and a step size of 0.03°. The morphology of the samples was characterized using a field emission scanning electron microscope (FESEM). The elemental

distribution was analyzed via energy-dispersive spectroscopy (EDS) using an Oxford IE450X-Max80 system. Raman spectroscopy (InVia, Renishaw, UK) was conducted with an excitation wavelength of 514.5 nm, covering a spectral range of 500–3500 cm⁻¹. The specific surface area (SSA) was determined by Brunauer-Emmett-Teller (BET) analysis based on N₂ adsorption-desorption isotherms measured using a Micromeritics Tristar 3000 at 77 K. The chemical composition and bonding configurations were investigated via X-ray photoelectron spectroscopy (XPS) using an ESCALAB 250Xi system (Thermo Fisher, USA) with Al-K α radiation (14.7 kV, 16 mA). Functional groups in the samples were characterized by Fourier-transform infrared spectroscopy (FTIR) using a Spectrum One spectrometer (PE Instruments, USA) within a test range of 400–2000 cm⁻¹.

Electrochemical Measurement.

The electrochemical performance was evaluated using both three-electrode and two-electrode configurations on an electrochemical workstation (AUTOLAB PGSTAT302N). For the three-electrode measurements, a 1 M H₂SO₄ solution was used as the electrolyte, with an Ag/AgCl electrode serving as the reference electrode and a Pt electrode as the counter electrode. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements were performed within a potential window of 0–0.8 V. Electrochemical impedance spectroscopy (EIS) was conducted with a voltage amplitude of 5 mV over a frequency range of 100 kHz to 10 mHz.

Capacitance values of the composite electrodes were calculated from the GCD curve according to the following equation

$$C_{g} = \frac{I\Delta t}{m\Delta U}$$

$$I\Delta t$$
(1)

$$C_{A} = A\Delta U \tag{2}$$

where C_g and C_A refer to the specific gravimetric capacitance and specific areal capacitance of a single electrode, respectively. I is the discharge current, Δt is the discharge time, m is the mass of a single electrode, A represents the electrode footprint, and ΔU is the potential window.

In the two-electrode configuration for device testing, two electrodes of equal mass were assembled into a symmetrical device with a sandwich structure. A 1 M PVA/H₂SO₄ gel electrolyte was used, and the device was encapsulated between PET films. The areal capacitance of the device was determined from GCD curves according to the following equation

$$C_{g,D} = \frac{I\Delta t}{2m\Delta U}$$
(3)
$$\underline{I\Delta t}$$

(4)

 $C_{A, D} = 2A\Delta U$

where $C_{g,D}$ and $C_{A,D}$ represent the gravimetric capacitance and areal capacitance of the symmetric supercapacitors, respectively. I denotes the discharge current, Δt is the discharge time, m is the mass of a single electrode, A is the electrode footprint, and ΔU is the potential window.

The Ragone plot was generated based on the areal energy density (E_A) and the corresponding areal power density (P_A), calculated using Equations (5) and (6), respectively.

$$E_{A} = \frac{CA\Delta U2}{2}$$

$$E_{A} = \frac{3600 \times EA}{\Delta t}$$
(5)
(6)

where C_A , ΔU , and Δt correspond to the areal capacitance, the potential window, and the discharge time, respectively, of the symmetric supercapacitor.

The diffusion relaxation time (τ_d) was determined by fitting the electrochemical impedance spectroscopy (EIS) spectrum of a measured electrode using an equivalent circuit incorporating restricted linear diffusion element M which is related to τ_d by Equation (7).^{1,2}

$$Z_{\rm M} (f) = \frac{{\rm Rd} \frac{{\rm coth} \sqrt{\tau {\rm dj} 2\pi f}}{\sqrt{\tau {\rm dj} 2\pi f}}}{(7)}$$

The MacMullin number (N_m) of the printed electrode was determined by analyzing the measured EIS spectrum using transmission line modeling (TLM). In this approach, the ionic resistance (R_{ion}) is correlated with and extracted from the complex capacitance.³ The N_m value was subsequently calculated using Equation (9).⁴

$$N_{\rm m} = (R_{\rm ion} \cdot A \cdot \sigma)/d \tag{9}$$

where, A is the cross-sectional area of the electrode, σ is the conductivity of the electrolyte, d is the thickness of the electrode, and R_{ion} is the ionic resistance.

2. Figures



Fig. S1 The Comparison in XRD patterns between (a) rGO and GO, (b) among PEDOT: PSS, HPA treated PEDOT:PSS and concentrated H₂SO₄ treated PEDOT:PSS. (c) the comparison of the (002) peak position among rGO, rGP, H-rGP electrodes.

The retention of the characteristic PSS peak at 18.9° suggests that HPA does not remove the PSS phase, whereas substantial PSS reduction occurs only after concentrated H₂SO₄ treatment on rGP as shown in Fig. S1b.



Fig. S2 FT-IR spectra compared among (a) H-rGP, rGP and GP; and (b) between rGO and GO.

In rGP, characteristic peaks of PEDOT:PSS are clearly observed, including S–O and S–phenyl bonds from the sulfonic acid group, as well as C=C, C–C, and C–S bonds from the thiophene backbone. After acid-mediated phase engineering, the FT-IR spectrum of H-rGP shows a weakened





Fig. S3 XPS survey spectra of (a) H-rGP, rGP and rGO. (b) The deconvoluted high-resolution C 1s spectra of (b) rGO, and (c) rGP.

The notable appearance of S 1s and S2p peaks attributed to PEDOT: PSS in the survey spectrum of rGP and H-rGP compared to that of rGO confirms the successful incorporation of PEDOT: PSS into the graphene matrix. Similarly, by comparing the high resolution deconvoluted C1s spectrum between rGO and rGP, a band corresponding to C-S bond contributed by PEDOT: PSS can be observed.



Fig. S4 (a) Comparison of the Raman spectra of H_2SO_4 -PEDOT:PSS and PEDOT:PSS to confirm the conformational change of PEDOT. (b) The D/G band ratio compared between rGP and H-rGP.

It should be noted that, due to the structural differences between rGO and PEDOT:PSS which result in markedly different polarizability changes during molecular vibrations⁵⁻⁷ as well as their substantial disparity in mass content,^{8, 9} the Raman signal of PEDOT:PSS is overwhelmed by the dominant signal from rGO as observed in Figure S4b.

Additionally, the D/G band ratio increases from rGP to H-rGP (Fig. S4b), suggesting that PEDOT conformational changes induce greater structural disorder in graphene, suggesting strong interfacial interactions between graphene and PEDOT:PSS, which may play a crucial role in regulating the reaction interface.



Fig. S5 Nitrogen adsorption-desorption isothermal curves of H-rGP and rGP.



Fig. S6 Electrochemical performance compared among rGP electrodes prepared from GO/PEDOT:PSS composites of varied GO contents in weight percentage to determine the optimal composition for desired supercapacitor performance. (a) The CV curves compared at a scan rate of 10 mV/s and (b) GCD curves measured and compared at a current density of 0.5 A/g for different composites. (c) the gravimetric capacitances vs. current densities compared among rGP electrodes of different GO weight contents, pure PEDOT:PSS, and H-PEDOT:PSS (H_2SO_4 -treated PEDOT:PSS).

The optimal composition of the GO/PEDOT:PSS composite for achieving superior electrochemical performance was determined through three-electrode performance testing on composite thin films with varying compositions. It was observed that pure rGO exhibits the highest gravimetric capacitance at low current densities. However, severe stacking and restricted ion diffusion in pure rGO result in a significant decline in rate capability. In contrast, the incorporation of PEDOT:PSS, owing to its mixed ionic-electronic conducting properties, enables a minimal compromise in gravimetric capacitance while substantially enhancing rate performance at a proper composition. By optimizing the ratio, the ideal composition was determined to be 80 wt% GO and 20 wt% PEDOT:PSS.

It is also observed that H-PEDOT:PSS exhibits excellent rate capability, as evidenced by minimal capacitance degradation over the adopted current density range. Its gravimetric capacitance is slightly improved relative to pure PEDOT:PSS, indicating a modest enhancement resulting from acid-induced phase engineering. Nevertheless, its capacitance remains significantly lower than that of the composite electrode containing 80 wt% GO. The result underscores the role of rGO as a high-capacitance matrix, ideally serving as the dominant component to provide charge storage, while PEDOT:PSS/H-PEDOT:PSS acts as an effective mediator to mitigate the kinetic limitations of rGO.

As for the prospect of 3D printing PEDOT:PSS for supercapacitor applications, the poor rheological behavior of inks formulated with pristine PEDOT:PSS and the inadequate mechanical integrity of the resulting printed constructs pose significant technical challenges.^{10, 11} Moreover, the electrical conductivity of PEDOT:PSS remains substantially lower than that of highly conductive carbon-based materials. When used as a standalone 3D-printed electrode under high loading conditions, PEDOT:PSS is more prone to pronounced ohmic polarization, which further compromises device performance. Therefore, pristine PEDOT:PSS is not considered suitable as a freestanding electrode material, particularly in high-loading-density 3D printing applications.



Fig. S7 (a) Raman spectra of rGO and acid-treated H-rGO; (b) CV curves of rGO and H-rGO electrodes measured at 10 mV/s; (c) GCD curves of rGO and H-rGO electrodes at 1 A/g; (d) Gravimetric capacitance as a function of current density for rGO and H-rGO electrodes.

The use of a balanced H₂SO₄ concentration and mild room-temperature treatment minimizes defect formation on rGO, consistent with literature reports¹². Raman spectroscopy was performed on both pristine rGO and acid-treated H-rGO to verify this. As shown in Fig. S7a, the I_D/I_G ratio remains nearly unchanged, indicating negligible defect introduction. Furthermore, cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) tests (Fig. S7b, c) demonstrate that the acid treatment has little impact on electrochemical performance, with rGO maintaining excellent capacitance and stability (Fig S7d).



Fig. S8 Electrochemical performance comparison among rGO, rGP, and H-rGP. (a) The CV curves compared at a scan rate of 10 mV/s and (b) GCD curves compared at a current density of 0.5 A/g.



Fig. S9 Comparison of active material mass loading on the 3D-printed H-rGP electrode before and after long-term cycling.

Given the establishment of π - π interactions between rGO and PEDOT:PSS, which effectively "cement" the two components together,^{13, 14} along with the graphene-dominated composition of the printed electrode,¹⁵ the risk of dissolution or structural disassembly of the composite during operation is significantly suppressed.¹⁵⁻¹⁷ This structural integrity is reflected in the observed minimal change in active material loading after long-term cycling (Fig. S9).



Fig. S10 The cycling stability test of printed (a) rGP and (b) rGO electrode performed at 4 A/g in 10000 cycles. Insets: A comparison in CV curves before and after the cycling at 20 mV/s.

The long-term cycling performance of the printed rGO, rGP alongside H-rGP electrodes (Figure 3g) has been evaluated. All electrodes exhibit excellent cycling stability, with capacitance retention exceeding 95% over 10,000 cycles.



Fig. S11 Comparison of diffusion relaxation times among printed rGO, rGP, and H-rGP electrodes, obtained by fitting the linear restricted diffusion element (M).

Diffusion relaxation times, derived from equivalent circuit fitting in the low-frequency region (Fig. S11), show H-rGP with a significantly lower time constant, indicating enhanced electrolyte transport to reactive interfaces. This improvement stems from conformational and topographical changes in PEDOT-rich regions, which exposes ion transport channels and enhances ionic percolation.



Fig. S12 Theoretical capacitance contributions of the constituent elements inferred using the Trasatti method. (a) Plots of the reciprocal of areal capacitance (1/C) versus the square root of the scan rate $(v^{1/2})$ for 3D-printed rGO, rGP, and H-rGP electrodes. Dashed lines represent the linear fitting curves for data points in the low scan rate region. (b) Illustration of the respective capacitance contributions from rGO and PEDOT:PSS in the printed rGP and H-rGP electrodes.



Fig. S13 Bar charts comparing the MacMullin numbers obtained from printed H-rGP and rGP electrodes.



Fig. S14 The electrochemical performance of the assembled symmetrical supercapacitor device from printed H-rGP electrodes. (a) The CV curves measured at varied scan rates and (b) GCD curves at different current densities of the assembled symmetric device; (c) the Regone plot comparing the performance of the H-rGP based device with representative existing works.¹⁸⁻²³ (d) A digital image of four assembled devices connected in series powering an LED display.

A symmetrical device was assembled using two printed 3D H-rGP electrodes, achieving an exceptional loading density of 87.8 mg/cm². Electrochemical evaluation revealed well-preserved rectangular CV curves (Fig. S12a) and symmetric isosceles triangular GCD curves (Fig. S12b), demonstrating stable charge storage behavior even at such high loading and electrode thickness. The printed symmetrical device exhibited outstanding performance, surpassing representative highly loaded graphene-based supercapacitors, as illustrated in the Ragone plot (Fig. S12c). To further demonstrate its practical applicability, Fig. S12d showcases the successful operation of an LED display, powered by four symmetrical devices connected in series, underscoring the feasibility of the proposed high-loading 3D-printed electrode design for real-world energy storage applications.

3. Table

Table S1. The electrochemical performance of the 3D-printed H-rGP electrode, with a focus on areal capacitance, loading density, and rate capability (measured within comparable current density ranges), tabulated and benchmarked against representative studies on highly loaded graphene for supercapacitor applications.

Sample	Areal capacitance (mF/cm ²)	mass loading (mg/cm ²)	Rate capability (%)	Reference
3D-GP	870.3	15.3	65.8%@(1.2-11.5 mA/cm ²)	24

N-CNFs/RGO/BC film	2544	8	76%@(1-50 mA/cm ²)	25
3DP graphene	639.56	12	71.4%@(5-40 mA/cm ²)	26
3D GA	2195	12.8	75%@(5-100 mA/cm ²)	27
Graphene film	372	2	80%@(1-40 mA/cm ²)	28
3D PG	1640	45	54%@(2-50 mA/cm ²)	29
rGO film	71	13.6	79%@(1-100 mA/cm ²)	30
This work	3457	48.1	79.5%@(6.8-68 mA/cm ²)	

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