Three-Dimensional Graphene-based Macro- and Mesoporous Frameworks for High-Performance Electrochemical Capacitive Energy Storage

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Experimental Section

Synthesis of 3D graphene aerogels (GAs)

Graphene oxide (GO) was prepared from natural graphite flakes by a modified Hummers method, the details of which were described elsewhere.[1-4] 3D GAs were synthesized by a combined hydrothermal and freeze-drying process.[5] Typically, the as-prepared GO was first dispersed in water by sonication reaching a concentration up to 1.5 mg mL^{-1}. Afterwards, a 15 mL GO aqueous dispersion was sealed in a Teflon-lined autoclave and hydrothermally treated at 180 °C for 12 h. Finally, the resulting sample was freeze-dried overnight to obtain GAs.

Synthesis of 3D graphene aerogel-mesoporous silica (GA-SiO₂) frameworks

The GA-SiO$_2$ was prepared by a sol-gel approach. In a typical experiment, the as-synthesized 3D GAs (10 mg) were firstly suspended in a 20 mL aqueous solution containing CTAB (480 mg), ethanol (4 mL) and NaOH (20 mg), and then kept at 40~50 °C for 6 h. After that, tetraethylorthosilicate (TEOS, 0.5 mL) was slowly added to the above mixture. After reaction for 6~12 h, the prepared sample was washed with warm ethanol and water, repeated for three times, and freeze-dried overnight. Finally, GA-SiO$_2$ was produced by thermal treatment at 800 °C for 3 h in argon gas.

Synthesis of 3D graphene aerogel-mesoporous carbon (GA-MC)

3D GA-MC was prepared using GA-SiO$_2$ as a template by a nanocasting technique. Typically, GA-SiO$_2$ was repeatedly infiltrated in an ethanol solution of sucrose at 40 °C for 6 h. The above infiltration steps were repeated to ensure a complete filling of the void spaces in mesoporous silica of GA-SiO$_2$ by sucrose. Then, the sucrose-filled sample was freeze-dried overnight and carbonized at 700 °C for 3 h in argon. Subsequently, the silica template was removed using a NaOH solution (2 M). After drying overnight, 3D GA-MC was obtained.

Synthesis of 3D graphene aerogel-Co₃O₄ (GA-Co₃O₄)

3D GA-Co$_3$O$_4$ was prepared using GA-SiO$_2$ as a template by a nanocasting approach. Typically, GA-SiO$_2$ was repeatedly impregnated in a 2-isopropanol solution (10 mL) of cobalt acetylacetonate and acetic acid (1 mL) at 100 °C overnight. The weight ratio between template and cobalt salt was fixed to

1:3. Then, the sample was freeze-dried overnight and heated at 350 °C for 3 h in air. Finally, the composites were etched in a NaOH solution (2 M) to remove SiO_2 and followed by drying to obtain 3D GA-Co_3O_4.

Synthesis of 3D graphene aerogel-RuO_2 (GA-RuO_2)

3D GA-RuO_2 was prepared using GA-SiO_2 as a template by a nanocasting approach. GA-SiO_2 was repeatedly impregnated in a 2-isopropanol solution (10 mL) of ruthenium acetylacetonate and acetic acid (0.5 mL) at 100 °C overnight. The weight ratio between template and ruthenium salt was fixed to 1:3. Then, the sample was freeze-dried overnight and heated at 150 °C for 2 h in air. Finally, the composites were etched in a NaOH solution (2 M) to remove SiO_2 and followed by drying overnight to obtain 3D GA-RuO_2.

Templating synthesis of mesoporous carbon (MC)

First, mesoporous silica was obtained by thermal treatment of GA-SiO_2 at 800 °C for 3 h in air to burn out graphene. Then, the obtained mesoporous silica was infiltrated in an ethanol solution of sucrose at 40~50 °C, and repeated several times. Afterward, the sucrose-filled sample was carbonized at 700 °C for 3 h in argon. Finally, the silica template was removed using a NaOH solution (2 M) for 24 h, and after drying at 70 °C overnight, MC sample was produced.

Synthesis of graphene powder

A 40 mL GO (0.1 mg mL^{-1}) aqueous dispersion was sealed in a Teflon-lined autoclave and

hydrothermally reduced at 180 °C for 12 h. The sample was filtrated, washed, and dried at 70 °C overnight.

Synthesis of 2D graphene-based mesoporous carbon sheets (GMC)

GMC was synthesized using 2D graphene-based mesoporous silica as a template by a nanocasting technique which was previously reported in our group.[6] Typically, graphene-based mesoporous silica sheets (50 mg) were repeatedly infiltrated in an ethanol solution of sucrose (100~150 mg) at 40~50 °C overnight. Then, the above infiltration steps were repeated to ensure a complete filling of the void spaces in 2D graphene-based mesoporous silica by sucrose. Afterward, the sucrose-filled sample was freeze-dried overnight and carbonized at 700 °C for 3 h in argon. Subsequently, the silica template was removed using a NaOH solution (2 M). After vacuum drying at 80 °C for 12 h, GMC was obtained.

Characterization

The morphology and structure of the samples were investigated by SEM (Gemini 1530 LEO), TEM, HRTEM and STEM (Philips Tecnai F20), AFM (Veeco Dimension 3100), EDX (Philips Tecnai F20), XPS (Omicron Multiprobe equipped with the monochromatic Al K_α source, electron analyzer resolution of 0.9 eV), XRD and thermogravimetry (TG, from 25 to 800 $^\text{o}$C in air with a heating rate of 10 $^\text{o}$C) measurements. Nitrogen adsorption and desorption isotherms and pore size distribution were measured at 77 K with a Micromeritcs Tristar 3000 analyzer (USA). Mercury instrusion porosimetry (AutoPore IV 9500 V1.09, Serial 915, Micromeritics Instrument Corporation) ranging from 100 to 400000 nm was conducted to evaluate the macroporosity, bulk and apparent densities of GAs. The mechanical property of monolithic GAs was evaluated by the nanoindentation technique (nano indenter MFP-3D, Asylum

Research, U.S.A). The measurement was carried out at constant strain rate of 5 S^{-1} by diamond indenter with a flat-punch-geometry tip (241 μm diameter).

Electrochemical measurements of electrochemical capacitors (ECs) were carried out on an EG&G potentiostat/galvanostat Model 2273 instrument. CV measurements and charge-discharge galvanostatic tests were performed in a three-electrode system. All the working electrodes for ECs were fabricated by physically mixing 80 wt% powdered active materials (4 mg), 10 wt% acetylene black, and 10 wt% polytetrafluoroethylene (PTFE) binder dispersed in ethanol solvent, and then pressed on a platinum mesh network serving as a current collector, a platinum plate as counter electrode, a saturated calomel electrode (SCE) as reference electrode, and 1 M H_2SO_4 as aqueous electrolyte.
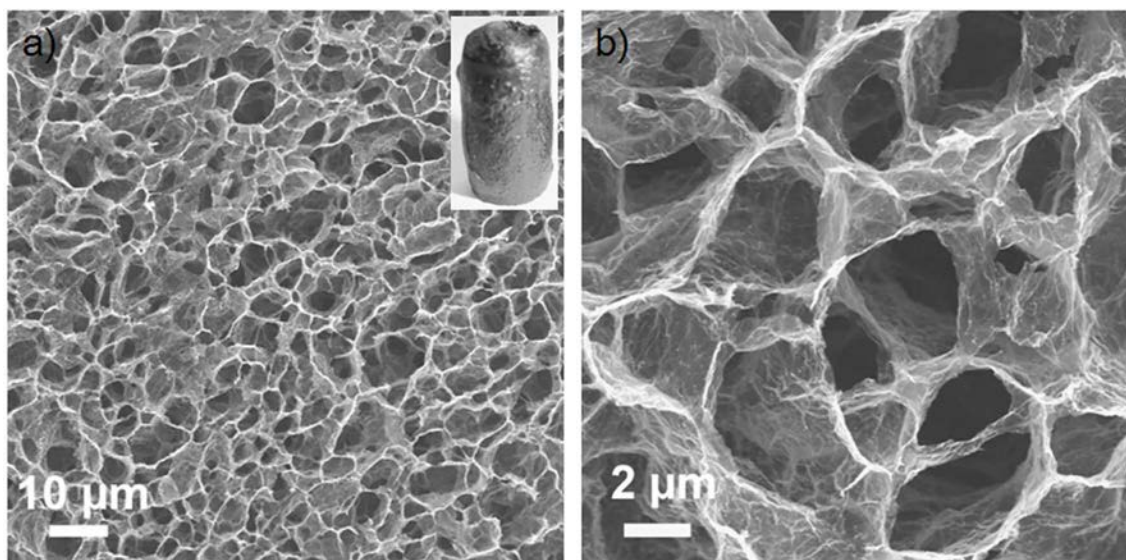
Figure S1. (a,b) SEM images of the as-prepared 3D GAs. Inset in (a) is the optical image of monolithic 3D GAs.
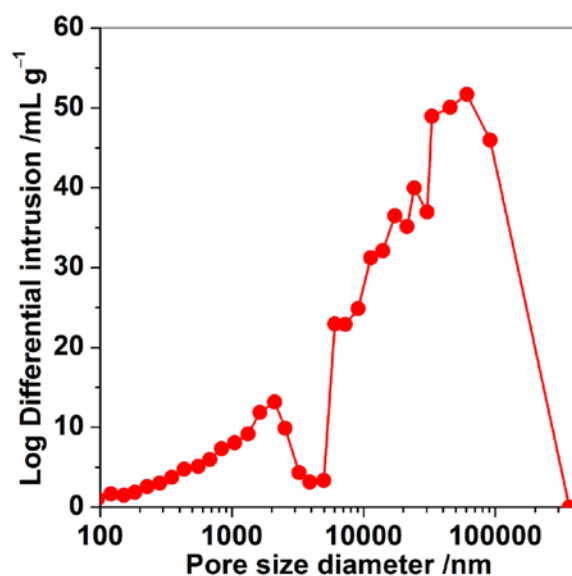
Figure S2. Macroscopic pore-size distribution of GAs obtained by mercury-intrusion porosimetry. Total intrusion volume measured is 82.5 mL/g, median pore diameter (volume) is 49345 nm, average pore diameter (4V/A) is 4762.1 nm, bulk density at 0.50 psia is 0.0106 g/mL, apparent (skeletal) density is 0.0825 g/mL, and the porosity is 87.2%. These results confirm both high macroporosity and connectivity of the as-synthesized graphene-based frameworks.
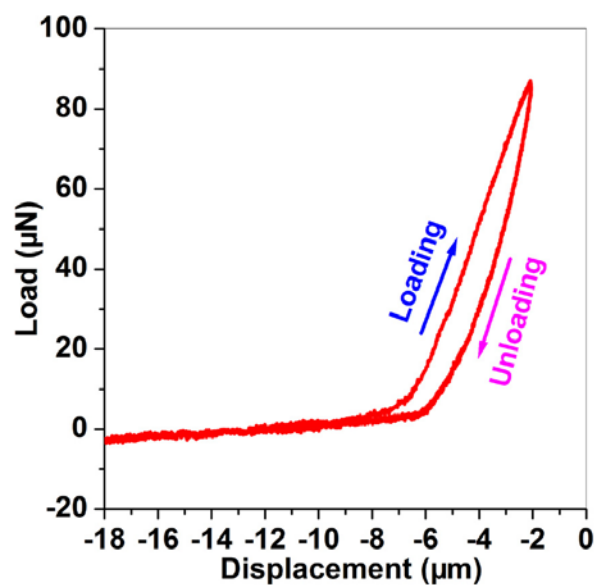
Figure S3. The Force-displacement curve of GAs measured by nanoindentation test: loading (the blue arrow) and unloading (magenta arrow) of an indenter tip. According to the Oliver-Pharr model,[7] the Young's modulus of graphene aerogels was calculated around 188 kPa.
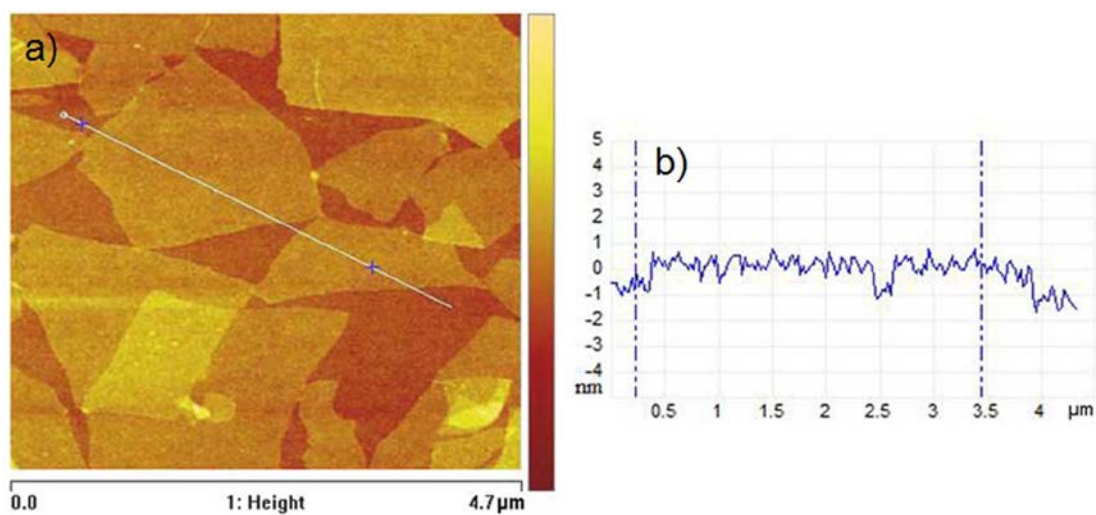
Figure S4. (a) Typical AFM image and (b) height profile of GO, with a thickness of about ~1 nm,

coated on silicon wafer.
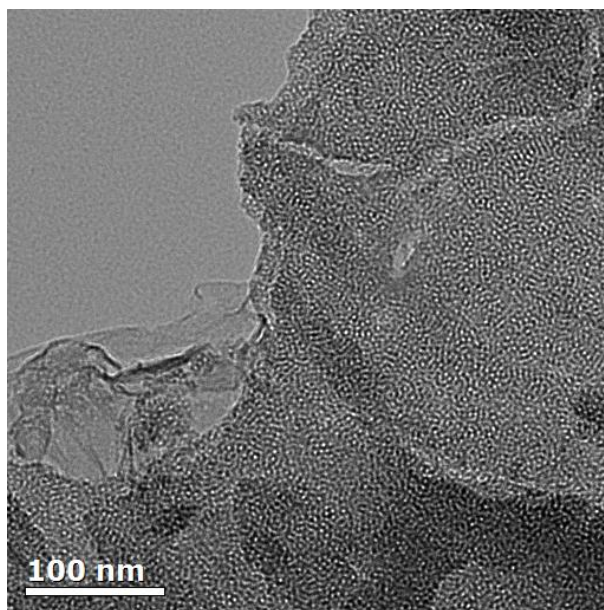
Figure S5. TEM image of GA-SiO$_2$, revealing that the graphene-silica walls have a mesoporous structure.
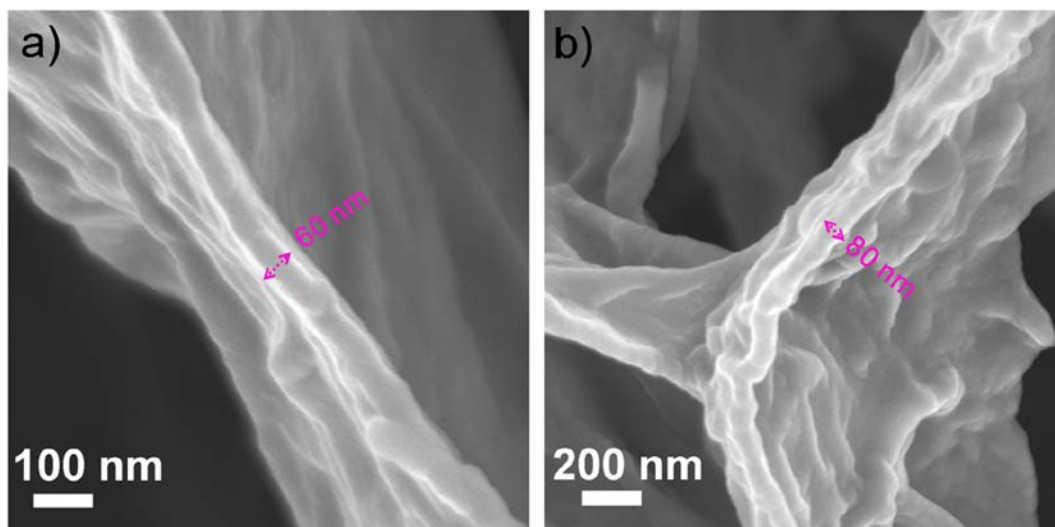
Figure S6. (a,b) Cross-sectional SEM images of sandwich-like silica walls in GA-SiO$_2$, showing the

increased thickness of about 60-80 nm after growth of mesoporous silica on 3D GAs at 45 °C for 12 h.
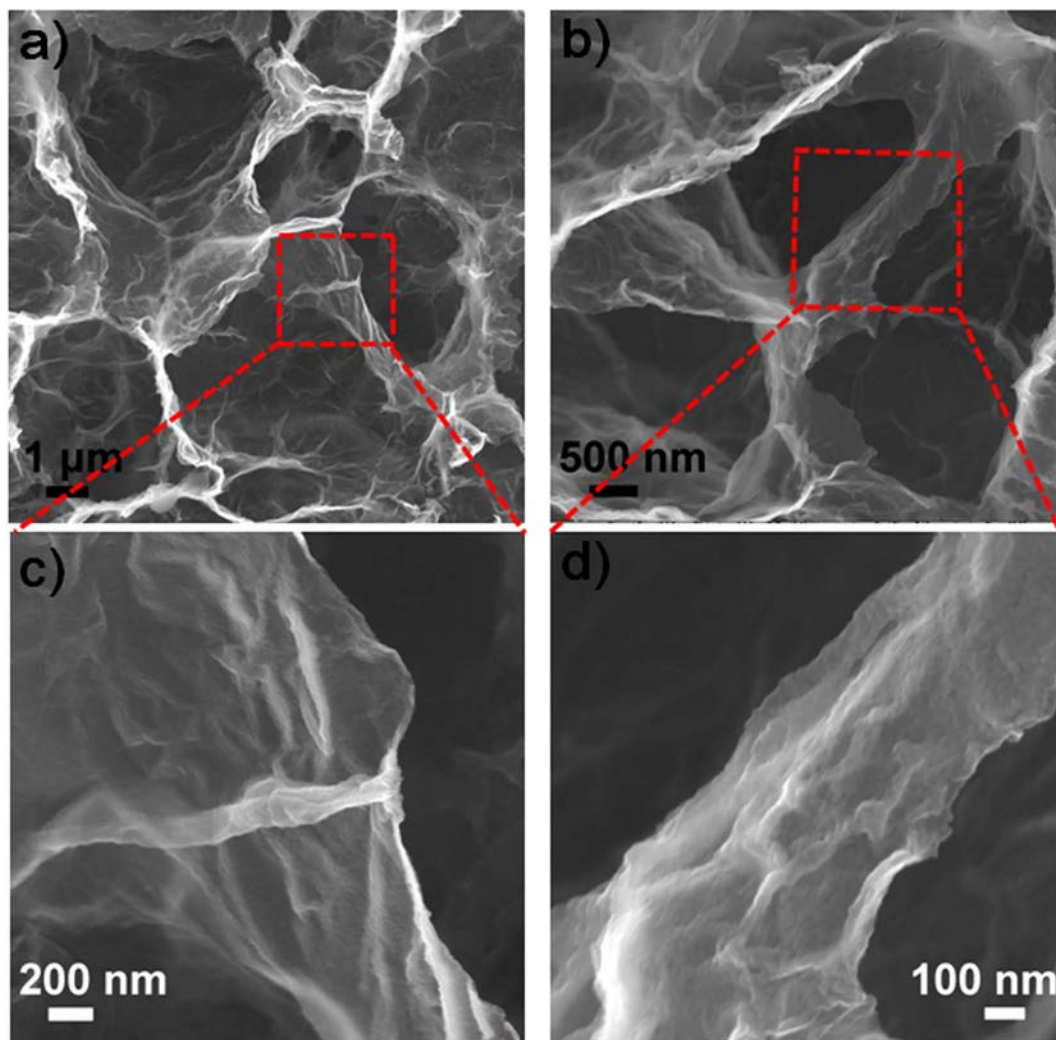
Figure S7. (a,b) SEM images of GA-SiO$_2$ and (c,d) high-magnification SEM images taken from the square regions in (a) and (b) after growth of mesoporous silica on 3D GAs at 45 °C for 6 h. The thickness is less than ~30 nm, as shown in Figure S5a.
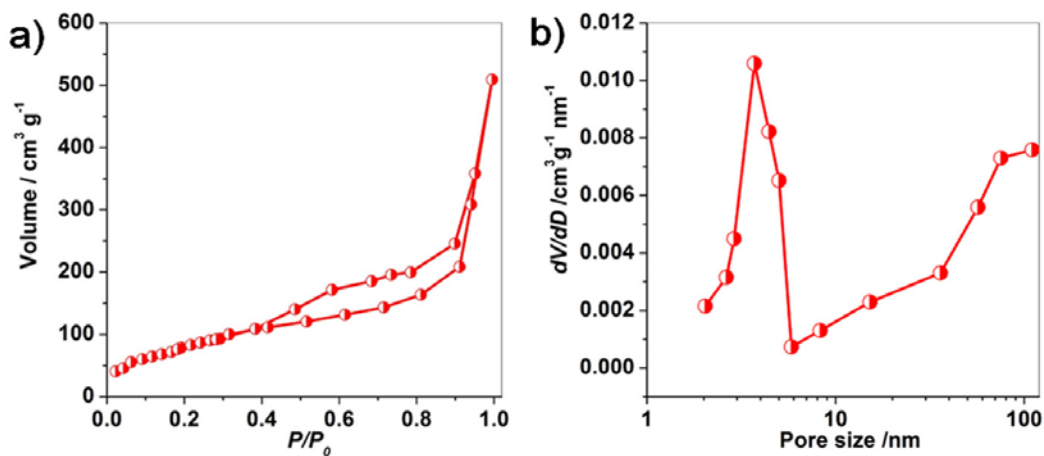
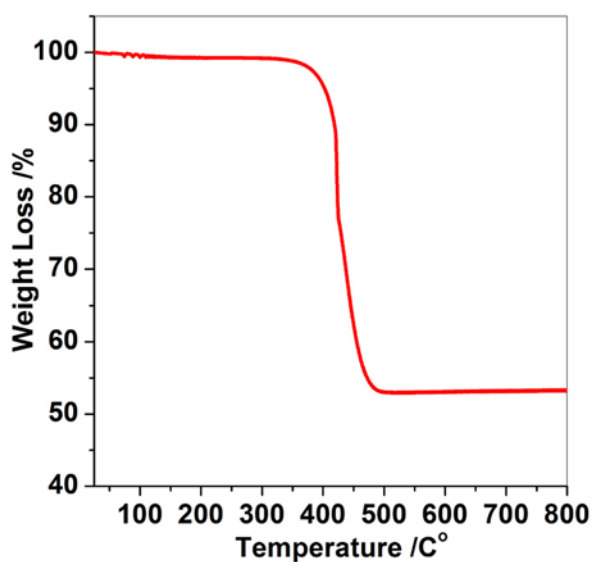**Figure S8**. (a) Nitrogen adsorption and desorption isotherm plot and (b) BJH pore distribution of GA-SiO$_2$.

Figure S9. The thermal stability of GA-SiO$_2$ measured by TG technique from 25 to 800 ^{o}C in air with a heating rate of 10 ^{o}C. The weight loss at around 420~460 ^{o}C can be attributed the combustion of graphene. After ~500 ^{o}C, no loss of weight can be observed. Therefore, the weight percentage of mesoporous SiO$_2$ left in air is ~53%.
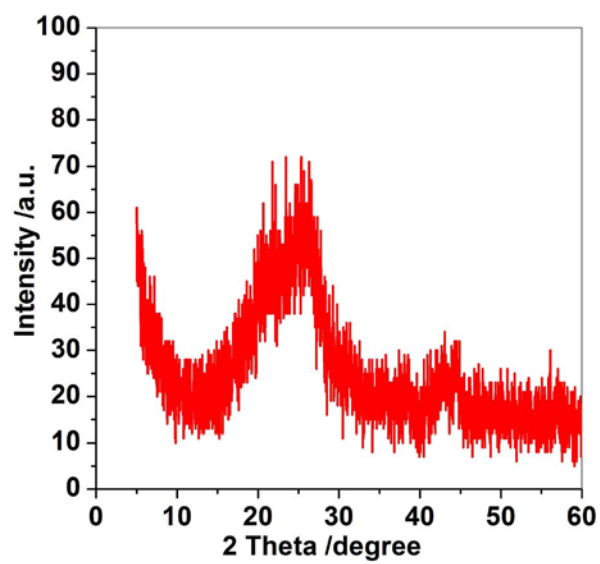
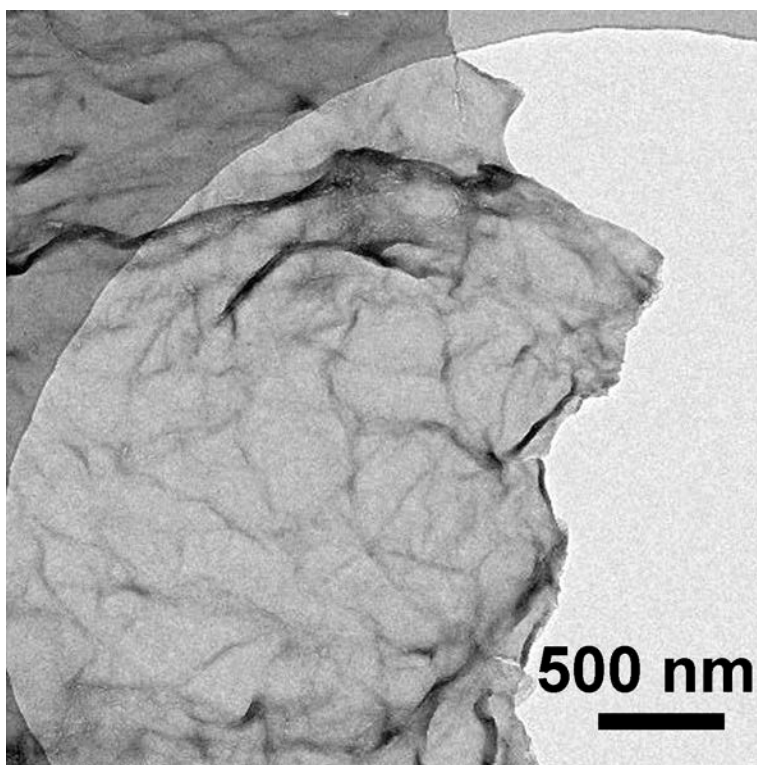**Figure S10**. XRD pattern of GA-MC.
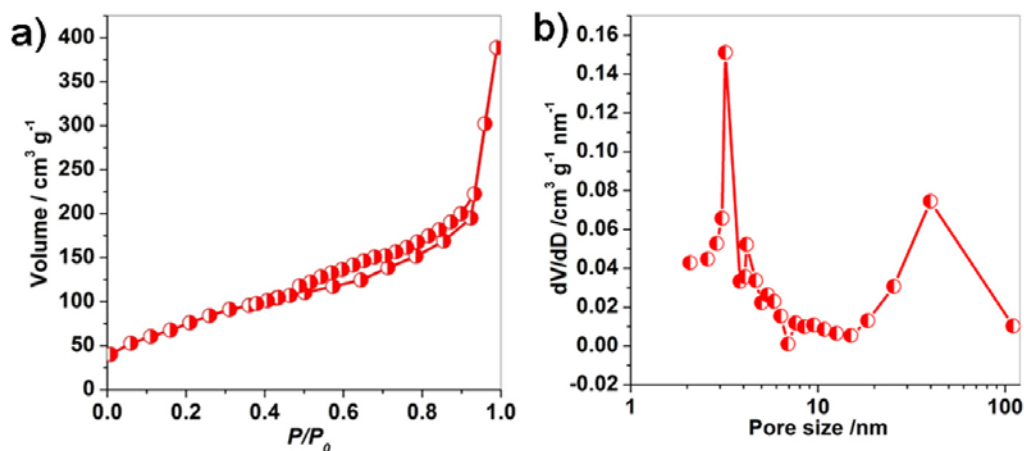

Figure S11. TEM image of GA-MC.

Figure S12. (a) Nitrogen adsorption and desorption isotherm plot and (b) BJH pore distribution of GA-MC. The mesopores in the range of around 2~4 nm are derived from the mesoporous silica in GA-SiO$_2$, while the mesopores with a size of 4~50 nm nm and macropores (50~100 nm) are originated from 3D aerogels (See Figure S6).
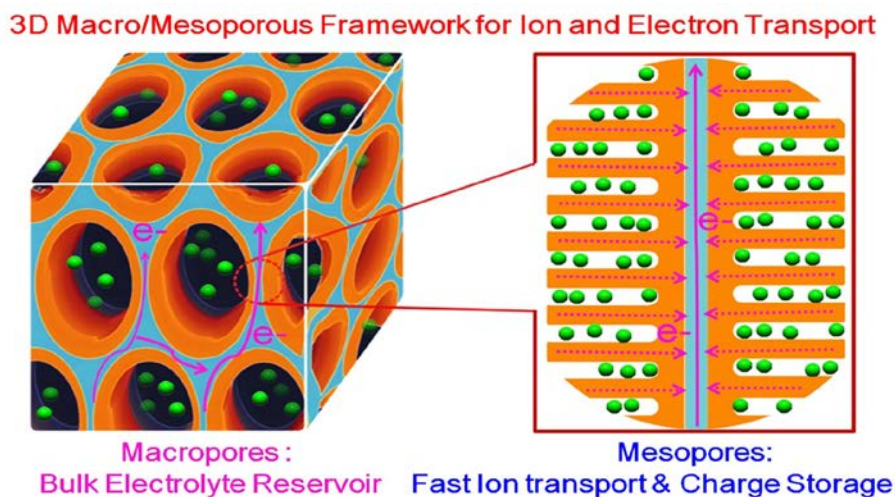

Figure S13. Schematic representation of the roles of macropores and mesopores for ECs in 3D hierarchical porous frameworks of GA-MC.
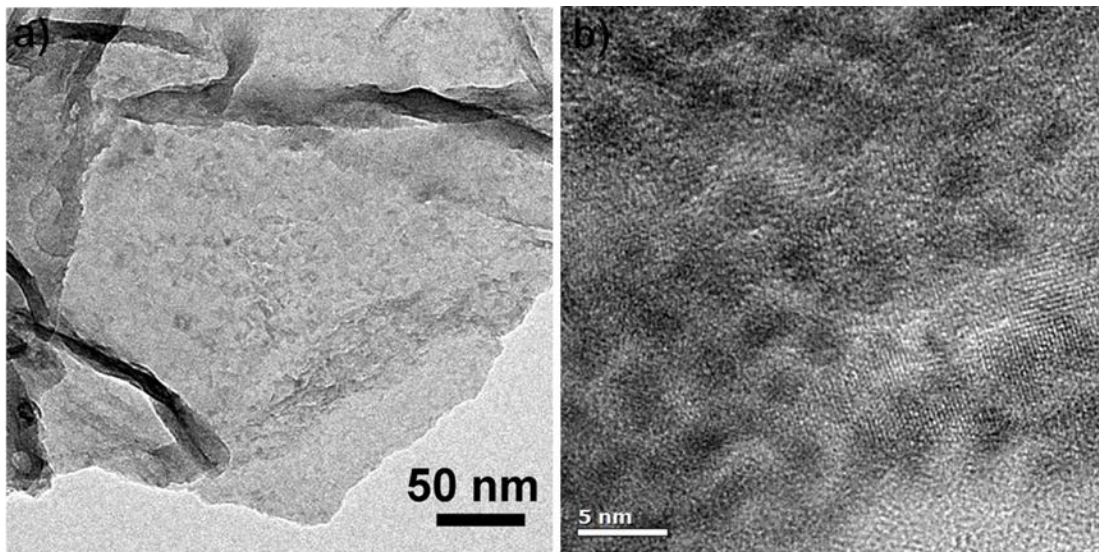
Figure S14. (a) TEM and (b) HRTEM images of GA-Co$_3$O$_4$ hybrids, revealing uniform decoration of ultrasmall Co$_3$O$_4$ nanoparticles with size of 2-3 nm on graphene surface. The black point-like regions in (b) are the Co$_3$O$_4$ nanoparticles, and the interval spacing between Co$_3$O$_4$ nanoparticles on the surface of 3D GAs discloses the nature of mesoporous structure.
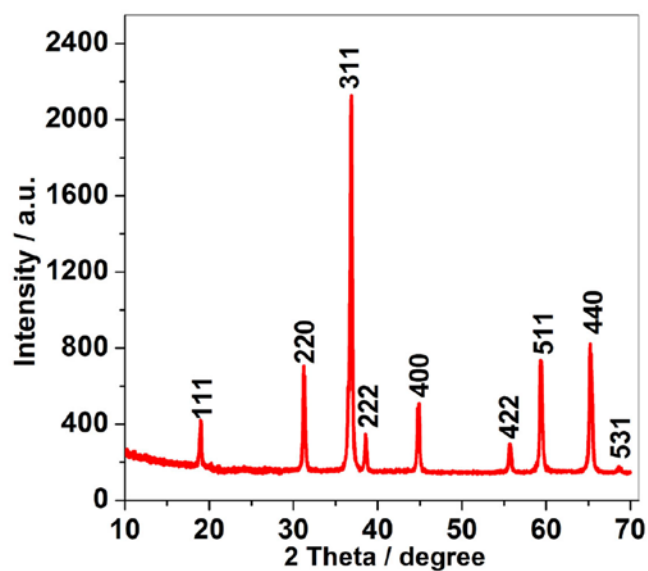
Figure S15. XRD pattern of GA-Co$_3$O$_4$ hybrids reveals the crystalline nature of Co$_3$O$_4$ (JCPDS No. 42-1467).
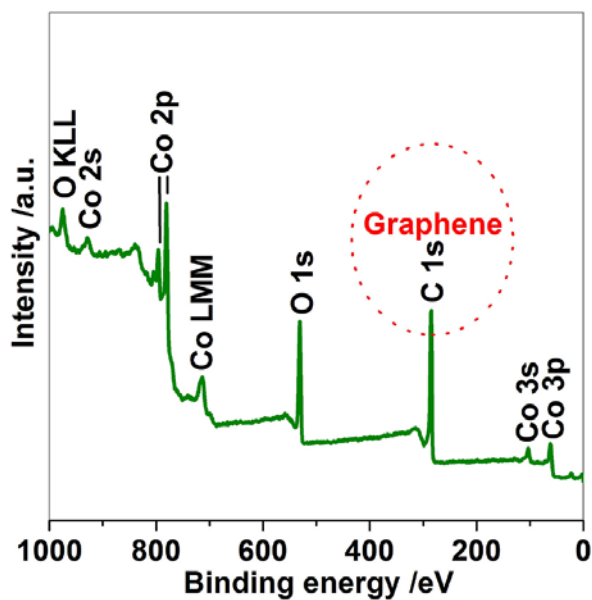

Figure S16. XPS analysis of GA-Co$_3$O$_4$ shows the existence of Co, O, C elements in the hybrids. Red dot ring indicates the carbon element which is derived from graphene.
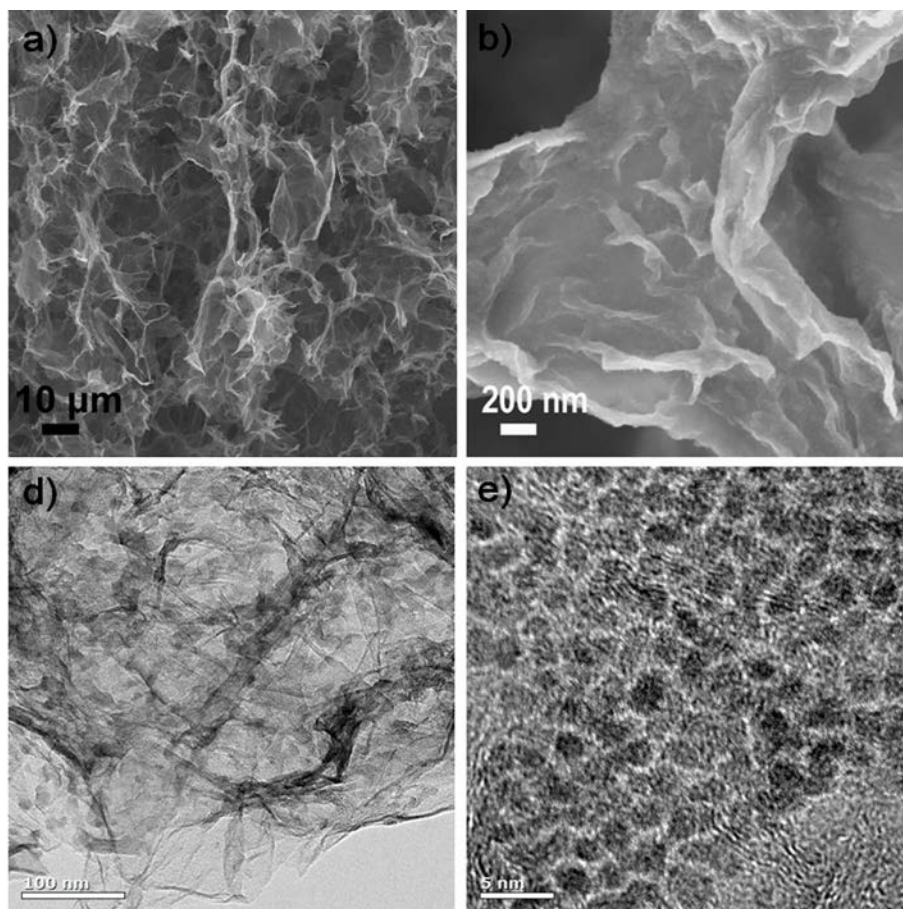
Figure S17. GA-RuO$_2$ hybrids derived from GA-SiO$_2$. (a, b) SEM images of GA-RuO$_2$, revealing the presence of macroporous interconnected frameworks with uniform RuO$_2$ nanoparticles on the graphene surface. (c) TEM and (d) HRTEM images of GA-RuO$_2$ demonstrate the uniform distribution of ultrasmall (2~3 nm) nanoparticles of RuO$_2$ on graphene sheets.
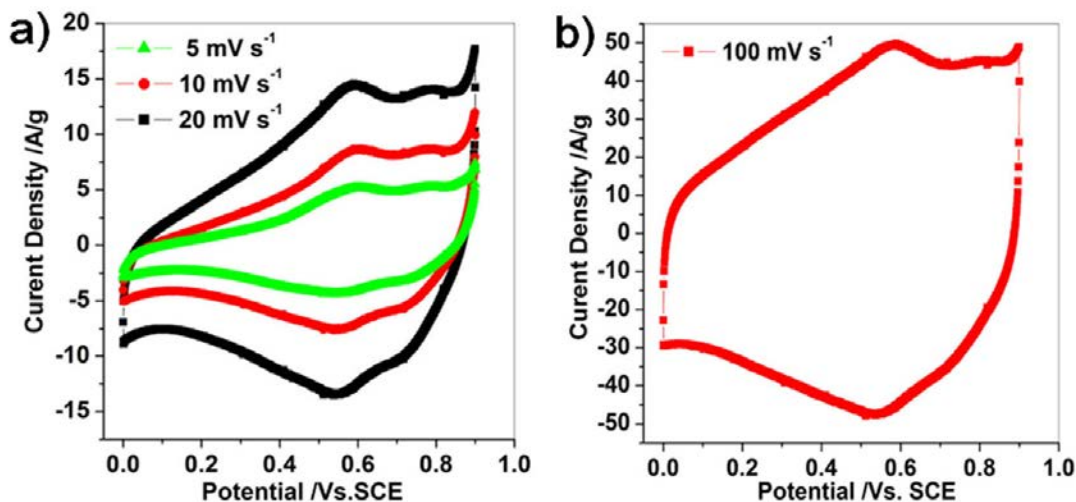
Figure S18. The electrochemical performance of GA-RuO$_2$ (~42 wt% RuO$_2$ in the hybrid) electrode for supercapacitors, measured at different scan rates of (a) 5, 10, 20, and (b) 100 mV s^{-1} in 1 M H$_2$SO$_4$ electrolyte. The CV curves show typical pseudocapactive behavior, and specific capacitance obtained at 5 and 100 mV s^{-1} is ~560 and ~348 F g^{-1}, respectively. The pseudocapactive utilization ($C_{sp}^{RuO_2}$) of RuO$_2$ in hybrid was calculated in the term of the following equation:

$$C_{sp}^{RuO_2} = (C_{sp}^{Hybrid} - C_{sp}^{GAs} \times 58\%)/42\%$$

Where the C_{sp}^{Hybrid} is the specific capacitance of GA-RuO$_2$ (560 F g^{-1}), C_{sp}^{GAs} is the specific capacitance of GAs (173 F g^{-1}). Thus, the specific capacitance of RuO$_2$ is calculated to be ~1090 F g^{-1}.

References

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