

Supporting information

Unravelling pseudocapacitive origin of graphene oxide-based aerogels by comparative insights

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Experiment

1. Materials

GO aqueous solution ($\sim 10 \text{ mg mL}^{-1}$, average size of $2.5 \text{ }\mu\text{m}$) was purchased from <http://www.gaoxitech.com/>, and was further diluted if needed. Deionized water was purchased from the College with resistivity higher than $18 \text{ M}\Omega\cdot\text{cm}$. All the commercial reagents of sulfuric acid (95.0-98.0%, Sinopharm Chemical Reagent Co., Ltd.), sodium sulfate ($\geq 99.0\%$, Shanghai ALADDIN Biochemical Technology Co., Ltd.), sodium bisulfite (99.99% metals basis, Shanghai ALADDIN Biochemical Technology Co., Ltd.), L-ascorbic acid (99.99% metals basis, Shanghai ALADDIN Biochemical Technology Co., Ltd.) and ethanol ($\geq 99.5\%$, Shanghai ALADDIN Biochemical Technology Co., Ltd.) were used without further purification.

2. Preparation of aerogels

For solvothermal strategies, 80 mL portion of 2 mg mL^{-1} GO solvent dispersion was sealed into a 100 mL Teflon-lined autoclave and maintained at $180 \text{ }^\circ\text{C}$ for 12 hours. Then, the autoclave was cooled to the room temperature and the resulting graphene hydrogels were taken out. Finally, the GAs was prepared by freeze-drying for 24 h to remove the solvent. The GAs were labeled as W-GA or A-GA according to the solvent of pure water or water/alcohol (1 : 1 in volume) mixture, respectively.

For reducing strategies, the GAs were prepared by mild chemical

reduction with NaHSO₃ or VC as reductant. Given quantity of reductant (the mass ratio of reductant to GO was 10:1) were added into 30 mL 2 mg mL⁻¹ GO aqueous dispersion. After 30 min ultrasonic treatment to dissolve reductant completely, the mixture was heated at 80 °C for 3 h without stirring. The obtained hydrogel was dialyzed in deionized water for 3 days to remove excessive unreacted reagents and biproducts, and was then freeze-dried for 24 h to obtain the GAs. The GAs were labeled as N-GA or V-GA according to the reductant of NaHSO₃ or VC, respectively.

3. Characterizations

Field-emission scanning electron microscopy (JEOL, Tokyo, Japan) was used to uncover the morphology of the GAs, as well as the energy dispersive spectroscopy mapping images. The specific surface area and pore diameter distribution of the GAs were obtained from nitrogen adsorption-desorption measurement (Micro ASAP2460). Raman spectra were collected using LabRAM Hr800 micro-Raman Spectrometer with 632 nm laser excitation. XRD were carried out by Bruker D8 Advance with Cu Ka radiation diffractometer and wavelength of 0.15406nm. TG analysis was based on TA SDT650. Elemental analysis was experimented by Elementar Vario EL. XPS spectra were collected by Thermo Fisher Scientific Nexsa. FTIR spectra were carried out by Thermo Nicolet iS5.

4. Electrochemical measurements

The electrochemical performance of the GA was tested by cyclic

voltammetry (CV) and galvanostatic charge/discharge (GCD). All the electrochemical measurements were carried out in 0.5 M H₂SO₄ or 0.5 M Na₂SO₄ solution by using a three-electrode system. For working electrode preparation, GA was initially prepared within thickness of ~2-5 mm. A piece of GA was placed between two pieces of stainless steel meshes, followed by roll-in process by electric tablet machine to form a paper-like electrode. A piece of platinum sheet was used as counter electrode and Ag/AgCl (with saturated potassium chloride) as reference electrode. The cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements were carried out on a RST5080F electrochemical workstation (RST instrument, Zhengzhou, China) with the potential range from -0.2 to 0.8 V. The mass specific capacitance (Cs) was calculated due to the following equation: $C_s = It/\Delta U$, while I is the discharging current density, t is the discharging time, ΔU is the real discharging potential.

Table S1. Electronic conductivity of aerogels under pressure of 10 MPa.

Aerogel	Electronic conductivity (S cm ⁻¹)
W-GA	4.6
A-GA	5.1
N-GA	3.3
V-GA	5.7
A-GA-1500	35.8

To fairly evaluate the electronic conductivity, precise condition of initial GO density (2 mg mL⁻¹) and applied testing pressure (10 MPa) has been set the same for all the tested aerogels. As a result, W-GA, A-GA, N-GA, V-GA and A-GA-1500 display ~4.6, 5.1, 3.3, 5.7 and 35.8 S cm⁻¹, respectively. As expected, highly-reduced A-GA-1500 surely have the highest conductivity among these samples. Considering that aerogel should be compressed for electrode, this result indicates that the aerogel conductivity is in order of N-GA < W-GA < A-GA < V-GA, which is the joint result of individual sheet chemistry and compressed aerogel framework.

Supporting figures

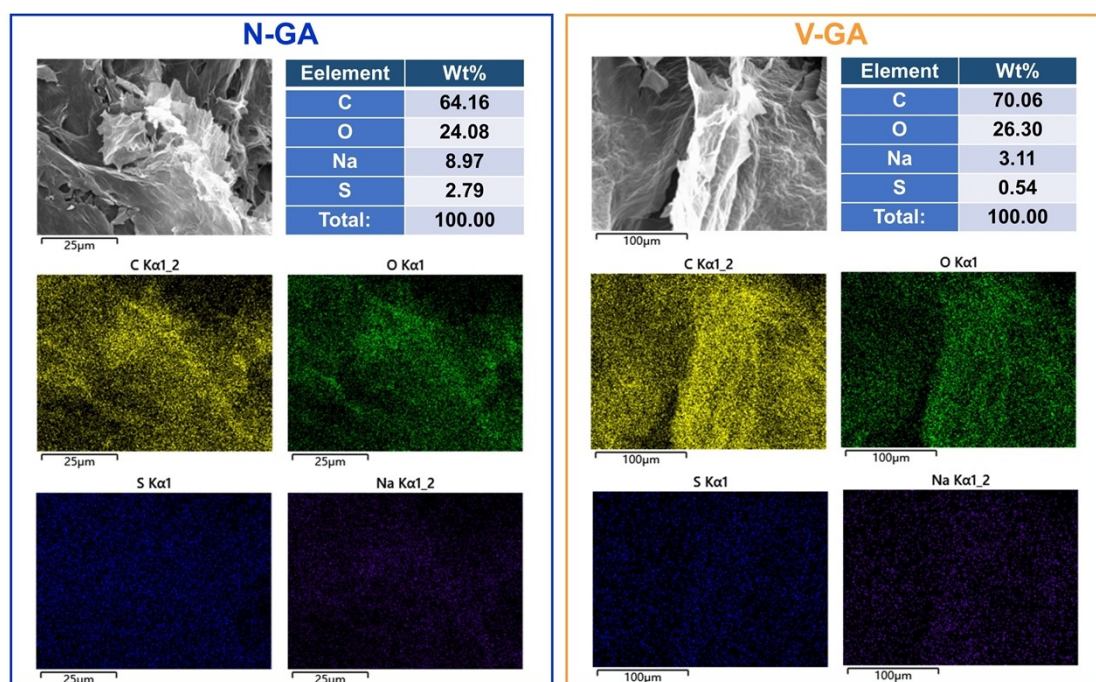


Fig. S1 EDS mapping images and corresponding element proportions of N-GA and V-GA.

EDS mapping images display that there is only 2.79 wt% of S left in N-GA, as well as that other elements (not C and O) take negligible proportion (< 5 wt%) in V-GA.

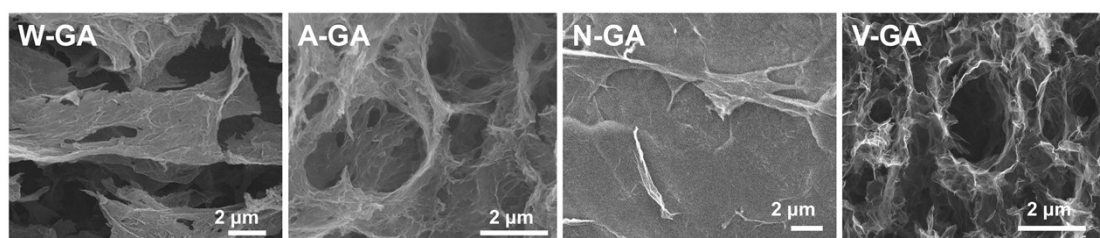


Fig. S2 Magnified SEM images of aerogels.



Fig. S3 Optical images of hydrogels prepared at different temperatures.

For solvothermal treatments, the autogenous pressure developed inside the sealed autoclave contributes to the reduction of GO sheets to graphene sheets (*Carbon*, 2008, **46**, 1994-1998.), also showing that ethanol will induce higher graphitization degree for GO than neat water when temperature raise up to 180 °C, which is in consistent with the sp^2 and sp^3 deconvolutions of C 1s in this work. NaHSO₃ as a weak reductant ($\varphi^\ominus \text{SO}_4^{2-}/\text{SO}_3^{2-} = 0.17$ V, in acid) has been used to establish interlayer connection by partially restore conjugated structure of adjacent GO sheets (*Chem. Eng. J.*, 2017, **327**, 142-149.), as well as its well-known ability to trigger addition reaction on carbonyl groups. For VC which is also a kind of weak oxidant ($\varphi^\ominus \text{C}_6\text{H}_6\text{O}_6/\text{C}_6\text{H}_8\text{O}_6 = 0.18$ V), it can release two active protons and change into dehydroascorbic acid (*Chem. Commun.*, 2010, **46**, 1112-1114.), leading to hydrogenation of hydroxyl and epoxide groups of GO for mild reduction.

For solvothermal treatments, reaction time of 1 and 6 hours have been used to find out the influence on the preparation. W-GH and A-GH both form irregular-shaped hydrogels after 1-hour reactions, while the residue on the walls of inner containers indicates that more GO sheets are combined into A-GH than in W-GH, illustrating that the mixture of ethanol/water is more reducible than neat water when under pressure. Longer-time reactions lead to increasing shrunk of W-GH and A-GH into regular cylinder shape, while 12-hour products have slight silver luster in comparison with black surfaces of 6-hour products. These results ensure that solvothermal reactions should be conducted for 12 hours.

For chemical reductions, we have conducted similar preparation method within reaction time of 1 and 2 hours. In N-GH, the color change of 1- and 2- hour products (from brown to black) indicates the reducing process, but they can not maintain solid state in this period. Only 3-hour reducing can result in shrunk of GO sheets into irregular hydrogels for N-GH. In V-GH, just 1-hour reducing can solidify the hydrogel, and longer-time reducing lead to more regular shape. To note, the change of solvent of V-GH (from colorless to yellow) confirm the oxidization of VC and thus reduction of GO after 3-hour reactions. These results ensure that chemical reductions should be conducted for 3 hours.

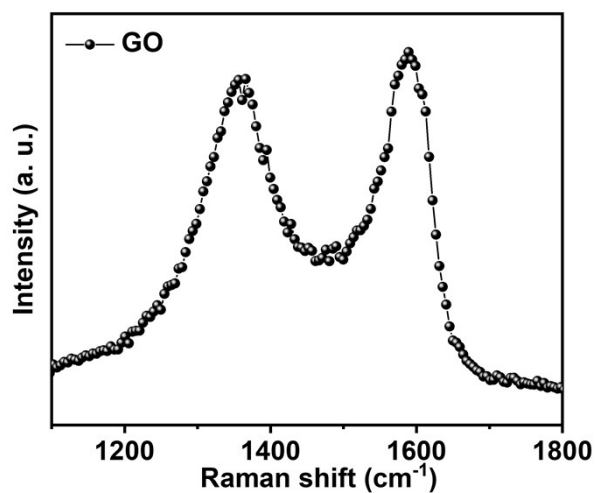


Fig. S4 Raman spectrum of GO.

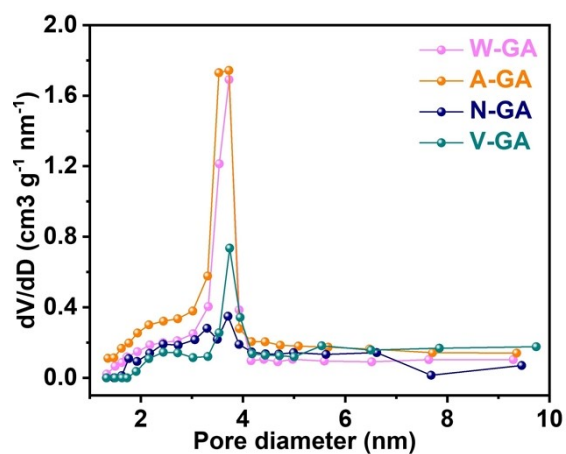


Fig. S5 Pore distribution of aerogels by BJH method.

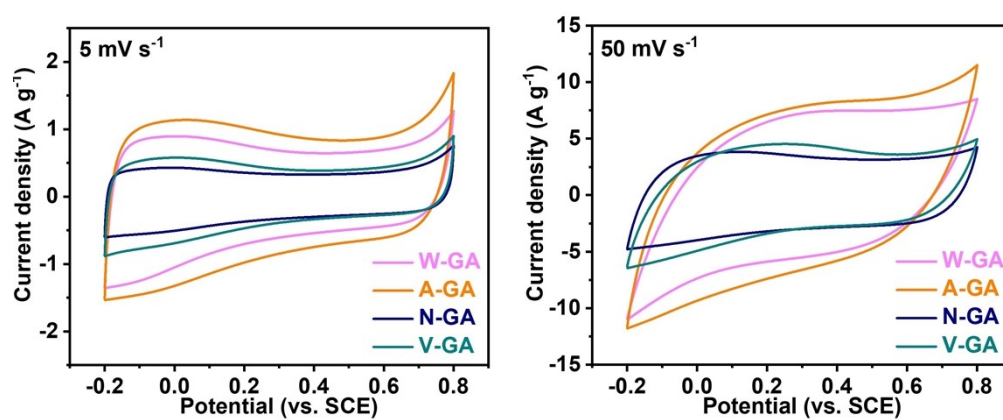


Fig. S6 CV curves of aerogels in Na_2SO_4 electrolyte at scan rate of 5 and 50 mV s^{-1} .

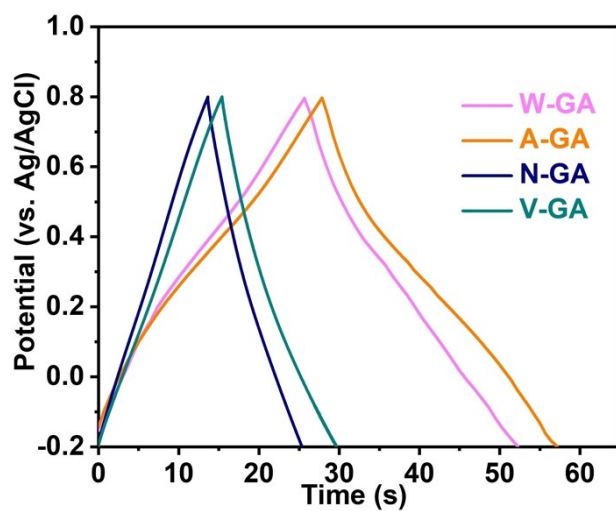


Fig. S7 GCD curves of aerogels under current density of 10 A g^{-1} in H_2SO_4 electrolyte.

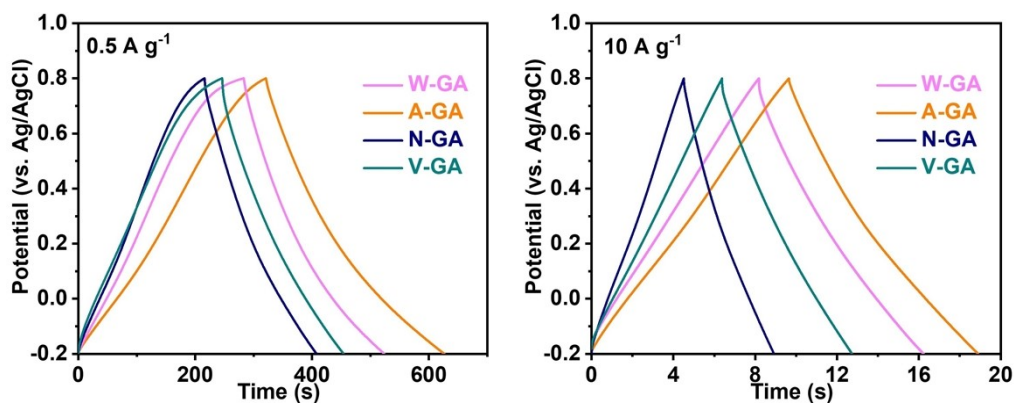


Fig. S8 GCD curves of aerogels under current density of 0.5 and 10 A g^{-1} in Na_2SO_4 electrolyte.

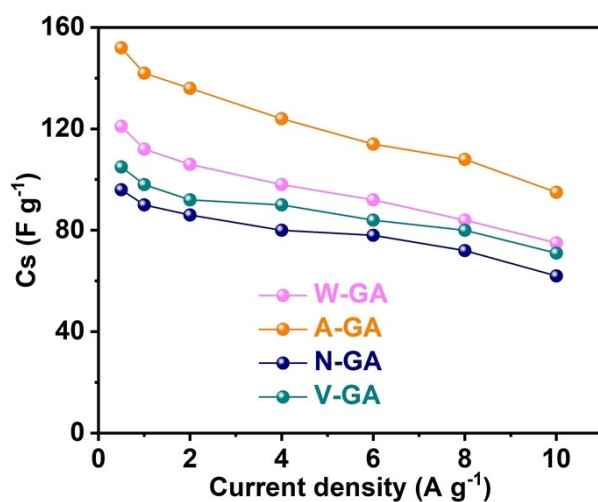


Fig. S9 Rate capabilities of aerogels in Na₂SO₄ electrolyte.

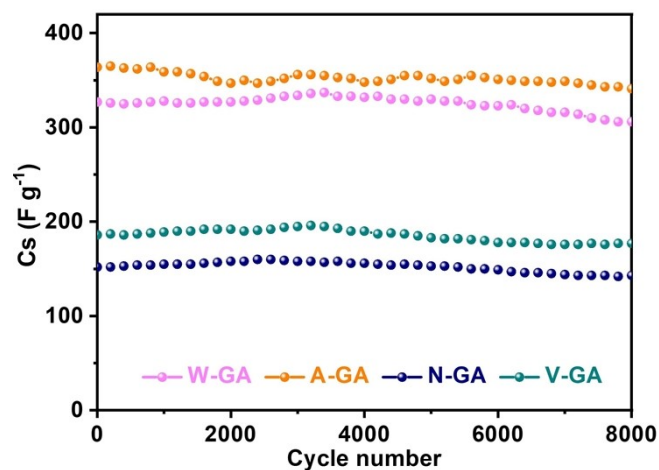


Fig. S10 Cycling stability of aerogels in H₂SO₄ electrolyte.

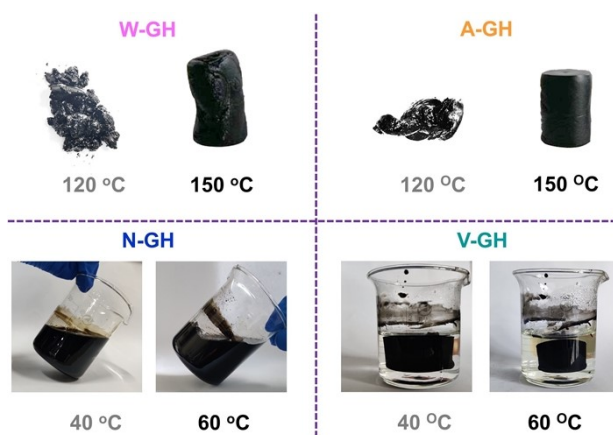


Fig. S11 Optical images of hydrogels prepared at different temperatures.

For solvothermal treatments of 12 hours, W-GH and A-GH within 120 °C can not maintain uniform state after solvothermal reactions and form into debris, as well as that W-GH and A-GH within 150 °C are irregular-shaped. For chemical reductions in aqueous solutions, lower temperature (40°C and 60 °C) results in viscous slurry (N-GH) or fragile bulk (V-GH) when under same staying time of 3 hours. Therefore, high temperature (180 °C for solvothermal treatments, 80 °C for chemical reductions) is need for aerogel preparation from GO solution. To note, it is dangerous to set high solvothermal temperature (>200 °C) due to the unstable polymer inner container of our autoclaves, and the boiling point of water (~100 °C) limits the highest temperature of chemical reductions.

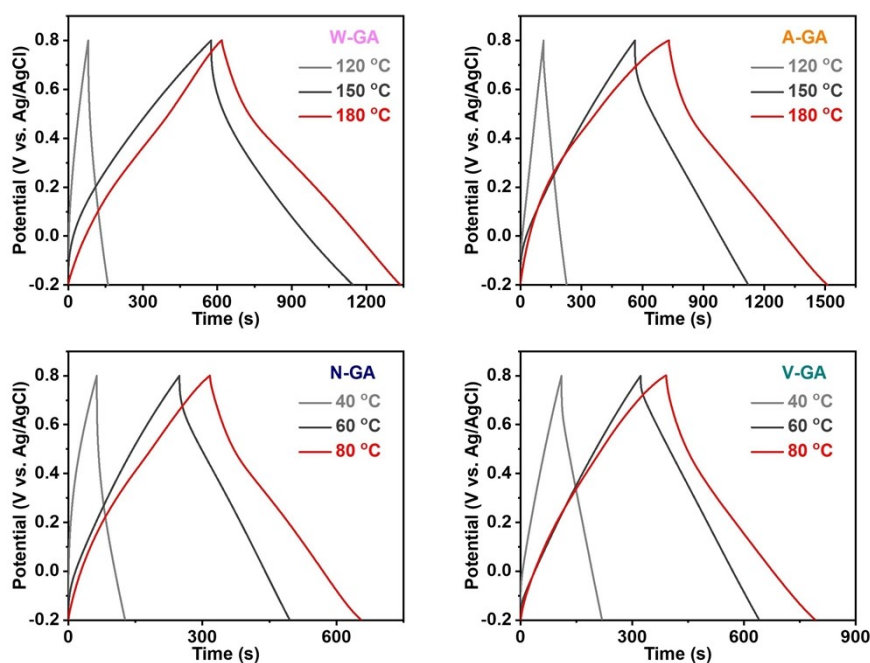


Fig. S12 GCD curves of aerogel electrodes prepared from hydrogels of different temperatures at current density of 0.5 A g⁻¹ in H₂SO₄.

These non-foamlike aerogels have been ground and mixed with conductive carbons and binders to fabricate electrodes. Consequently, samples under low-temperature treatments show unsatisfactory electrochemical performance when compared with high-temperature-prepared aerogel electrodes, partially due to the high IR drop of the low-degree reduced states of GO skeletons by low temperatures.

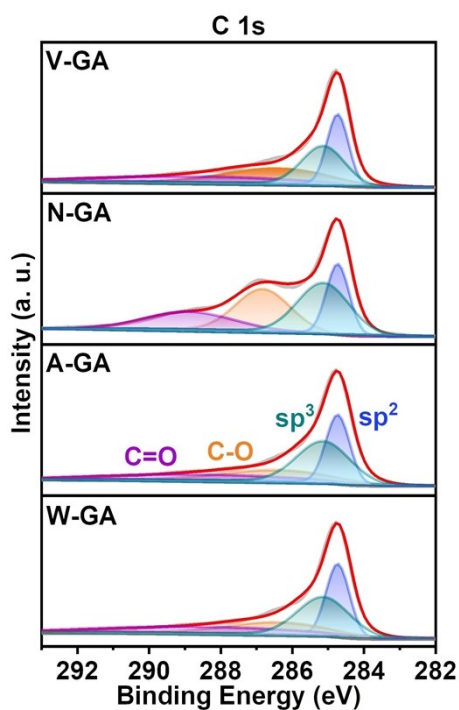


Fig. S13 XPS deconvolutions of C 1s for aerogels.

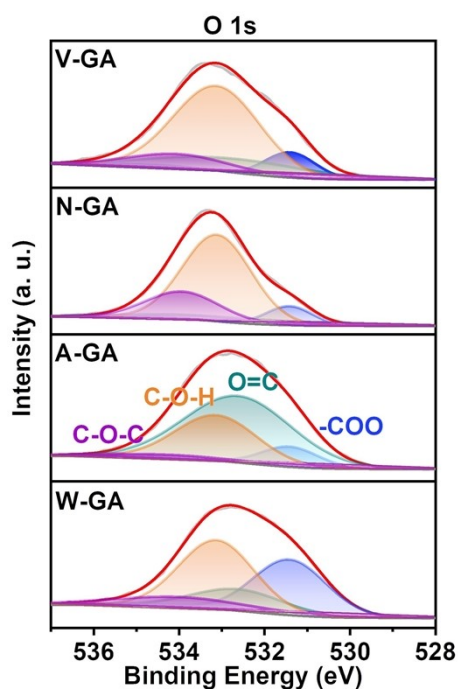


Fig. S14 XPS deconvolutions of O 1s for aerogels.

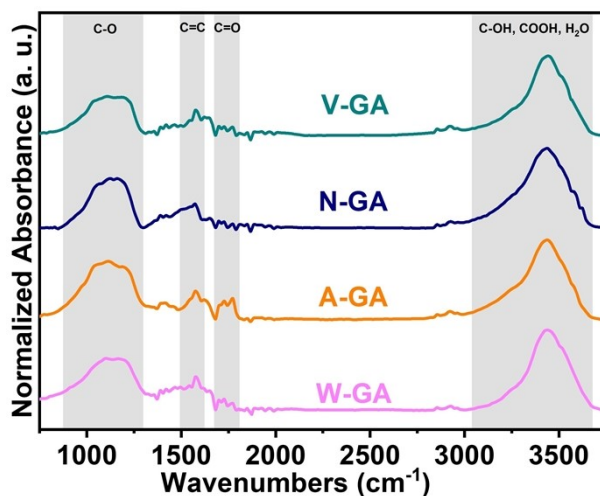


Fig. S15 FT-IR spectra of aerogels.

FTIR spectra of N-GA can not match typical molecular vibration peaks of NaHSO₃ (SDBS No. 11316), validating the absence of NaHSO₃ after repeated washing of N-GA.

Carbonyl (O=C), hydroxyl (C-O-H), carboxyl (-COO) and epoxide (C-O-C) all remain in these aerogels. This indicate that the carbon rings are

partially restored under mild reducing strategies of solvothermal treatments and chemical reductions. Specifically, the relative intensities of carbonyl groups of different samples have similar regularity of the XPS spectra, displaying that A-GA has the strongest signal of carbonyl groups among tested aerogels.