Supporting Information for

Viable Synthesis of Highly Compressible, Ultra-Light Graphene-Carbon Nanotube Composite Aerogel without Additional Reductant and its Applications for Strain-Sensitivity

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The Schematic of Synthesis Process

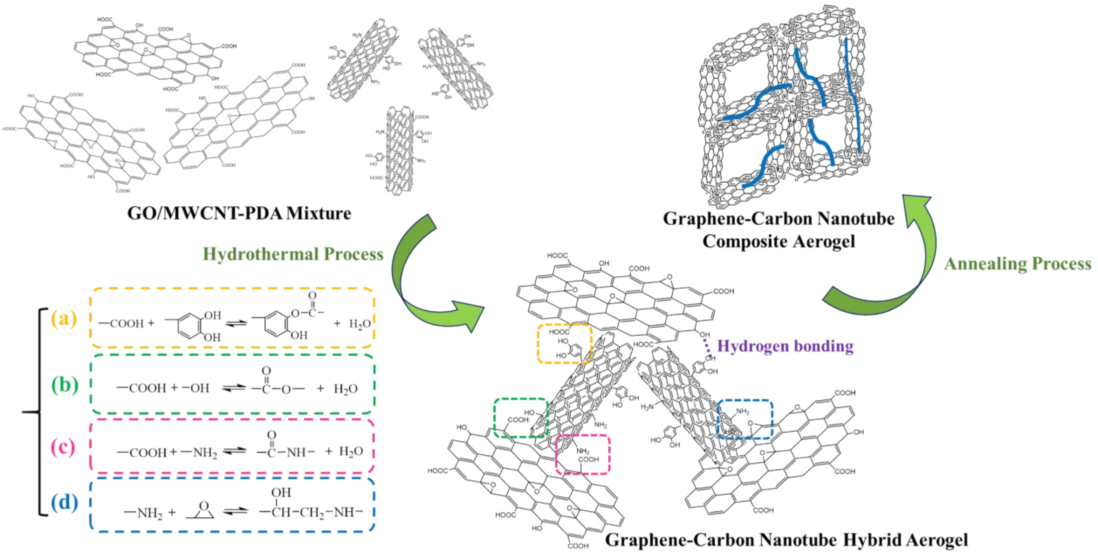

Fig. S1. Schematic illustration of the synthesis process of as-prepared graphene-carbon nanotube composite aerogel.

Experimental Details

Materials.

The commercial carboxyl-functionalized MWCNT (MWCNT-COOH) (purity, ≥95%; diameter, 10-20 nm) were supplied by Chengdu Organic Chemical Co. Ltd., Chinese Academy of Sciences, China.

Nature graphite flakes with an average diameter of 500 μm were purchased from Xianfeng Nanomaterials Technology Co. Ltd., Nanjing, China. Potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), concentrated sulfuric acid (H_2SO_4, 98 %) and hydrogen peroxide (H_2O_2, 35 %) were obtained from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Dopamine hydrochloride and tri (hydroxymethyl) aminomethane (Tris) were purchased from Sigma-Aldrich Co.Ltd., USA. All reactants were analytical purity and used as received. Deionized water was used throughout the experiments.

Preparation of Polydopamine Modified Carbon Nanotube and Graphene Oxide.

Polydopamine modified carbon nanotube (MWCNT-PDA) was prepared according to the method reported in our previous study[1]. 100 mg MWCNT-COOH was dispersed into 200 mL deionized water by using 400 W ultrasonication with a digital sonifier (JY-99 II, Ningbo Xinzhi Biotechnology Co., Ltd., China) for 20 min. To avoid overheating, the ultrasonication was set to work for 10 s at intervals of 15 s. After the treatment, 200 mg dopamine hydrochloride was added to the suspension under stirring. The pH value of the mixture was adjusted to 8.5 by using Tris-HCl buffer solution. The suspension was continuously stirred at 25 °C for 48 h, and then the resulting MWCNT-PDA was washed several times with deionized water, followed by 3000 rpm centrifugation. Later the dialysis treatment was used to completely remove the free polydopamine (PDA) and finally the MWCNT-PDA was obtained after freeze-drying for 24 h. About a 5 nm uniform transition layer was found on the surface of MWCNT-PDA, as shown in HRTEM image (**Fig.S2 (a)**).

Graphene oxide (GO) was prepared based on the modified Hummers method[2]. Typically, 5 g of nature graphite flakes and 2.5 g of $NaNO_3$ were mixed with 110 mL of H_2SO_4 (98 %) in a 500 mL breaker. The mixture was stirred for 0.5 h in an ice bath. Then 15 g $KMnO_4$ was carefully added into the suspension under moderate stirring. The mixture was first kept at 0 °C ~5 °C, and then the temperature was increased to 35 °C followed by continuous stirring for 12 h. After that, 200 mL deionized water was slowly added into the mixture. The diluted suspension was stirred for another 30 min before 25 mL H_2O_2 (35 %) was added to the mixture. Next, the mixture solution was treated under ultrasonication for 3 h and dialyzed for several days until the pH value of the solution became neutral. Eventually, GO dispersion solution (**Fig.S2 (b)**) was obtained after centrifugation as 3000 rpm. The concentration of GO in the suspension was determined by freeze-drying small amount of suspension and then weighing the dried sample.

Preparation of 3D GO/MWCNT-PDA Composite Aerogel.

The GO/MWCNT-PDA **composite** aerogel (**GCPCA**) was synthesized by hydrothermal reduction of a mixture of the GO and MWCNT-PDA, followed by freeze-drying and annealing. **Fig.S2 (c)** illustrates the method for the fabrication of three-dimensional **GCPCA**. First, GO and MWCNT-PDA with a mass ratio of 3:1 were dissolved in deionized water, and the concentration of GO was 2 mg/mL. The mixture was then sonicated for 30 min before it was held in an oil bath at 90 °C for 12 h. The ultra-light highly compressible composite aerogel was formed after the freeze-drying process for 24 h and subsequently annealing at 750 °C in a carbonized oven under N_2 atmosphere for 3 h. The PDA layer on the surface of MWCNT-PDA partly pyrolyzed after annealing process. The obtained 3D **GCPCA** was ultra-light, highly compressible and conductive.

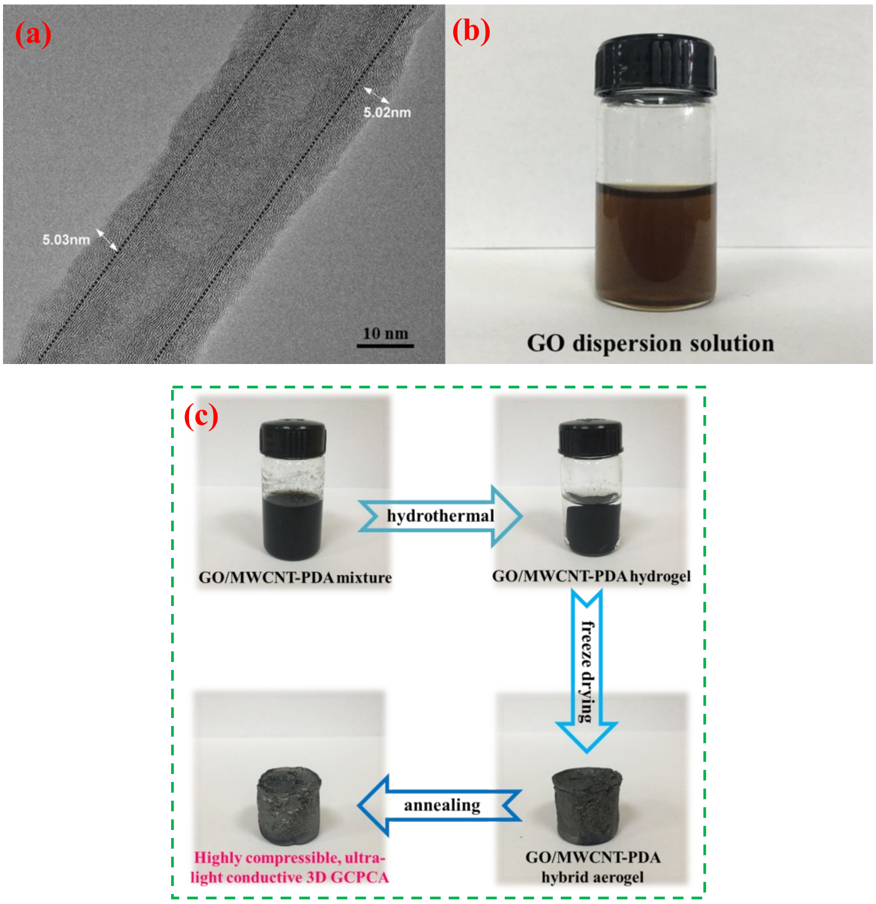

Fig. S2. The microstructure of the as-prepared MWCNT-PDA (a), the appearance of GO dispersion solution (b), and the schematic illustration for the synthesis of 3D **GCPCA** (c).

Characterizations.

The initial density of GCPCA samples were calculated as the final mass of the samples divided by their corresponding volumes, where the density of the air occupied in the pores was also included[3]. The morphology and microstructure of as-prepared **GCPCA**s were characterized by using scanning electron microscope (SEM, Hitachi S-4700, Japan) **equipped with an energy dispersive X-ray spectroscopy (EDS)** and high resolution transmission electron microscopy (HRTEM, Tecnai G2 F30 S, Japan). **GCPCAs were measured by adsorption and desorption of nitrogen using a Brunauer–Emmett–Teller (BET) surface area measurement system (JW-BK200C, China). The specific surface area and pore size distribution were then determined from the measured isotherms at 77 K using Barrett−Joyner−Halenda (BJH) methods. High resolution X-ray**

photoelectron spectroscopy (XPS) was performed to analyze the chemical composition of GCPCAs on an ESCALAB 250 (Thermo Fisher Scientific, USA) using monochromatic Al Kα X-ray source at a constant analyzer. Raman spectroscopy was performed using a Senterra R200-L (Bruker Optics, Germany) with an excitation wavelength of 514 nm. Ten percent of the maximum power of the laser was employed during general scanning. Dynamic compression properties of **GCPCA** samples were measured at 25 °C using Goodrich Flexometer (GABOMETER 2000, Germany). The testing frequency was 1 Hz for all compressive strains. **Electrical conductivity of the GCPCA samples was measured by using two-probe method under mechanical deformation. During the measurement, two pieces of nickel foam serving as electrodes were connected to aerogels and digital multimeters (DMM, Agilent 34401A, USA). It is notable that the electrical resistance of nickel foam was excluded from the experimental result. To ensure the accuracy of the data, three specimens were tested for every case and the average values were taken.**

Supporting Results

Fig. S3 shows the dispersion stability behavior of different functionalized MWCNT (pristine MWCNT, MWCNT-COOH, ethylenediamine-functionalized MWCNT (MWCNT-NH_2)**[4]** and MWCNT-PDA) in deionized water before mixing with GO dispersion solution. It was clear to see that MWCNT-PDA showed outstanding water-solubility and dispersion stability in deionized water compared to the others. The abundant catechol groups on the sidewall of MWCNT-PDA can significantly enhance the hydrophilic of MWCNTs. And it can promote the dispersity of MWCNT-PDA in GO dispersion solution, which was an important prerequisite for realizing performance improvement of the resulting **GCPCA**.

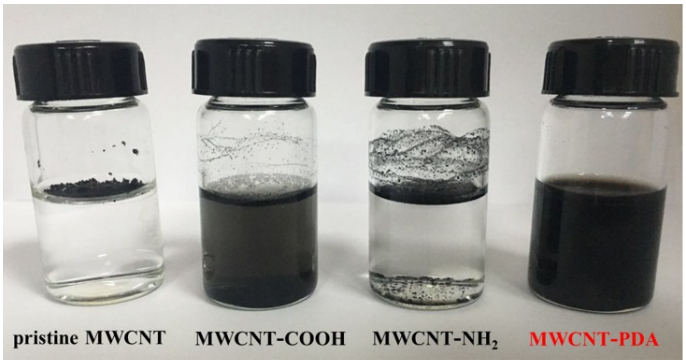

Fig. S3. The water-solubility and dispersion stability of different functionalized MWCNTs (pristine MWCNT, MWCNT-COOH, MWCNT-NH_2 and MWCNT-PDA) in deionized water (1 mg/mL) before mixing with GO dispersion solution.

Table S1 Comparison of the initial density between different GO/CNT aerogels

Samples	**GO** (mg/mL)	**GO/CNT** (weight ratio)	**Reducing or cross-linking agent**	**Reaction temperature and times**	**Thermal annealing temperature** (°C)	**Density** (mg/cm^3)
CNT/graphene aerogels[5]	2	5:1-5:4	PVA	/	1050	5-8
GO/CNTs hybrid sponge[6]	3.2	4:1	/	/	800	2.6
Gr/CNT aerogel[7]	2	3:1	/	180 °C for 12 h	/	23
graphene–CNT aerogels[8]	2.5	3:1	PVP, EDA	120 °C for 12 h	/	12.8
graphene/CNT aerogels[9]	2	3:1	/	180 °C for 12 h	/	2.8
graphene/CNT aerogel[10]	2	1:1	Vc	50 °C for 12 h	/	54.4
GO/MWCNT-PDA composite aerogel (This work)	2	3:1	/	90 °C for 12 h	750	**2.5**

Table S1 gives the initial density of some GO/CNT compressible materials. It can be seen that the **GCPCA** obtained in this work exhibited an ultra-light material characteristic compared to GO/CNT compressible materials reported previously.

The more detailed porous properties and specific surface area (SSA) of as-prepared GCPCA

were further confirmed by nitrogen adsorption–desorption measurements. The adsorption–desorption isotherms of GCPCA exhibited a typical hysteresis loop, which suggested a great number of mesopores in the framework of the composite aerogel (Fig. S4a). By fitting the isotherm curves with the BET model, the specific surface area of GCPCA was calculated to be 133 m^2·g^{-1}. The distribution curve of the pore size measured by the BJH method showed that most of the pore volumes of GCPCA were within a diameter of 2–55 nm (Fig. S4b). Besides, the total pore volume was determined to be 0.568 cm^3·g^{-1}.

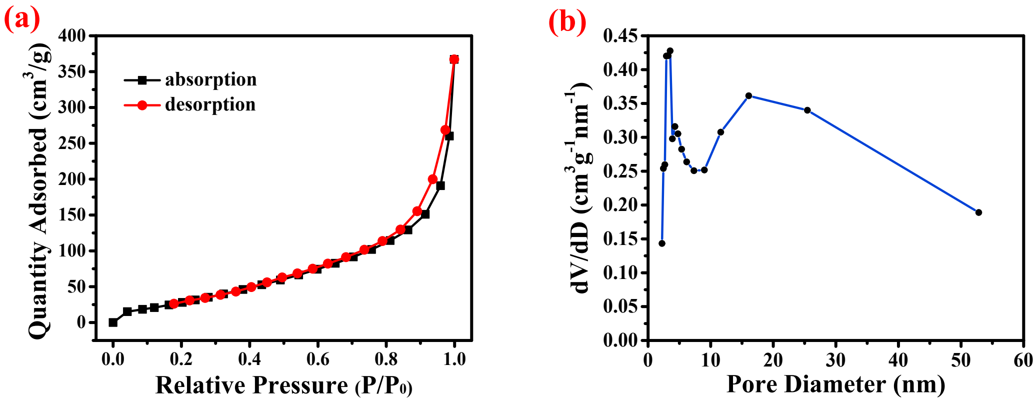

Fig. S4. Typical nitrogen adsorption/desorption isotherm (a) and BJH pore diameter distribution (b) of as-prepared GCPCA.

The elemental mappings of GCPCA samples presented uniform distribution of C, O, N elements in the selected region, which was consistent with the EDS spectrum in Fig. S5 (a). To further elaborate on the order/disorder degree in graphite structure of the aerogel network, Raman spectra of GCPCA before and after annealing treatment was shown in Fig. S5 (b). The G band at 1607 cm^{-1} is associated with the sp^2 carbon atoms in the hexagonal carbon framework, while the D band at 1344 cm^{-1} corresponds to the sp^3-hybridized carbon atoms at the edges or defects on the graphene basal plane. A slight decrease of I_D/I_G ratio from 1.25 to 1.19 suggested

a reduction of defects and disorder structure because both GO and MWCNT-COOH were reduced to rGO and MWCNT during pyrolysis process. XPS was used to analyze the chemical composition and atomic ratio of each element in the structure of GCPCA. After pyrolysis, a significant decrease in the O and N contents was observed (Table S2) due to chemical reduction and graphitization, which was in good agreement with Raman analysis results. The high resolution N 1s spectra as shown in Fig. S5 (c)-(d) displayed three peaks at 398.8 eV, 399.7 eV and 401.3 eV relating to pyridinic-N, pyrrolic-N and graphitic-N, respectively. And the adsorption peak belonging to pyridinic-N became weakened and the peak intensity of graphitic-N was increased after thermal annealing process. From these structural transformations, we can conclude that GCPCA exhibited a microstructure analogous to nitrogen-doped multilayer graphitic planes [11, 12].

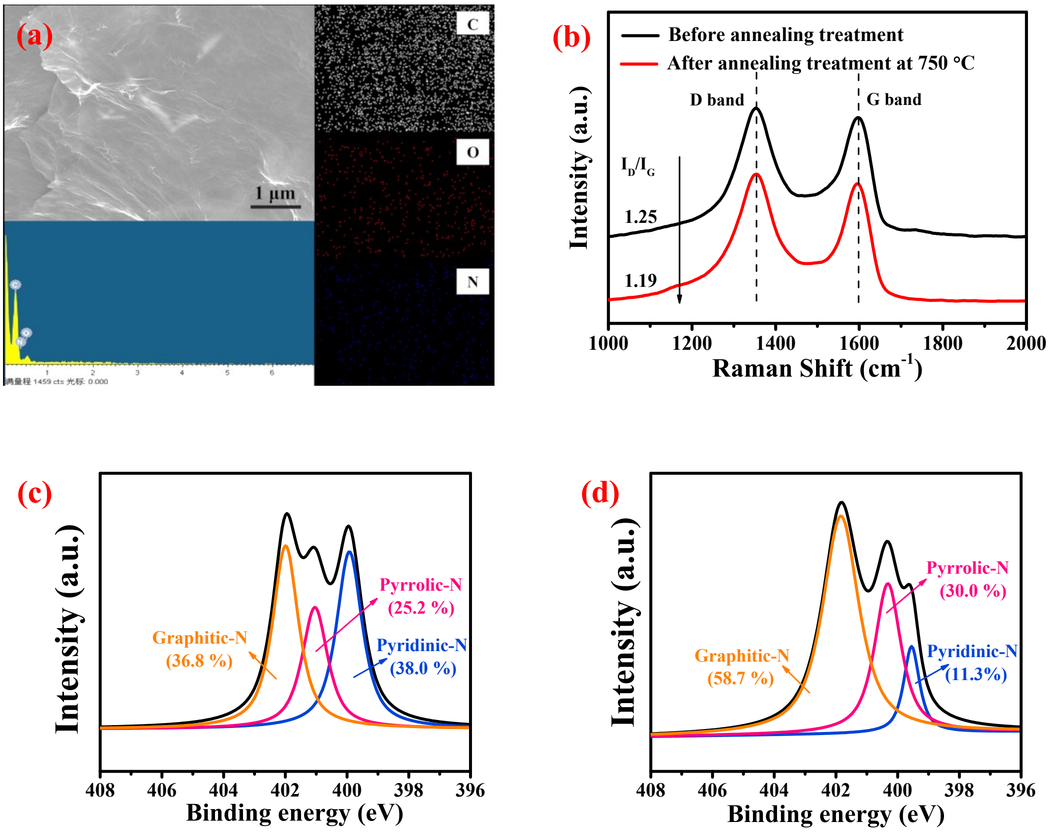

Fig. S4. (a) SEM image of GCPCA and the corresponding elemental mappings of C, O, N as well as EDS spectrum; (b) Raman spectra of GCPCA before and after annealing treatment at 750 °C; The deconvolution curves of N 1s X-ray photoelectron spectra obtained for the nitrogen-doped GCPCA before (c) and after (d) annealing treatment at 750 °C.

Table S2 Surface element analysis of as-prepared GCPCA before and after annealing treatment

GCPCA Samples	Element content (%)			Atomic ratio	
	C	O	N	O/C	N/C
Before annealing treatment	72.73	24.03	3.24	0.33	0.04
After annealing treatment	90.21	8.46	1.33	0.09	0.01

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