

## Supporting Information for

### **Green Synthesis of Carbon Nanotube/Graphene Hybrid Aerogels and Their Use as Versatile Agents for Water Purification**

By *Zhuyin Sui, Qinghan Meng, Xuotong Zhang\**, Rui Ma and Bing Cao

School of Materials Science & Engineering, Beijing Institute of Technology, Beijing, 100081, P. R. China

College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing, 100029, P. R. China

## **Experimental**

**Materials:** All chemicals including Vitamin C, various dyes and metal salts were purchased from Beijing Chemical Reagents Company with their purity being of analytical grade. All chemicals were used without further purification. Graphene oxide (GO) [1], pristine (MWCNT) [2] and acid treated (c-MWCNT) [3] multi-wall carbon nanotubes used in this case were synthesized and reported in our previous studies.

**Synthesis of graphene/MWCNT hybrid hydrogel:** In a typical procedure, 40 mg MWCNTs were added into 10 mL deionized water, and the resulting mixture was sonicated for about 3 hours, and then 10 mL GO suspension (4 mg/mL) were added into the above mixture and sonicated for another 4 hours to form a uniform GO/MWCNT dispersion. After that, a few droplets of 0.1 M HCl and 200 mg VC were added into the above dispersion and sonicated for a short while to dissolve VC completely. Finally, the resultant mixture was left without stirring for 12 hours at 50 °C to form graphene/MWCNT hybrid hydrogel.

**Synthesis of graphene/c-MWCNT hybrid hydrogel:** In a typical procedure, 40 mg c-MWCNTs were added into 10 mL deionized water, and the resulting mixture was sonicated for 2 hours to form a dispersion, and then 10 mL GO (4 mg/mL) suspension was added into the c-MWCNTs dispersion and sonicated 0.5 hours to form a uniform GO/c-MWCNT

dispersion. After that, a few droplets of 0.1 M HCl and 200 mg VC were added into above dispersion and sonicated for a short while to dissolve VC completely. Finally, the resulting mixture was left without stirring for 12 hours at 50 °C to form graphene/c-MWCNT hybrid hydrogel.

**Supercritical drying of the as-synthesized hydrogels:** The obtained graphene/MWCNT and graphene/c-MWCNT hybrid hydrogels were first purified in a large amount of distilled water for at least a week to wash out low molecular weight components of the system including excess VC and its oxidized product dehydroascorbic acid. Finally, the purified graphene/MWCNT and graphene/c-MWCNT hydrogels were further turned into alcogel by using alcohol to replace the water within the network of the hydrogels, and then dried with supercritical CO<sub>2</sub> to obtain the corresponding graphene/MWCNT and graphene/c-MWCNT hybrid aerogels.

**Capacitive deionization:** The resulting hybrid aerogels as active substances, carbon black as conductive additive and PTFE as binder, were used to fabricate the working electrode and their percentages in the final electrode were 75%, 20% and 5%, respectively. In order to achieve adhesion among active substance, conductive additive and binder, the mixture was carefully grinded for ca. one hour. Subsequently, ethanol was added dropwise to the mixture to increase the moisture and then the mixture was pressed onto a nickel foam plate with a diameter of 82 mm. The resultant electrodes were allowed to dry at 353 K for 12 hours. The total mass loadings of the graphene/MWCNT aerogel electrode and the graphene/c-MWCNT aerogel electrode were 0.579 g and 0.719 g, respectively. Each electrode had an active area of 20 cm<sup>2</sup> and had a flow-through hole with a diameter of 4 mm. Finally, the electrodes were

assembled into a CDI device and a separation distance between two electrodes was maintained by using a silicone gasket (hollow at the center) with the thickness of 2 mm. In order to investigate the desalination capacity of the CDI system with the graphene/MWCNT and the graphene/c-MWCNT hybrid aerogel electrodes, batch mode experiments were made in a continuously recycling system including an electrosorption unit cell. In each experiment, the solution was continuously pumped from a peristaltic pump into the cell and the effluent returned to the feed tank. The temperature of the solution was maintained at ~293 K and the flow rate was kept constant at 20 mL/min. In the meanwhile, when the initial concentrations of NaCl in aqueous solution were 100, 200, 400, 800, 1600, 3200, 4000 mg/L, the applied voltage was adjusted to 1.6 V at which no electrolysis of water occurred. The solution volume was maintained at 200 mL in the system and the approximate volume of the solution in the electrosorption unit cell was 15 mL. The experimental details can be found elsewhere [4]. Regeneration of working electrode was carried out by shorting and washing electrodes with a large amount of water. The concentration variation of NaCl solution was continuously monitored and measured by using an ion conductivity meter (type 308A, Leici Company). The relationship between conductivity and concentration was acquired according to a calibration table made prior to the experiment.

In our experiment, the desalination capacity was defined as follows:

$$\text{Desalination Capacity (mg g}^{-1}\text{)} = \frac{(C_0 - C_e) \times V}{M}, \text{ where } C_0 \text{ and } C_e \text{ (mg/L) are the}$$

initial and equilibrium concentration of NaCl, respectively, while  $V$  is the volume of the NaCl solution (L) in the system and  $M$  is the total mass loading of the graphene/MWCNT or graphene/c-MWCNT hybrid aerogel (g).

**Dye adsorption:** Three basic dyes (rhodamine B, fuchsin and methylene blue) and one acid dye (acid fuchsin) were investigated for their adsorption behavior with the as-synthesized graphene/CNT hybrid aerogels. In a typical experiment, 20 mg of as-synthesized hybrid aerogel was added into 200 mL of 20 mg/L aqueous dye solution followed by slowly stirring at room temperature. Before mixing, a few droplets of ethanol was dropped onto the surface of the graphene/CNT hybrid aerogel in order to increase their hydrophilicity [5]. At a series of intervals, the mixture was sampled and the dye concentration remaining in the mixture was measured after centrifugation. The dye concentration was determined through a UV/vis spectrometer and calculated by the standard spectrophotometric method at the maximum absorbance of each dye. The amount of dye  $q_t$  ( $\text{mg g}^{-1}$ ) absorbed with the hybrid aerogel at time  $t$ , was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t) \times V}{M}, \text{ where } C_0 \text{ and } C_t \text{ (mg/L) are the initial and time } t \text{ concentration}$$

of the dye, respectively, while  $V$  is the volume of dye solution (L) and  $M$  is the mass of the hybrid aerogel used (g).

The pseudo-first-order kinetic equation is presented as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t, \text{ and pseudo-second-order kinetic}$$

equation is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \text{ where } q_e \text{ and } q_t \text{ (mg g}^{-1}\text{) are the dye amount}$$

adsorbed with the graphene/CNT hybrid aerogel at equilibrium and time  $t$ , respectively;  $k_1$  and  $k_2$  represent the pseudo-first-order ( $\text{min}^{-1}$ ) and pseudo-second-order ( $\text{g mg}^{-1} \text{min}^{-1}$ ) rate constant, respectively.

Cetyl trimethylammonium bromide (CTAB) has been chosen as a regenerant to

investigate the desorption behavior of the loaded dye within the graphene/CNT hybrid aerogel. After adsorption, the mixture of the dye and hybrid aerogel was filtered with a large amount of water. Then the graphene/CNT hybrid aerogel containing the adsorbed dye was added into 200 mL of DI water and an appropriate amount of CTAB (with the mass ratio of CTAB to adsorbed dye 1:1, 5:1 10:1, 20:1, 50:1 and 100:1, respectively) was added into above suspension to desorb the dye from the graphene/CNT hybrid aerogel.

**Heavy metal ion binding:** The heavy metal  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$  and  $\text{Cu}^{2+}$  ions were investigated in our case. To estimate the binding capacity, 10 mg of the resulting hybrid aerogel and 50 mL of heavy metal ion solution with concentration of 50 mg/L were mixed under stirring at room temperature for 5 days to reach binding equilibrium. Before mixing, a few droplets of ethanol were dropped onto the surface of the graphene/CNT hybrid aerogels. The heavy metal ions concentration was measured with atomic adsorption spectrometry and the binding capacity of these heavy metal ions onto the graphene/CNT hybrid aerogels were calculated using the following equation:

$$\text{Binding Capacity} = \frac{(C_0 - C_e) \times V}{M}, \text{ where } C_0 \text{ and } C_e \text{ (mg/L) are the initial and}$$

final concentrations of the heavy metal ions in aqueous solution, respectively, while  $V$  is the volume of heavy metal ion solution (L) and  $M$  is the mass of the hybrid aerogels (g).

**Characterization:**

The compression tests were carried out by a single-column system (CMT6104) with loading capacity from 10 to 104 N at a constant downward speed of 2 mm/min and the compressive modulus was calculated from the slope of the initial stress-strain curve (the size of samples is 10.5 mm in diameter and 14.5 mm in height for graphene/MWCNT hybrid aerogel with a

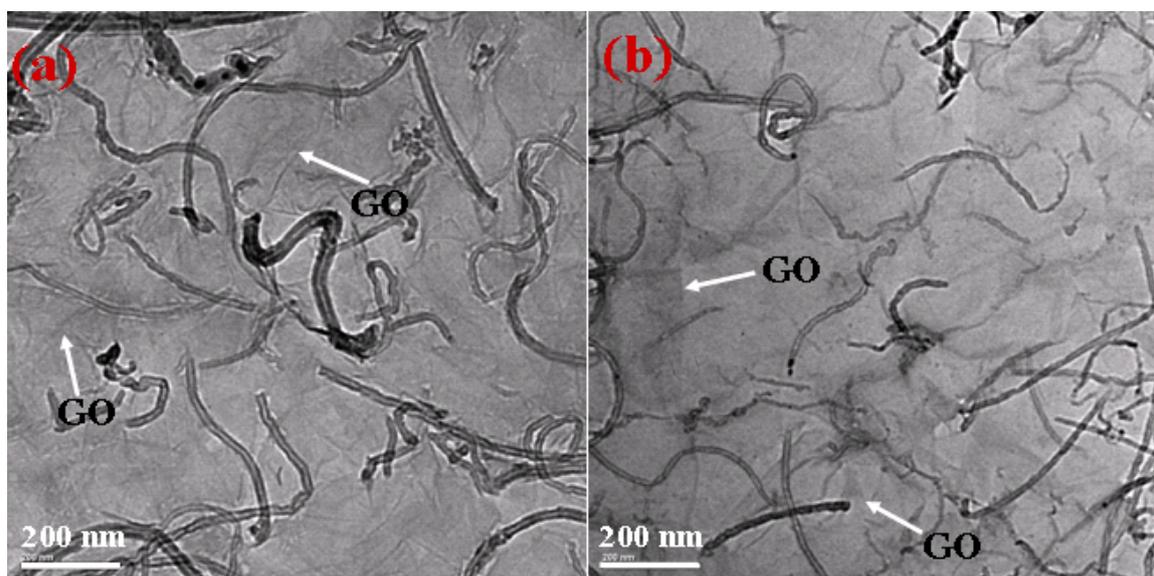
density of  $54.4 \text{ mg cm}^{-3}$  and 12.6 mm in diameter and 17.8 mm in height for graphene/c-MWCNT hybrid aerogel with a density of  $31.8 \text{ mg cm}^{-3}$ , respectively). Scanning electron microscopy (SEM) was acquired at a Hitachi S-4800 field-emission-gun scanning electron microscope at 5-10 kV. TEM was conducted at a FEI Tecnai 20 transmission electron microscope with an acceleration voltage of 200 kV. Raman scattering was performed on a Renishaw system 1000 using a 514.5 nm laser source. UV spectroscopy was performed on UV-6100 double beam spectrophotometer (Shanghai Mapada). X-Ray photoelectron spectroscopy (XPS) was conducted using an AXIS Ultra spectrometer with a high-performance Al monochromatic source operated at 15 kV. Nitrogen sorption measurements were performed with ASAP 2010 (Micromeritics, USA) to obtain pore properties such as the BET-specific surface area, pore size distribution, and total pore volume. Before measurement, the sample was outgassed under vacuum at  $250 \text{ }^\circ\text{C}$  for ca. 10 hours until the pressure less than  $5 \text{ }\mu\text{mHg}$ . A Keithley 4200 Semiconductor Characterization System was used to measure the electrical conductivities (four-probe method) of the samples. Powder X-ray diffraction (XRD) analyses were performed on X'Pert Pro MPD (PANalytical, The Netherlands) diffractometer with  $\text{Cu K}\alpha$  radiation. The diffraction data was recorded for  $2\theta$  angles between  $5^\circ$  and  $70^\circ$  with a scanning speed of  $0.01 \text{ }^\circ/\text{s}$  and the accelerating voltage and the applied current were 40 kV and 40 mA, respectively. The heavy metal ions concentration was measured with the AA-6800 atomic absorption spectrometry.

Tables

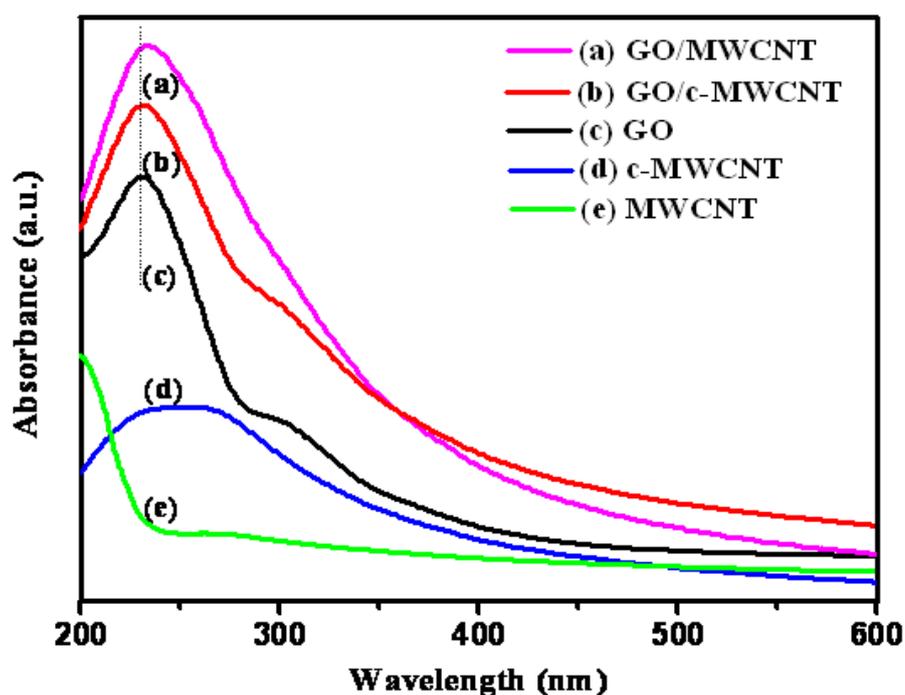
**Table SII** Adsorption capacities of various adsorbents in the initial concentration 20 mg/L aqueous dye solution

Adsorbent	Adsorption Capacity (mg g <sup>-1</sup> )			
	Rhodamine B	Methylene blue	Fuchsin	Acid fuchsin
Graphene/c-MWCNT	150.2	191.0	180.8	35.8
Graphene aerogel	133.6	152.8	142.7	43.2
Graphene/MWCNT	146.0	134.9	123.9	66.4
MWCNT powder	56.6	21.8	18.9	89.1

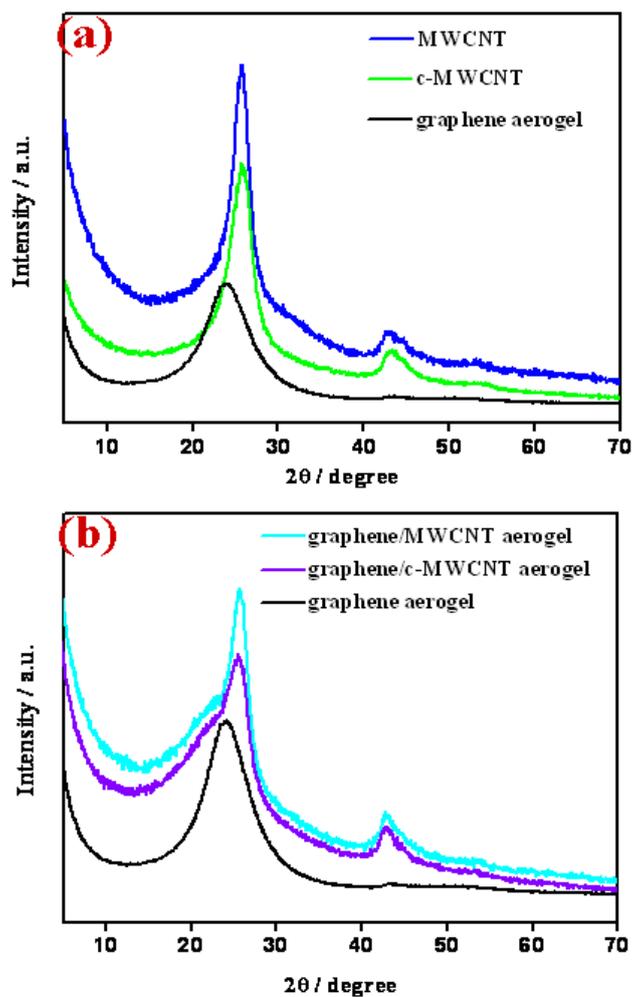
## Figures



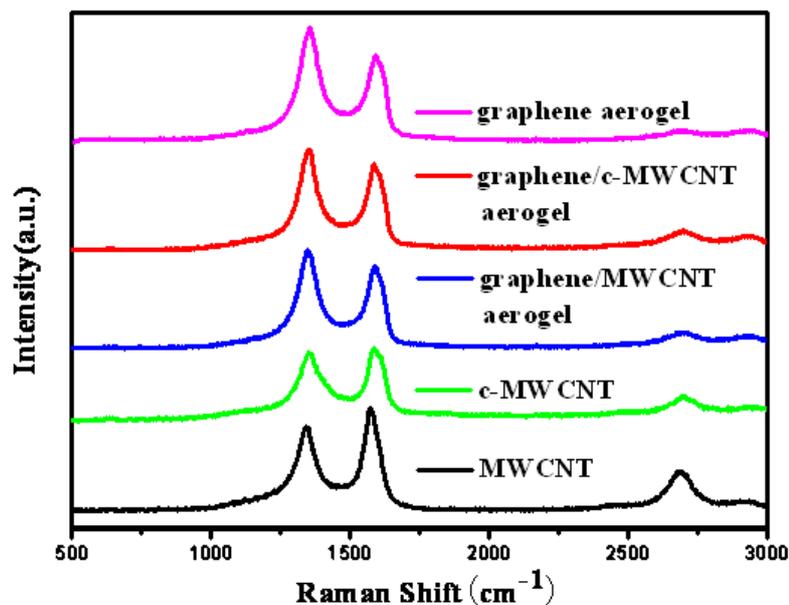
**Figure S11.** TEM images of GO/MWCNT (a) and GO/c-MWCNT (b) aqueous dispersions, indicating either MWCNTs or c-MWCNTs with hollow cores are individually attached onto the surfaces of GO sheets without obvious aggregation.



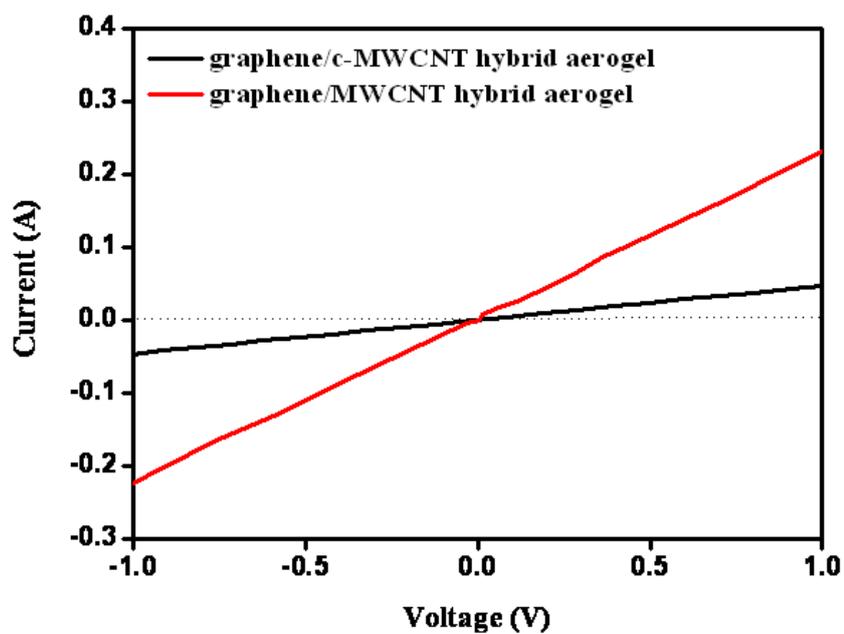
**Figure SI2.** UV-vis absorption spectra of the diluted GO/MWCNT (a), GO/c-MWCNT (b), GO (c), c-MWCNT (d) and MWCNT (e) aqueous dispersions. The adsorption peaks of the GO aqueous solution mainly center at 230 nm and 300 nm, respectively, corresponding to  $\pi$ - $\pi$  transitions of aromatic C-C bonds and the n- $\pi$  transitions of C=O bonds, in accordance with results reported elsewhere [6]. After the noncovalent adsorption of either MWCNTs or c-MWCNTs onto GO sheets, we observe that the adsorption peak of GO/MWCNT and GO/c-MWCNT turns up at 233nm and 235nm, respectively, indicative of interaction between GO sheets and CNTs.



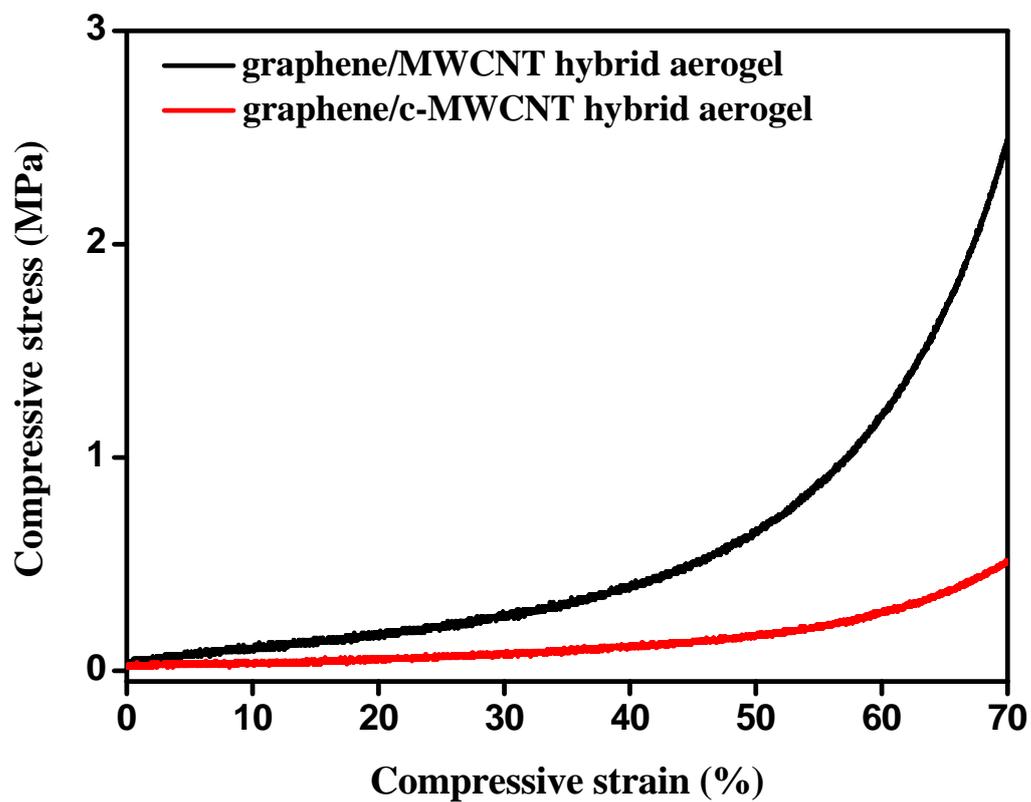
**Figure S13.** XRD patterns of the resultant graphene/MWCNT aerogel, graphene/c-MWCNT aerogel, MWCNT powder, c-MWCNT powder and graphene aerogel.



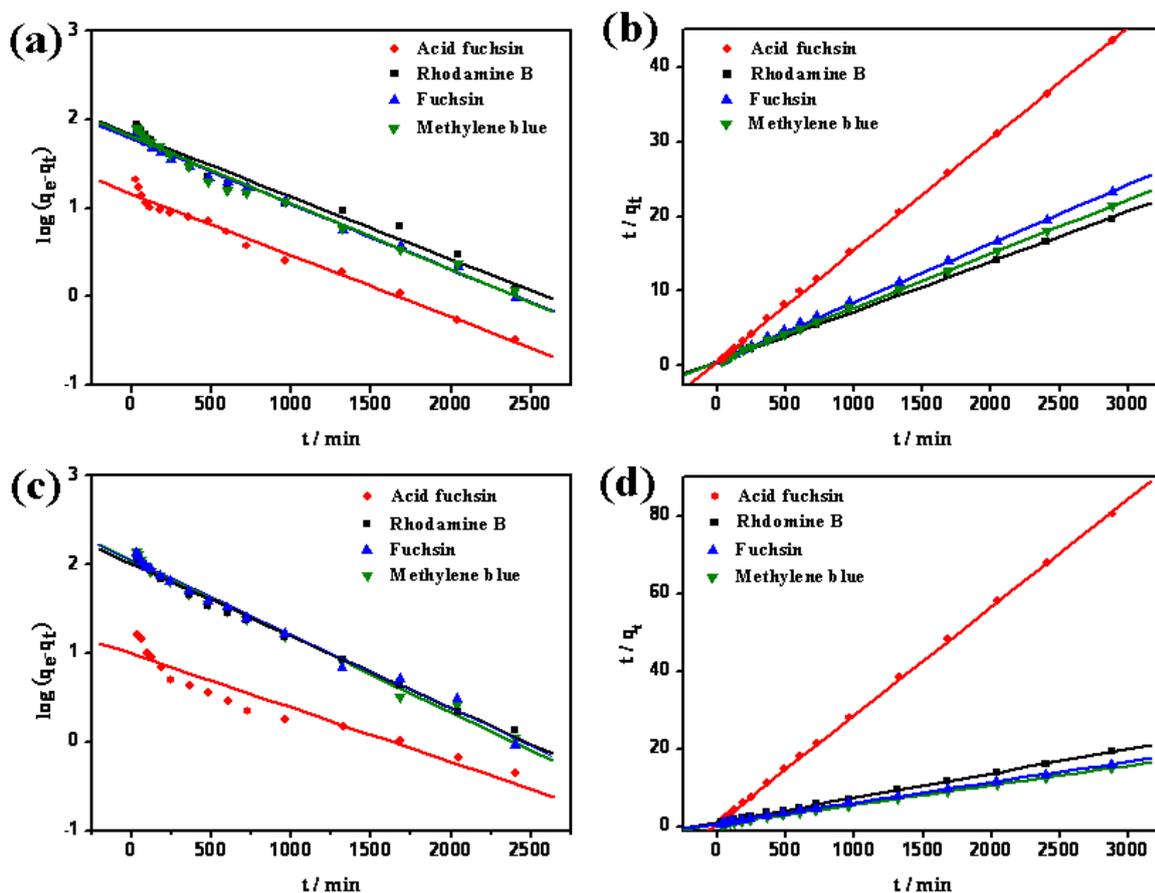
**Figure SI4.** Raman spectra of the resulting graphene aerogel, graphene/c-MWCNT hybrid aerogel, graphene/MWCNT hybrid aerogel, c-MWCNT powder and MWCNT powder. It should be noted that for mechanically exfoliated graphene, the 2D peak is sharp and exhibits higher intensity than the G peak [7]. In our pure graphene aerogel, the 2D peak intensity is quite weak due to increasing disorder [8] that is formed in the course of oxidation and reduction. Therefore, there is an obvious decrease in the 2D peak intensity due to average effect when integrating these graphene sheets with MWCNTs into graphene/MWCNT hybrid aerogel. Our result is also in accordance with the results observed by others [9][10].



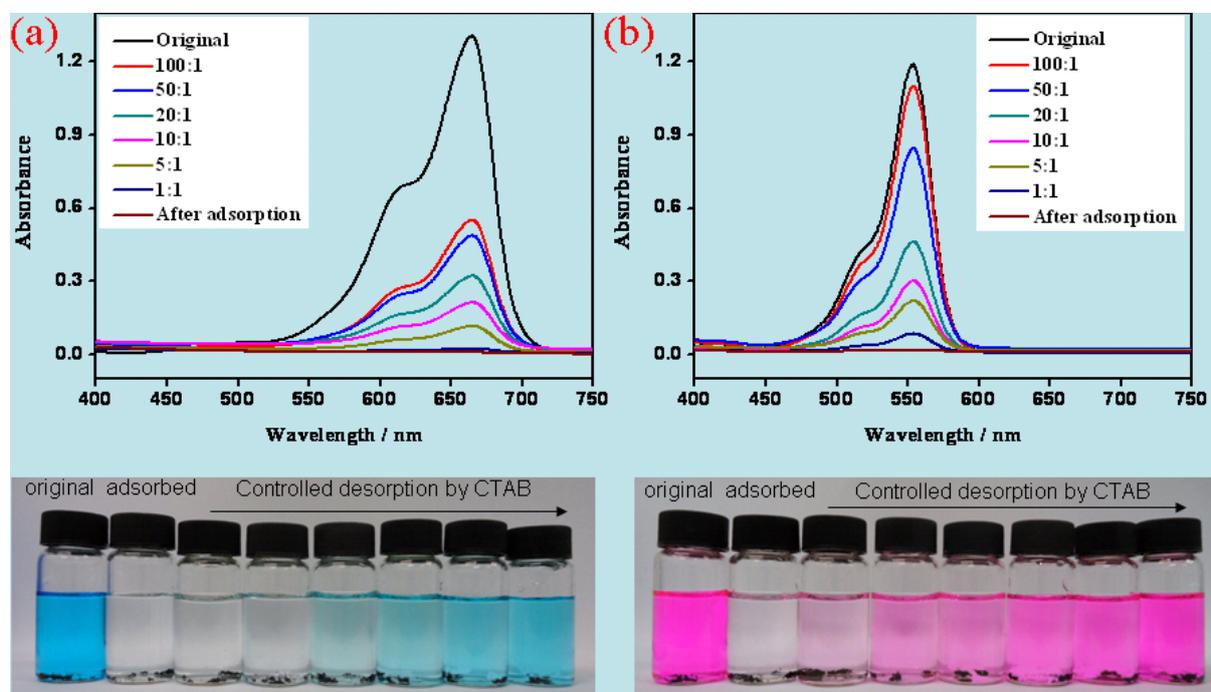
**Figure SI5.** I-V curves of graphene/MWCNT and graphene/c-MWCNT hybrid aerogels



**Figure SI6.** Compressive stress-strain curves of the graphene/CNT hybrid aerogels



**Figure SI7.** Pseudo-first order (a, c) and pseudo-second order (b, d) sorption kinetic curves of basic dyes (rhodamine B, methylene blue, fuchsin) and acid fuchsin by the graphene/MWCNT (a, b) and graphene/c-MWCNT (c, d) hybrid aerogels



**Figure SI8.** Controllable desorption of methylene blue embedded in the graphene/c-MWCNT hybrid aerogel (a) and controllable desorption of rhodamine B embedded in the graphene/MWCNT hybrid aerogel (b) by the surfactant CTAB (the mass ratio of CTAB to adsorbed dye is 1:1, 5:1, 10:1, 20:1, 50:1 and 100:1, respectively)

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