Supporting Information

Bicomponent supramolecular hydrogels derived from Ga-based metal-organic cube and carbon-based nanomaterials

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1. Materials

4,5-Imidazoledicarboxylic acid (H_3ImDC), Gallium(III) nitrate hexahydrate [$Ga(NO_3)_3.6H_2O$], graphite flakes and amine functionalized carbon nanotube ($CNT-NH_2$) were procured from Sigma-Aldrich chemical Co. Ltd Sodium nitrate ($NaNO_3$), Sulphuric acid (H_2SO_4) were purchased from Thomas Baker and used without further purification. All solvents and triethylamine (NEt_3) were obtained from Spectrochem Pvt. Ltd. (Mumbai, India).

2. Synthesis

Synthesis of Ga(III) Metal-Organic Cube: We followed a previously reported procedure for the synthesis of the compound.[1] H_3ImDC (0.5 mmol, 78 mg), $Ga(NO_3)_3 \cdot 6H_2O$ (0.5 mmol, 128 mg), and 10 mL of DMF were mixed in a 20 mL Teflon-lined container and stirred at room temperature for 30 minutes. Subsequently, 15 µL of triethylamine (NEt_3) was added to the reaction mixture, followed by an additional 30 minutes of stirring. The Teflon container was then sealed inside a stainless steel autoclave and heated at 120 °C for 24 hours. After the reaction was complete, the autoclave was allowed to cool gradually to room temperature. The resulting white product was collected by centrifugation, washed repeatedly with methanol, and dried in air. The purity of the synthesized compound was confirmed by powder X-ray diffraction (PXRD) (Figure S1a), matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) (Figure S1b), and Fourier-transform infrared spectroscopy (FTIR) (Figure S1c). The molecular formula of the **Ga-MOC** was determined to be $[(Ga_8(ImDC)_{12})(7H^+)(2Na^+)(H_2O)]^{3-}$, with a calculated molecular mass of 2467.32 Da. The MALDI-MS spectrum showed a prominent peak at $m/z = 822$, corresponding to a triply charged species ($z = 3$), supporting the presence and stability of the discrete monomeric unit. FTIR analysis revealed characteristic peaks at 3447 (broad), 3086 (medium), 2775 (medium), 1676 (strong), 1473 (strong), 1363 (strong), 1100 (strong), 857 (medium), 660 (medium), and 550 cm^{-1} (medium), which are consistent with previously reported data.

Synthesis of Graphene oxide (GO): Graphene oxide (GO) was synthesized using a modified Hummer's method.[2] Concentrated sulfuric acid (H_2SO_4, 69 mL) was added to a mixture of graphite flakes (3.0 g, 1 wt equiv) and sodium nitrate ($NaNO_3$, 1.5 g, 0.5 wt equiv), and the mixture was cooled to 0 °C. Potassium permanganate ($KMnO_4$, 9.0 g, 3 wt equiv) was then added slowly in portions, maintaining the temperature below 20 °C. The reaction was warmed to 35 °C and stirred for 30 min. Water (138 mL) was then added gradually, producing an exothermic reaction that raised the temperature to about 98 °C. This temperature was maintained for 15 min, followed by cooling in a water bath for 10 min. Subsequently, additional water (420 mL) and 30% hydrogen peroxide (H_2O_2, 3 mL) were introduced, causing another exothermic response. After cooling to room temperature, the product was purified by sieving, filtration, repeated washing, centrifugation, and decantation, and then vacuum-dried. This process yielded about 1.2 g of solid GO. The obtained material was characterized using powder X-ray diffraction (PXRD),[3] Raman spectroscopy,[4] and field emission scanning electron microscopy (FESEM) with energy-dispersive X-ray elemental mapping.

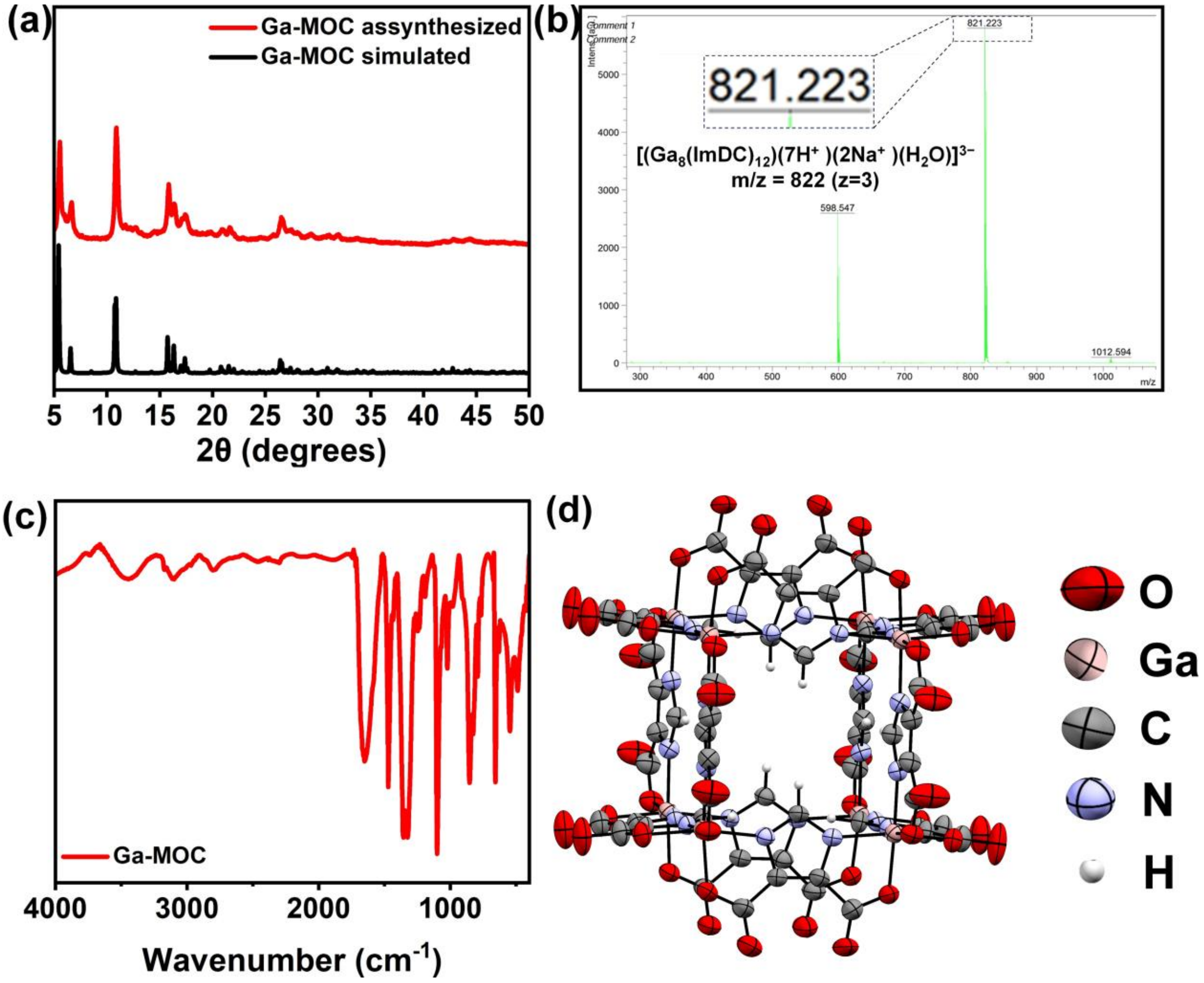
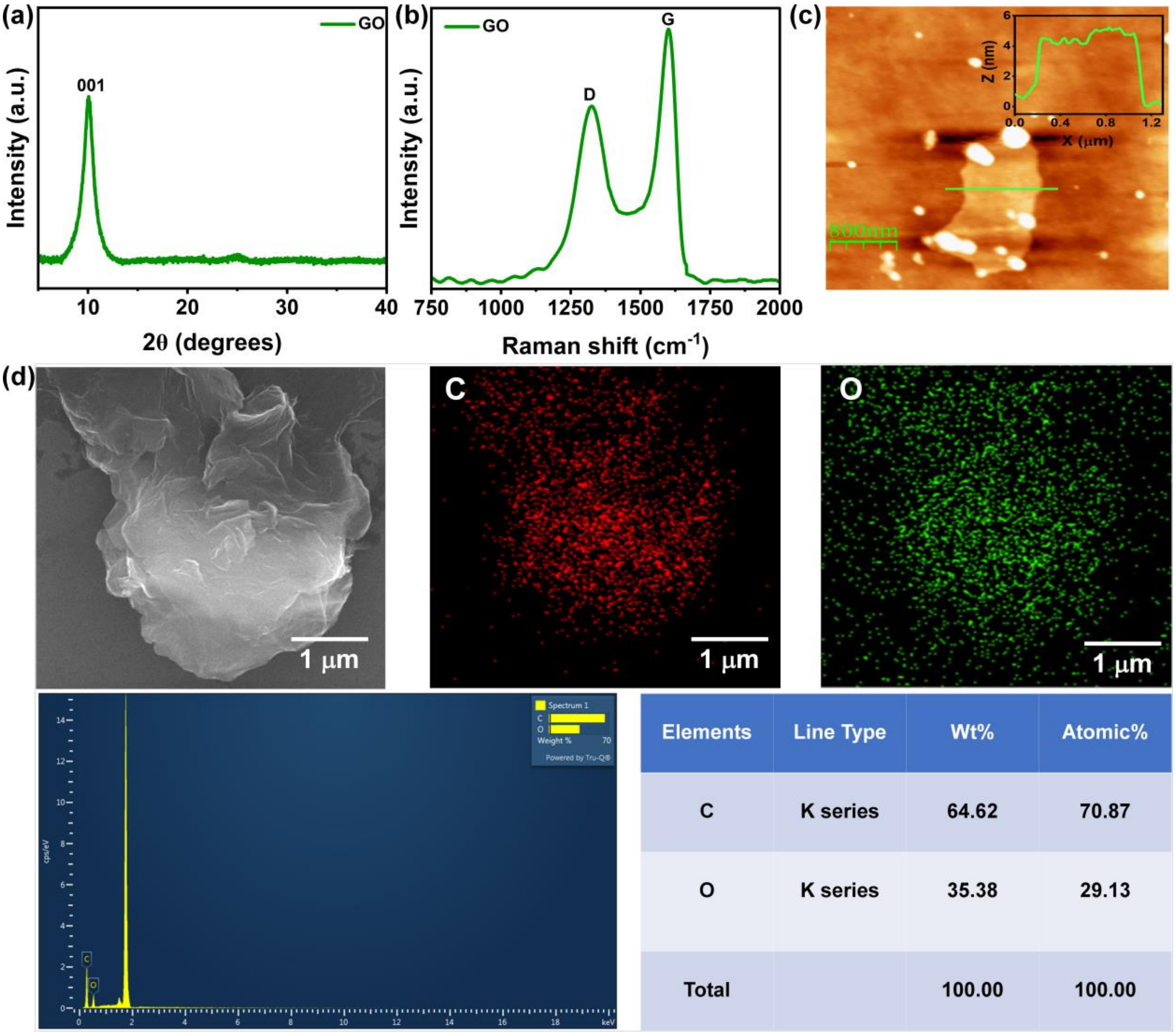


Figure S1: (a) PXRD pattern of **Ga-MOC** simulated (black) and as synthesised (red). (b) MALDI-TOF mass spectrum of **Ga-MOC**. Calculated m/z = 822 (z = 3) and observed 821.223 (z = 3). (c) FTIR spectrum of as synthesised **Ga-MOC**. (d) ORTEP diagram of **Ga-MOC** (Ellipsoids are shown at 50 % probability).



Elements	Line Type	Wt%	Atomic%
C	K series	64.62	70.87
O	K series	35.38	29.13
Total		100.00	100.00

Figure S2: GO characterizations: (a) PXRD, (b) Raman, (c) AFM (inset: the height profile of sheet), (d) EDS.

3. Methods

Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Discover diffractometer equipped with Cu-Kα radiation. Morphological characterization was performed using a Bruker Leica-S440I Field Emission Scanning Electron Microscope (FESEM). Samples were mounted on silicon wafers and examined under high vacuum at an accelerating voltage of 100 kV. Transmission electron microscopy (TEM) was conducted on a JEOL JEM-3010 instrument operated at 300 kV. Energy-dispersive X-ray spectroscopy (EDS) analysis was carried out using an EDAX Genesis system attached to the FESEM column. Raman spectra were collected on a Renishaw in via Raman microscope using a 785 nm excitation laser. Rheological measurements were performed on an Anton Paar MCR 92 rheometer equipped with a Peltier-controlled plate-plate geometry. The bottom glass plate had a diameter of 60 mm, and the upper measuring plate was 25 mm. Gel samples were subjected to stress sweep tests at constant frequency (25 °C), followed by frequency sweep tests at constant stress within the linear viscoelastic region to determine the storage (G′) and loss (G″) moduli. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Bruker Autoflex Speed instrument by drop-casting an aqueous **Ga-MOC** solution onto the matrix. Zeta potential measurements were conducted using a Malvern Zetasizer Ultra system operating with a 532 nm laser. CO_2 adsorption–desorption isotherms of the **Ga-CNT** and **Ga-GO** aerogels were measured at 298 K using a QUADRASORB-SI and an AUTOSORB IQ2 analyzer.

4. Additional figures

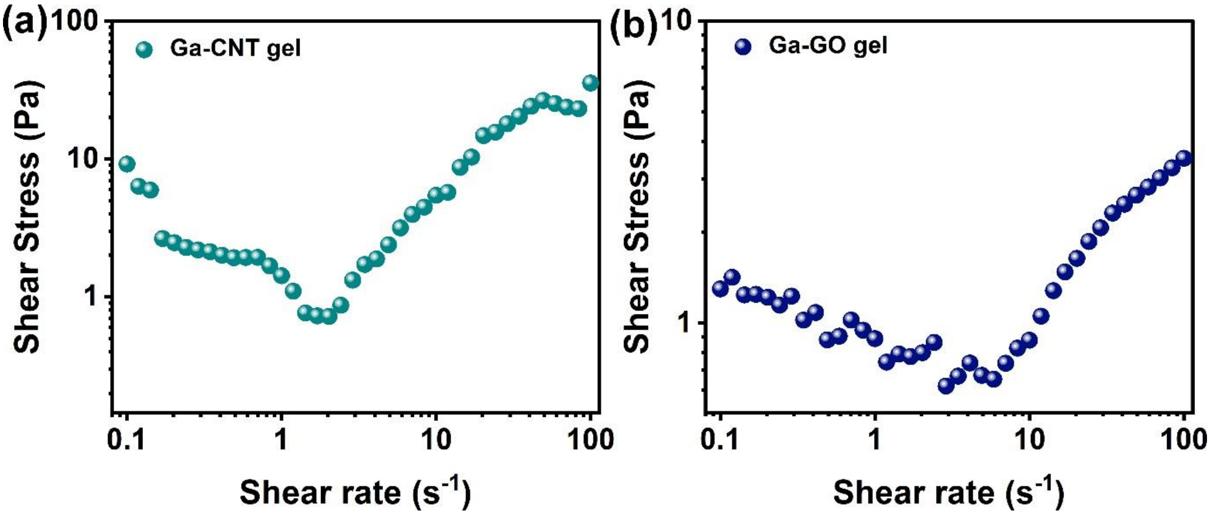


Figure S3: Shear stress vs Shear rate plot of (a) **Ga-CNT** gel and (b) **Ga-GO** gel.

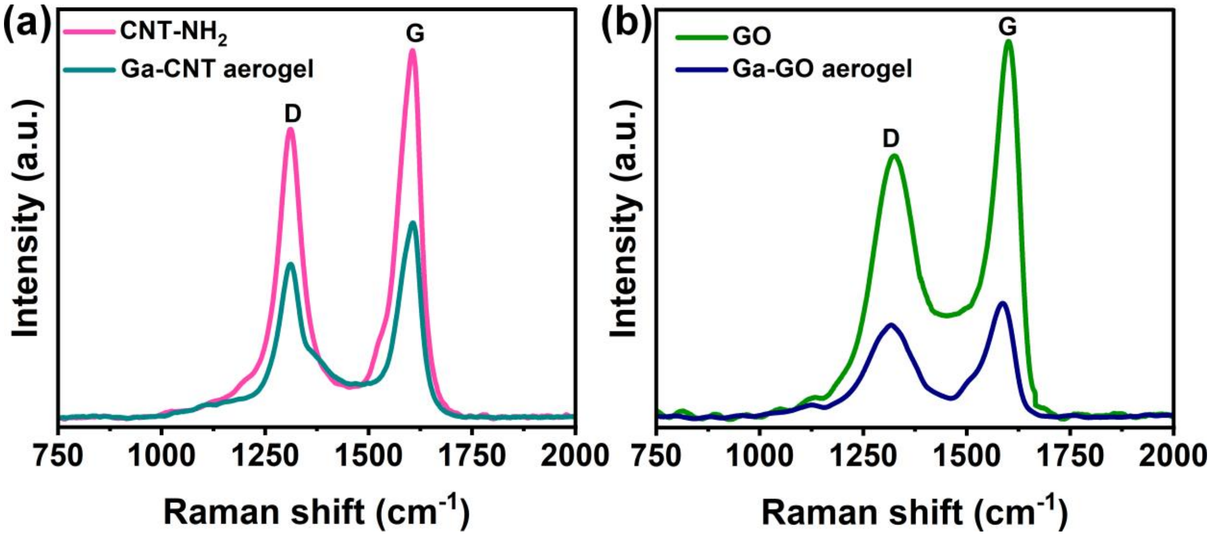


Figure S4: (a) Raman spectroscopy of CNT-NH_2 and **Ga-CNT** aerogel.[5] (b) Raman spectroscopy of GO and **Ga-GO** aerogel.

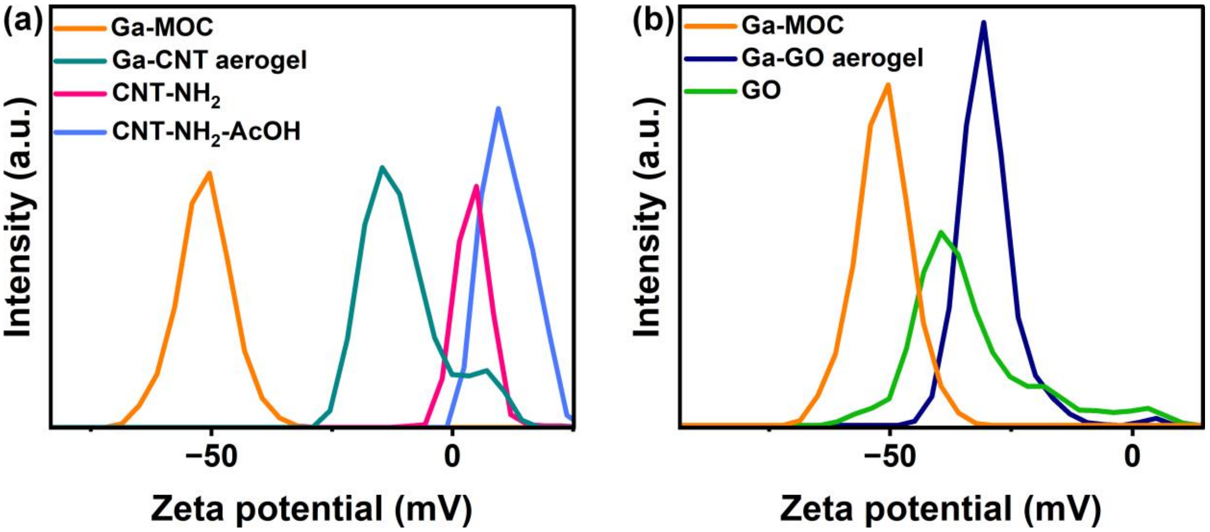


Figure S5: (a) Zeta potential of CNT-NH$_2$, **Ga-MOC**, **Ga-CNT** aerogel in water and CNT-NH$_2$ in AcOH/water. (b) Zeta potential of GO, **Ga-MOC** and **Ga-GO** aerogel in water.

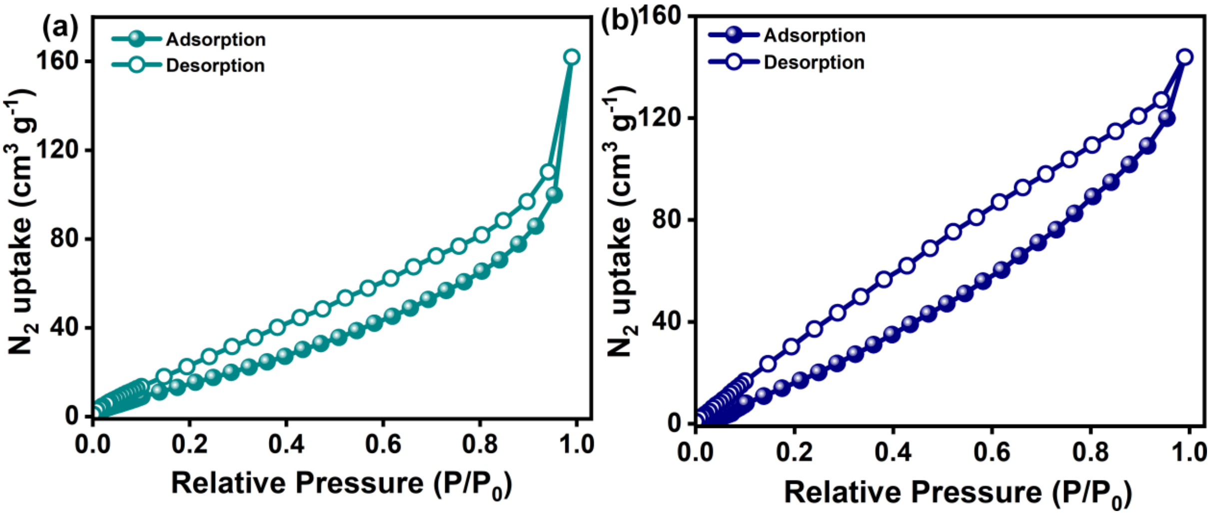


Figure S6: N$_2$ adsorption-desorption isotherms at 77 K (a) **Ga-CNT** aerogel, (b) **Ga-GO** aerogel.

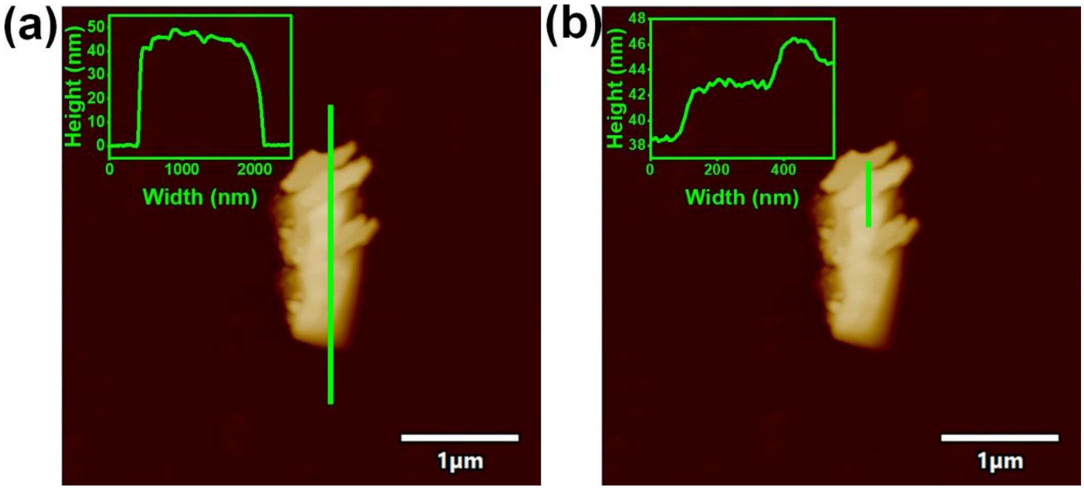


Figure S7: (a) and (b) AFM image of **Ga-GO** aerogel (inset: height profile).

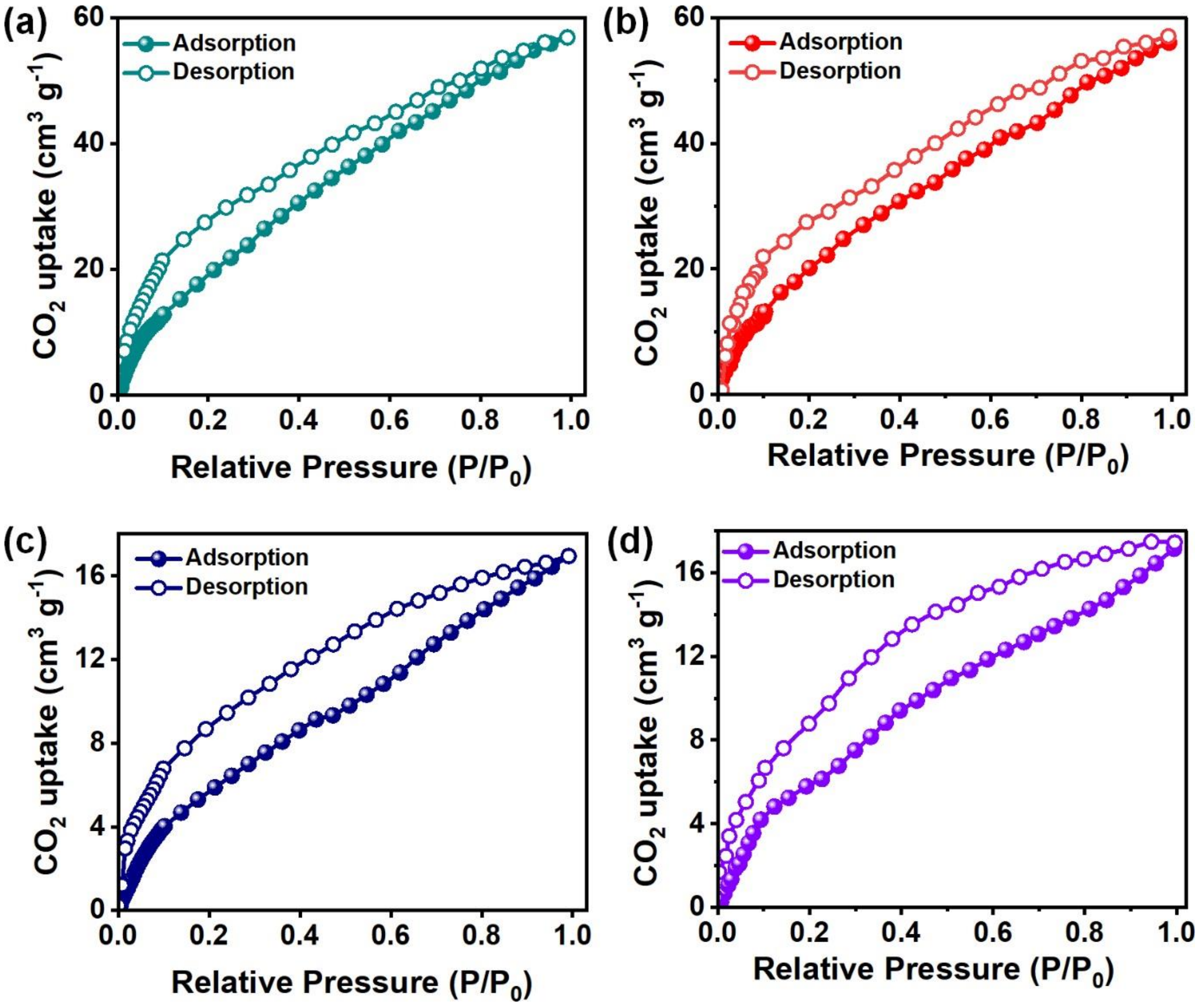


Figure S8: CO_2 adsorption-desorption isotherms of the **Ga-CNT** aerogel measured at 298 K: (a) first cycle and (b) second cycle. CO_2 adsorption-desorption isotherms of the **Ga-GO** aerogel measured at 298 K: (a) first cycle and (b) second cycle.

References

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