

## Supplementary Information

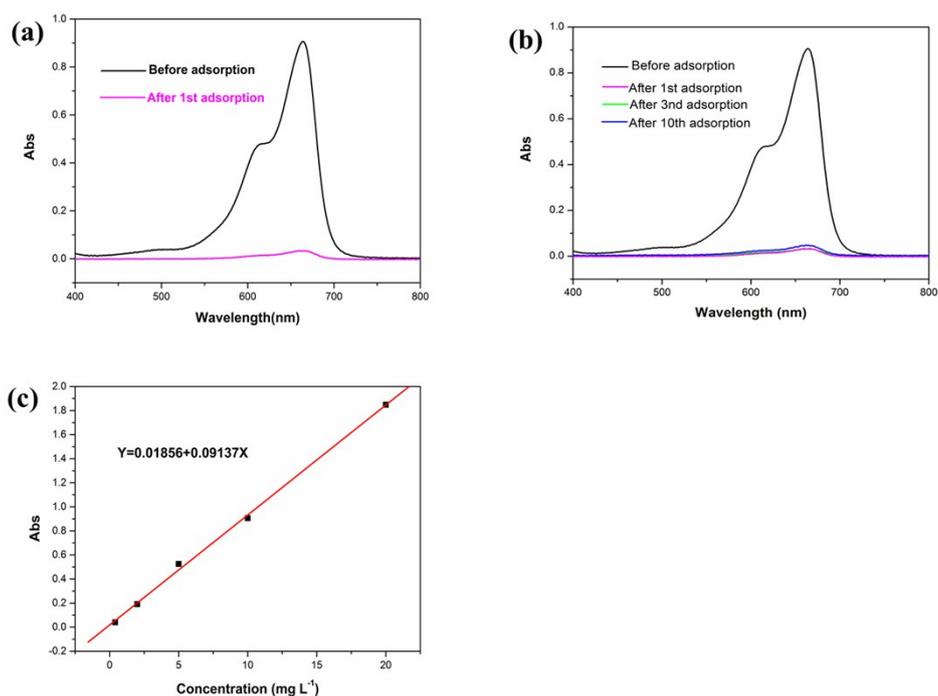
### Using multiple hydrogen bonding cross-linker to access reversibly responsive three dimensional graphene oxide architecture

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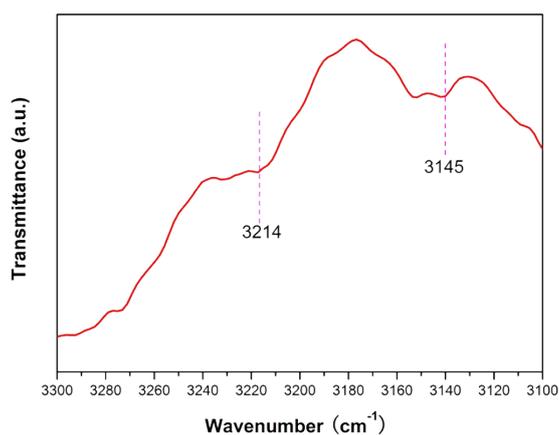
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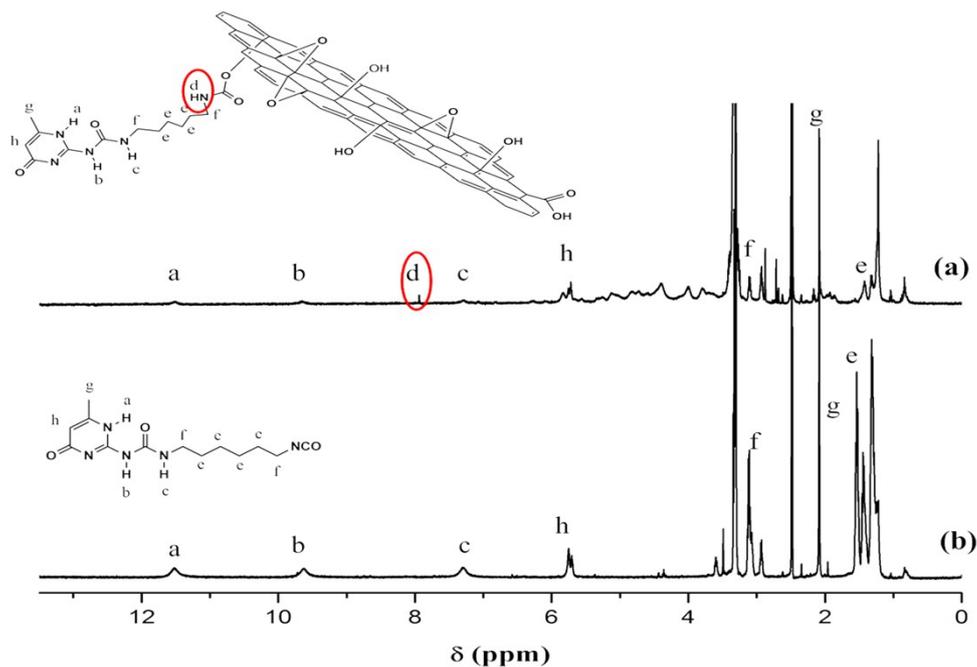
**Fig. S1** (a) UV-Vis spectra of 10mg L<sup>-1</sup> MB before and after adsorption (b) UV-Vis spectra of MB after 1st, 3rd and 10th adsorption (c) Calibration curve of MB.

After 10 adsorption-desorption cycles, the UGO bulk still maintain a good adsorption performance as is shown in Fig. S1b. However, the absorbance of MB after 10th adsorption is higher than that of 1st and 3rd, indicating the slightly decline of adsorption performance probably attributed to permanent electrostatic adsorption of some MB molecules on the surface of UGO sheet.



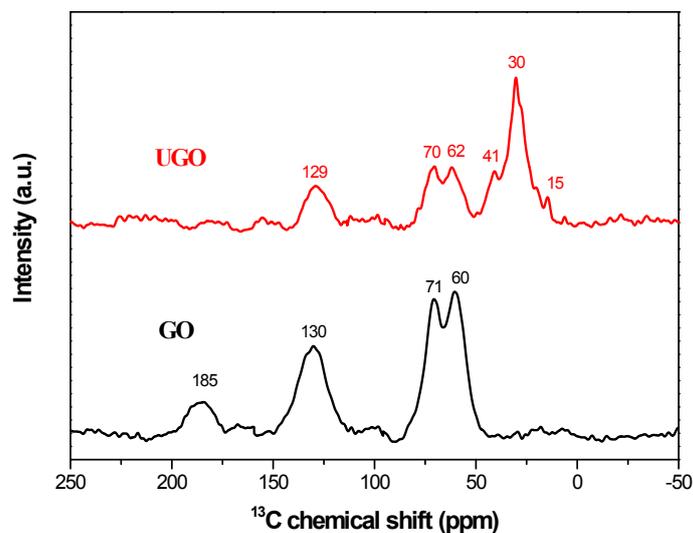
**Fig. S2** The FT-IR spectra of the UGO from wavenumber 3100 cm<sup>-1</sup> to 3300 cm<sup>-1</sup>

The presence of peaks at 3145 cm<sup>-1</sup> and 3214 cm<sup>-1</sup> in the FT-IR spectra of the UGO suggests the formation of the self-complementary hydrogen bonds.



**Fig. S3**  $^1\text{H}$  NMR spectra recorded in  $\text{DMSO-d}_6$  for: (a) UGO, and (b) UPy.

Fig. S3 shows the  $^1\text{H}$  NMR spectra for the UPy and UGO. For the UPy, the characteristic signals can be clearly distinguished. After the reaction of UPy and GO, the  $^1\text{H}$  NMR spectrum of UGO demonstrates the appearance of these UPy characteristic peaks with a significant decrease in the intensities caused by diamagnetic ring currents in GO,<sup>1</sup> indicating UPy has been grafted onto GO surface successfully. Besides, an emerging d peak (marked with red circle) is attributed to the newly generated amide group.

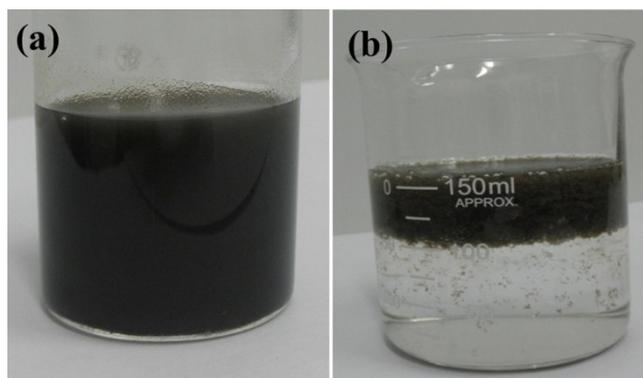


**Fig. S4**  $^{13}\text{C}$  solid state NMR spectra of GO and UGO

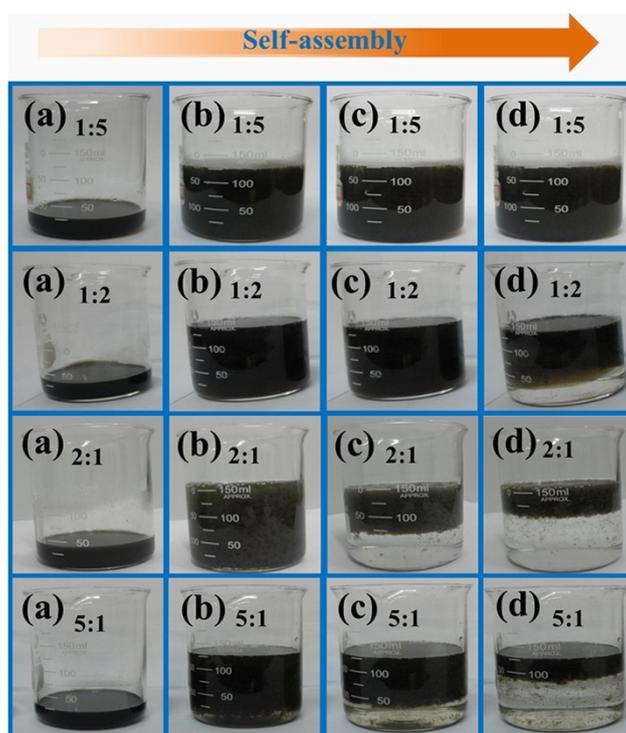
Comparison of the GO and UGO  $^{13}\text{C}$  NMR spectra provides information about the structures appended on the surface of GO. The  $^{13}\text{C}$  NMR spectrum of GO confirms the presence of abundant hydroxyl, epoxide and carbonyl groups (shifts centered at 71 ppm, 60 ppm and 185 ppm). The resonance at 130 ppm belongs to the un-oxidized  $\text{sp}^2$  carbons of GO.<sup>2</sup>

In the  $^{13}\text{C}$  spectrum of UGO, the peak from the carbonyl carbons is absent. The presence of three distinct resonances (15, 30 and 41 ppm) is attributable to the carbons in the UPy. The resonance centered at 30 ppm is attributable to the carbons in the  $\text{CH}_2$  groups of UPy. And the peaks emerging at 15 ppm and 41 ppm are attributable to the  $\text{CH}_3$  and  $\text{CH}$  groups of UPy respectively.<sup>3</sup>

In this paper, it is speculated that the pairing of quadruple hydrogen bond formed in the aqueous environment. However, UGO didn't dissolve in  $\text{D}_2\text{O}$ , making the detection of hydrogen bond by NMR characterizations in liquid impossible. Hydrogen bonding between individually separated UGO nanosheets can only be detected by FTIR (Fig. S2) while the UGO sheets are in solid states.

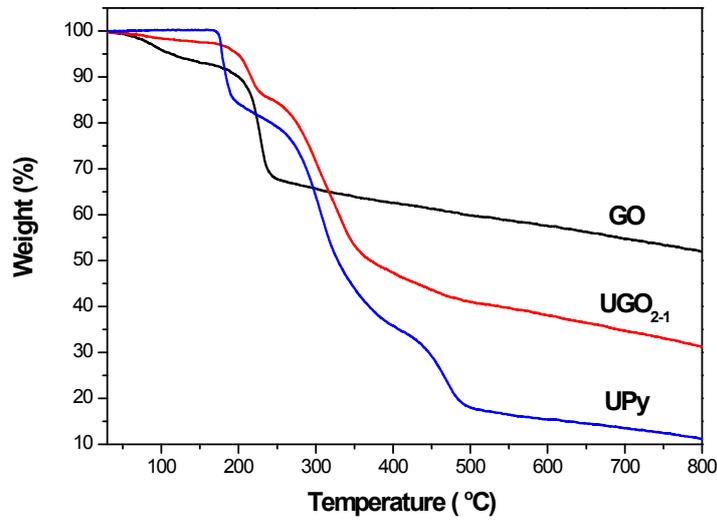


**Fig. S5** (a) Optical photograph showing homogeneous DMF solution of isolated UGO sheets. (b) Optical photograph showing 3D UGO assembly on the upper of the solution.



**Fig. S6** Photographs showing the phenomena brought by different reaction molar ratio between UPy and GO. (a) Isolated UGO sheets in DMF. (b) Water was added in. (c) 10 minutes later. (d) 30 minutes later.

Different mass ratio reaction between UPy and GO (1:5, 1:2, 2:1, 5:1) was conducted in the experiments. The obtained UGO were denoted as UGO<sub>1-5</sub>, UGO<sub>1-2</sub>, UGO<sub>2-1</sub> and UGO<sub>5-1</sub> correspondingly. The UGO were initially dispersed in DMF. After water was added in, an interesting phenomenon was observed. The UGO<sub>1-2</sub>, UGO<sub>2-1</sub> and UGO<sub>5-1</sub> showed an obvious self-assembly behavior, and a phase separation process was observed. However, the self-assembly process of UGO<sub>1-5</sub> doesn't occur. The UGO<sub>2-1</sub> showed the fastest assembly rate among them.



**Fig. S7** TGA curves of UPy, GO and UGO<sub>2-1</sub>

$$D_g(\%) = \frac{R_g - R}{R_g - R_u} \times 100\% \quad \dots\dots\dots (1)$$

The amount of UPy grafted on GO was comprehensively estimated by the atomic percentage of the emerging nitrogen in XPS spectra (Tab. S1) and the weight loss at three different temperatures in the TGA curve (Fig. S7).<sup>4</sup> The grafting density ( $D_g$ ) can be calculated at three different temperatures (600 °C, 700 °C and 800 °C) according to eqn (1), wherein,  $R_g$ ,  $R$  and  $R_u$  represent the residual weight percentage (wt %) of GO, UGO<sub>2-1</sub> and UPy, respectively (Tab. S1).

**Tab. S1** The grafting density of UPy on GO calculated by TGA and XPS data

Temperature (°C)	Residual weight			Grafting density			weight percentage [a]
	600	700	800	weight percentage			
	600	700	800	700	700	800	
UPy	15.45%	13.5%	11.18%	-	-	-	-
GO	57.58%	54.83%	51.97%	-	-	-	-
UGO <sub>2-1</sub>	38.04%	34.78%	31.22%	46.4%	48.5%	50.8%	46.9%

[a] Data is estimated by XPS spectra

Here, we defined the bulk-average grafting density ( $D_f$ ) as the average number of carbon atoms supporting one UPy. Specifically, the density is  $1/24 \sim 1/28$ . The above results indicate that one UPy molecule is approximately covalently supported by per 24 ~ 28 carbon atoms of GO.

## References

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