Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Self-Healing Stable Polymer Hydrogel for pH Regulated Selective Adsorption of Dye and Slow Release of Graphene Quantum Dots

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Characterisation of Graphene Oxide

1. Synthesis and Characterisation of Graphene Oxide

GO was synthesized from graphite powders according to the modified Hummer's method. Graphite powder (1g) and $NaNO_3$ (1g) were added to 46 mL of cold (0 °C) concentrated H_2SO_4 in a 250 mL flask. The mixture was stirred for 30 min in an ice bath. Subsequently, $KMnO_4$ (3g) was added slowly into the solution and still kept in an ice bath with stirring for 2 h. Then the mixture was kept at 35 °C for 3 h, followed by adding 30 mL of deionized water slowly. The hybrid was kept at 98 °C for 0.5 h, followed by adding 10 mL of 30 wt% H_2O_2. For purification, the mixture was washed with 5% of HCl solution and deionized water several times and separated via centrifugation until the pH value of the decantated reached 6, and subsequently dried in a vacuum oven at room temperature.

The UV-visible spectrum of GO was recorded at room temperature and is shown in figure S 1a. The absorption peak centred at 231 nm is assigned to the π-π^* transition of C=C bonds whereas the broad band around 300 nm arises due to the n-π^* transition of C=O bonds in graphene oxide.

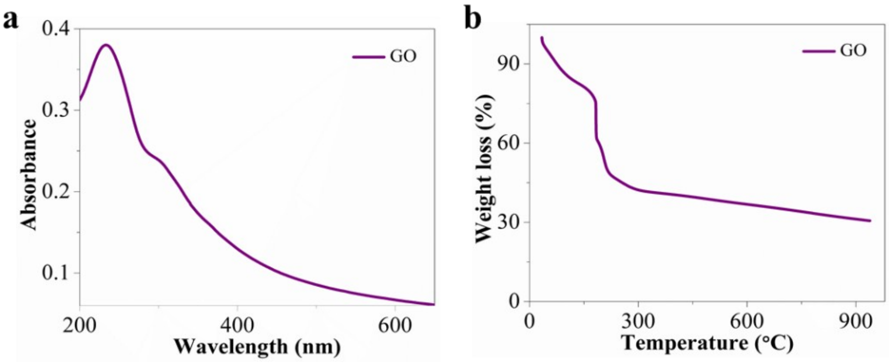

Figure S1. (a) The UV-visible absorption spectrum of aqueous dispersion of graphene oxide (GO) and (b) TGA thermogram of GO

The thermogravimetric analysis of GO done in nitrogen atmosphere is shown in figure S 1b. Small weight loss (~20%) below 150 °C is presumably due to the losses of adsorbed water molecules and the major weight loss (~55%) in the temperature range of 200–400 °C is could be due to the removal of most labile oxygen functional groups present in GO (e.g., CO, CO_2 etc.). A slow weight loss in the range of 500–900 °C is due to the removal of more stable oxygen functionalities.

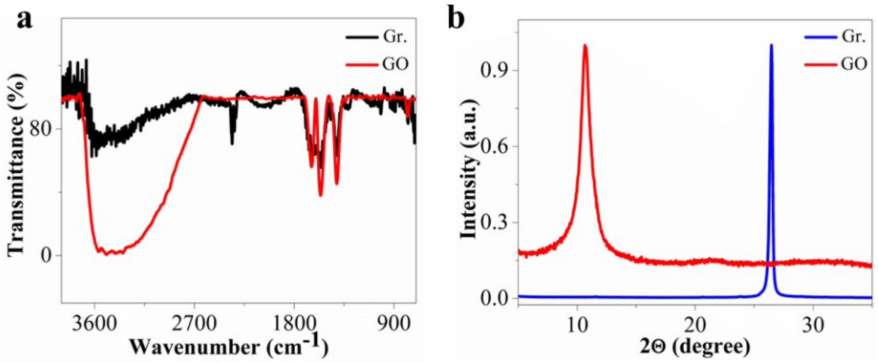

Figure S2. (a) FT-IR spectra, (b) XRD of graphene (Gr.) and GO

FT-IR spectra of shown in figure S 2a shows the intensities of peaks corresponds to stretching (str.) frequencies of C=O (1720 cm^{-1}), epoxy C-O (1227 cm^{-1}) and alkoxy C-O (1048 cm^{-1}), O-H (3400 cm^{-1}) and O-H deformation (deform.) vibrations (1395 cm^{-1}).

The layer-to-layer distance (*d*-spacing) for the graphene oxide has been calculated to be 8.41 Å (with a 2θ value of 10.5°; for 002 planes), whereas 3.36 Å (with a 2θ value of 26.3°; for 002 planes) has been calculated for the graphite (Figure S 2b). The presence of oxygen containing functional groups at the basal plane of graphene oxide and intercalation of the water molecules in between the of graphene oxide planes results in increase in the *d*-spacing in graphene oxide.[1–5]

The synthesized GO was sonicated for 2-3 h and sample was prepared by drop casting an aqueous solution of dispersed graphene oxide on an ITO glass plate. The SEM image shown in figure S3 shows the sheet type structure of GO.

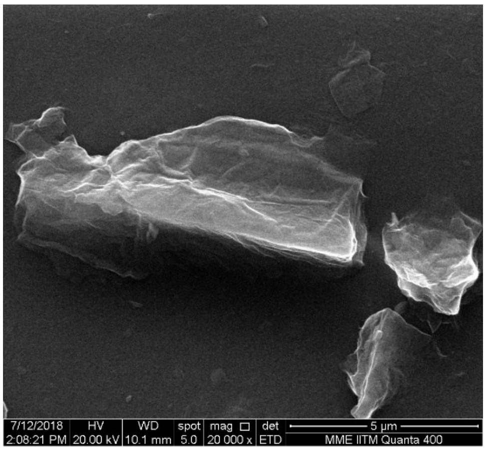

Figure S3. SEM image of GO

2. SEM images of the hydrogels

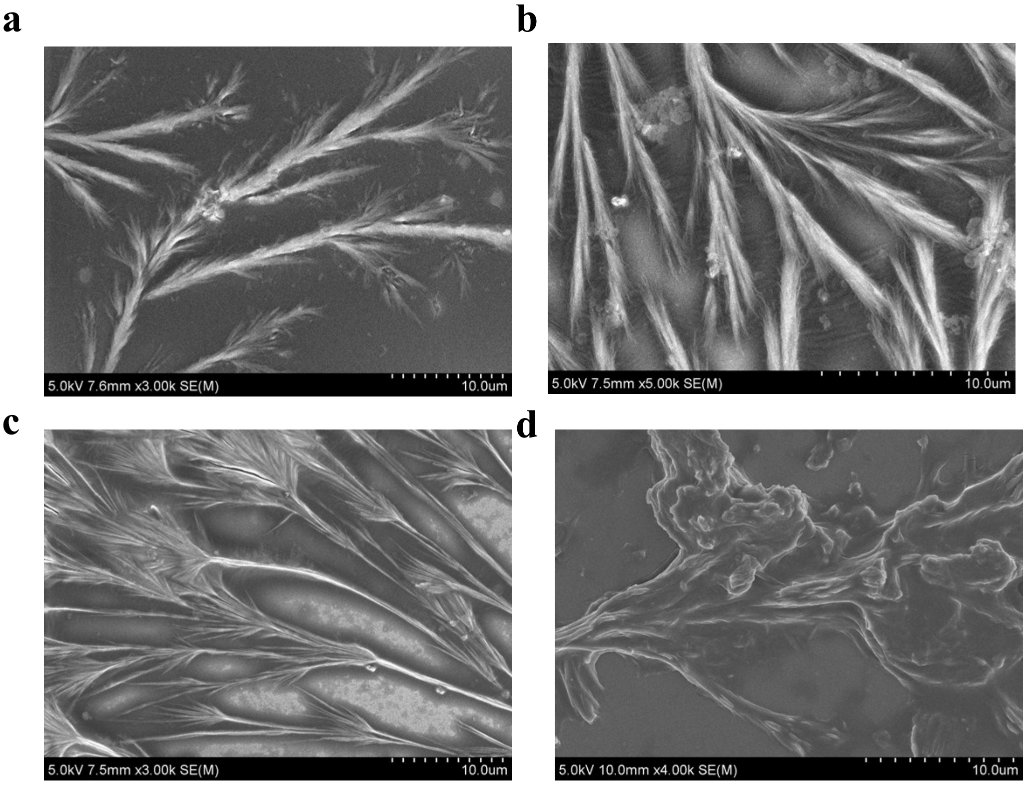

Figure S4. SEM image of (a) AAM, (b) $GO_{0.15}AAM$, (c) $GO_{0.5}AAM$, (d) $GO_{1.0}AAM$ hydrogels

3. Images of hydrogels after complete swelling

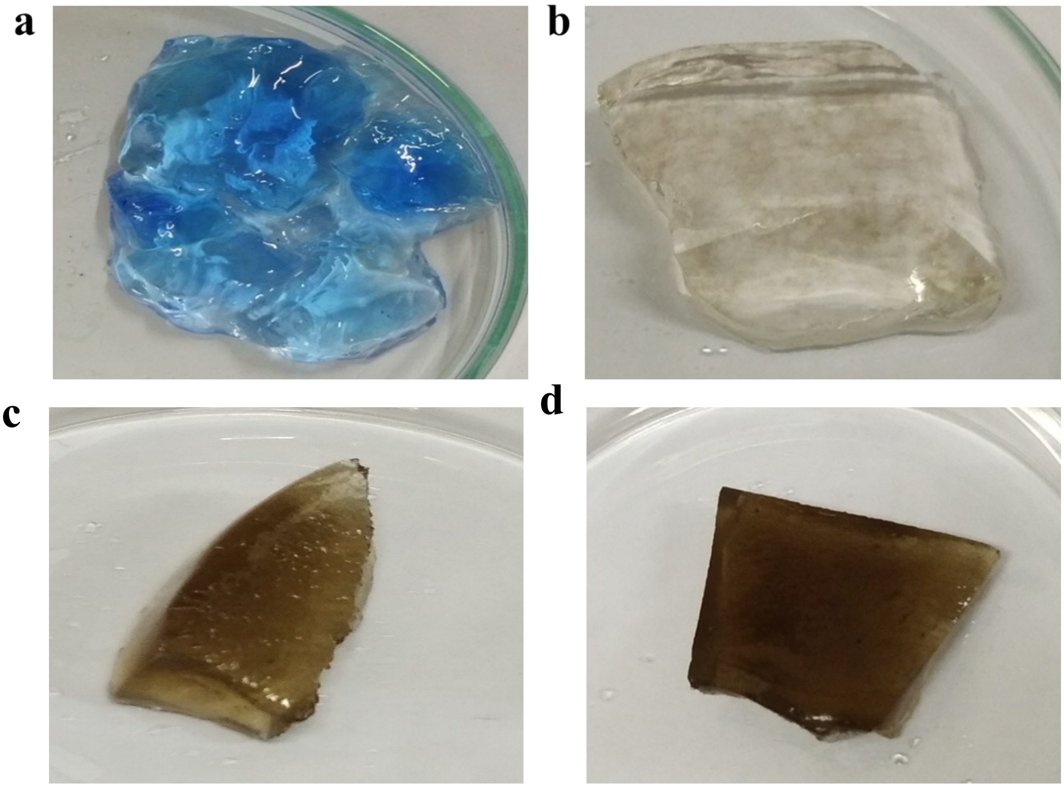

Figure S5. photographs of (a) AAM, (b) $GO_{0.15}AAM$, (c) $GO_{0.5}AAM$, (d) $GO_{1.0}AAM$ hydrogels after swelling

4. Images of AAM hydrogel during tensile stress-strain experiment

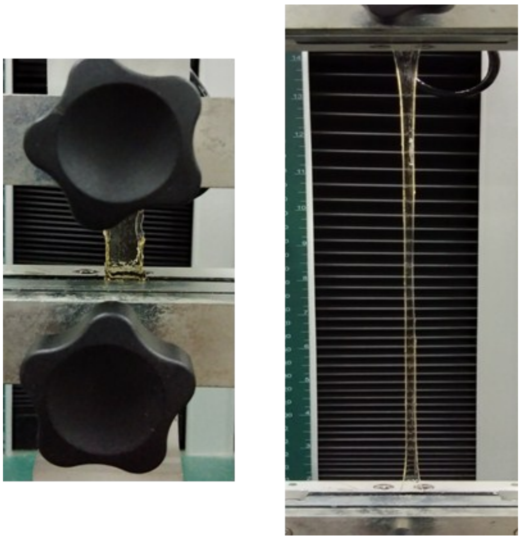

Figure S6. AAM hydrogel before and after elongation

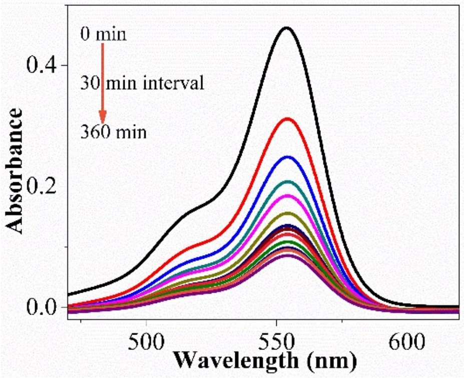

Figure S7. UV-Vis spectra of Rh B dye adsorption on AAM hydrogel

Table S1.

Models		Pseudo first order			Pseudo second order			Intraparticle diffusion		
Hydrogels (in mg)	Dye	k_1 (1/min)	Δq (%)	R^2	k_2 (g/mg min)	Δq (%)	R^2	k_3 (min-$^{0.5}$)	C	R^2
GO$_{0.5}$AAM	MB	0.021	57.52	0.974	0.001	2.56	0.997	8.90	38.66	0.737
	Rh B	0.011	14.32	0.974	0.009	22.9	0.998	3.81	5.392	0.971

5. Kinetic studies of Organic dyes adsorption experiments

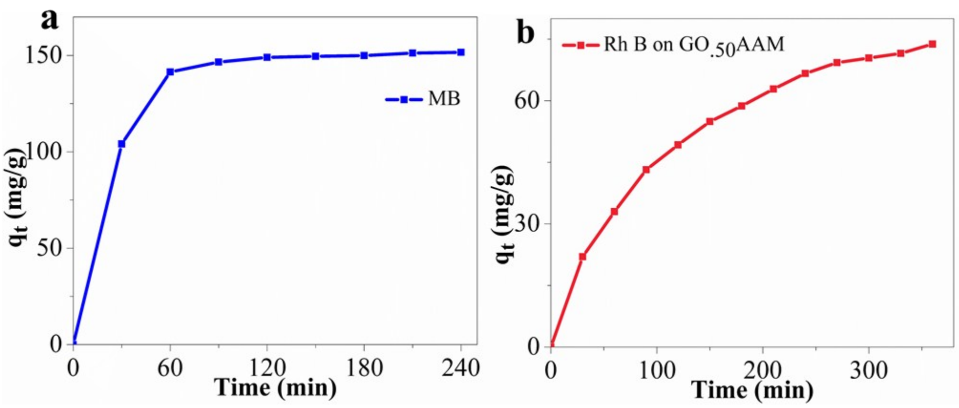

Figure S8. Effect of contact time on the adsorption capacity of (a) MB and (b) Rh B on GO$_{0.5}$AAM

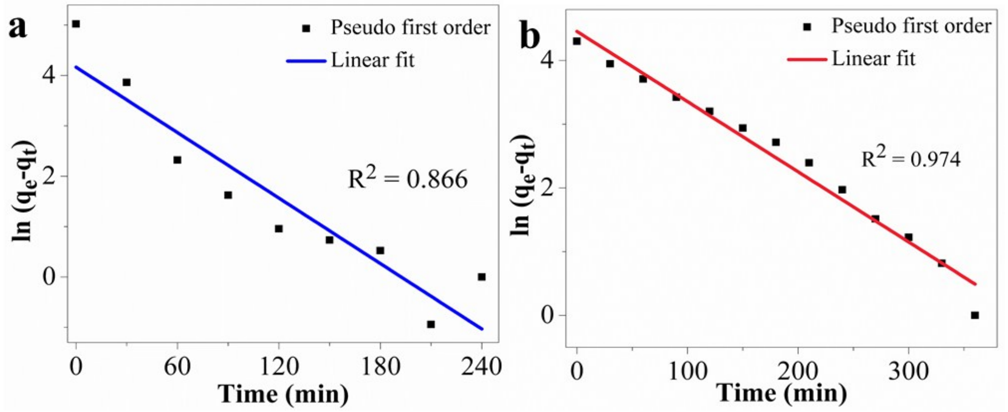

Figure S9. Pseudo-first-order fitting of adsorption kinetics for (a) MB and (b) Rh B.

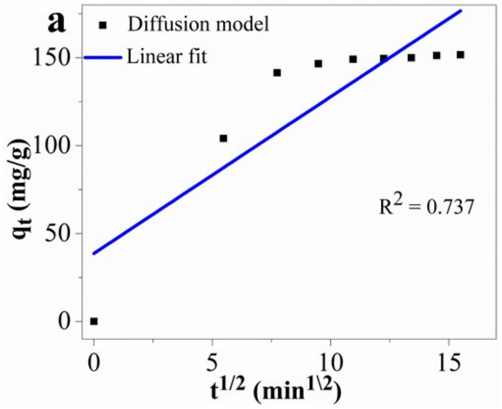

Figure S10. Diffusion model fitting of MB on $GO_{0.5}AAM$ hydrogel

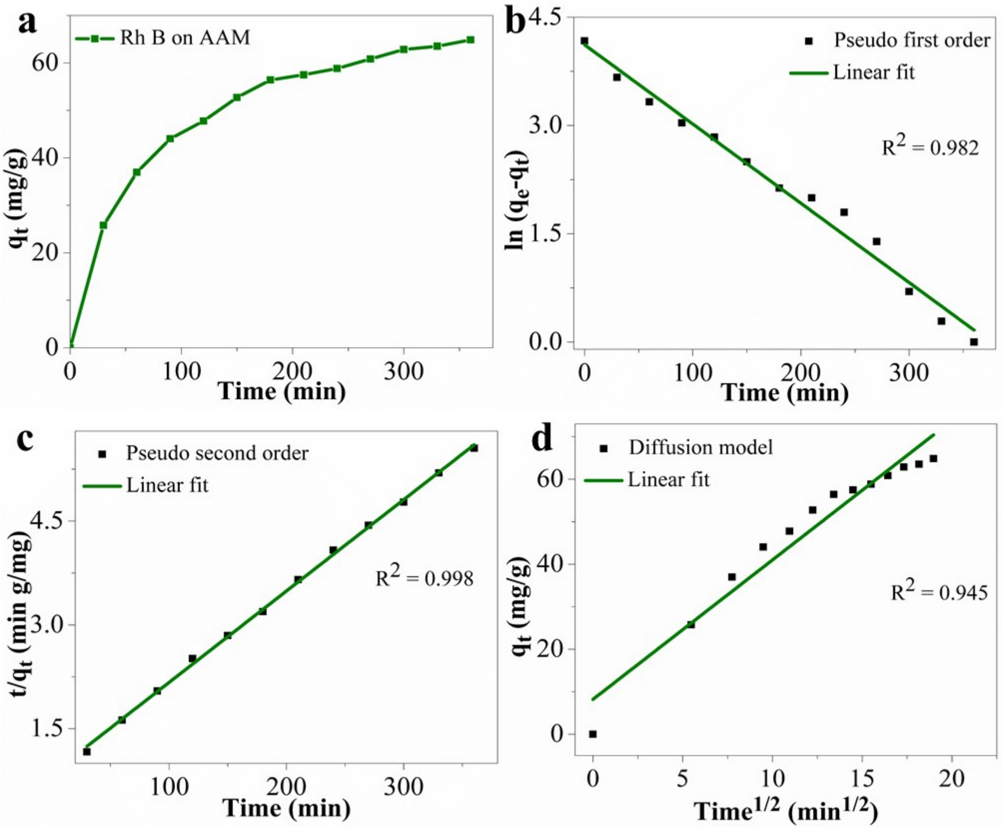

Figure S11. (a) Effect of contact time on the adsorption capacity, (b) Pseudo-first-order, (c) Pseudo-second-order and (d) diffusion model of adsorption kinetics for Rh B on AAM hydrogel

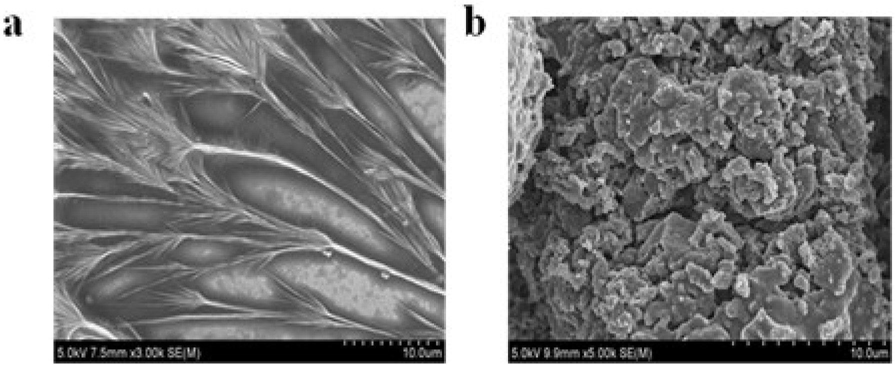

Figure S12. SEM image of hydrogels (a) before, (b) after MB adsorption

6. SEM images of the hydrogel after adsorption of MB

7. PL spectra of GQDs at different excitation wavelength

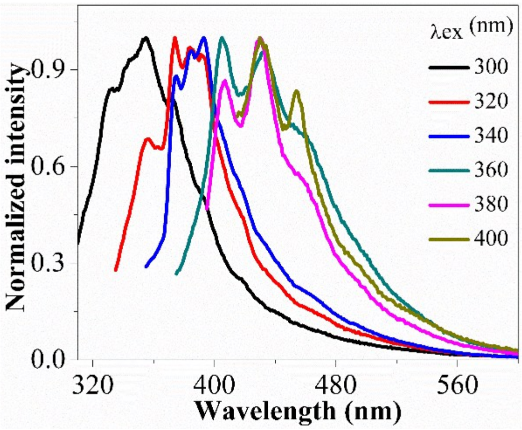

Figure S13. Emission spectra of GQDs at different excitation wavelength

References

1 J. Long, S. Li, J. Liang, Z. Wang and B. Liang, *Polym. Compos.*, 2019, **40**, 723.

2 X. Tong, H. Wang, G. Wang, L. Wan, Z. Ren, J. Bai and J. Bai, *J. Solid State Chem.*, 2011, **184**, 982.

3 Y. Piao and B. Chen, *J. Polym. Sci. Part B Polym. Phys.*, 2015, **53**, 356.

4 M. Sabzevari, D. Cree and L. Wilson, *Journal of Nanomaterials.,* 2014, **2014**, 1.

5 S. Bykkam, V. Rao, S. Chakra and T. Thunugunta, *Int. J. Adv. Biotechnol. Res.*, 2013, **4**, 142.