Electronic Supplementary Information

Environment-friendly reduced graphene oxide as a broad-spectrum adsorbent for anionic and cationic dyes *via* π-π interaction

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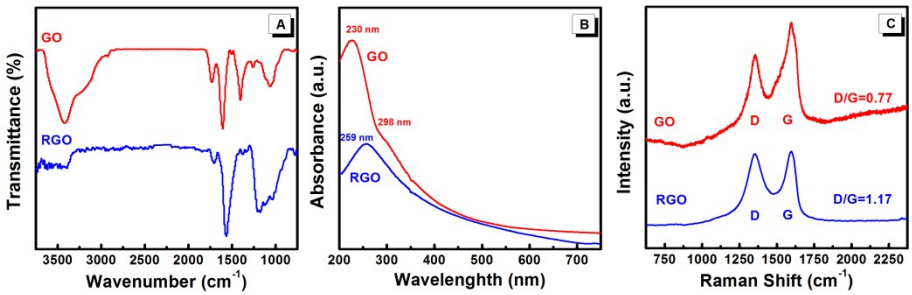


Fig. S1 FT-IR (A), UV-Vis (B) and Raman (C) spectra of GO and RGO.

In (A), the absorption peaks such as C=O (carbonyl) at 1732 cm^{-1}, O-H at 3405 cm^{-1} and 1385 cm^{-1}, C-O (epoxy) at 1260 cm^{-1}, and C-O (alkoxy) at 1064 cm^{-1} in GO [1,2] decrease dramatically after reduction, suggesting that most oxygen functionalities are removed. In (B), the UV-Vis curve of GO dispersion exhibits a peak at 230 nm and a shoulder at 298 nm, attributed to $\pi \rightarrow \pi^*$ transition of phenyl and $n \rightarrow \pi^*$ transition of C=O bonds, respectively. For the RGO, the shoulder at 298 nm disappears and the peak at 230 nm red-shifts to 259 nm due to the restored electronic conjugation.[3] In (C), GO displays a D band at 1351 cm^{-1} and a G band at 1595 cm^{-1}, attributed to the first order scattering of the E2g mode[4] and the reduction in size of the in-plane sp^2 domains,[3] respectively. RGO also contains both D (at 1349 cm^{-1}) and G bands (at 1593 cm^{-1}) but its D/G ratio is higher than GO, suggesting that more sp^2 domains are formed.[3,5] All these results suggest the effective reduction of GO using *L*-cysteine.

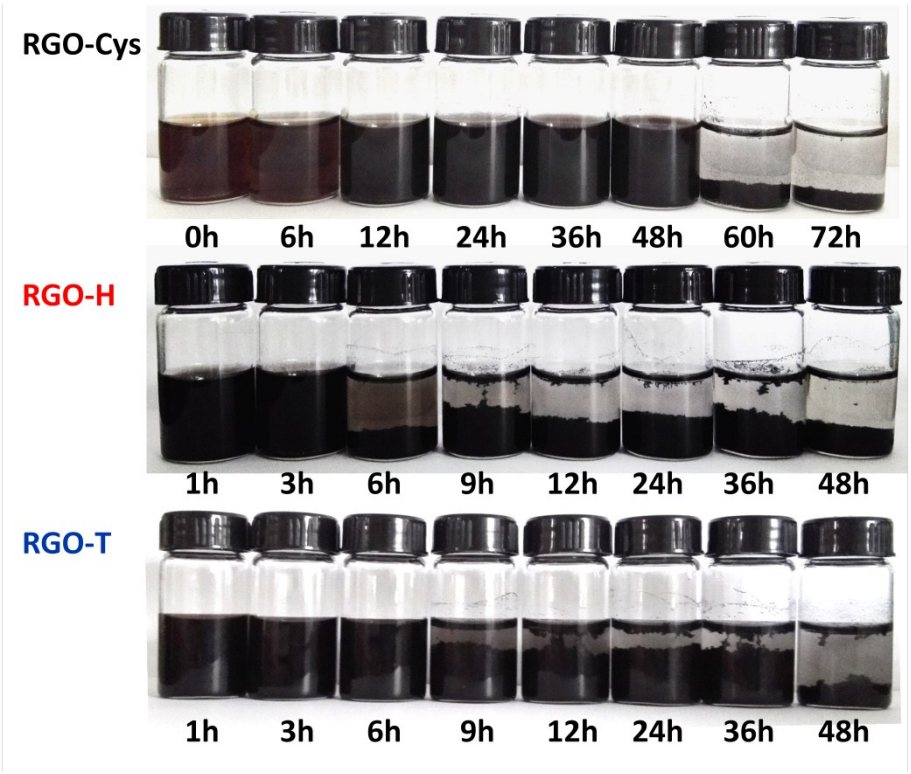


Fig. S2 Effects of reacting time on dispersity of RGO in aqueous solution (0.5 mg/mL) reduced using different methods. All suspensions were stilled for 24 h.

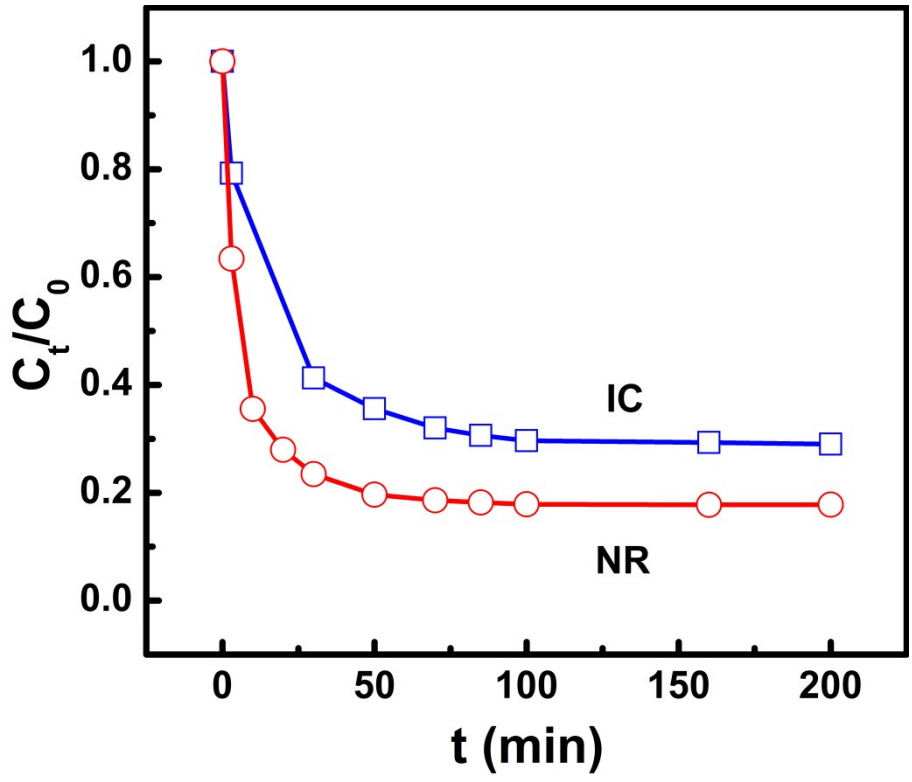


Fig. S3 Changes of C_t/C_0 of IC and NR with the adsorption time increases.

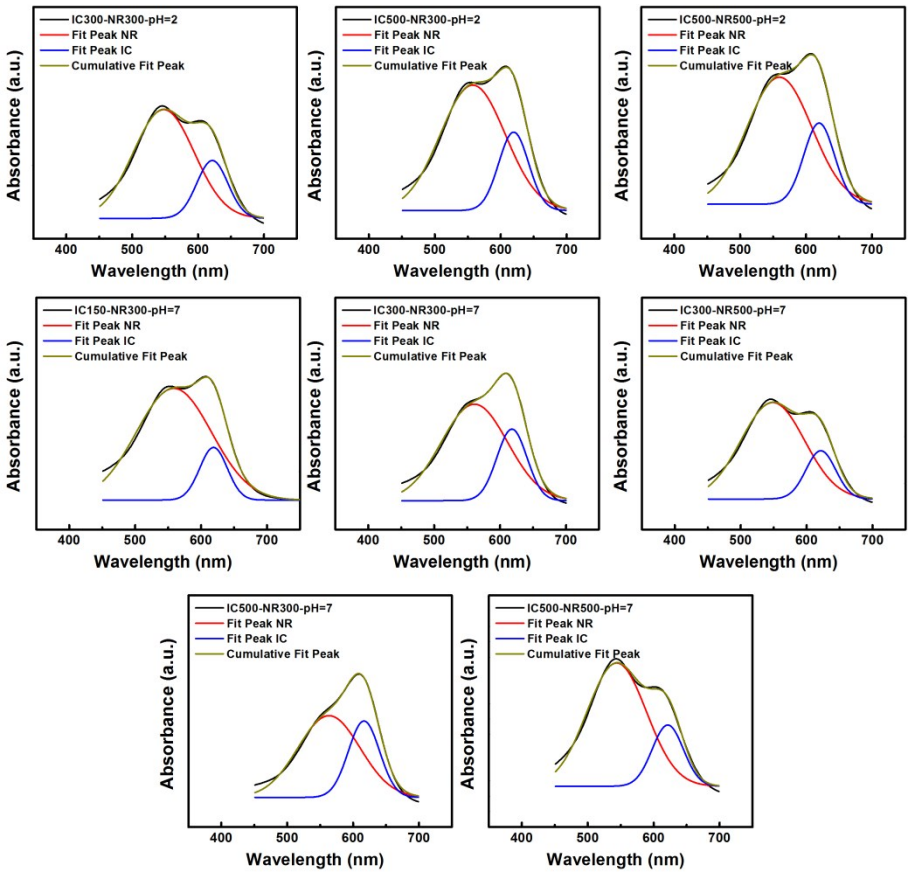


Fig. S4 The peak-differentation-imitating of UV-Vis spectra of mixed dye solutions after absorption using RGO-Cys.

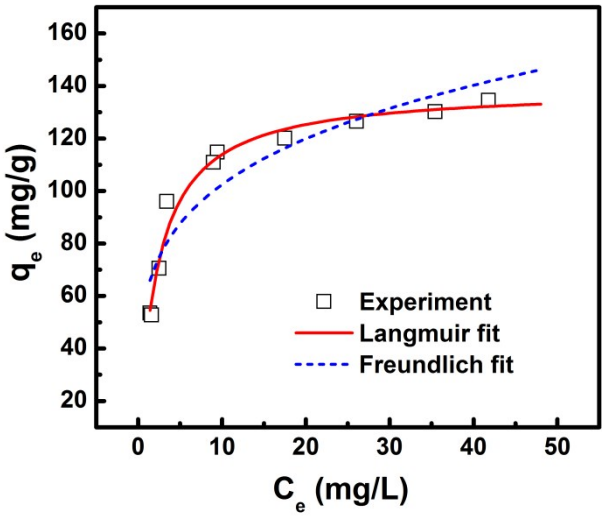


Fig. S5 Adsorption isotherm plots and curves fitted with Langmuir (solid line) and Freundlich (dot line) models of Cu^{2+}

Table S1 The relative contents of different functional groups on GO and RGO-Cys.

Content (%)	C=C	–OH/C–O–C	–COOH
GO	45.4	44.0	10.6
RGO-Cys	72.5	17.7	9.8

Table S2 Thermodynamic parameters for the adsorption of IC and NR

Dyes	C_0	ΔH^0	ΔS^0	ΔG^0 (kJ/mol)			
	(mg/L)	(kJ/mol)	(J/mol/K)	30 °C	35 °C	40 °C	50 °C
IC	300	66.48	235.2	-4.786	-5.961	-7.137	-9.490
	400	36.83	130.8	-2.802	-3.456	-4.110	-5.418
	500	32.89	112.4	-1.167	-1.729	-2.291	-3.415
NR	300	17.11	96.96	-12.27	-12.75	-13.24	-14.21
	400	10.63	53.85	-5.686	-5.956	-6.225	-6.764
	500	4.371	22.94	-2.583	-2.698	-2.809	-3.039

Table S3 Knetic parameters for the adsorption of IC and NR

Dyes	Pseudo-first-order			Pseudo-second-order		
	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/mg/min)	R^2
IC	825.3	0.0822	0.986	897.7	0.0001	0.999
NR	963.1	0.1739	0.989	1022.1	0.0003	0.998

Table S4 Langmuir and Freundlich isotherm parameters for adsorption of IC and NR

Dyes	Langmuir			Freundlich		
	q_m (mg/g)	b	R^2	K ($(L/mg)^{1/n}$)	n	R^2
IC	1005.7	0.243	0.994	707.4	16.4	0.849
NR	1301.8	0.293	0.995	920.2	16.7	0.828

Table S5 q_m of different adsorbents towards IC and NR

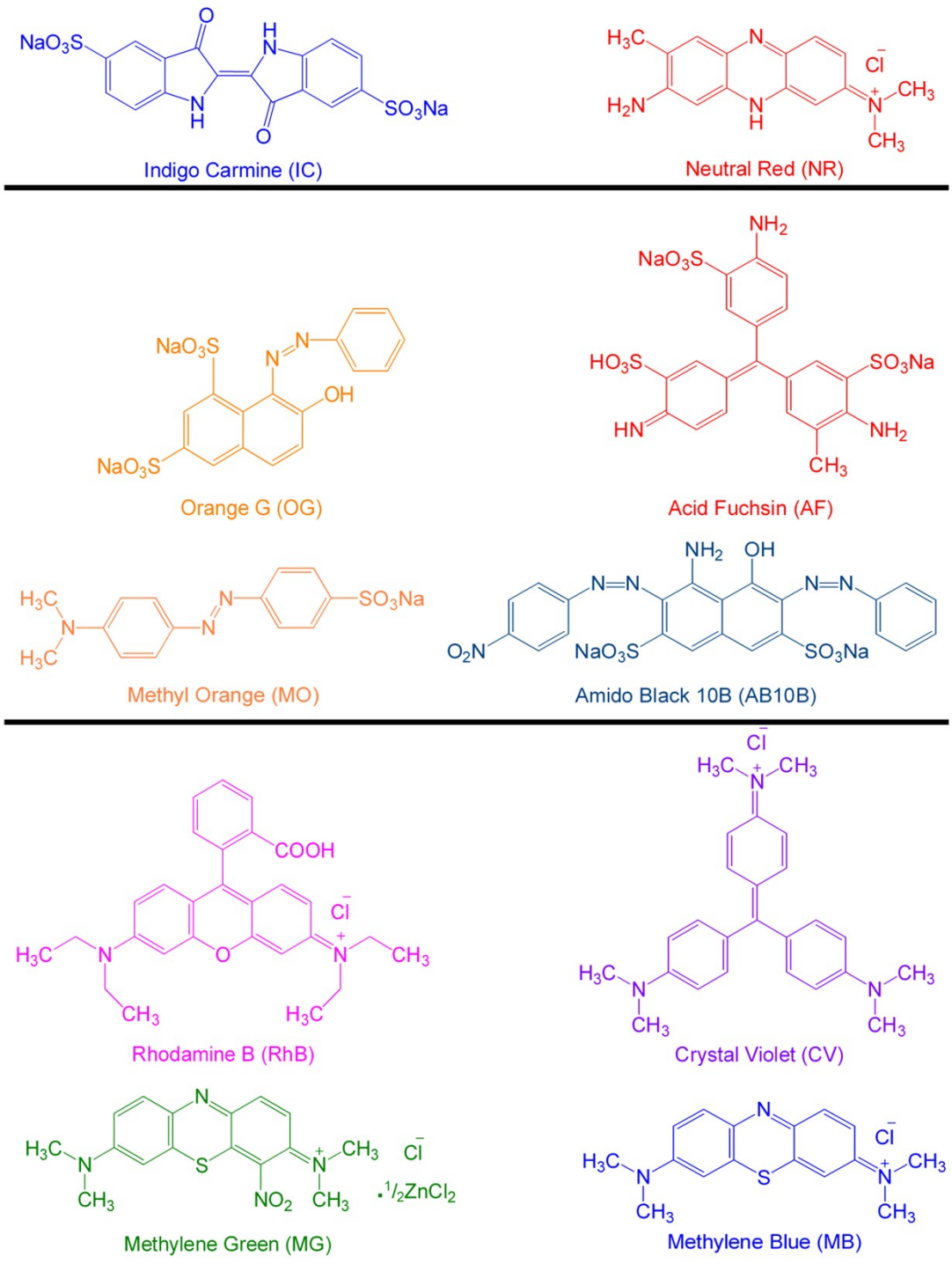
Dyes	Adsorbents	q_m (mg/g)	*Ref.*
IC	Apricot stone actived carbon	552.5	6
	Chitin	5.8	7
	Chitosan	71.8	
	halloysite nanotubes	54.8	8
	Polyampholyte hydrogel	320.0	9
	Polyacrylic acid/SiO_2 nanofiber	523.1	10
	Polyvinyl alcohol/SiO_2 nanofiber	340.0	11
	RGO-Cys	1005.7	This work
NR	Multiwalled carbon nanotube	20.51	12
	Fe3O4 hollow nanosphere	105.0	13
	Chitosan hydrogel/SiO_2	254.1	14
	Chitin hydrogel/SiO_2	306.1	
	Chitin/GO composite	165.0	15
	GO/Fe_3O_4 composite	171.3	16
	Sulfonic graphene//Fe_3O_4	216.8	17
	Mn-impregnated activated carbon	285.7	18
	Triphenylene-modified chitosan	1552.1	19
	RGO-Cys	1301.8	This work

Table S6 Some absorbents and their q_m towards anionic and cationic dyes

Absorbents	Anionic dyes	q_m (mg/g)	Cationic dyes	q_m (mg/g)	*Ref.*
Dual-mesoporous silica	Congo red	5-30	Brilliant green	59-72	20
Kaolin	Congo red	5.5	Brilliant green	65.4	21,22
Maize stem parenchymatous ground tissue	Eriochrome black T	167.0	Methylene blue	160.8	23
Maize cob	Telon blue	47.7	Atrazon blue	160	24
	Erionyl red	41.4	Maxilon red	94.5	
Amine/Fe_3O_4 functionalized raw corn stalk	Methyl orange	101.0	Methylene blue	<5	25
	Reactive brilliant red	222.2			
	Acid red 18	99.4			
Polyallylamine modified yeast	Congo red	167.3	Rhodamine B	14.4	26
Mesoporous carbon nanospheres	Direct red 23	769.2	Basic yellow 28	909.1	27
Porous boron nitride whiskers	Methyl blue	13973.0	Rhodamine B	210.1	28
Activated carbon	Metanil yellow	386	Methylene blue	35-533	29-32
	Telon blue	175	Deorlene yellow	200	
	Remazol black	0-325	Victoria blue	5.5	
	Remazol reactive red	0-279	Disperse blue 7	25	
Porous carbon	Eosin yellow	400	Methylene blue	402.2	33
Magnetite activated carbon	Congo red	116.1	Thionine Janus green	343.8, 612.9	34
	Reactive blue 19	104.6			
	Methylthymol blue	174.6			
	Mordant blue 29	213.4			
Exfoliated GO	Rhodamine B	1.2	Methylene blue	17.3	35
			Methyl violet	2.5	
Magnetic GO	Reactive black 5	164-188	Methylene blue	64.2	36,37
	Orange G	20.8			
Polydopamine (15%) layer coated GO	Coomassie brilliant blue	2100	Methylene blue	1800	38
			Methyl violet	2100	
			Malachite green	2000	
	Methyl orange	30	Basic fuchsin	1700	
			Neutral red	1400	
			Rhodamine B	100	
GO/chitosan hydrogel	Eosin Y	326	Methylene blue	390	39
Magnetic GO/chitosan	Methyl blue	95.3	Methylene blue	180.8	40,41
RGO sponge	Methyl orange	11.5	Methylene blue	184.0	42
			Rhodamine B	72.5	
RGO/Fe_3O_4 nanoparticle	Acid blue 92	45-93	Rhodamine 6G	20-30	43
	Orange 2	44-88	Rhodamine B	37-41	
	New coccine	21-45	Malachite green	35-53	
$CoFe_2O_4$-functionalized RGO	Methyl orange	71.5	Methyl green	204-313	44,45
Amine- RGO/CNT	Methyl orange	294	Methyl violet	298	46
Carbon nanotube/graphene aerogels	Acid fuchsin	35.8	Rhodamine B	150.2	47
			Methylene blue	191.0	
			Fuchsine	180.8	

Table S7 Langmuir and Freundlich isotherm parameters for the adsorption of Cu^{2+}

Langmuir			Freundlich		
q_m (mg/g)	b	R^2	K ((L/mg)$^{1/n}$)	$1/n$	R^2
139.23	0.45	0.977	60.82	0.23	0.881



Scheme S1. Structures of dye stuffs used in this work.

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