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Efficient adsorption of organic dyes on a flexible single-wall carbon nanotube film

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ELECTRONIC SUPPLEMENTARY INFORMATION

Experimental section

Origin of raw single-wall carbon nanotubes (SWCNTs)

The SWCNTs used in this study were purchased from Shenzhen Nanotech Port Co. Ltd, China. No further purification was performed before the fabrication of the SWCNT films.

Fabrication of flexible SWCNT films

Flexible SWCNT films were fabricated by a simple filtration method. About 20 mg of SWCNTs were ultrasonicated in 200 mL of a 0.5 wt% sodium dodecyl sulfate (SDBS) water solution. The suspension was then filtered using a porous cellulose membrane filter with a pore diameter of 0.42 mm. The sheet resistivity of the films was measured by a four-point probe meter (4-probe tech.).

Characterization

The morphology and structure of the SWCNT films were characterized by scanning electron microscopy (SEM, Nova NanoSEM 430), Raman spectroscopy (Jobin Yvon HR800), thermogravimetric analysis (NETZSCH STA 449C), and transmission electron microscopy (TEM, Tecnai F20, 200 kV). The specific surface area and pore structure of the samples were investigated with an automatic volumetric sorption analyzer (ASAP 2020 M) using N_2 as the adsorbate at −196 °C. The UV−*vis* absorption spectra were obtained using a SP-1900 UV−*vis* spectrophotometer.

HNO_3 treatment of the SWCNT films

To remove residual metal catalyst, the SWCNT films were treated by dipping in a 67% HNO_3 solution for 30 min.

Dye adsorption and desorption

Four dyes, Rhodamine B (RhB), methylene blue (MB), methylene orange (MO), and congo red (CR), were used to investigate the adsorption performance of the as-prepared SWCNT films. In a typical experiment, a SWCNT film (~5 mg) was put into an aqueous dye solution (100 mL, 10 mg L^{-1}), followed by stirring at room temperature. At predetermined time intervals of 30 min, the dye concentration was measured by using a UV-*vis* spectrophotometer at the maximum absorbance of each dye (553 nm, 664 nm, 465 nm, and 490 nm for RhB, MB, MO, and CR, respectively). For desorption, the SWCNT film containing the dye was put into ethanol followed by shaking. The adsorbed RhB gradually desorbed from the film and changed the color of the ethanol to pink. After repeatedly washing with ethanol until the solution was colorless, the SWCNT film was dried at 50 °C for 10 h for repeated use.

The dye adsorption amount q_t (mg g^{-1}) was calculated by: $q_t = (C_0 - C_t)V/W$. Where, C_0 and C_t (mg L^{-1}) are the liquid-phase concentration of dyes at the beginning and after time t (min), respectively. V (L) is the volume of the solution, and W (g) is the mass of the SWCNT film used.

SEM and TEM characterizations of the SWCNT film

As shown in Fig. S1a, the film is composed of numerous entangled CNT bundles that are tens of micrometers in length. These bundles have a clean surface and straight tube walls (Fig. S1c). HRTEM observations reveal that there is occasionally an amorphous carbon coating on the outer surface of the SWCNTs (Fig. S1d). Moreover, the walls of the SWCNTs are well resolved, indicating good structural integrity.

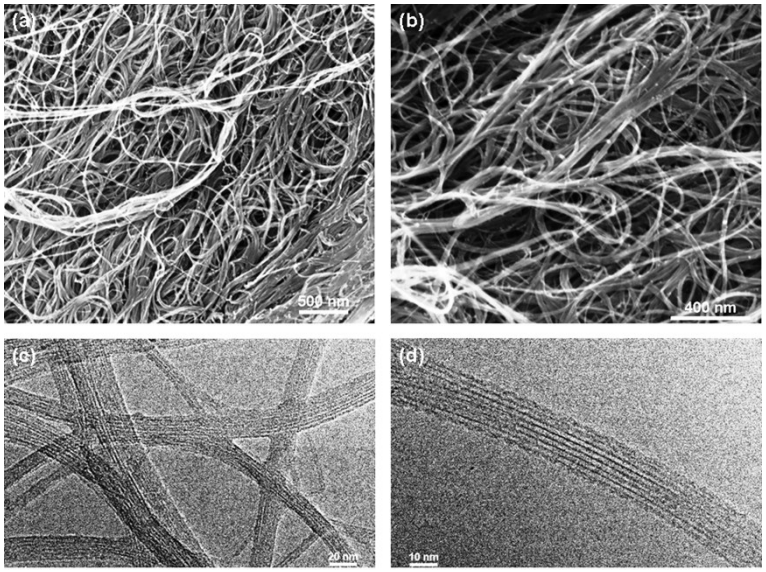

Fig. S1 Typical SEM images of the SWCNT films (a) before and (b) after HNO_3-treatment. (c, d) TEM images of the purified SWCNTs showing their high purity.

Raman spectroscopy of the SWCNTs

Fig. S2 shows a typical Raman spectrum of the SWCNTs excited by a 633 nm laser. The G-band is very narrow and strong, while the D-band is very weak and almost invisible. The I_G/I_D ratio was calculated to be ~62, indicating the high quality of the SWCNTs.

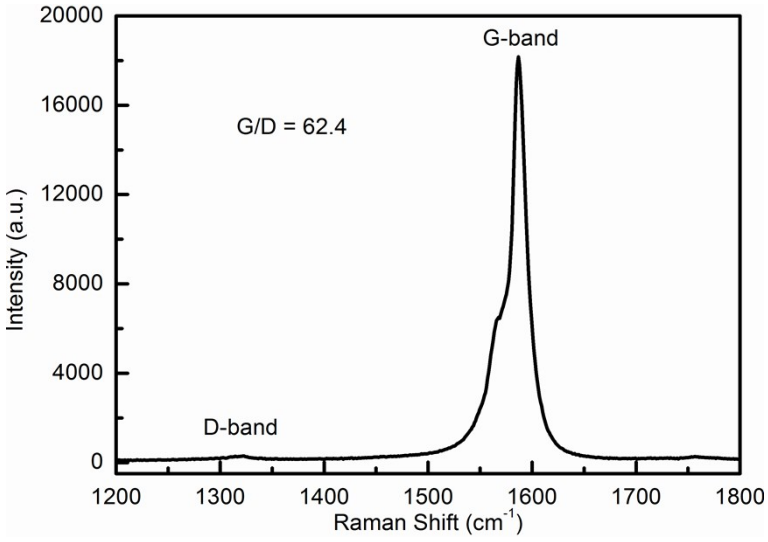

Fig. S2 Raman spectrum of the SWCNTs excited with a 633 nm laser.

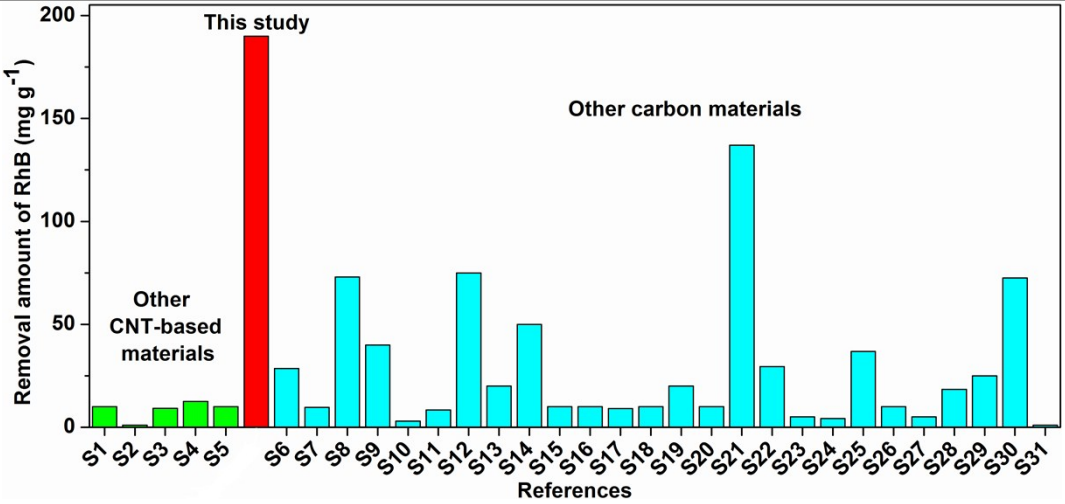

Fig. S3 A comparison of the RhB removal performance of different carbon materials.

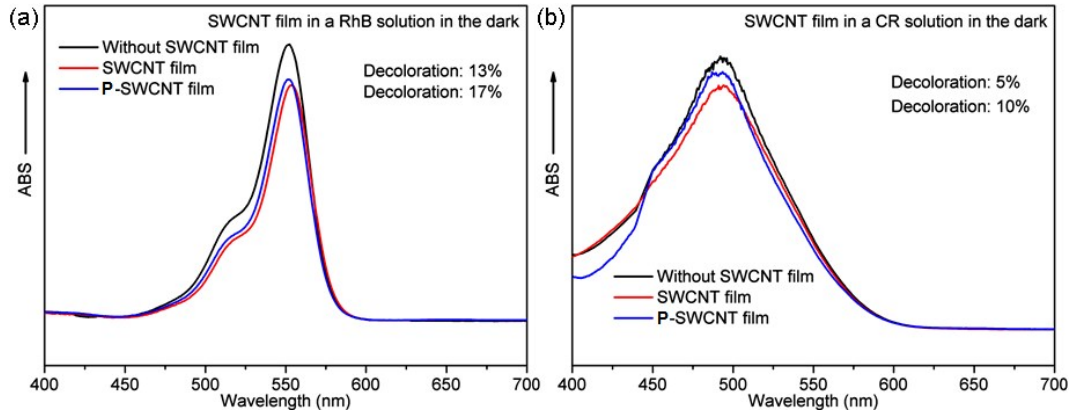

Fig. S4 UV−*vis* absorption spectra of (a) RhB and (b) CR solutions after 240 min in dark. The initial concentrations of RhB and CR: 10 mg L^{-1}; the amount of adsorbent: 5 mg.

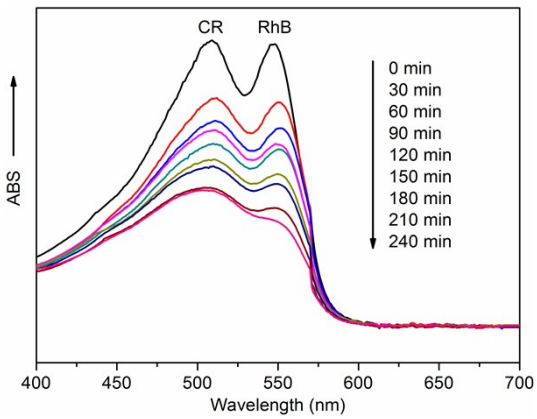

Fig. S5 The UV−*vis* absorption spectra of a mixed RhB and CR aqueous dye solution in the presence of an SWCNT film.

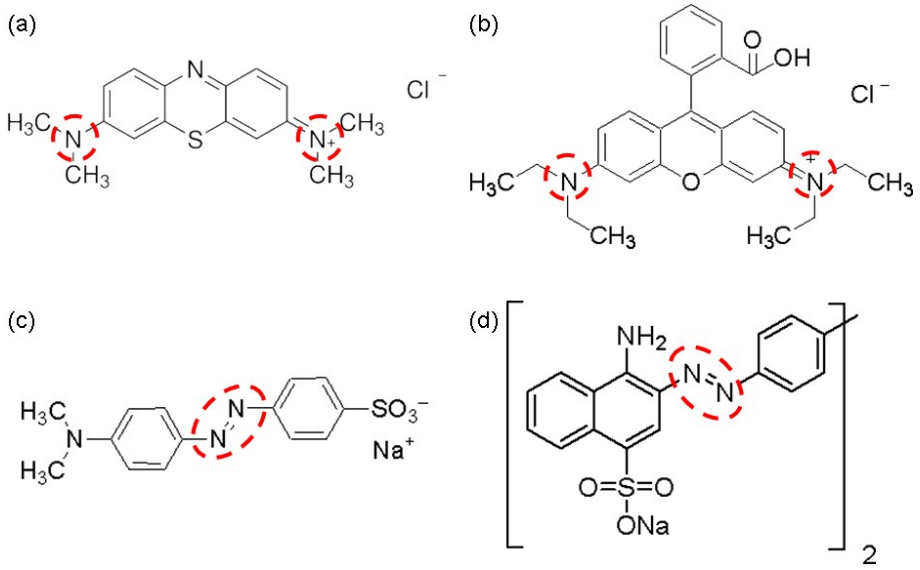

Fig. S6 Molecular formulae of (a) MB, (b) RhB, (c) MO, and (d) CR.

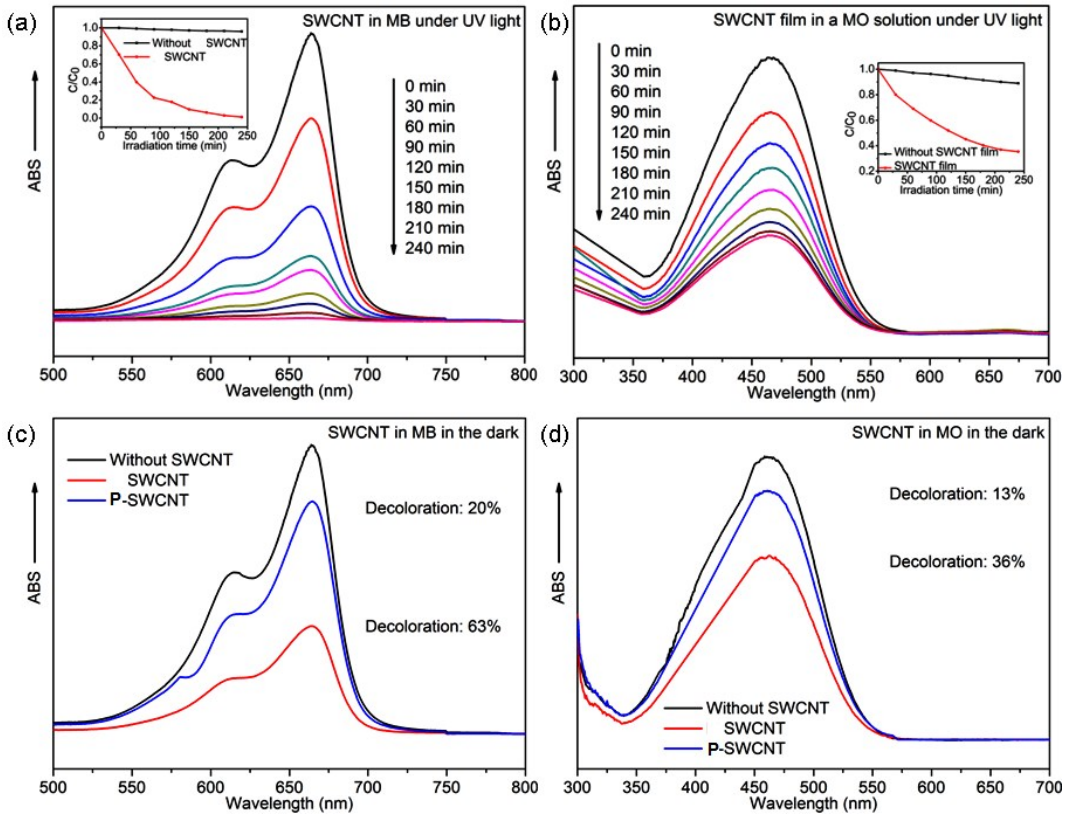

Fig. S7 UV−*vis* absorption spectra of (a) MB and (b) MO solutions after different times of UV light irradiation. Inset: decolorization rates of (a) MB and (b) MO with and without SWCNTs. UV−*vis* spectra of (c) MB and (d) MO solutions after 240 min in the dark. The initial concentration of RhB was 10 mg L^{-1} and the amount of adsorbent was 5 mg.

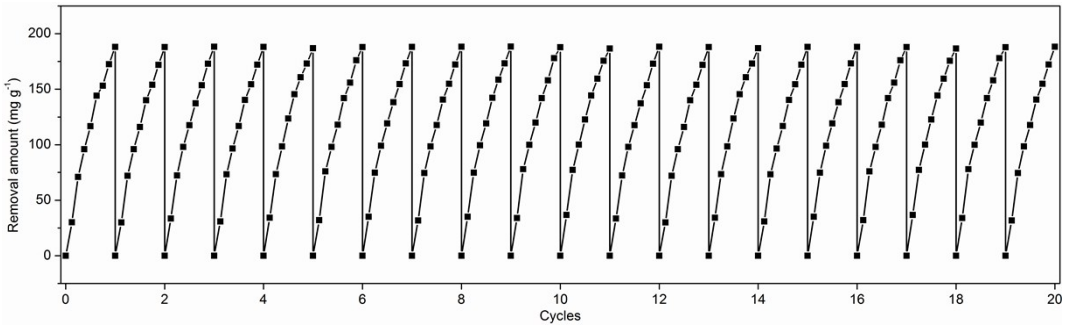

Fig. S8 The cycling stability of the adsorption/desorption of RhB on the SWCNT film.

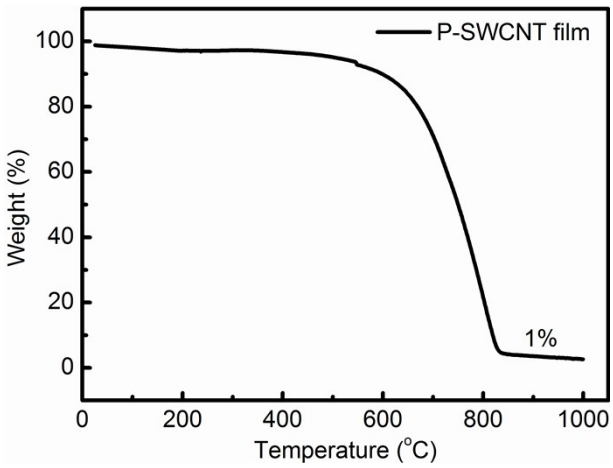

Fig. S9 TGA curve of a P-SWCNT film.

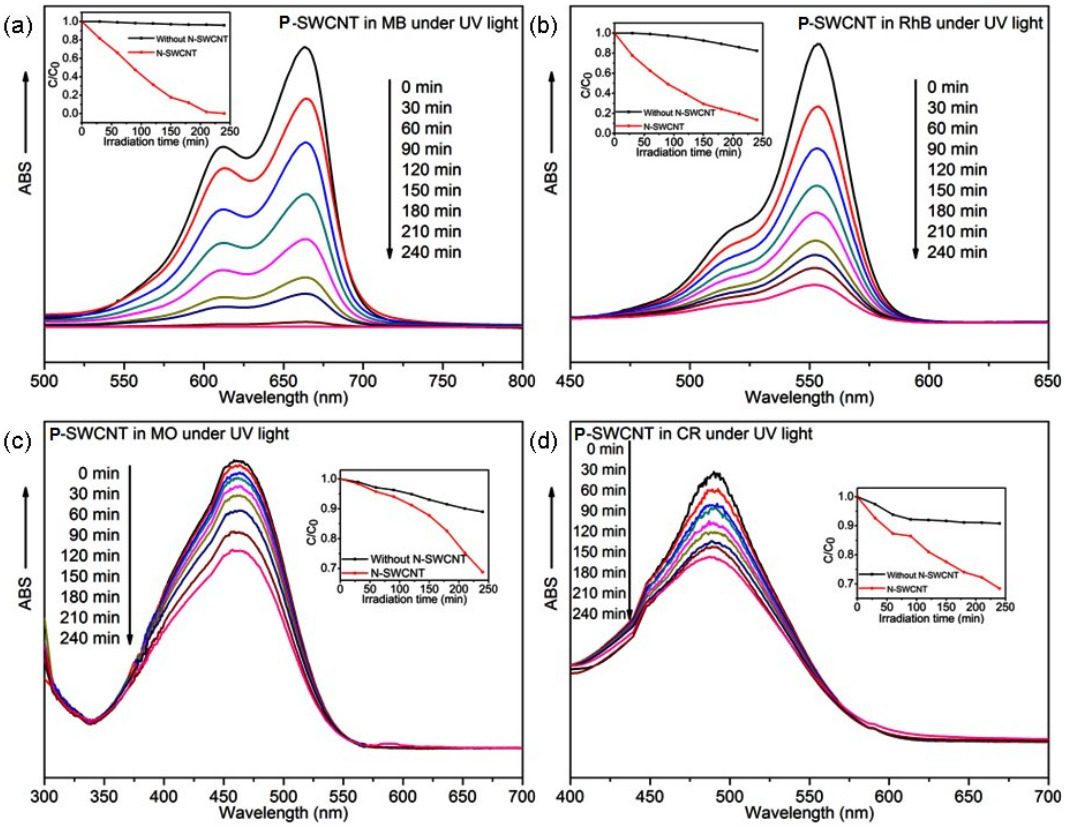

Fig. S10 UV−*vis* absorption spectra of (a) MB, (b) RhB, (c) MO, and (d) CR solutions after different times of UV light irradiation in the presence of the P-SWCNT adsorbent. Inset: decolorization rates of MB, RhB, MO, and CR. The initial concentration of the MB, RhB, MO,and CR solutions was 10 mg L^{-1} and the amount of adsorbent (P-SWCNT) was 5 mg.

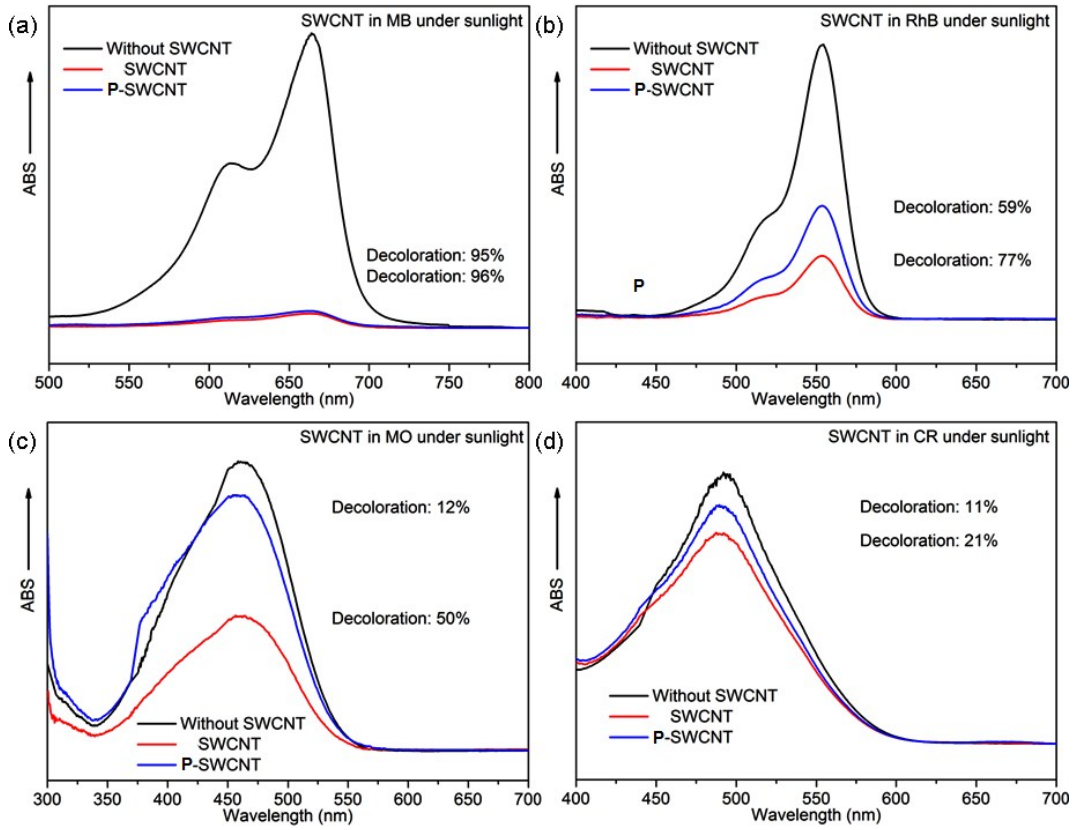

Fig. S11 UV−*vis* absorption spectra of (a) MB, (b) RhB, (c) MO, and (d) CR solutions after 240 min under sunlight in the presence of a SWCNT film. The initial concentration of the MB, RhB, MO, and CR was 10 mg L^{-1} and the amount of adsorbent was 5 mg.

Table S1 Comparison of the dyes adsorption performance of the SWCNT film with that of other reported carbon or carbon-containing materials.

Dye	Adsorpter	Removal amount (mg g^{-1})	Reference
RhB	CNT/Ag_3PO_4	10	S1
	$Ni_{1-x}Co_xFe_2O_4$/MWCNTs	1	S2
	CNT/TiO_2	9.23	S3
	ZnO/N-CNTs	12.5	S4
	MWCNT/BiOBr	10	S5
	CdS/N-rGO	28.6	S6
	AgI-RGO	9.68	S7
	MPGC-900	73	S8
	SiO_2/GO	40	S9
	g-C_3N_4/SiO_2-HNb_3O_8	3	S10
	Ti/g-C_3N_4	8.33	S11
	CNG	75	S12
	g-C_3N_4	20	S13
	g-C_3N_4/BiOBr	50	S14
	g-C_3N_4/TiO_2	10	S15
	SnO_{2-x}/g-C_3N_4	10	S16
	WO_3 NRs/g-C_3N_4	9.1	S17
	Ag_3VO_4/g-C_3N_4	10	S18
	Al_2O_3/g-C_3N_4	20	S19
	CeO_2/C_3N_4/N-rGO	10	S20
	3D-MGFs	137	S21
	3D RGO-based hydrogels	29.44	S22
	mC/C-ZnO	5	S23
	MRGO	4.23	S24
	Ptp-CN	36.8	S25
	SiO_2-C_3N_4	10	S26

	Zn_2SnO_4/g-C_3N_4	5	S27
	$CuFe_2O_4$/g-C_3N_4	18.4	S28
	Bi-Bi_2O_3/C	25	S29
	GSs	72.5	S30
	Fe_3O_4/C/Cu_2O	0.96	S31
	SWCNT film	190	This work
MB	Graphene nanosheet	111.6	S32
	Ni/C nanomaterial	175.2	S33
	SWCNT film	198	This work
	Fe/ordered mesoporous carbon	316	S34
	Calcium alginate/MWCNTs	606.1	S35
MO	Chitosan/Fe_2O_3/MWCNTs	66.9	S36
	SWCNT film	130	This work
	Mesoporous carbon	294.1	S37
	Pinecone derived activated carbon	404.4	S38
	MWCNTs/Fe3O4/PANI	544.99	S39
CR	SWCNT film	90	This work
	Functionalized MWNTs	148	S40
	Activated carbon	300	S41
	Activated carbon fibers	557	S42
	CNT/Mg(Al)O nanocomposites	1250	S43

Scheme S1 The adsorption amount (mg g^{-1}) and color change of dye solutions.

SWCNT	Dye	UV light	Sunlight	Dark
Original	MB	198	192	126
	RhB	190	154	34
	MO	130	100	72
	CR	90	42	20
HNO_3-purified	MB	198	190	40
	RhB	174	118	26
	MO	64	24	26
	CR	64	22	10

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