Electronic Supplementary Material (ESI) for Analytical Methods.

Interfacial Growth of Metal-Organic Framework on Carboxyl-Functionalized Carbon Nanotube for Efficient Dye Adsorption and Separation

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Experimental Section

Materials

Zirconium tetrachloride, 2-amino-1,4-benzenedicarboxylic acid ($H_2BDC\text{-}NH_2$), N,N-dimethyl formamide (DMF), methyl orange (MO), methylene blue (MB) and chloroform were supplied from Sinopharm Chemical Reagent Co., Ltd. All of the chemicals were used as-received without any purification. CNTs-COOH (-COOH content of 3.86%) was purchased from Beijing DK Nanotechnology Co., Ltd.

Characterizations

Powder X-ray diffraction (PXRD) patterns are collected from a BRUKER D8 ADVANCE X-ray diffractometer in the range of 2θ = 5-50^o by step scanning. The size and morphology of composites are determined by a transmission electron microscope (TEM, JEM-2100 plus) and a scanning electron microscope (SEM, Hitachi S4800). Fourier transform infrared spectrum (FT-IR) measurement is performed on a PerkinElmer FT-IR C94349 spectrometer in the range of 650-4000 cm^{-1}. Thermogravimetric analysis (TGA) is carried out under nitrogen atmosphere (20 mL min^{-1}) from 50-700 ^{o}C using PerkinElmer Pyris 1 at a rate of 20 ^{o}C min^{-1}. X-ray photoelectron spectroscopy (XPS) is obtained from an ESCALab220i-XL electron spectrometer with 300W AlKα radiation. C1s line at 284.8 eV from adventitious carbon is used as the binding energy reference. N_2 adsorption-desorption isotherms at 77 K from a Quadrasorb SI-MP system is applied for porosity characterization. Prior to analysis, the samples are activated at 150 ^{o}C for 24 h on a Micrometrics Smart VacPrep System. Zeta potential is measured on a Brookhaven ZetaPALS instrument.

Table S1 Porous properties of CNTs-COOH, UiO-66-NH_2 and their composites

Samples	BET surface area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)	Langmuir
CNTs-COOH	109.4	0.329	--
UiO-66-NH_2	572.3	0.302	737.6
CNTs/UiO-66-NH_2	518.0	0.223	601.8
CNTs-CONH-UiO-66	539.3	0.311	735.0
CNTs@UiO-66-NH_2	692.4	0.359	873.0

Table S2 Contribution of nitrogen peaks resulting from the fitting of Gaussian components to N 1s photoelectron spectra for adsorbents

Adsorbents	Peak area (%)	
	$PhNH_2$ N1s	$PhNH_3^+$ N1s
UiO-66-NH_2	69.79	30.21
CNTs@UiO-66-NH_2	37.60	62.40

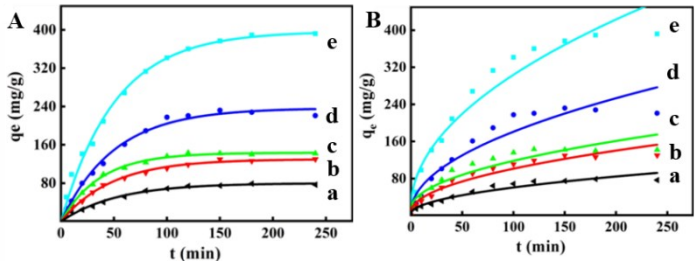


Fig. S1 (A) Fitting of pseudo-first-order kinetic model (B) Fitting of pseudo-second-order kinetic model for different adsorbents: (a) CNTs-COOH, (b) CNTs/UiO-66-NH_2, (c) UiO-66-NH_2 (d) CNTs-CONH-UiO-66, (e) CNTs@UiO-66-NH_2

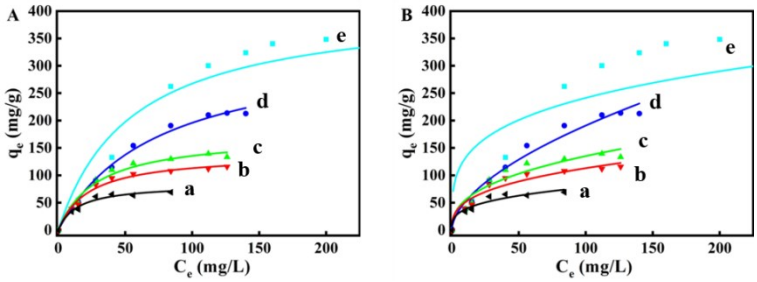
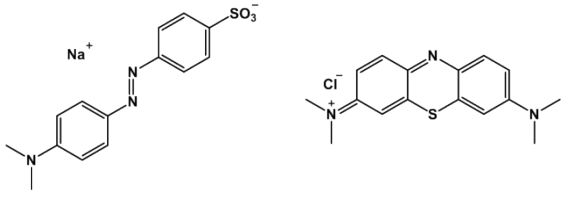


Fig. S2 Fittings of (A) Langmuir and (B) Freundlich kinetic models for different adsorbents: (a) CNTs-COOH, (b) CNTs/UiO-66-NH_2, (c) UiO-66-NH_2 (d) CNTs-CONH-UiO-66, (e) CNTs@UiO-66-NH_2



MO (3.1 Å × 4.3 Å × 14.5 Å) MB (4.2 Å × 5.0 Å × 13.4 Å)

Scheme S1. Schematic drawing of dyes.

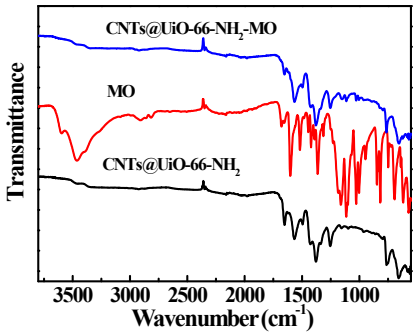


Fig. S3 FTIR spectra of CNTs@UiO-66-NH_2 before and after adsorption of MO.