Fast capture of methyl-dyes from wastewater over hierarchical amino-Co$_{0.3}$Ni$_{0.7}$Fe$_2$O$_4$@SiO$_2$ nanofibrous membrane

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Materials:

Poly(viny alcohol) (PVA; *MW* ranging from 85000 to 124000 g/mol) was purchased from Sigma, tetraethyl orthosilicate (TEOS, 98 wt%) was pruchased from Lingfeng Chemical Co., Ltd., China. Phosphoric acid (H_3PO_4, 85 wt%), $Co(NO_3)_2·6\ H_2O$, $Ni(NO_3)_2·6\ H_2O$, $Fe(NO_3)_3·9\ H_2O$ were purchased from Aladdin Chemical Reagent Co., Ltd., China. Dopamine and Tris-HCl were purchased from Shanghai Richjiont Chemical Reagents Co., Ltd China. Paperadhensive was purchaed from Shanghai petrocchemical adhesive factory Co., Ltd., China. DI water was obtained from a Millipore system. All chemicals were of analytical grade and were used as received without further purification.

Preparation of SiO₂ NFMs

The electrospun SiO_2 NFMs were fabricated as follows. The precursor solution was prepared by dissolving PVA in DI water at 70 °C with vigorous stirring for 12 h. A silica sol with a molar ratio of $SiO_2:H_2O:H_3PO_4:=1:11:0.01$ was prepared through hydrolysis TEOS in phospheric acid solution. Then, 10 g of resultant silica sol was mixed with 10 g of PVA solution to improve the electrospinnability of the PVA/SiO_2 solution. The electrospinning process was performed at a fixed voltage of 20 kV and a fixed feed rate of 1.0 mL h^{-1} with a distance of 20 cm between the needle tip and the round collector. The chamber temperature and relative humidity during electrospinning were 23±2 °C and 42±3%. Finally, the electrospun SiO2 nanofiber membrane(NFM) was collected on a aluminum foil then calcined at 800 °C in air to remove the PVA. Thus, a pure SiO_2 NFMs was obtained for future experiments.

Fabrication of Co₀.₃Ni₀.₇Fe₂O₄@SiO₂ NFMs

Mixed salts solution was prepared by dissolving $Fe(NO_3)_3·9\ H_2O$, $Co(NO_3)_2·6\ H_2O$ and $Ni(NO_3)_2·6\ H_2O$ in DI water with an atomic raito of 0.3Co: 0.7Ni:2Fe of 1 , 2 and 4 wt% of $Fe(NO_3)_3·9\ H_2O$, were dissolved in distilled water, and guarentee the $Co(NO_3)_2·6\ H_2O$ and $Ni(NO_3)_2·6\ H_2O$, a mole ratio corresponding to the nominal

composition of Co: Ni: Fe ratio of 0.3: 0.7: 2, and Then paperadhesive solution (with various concentrations: 0.5, 1 and 2 wt%) was mixed with the above salt solution and vigrouly stirred until a homogeneous   gelatin sol was obtained. Subsequently, the SiO_2 NFMs was dipped in the mixed sol for 10 min with mildstirring. After dipcoating,   the membranes were dried in a oven at 50 °C for 30 min, leading to the formation of the crosslinked gelatin layer on fiber surface which contained homogeneouly distributed $Co(NO_3)_2$, $Ni(NO_3)_2$ and $Fe(NO_3)_3$. Then , the gelatin/SiO_2 NFMs were calcined at 700 °C for 2 h with a heating rate of 5 °C/min in N_2 flow and yielded the $Co_{0.3}Ni_{0.7}Fe_2O_4$@SiO_2 NFMs. Different concentration of paper adhesive and salt concentration was denoted as A-x-SiO_2 NFMs-M-y in the subsequent supporting information discussion, where A and M stands for adhesive and metal ion, and x and y stands for the concentration of adhesive and $Fe(NO_3)_3·9$ H_2O.

Surface modification of $Co_{0.3}Ni_{0.7}Fe_2O_4$@SiO_2 NFMs by dopamine

$Co_{0.3}Ni_{0.7}Fe_2O_4$@SiO_2 NFMs were surface modified with aqueous solutions of dopamine and HCl (2 mg/ml dopamine in l0 mM Tris-buffer, pH=8.5). The pH of the solution was monitored with a pH meter (Mettler Toledo FE-20). The $Co_{0.3}Ni_{0.7}Fe_2O_4$@SiO_2 NFMs was stirred in the dopamine solution at 50 °C for 24 h, and the color of the solution changed from brown to dark brown. The $Co_{0.3}Ni_{0.7}Fe_2O_4$@SiO_2 NFMs coated with PDA were suction filtered, rinsed thoroughly with deionized water at least three times, and dried in a vacuum oven at 50 °C for 6 h. The PDA coated $Co_{0.3}Ni_{0.7}Fe_2O_4$@SiO_2 NFMs was denoted as PDA-$Co_{0.3}Ni_{0.7}Fe_2O_4$@SiO_2 NFMs.

Characterization

The morphology of NFMs was examined by a scanning electron microscope (SEM, Hitachi, S4800). TEM and selected area electron diffraction patterns were acquired by a JEM-2100F, JEOL Ltd., Japan. X-ray diffraction (XRD) patterns of NFMs were

obtained on an X-ray diffractometer (Rigku, ultima IV). Thermal degradation measurements were performed using a thermogravimetric analyzer (TG) (NETZSCH, STA 449F3). Fourier-transform infrared spectroscopy (FT-IR, Thermo Scientific, Nicolet 6700) was applied to detect the presence of dopamine. BET surface area and pore size distribution were obtained by measuring N_2 adsorption-desorption isotherms on a Micromeritics, physisorption analyzer, ASAP 2020. The concentration of dye in the solution was measured by a UV–Vis spectrometer (Shimadzu, UV-1800). The near-surface chemical information of materials were analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha, Al Kα radiation, 1486.6 eV, 12 kV, 3 mA). XPS peak positions were calibrated with the help of the C 1s peak at 285.0 eV. The N content of hybrid membrane before and after adsorption was analyzed by an organic elemental analyzer (Thermo Flash 2000).
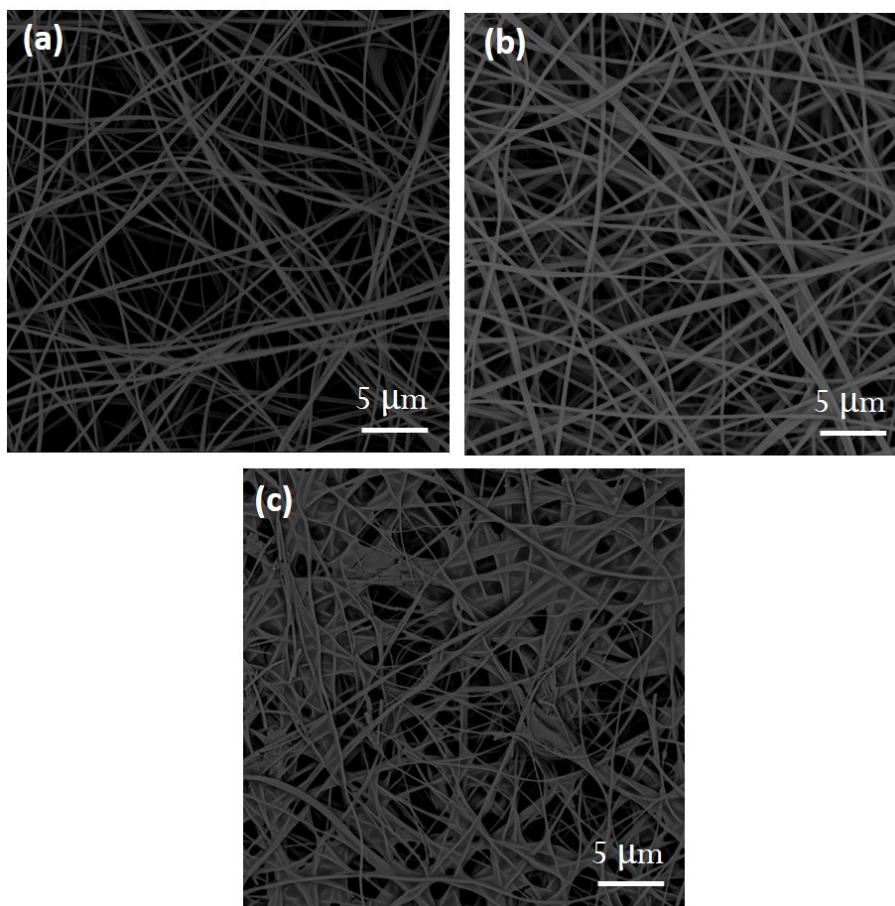
Fig. S1. FE-SEM images of SiO$_2$ NFMs dip-coated in aqueous paper adhesive solutions with various concentrations (a) 0.5wt%, (b) 1.0wt% and (c) 2 wt%, respectively.
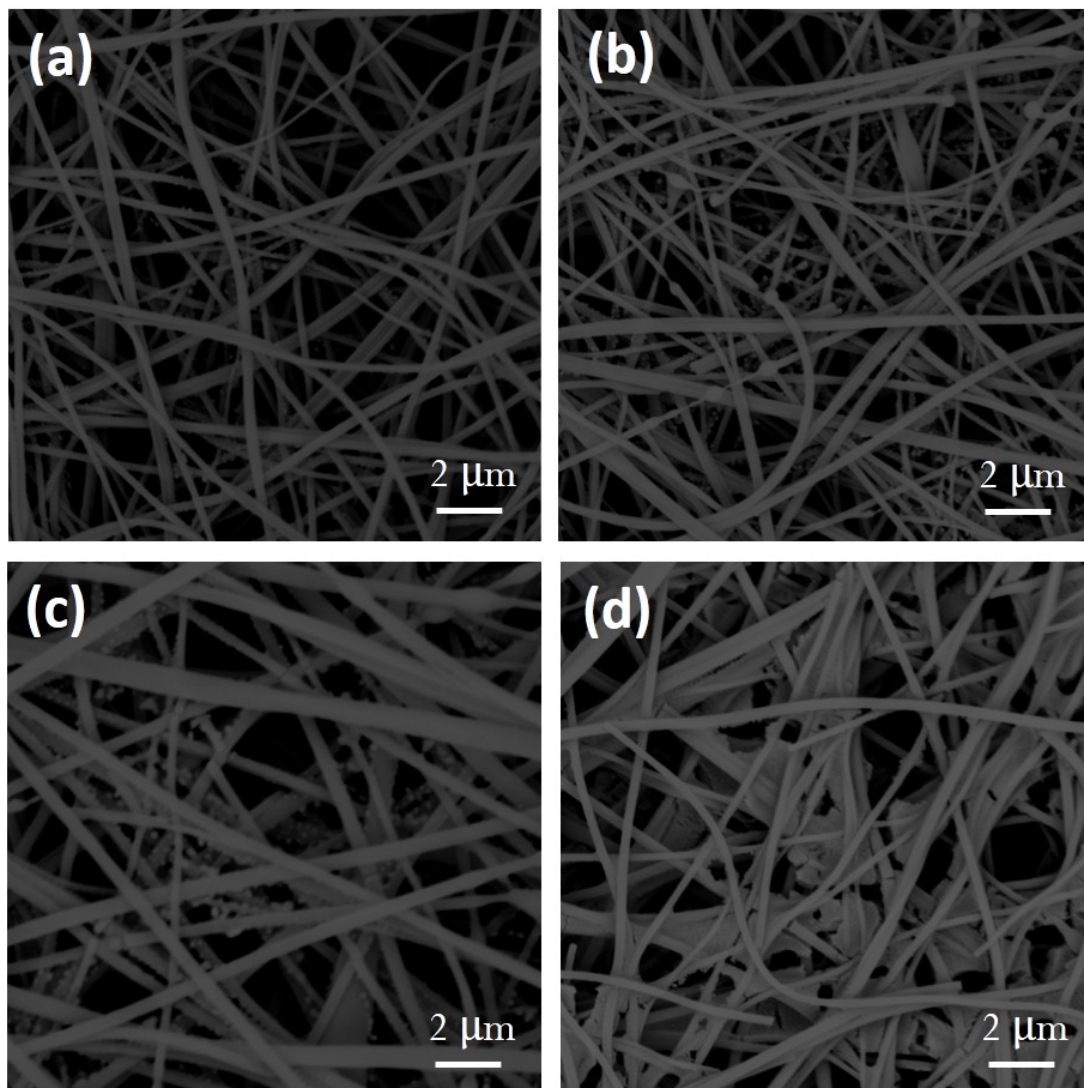
Fig. S2. FE-SEM images of A-1-SiO$_2$ NFMs dipcoated in solutions with various concentrations of salts (a) 1wt%, (b) 2wt%, (c) 4 wt% and (d) 8 wt%, respectively.
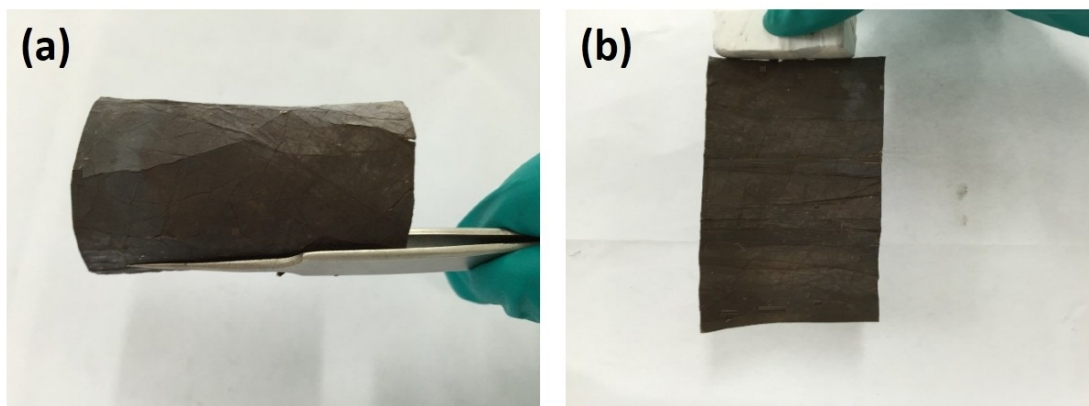
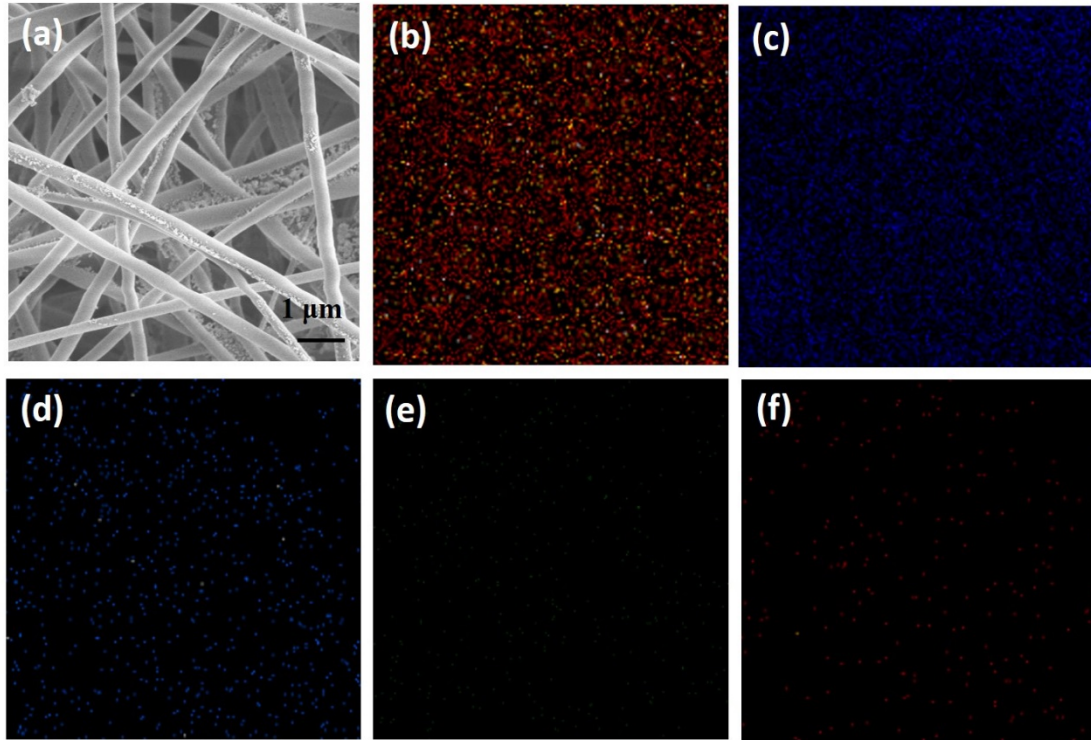Fig. S3 Demonstrations of the (a) flexibility and (b) magnetism of the NFMs.

Fig. S4. (a) FE-SEM images of $Co_{0.3}Ni_{0.7}Fe_2O_4@SiO_2$ NFMs and corresponding elemental mapping, (b) oxygen, (c) silicon, (d) iron , (e) cobalt and (f) nickel.
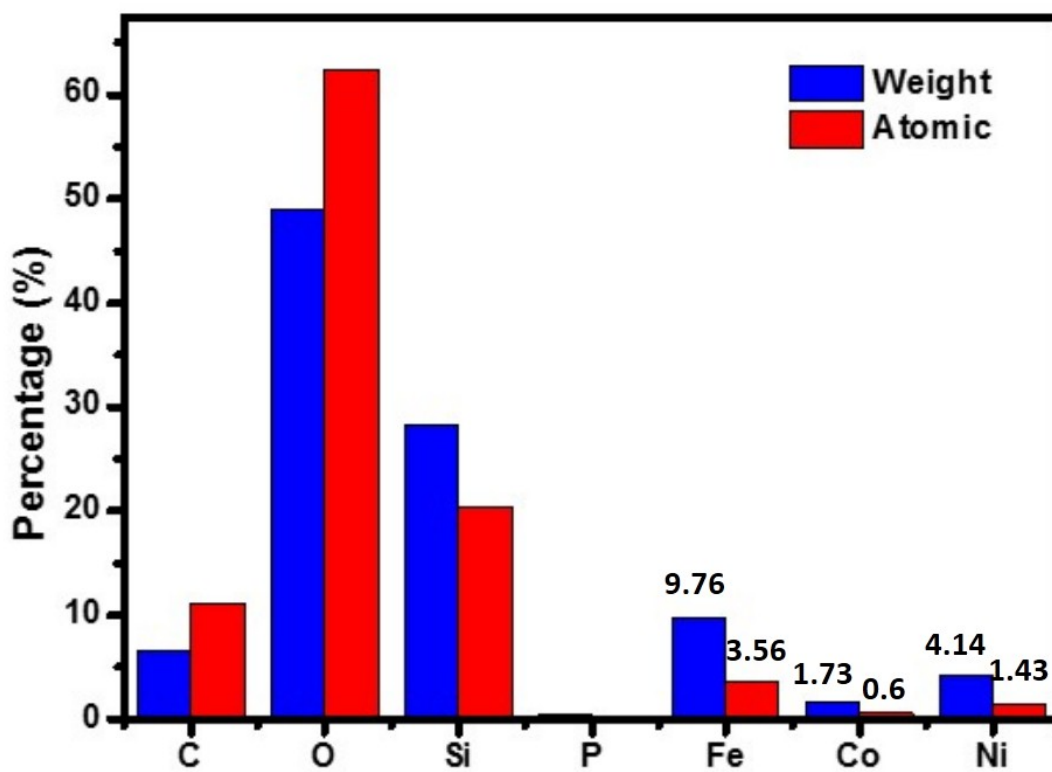
Fig. S5. EDS results of the weight and atomic percentage of C, O, Si, P, Fe, Co and Ni of $Co_{0.3}Ni_{0.7}Fe_2O_4@SiO_2$ NFMs.
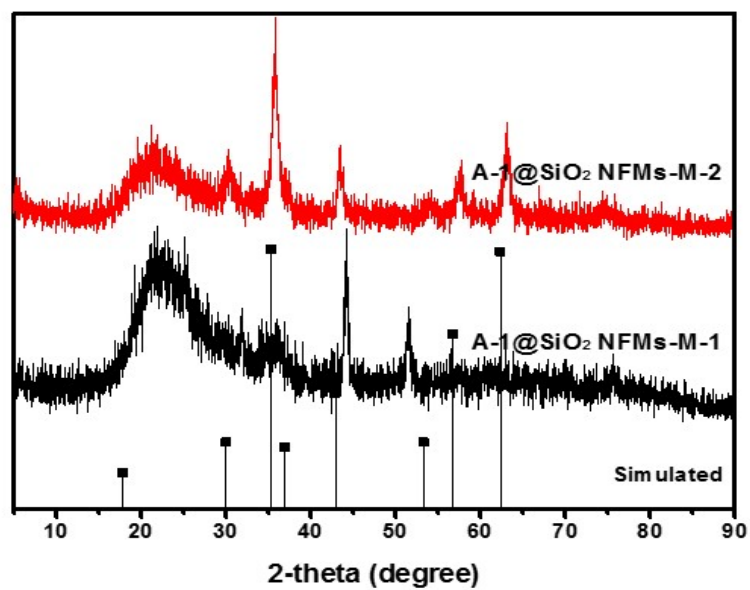
Fig. S6. XRD diffraction patterns of $Co_{0.3}Ni_{0.7}Fe_2O_4@SiO_2$ NFMs prepared with various salt concentrations.

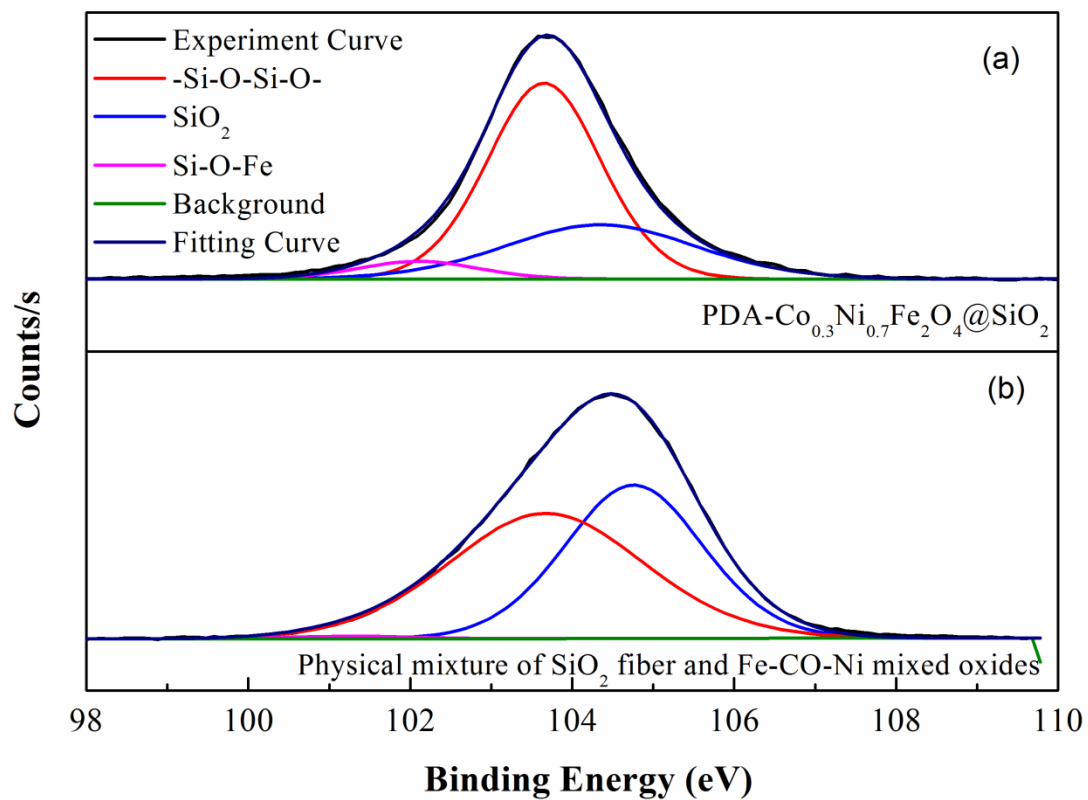Fig. S7 Si2p spectra of PDA-Co$_{0.3}$Ni$_{0.7}$Fe$_2$O$_4$@SiO$_2$ NFM (a) and physical mixed SiO$_2$/Fe-Co-Ni oxides (b).
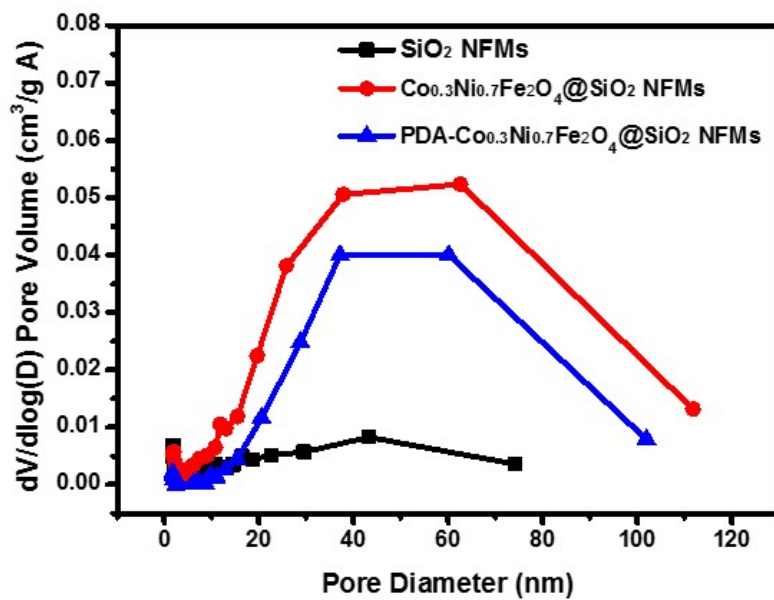
Fig. S8. Pore size distributions (calculated from N_2 adsorption-desorption isotherms) of SiO_2, $Co_{0.3}Ni_{0.7}Fe_2O_4@SiO_2$ and PDA-$Co_{0.3}Ni_{0.7}Fe_2O_4@SiO_2$ NFMs.
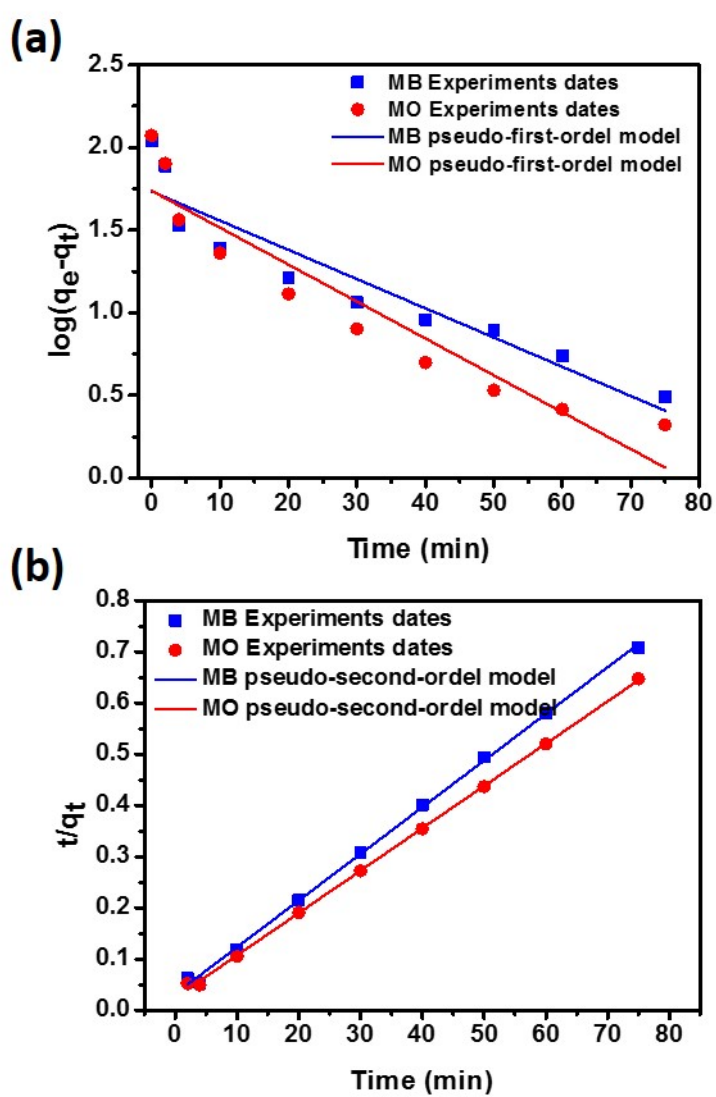
Fig. S9. Adsorption kinetics for MO and MB onto PDA-$Co_{0.3}Ni_{0.7}Fe_2O_4$@SiO_2 NFMs. (a) pseudo-first-order and (b) pseudo-second-order.

Table S1 Comparison of the adsorption capacity of NFMs .

Adsorbents	Dye	Concentration (g/L)	pH	Adsorption capacity (mg/g)	Responsive time (h)	Ref
Acid/carbon	MO	0.5-0.6	6	88	48	[1]
γ-Fe$_2$O$_3$ /MWCNTs/chitosan	MO	0.05	6.5	61.43	3	[2]
hollow α-Fe$_2$O$_3$ nanofibers	MO	0.1	7	80.6	0.25	[3]
Keratin nanofibrous	MB	0.25	6	170	0.83	[4]
Fe$_3$O$_4$/graphene nanocomposite	MB	0.25	-	70	3	[5]
PVA/PAA@PDA	MB	0.05	3-4	445.7	1.25	[6]
PDA-Co$_{0.3}$Ni$_{0.7}$Fe$_2$O$_4$ NFMs	MO	0.02	7	116.2	0.66	This work
PDA-Co$_{0.3}$Ni$_{0.7}$Fe$_2$O$_4$ NFMs	MB	0.02	7	107.5	1	This work

Reference

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