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Supporting information

One-step preparation of CdS-modified mesoporous titanate nanobelts: its application as high-performance cationic dye adsorbents

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SI-1 Experimental section

The synthesis of TiO_2 nanobelts: 2 g TiO_2 (Degussa P25) was dispersed in a mixed solution containing 40 mL NaOH (10 mol·L^{-1}) and 40 mL ethanol, then transferred into a 100 mL of Teflon-lined stainless autoclave and maintained at 180 °C for 12 h. The white precipitates were washed by deionized water for several times, followed by constant stirring in 0.1 mol·L^{-1} HCl solution for 24 h. The obtained precipitates were washed with deionized water and ethanol alternately until pH=7, and died in vacuum oven at 80°C over night. TiO_2 nanobelts were obtained through calcination of the solid at 400 °C in the air for 2 h.

The synthesis of CdS quantum dots: 1.68 g $Na_2S·9H_2O$, 0.90 g $CdSO_4$, 0.10 g polyvinylpyrrolidone (PVP) and 70 mL deionized water were mixed in 100 mL of Teflon-lined stainless autoclave, and maintained at 160 °C for 2 h. The obtained yellow products were washed by deionized water for several times and dried in vacuum oven at 80°C over night.

Table S1. Sample numbers and corresponding experimental conditions

Samples	m_{CdS} (mg)	m_{TiO2} (mg)	V_{NaOH} (mL)	Absolute ethanol (mL)	Solvothermal time (h)	Solvothermal temp (ºC)
CTNS-1	0	500	40	40	2	180
CTNS-2	0.5	500	40	40	2	180
CTNS-3	5	500	40	40	2	180
CTNS-4	25	500	40	40	2	180
CTNS-5	50	500	40	40	2	180
CTNS-6	100	500	40	40	2	180
CTNS-7	150	500	40	40	2	180

SI-2 The adsorption effect of CTNS-3 on MB and NR

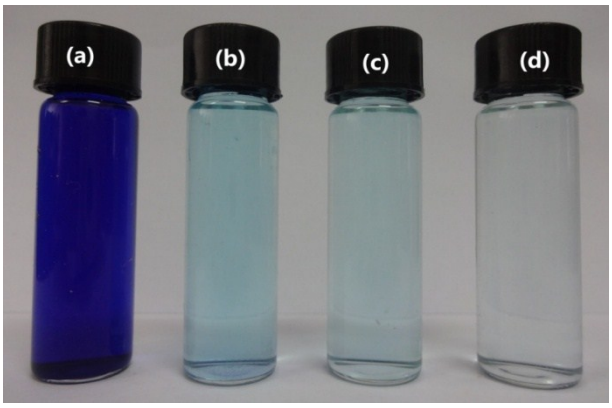

Fig. S1. Comparison of MB adsorption effect in the absence (a) and presence of CTNS-3 (b, 25 ºC; c, 45 ºC and d, 65 ºC).

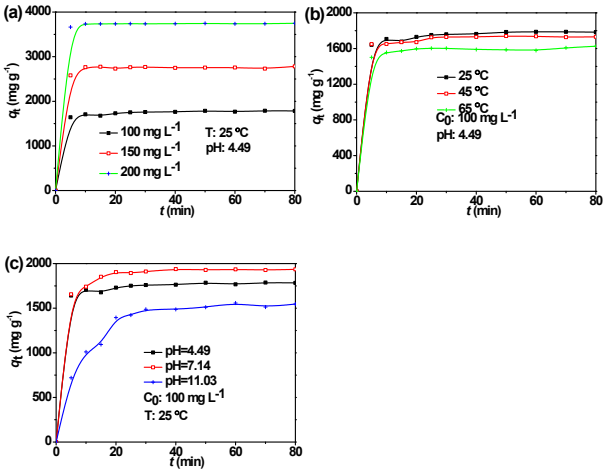

Fig. S2. The effect of intial NR concetration (a), temperature (b) and pH (c) on the adsorption capacity of MB in the presence of CTNS-3.

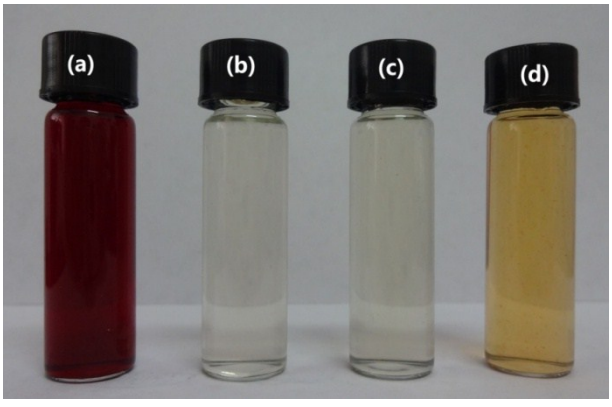

Fig. S3. Comparison of NR adsorption effect in the absence (a) and presence of CTNS-3 (b, 25 ºC;

c, 45 ºC and d, 65 ºC).

SI-3 Adsorption isotherms

Taking MB as the model cationic dye for the study of adsorption isotherms, and the adsorption isotherms are obtained by varying the initial concentrations of MB. The Langmuir and Freundlich models are used [1]. The Langmuir model is described in equation S1:

$C_e/q_e = C_e/q_m + 1/(K_L q_m)$ (S1)

where q_e and C_e are the amount (mg g^{-1}) adsorbed and concentration (mg L^{-1}) of the MB at equilibrium, q_m is the maximum adsorption capacity and K_L is the Langmuir constant. The q_m and K_L represents a monolayer on the adsorbent and the affinity grade between the sorbent and adsorbent respectively.

The Freundlich model is shown in equation S2:

$\log q_e = \log K_F + (1/n)\log C_e$ (S2)

where q_e and C_e are the amount (mg g^{-1}) adsorbed and concentration (mg L^{-1}) of the MB at equilibrium respectively, K_F and n are parameters of the Freundlich model. Where n represent the heterogeneity. The parameter of n can indicates the favorable tendency of adsorption process.

The fitting results of Langmuir and Freundlich models depending on the Equation (S1) and (S2) and the experimental data are shown in the Figure S4. The correlation coefficients of Langmuir and Freundlich models are 0.9978 and 0.9922 respectively. It can be seen that the correlation coefficients of Langmuir and Freundlich models are very close. As the nitrogen adsorption-desorption isotherm of CTNS-3 belongs to type-IV isotherm, which is representative of mesoporous material, and the Langmuir model usually corresponds to the type-Iisotherm. So, the Langmuir model does not fit the actual adsorption process of MB, and the whole adsorption process of MB for CTNS-3 is attributed to the Freundlich adsorption model.

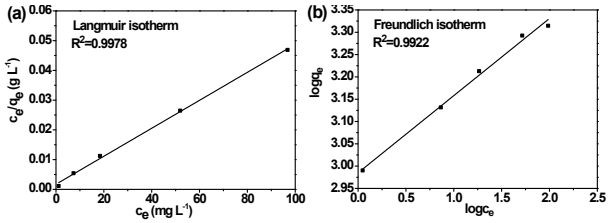

Fig. S4. Langmuir adsorption isotherm and Freundlich adsorption isotherm of CTNS-3 for MB at

25°C.

SI-4 Adsorption kinetics

To better understand the adsorption process of cationic dyes onto CTNS-3, first-order kinetic and second-order kinetic models are used respectively, and MB is chosen as model cationic dye for the study of adsorption kinetics. The first-order rate expression is equation S3 [2]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{(S3)}$$

where q_e and q_t are adsorption capacity of MB adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, and k_1 the rate constant of adsorption (min^{-1}). Values of k_1 are calculated from the slope of plots in Figure S5 at different initial MB concentrations, temperature and pH. The values of k_1, q_e, and correlation coefficients are summarized in Table S2.

The second-order kinetic model is expressed in equation S4 [3]:

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad \text{(S4)}$$

where k_2 is the rate constant of second-order adsorption (g mg^{-1} min^{-1}). Figure S6 shows the second-order kinetic of MB onto CTNS-3 at different initial concentrations, pH and temperatures. Values of k_2 and q_e can be calculated from the intercept and slope of plots of t/q_t versus t. Results show that the plots of t/q_t versus t for the experiment has a good linear relationship, and the experimental values of q_e agree with the calculated q_e values better (Table S2). Almost all the correlation coefficients for the second-order model is greater than 0.999. In the view of all these results, it can be concluded that the second-order kinetic model belong to the actual adsorption process of MB onto CTNS-3.

The half adsorption time ($t_{1/2}$) of MB, i.e. the time required for the CTNS-3 to uptake half of the amount adsorbed at equilibrium. The important parameter to assess the adsorption rate for the second-order process is $t_{1/2}$. The equation of calculating $t_{1/2}$ is as below [4]:

$$t_{1/2} = 1/(k_2 q_e) \quad \text{(S5)}$$

The calculated values of $t_{1/2}$ are listed in Table S2.

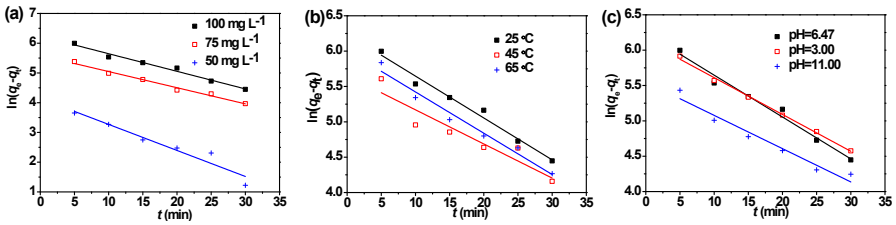

Fig. S5. First-order kinetics of MB onto CTNS-3 at different initial concentrations (a), temperatures (b) and pH (c).

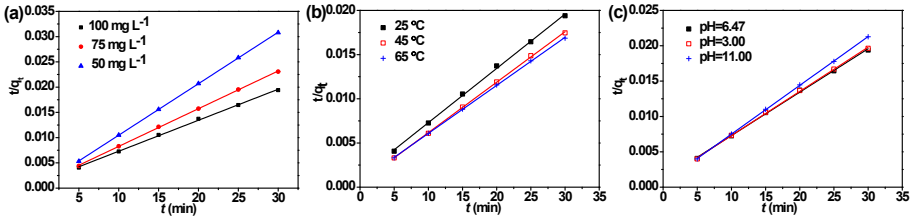

Fig. S6. Second-order kinetic of MB onto CTNS-3 at different initial concentrations (a), temperatures (b) and pH (c).

Table S2. Kinetics values calculated from MB adsorption onto CTNS-3

Parameters			First-order kinetic model				Second-order kinetic model			
T (ºC)	C_0 (mg·L^{-1})	pH	q_e (exp.) (mg·g^{-1})	k_1 (min^{-1})	q_e (calculated) (mg·g^{-1})	R^2	k_2 (g·mg^{-1}·min^{-1})	q_e (calculated) (mg·g^{-1})	R^2	$t_{1/2}$ (s)
25	50	6.47	978	0.0875	63	0.9208	1.02×10^{-3}	980	0.9999	60
25	75	6.47	1300	0.0731	333	0.9803	7.59×10^{-4}	1318	0.9997	60
25	100	6.47	1632	0.0592	512	0.9771	6.14×10^{-4}	1629	0.9987	60
45	100	6.47	1783	0.0483	285	0.8601	5.71×10^{-4}	1752	0.9996	59
65	100	6.47	1851	0.5838	406	0.9671	5.43×10^{-4}	1841	0.9998	60
25	100	3.00	1625	0.0521	460	0.9955	6.25×10^{-4}	1600	0.9993	59
25	100	11.00	1480	0.0471	257	0.9499	6.89×10^{-4}	1451	0.9999	59

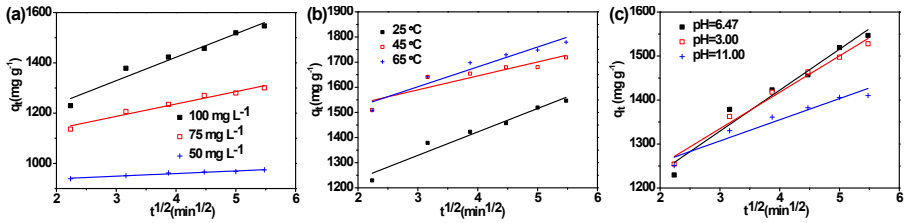

Fig. S7. Intra-particle diffusion of MB onto CTNS-3 at different initial concentrations (a), temperatures (b) and pH (c).

Table S3. The parameters of intraparticle diffusion model for CTNS-3

T (ºC)	C_0 (mgL^{-1})	*pH*	k_t (mg·min$^{-1/2}$·g^{-1})	C	R^2
25	50	6.47	93.17	1049.7	0.9538
25	75	6.47	49.25	1039.3	0.9622
25	100	6.47	10.43	917.9	0.9584
45	100	6.47	55.48	1423.4	0.8100
65	100	6.47	79.00	1365.2	0.9179
25	100	3.00	82.73	1086.7	0.9796
25	100	11.00	48.15	1162.5	0.9267

References

[1] L.A. Sepulveda, F.A. Cuevas, E.G. Contreras, Valorization of agricultural wastes as dye adsorbents: characterization and adsorption isotherms, Environ. Technol., 36 (2015) 1913-1923.

[2] H. Yuh-Shan, Citation review of Lagergren kinetic rate equation on adsorption reactions, Scientometrics, 59 (2004) 171-177.

[3] Y.-S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chemical Engineering Journal, 70 (1998) 115-124.

[4] M. Doğan, M. Alkan, A. Türkyilmaz, Y. Özdemir, Kinetics and mechanism of removal of methylene blue by adsorption onto perlite, Journal of hazardous materials, 109 (2004) 141-148.