Electronic Supplementary Material

Hyperbranched magnetic polymer: highly efficient removal of Cr(VI) and application in electroplating wastewater

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Text S1

A certain amount of absolute ethanol, cyanuric chloride and 80% hydrazine hydrate were added to a 250 ml three-necked flask, placed in a constant temperature oil bath heating stirrer, heated to 50 ℃ and kept for 2 h. After that, Na_2CO_3 solution was added to the obtained liquid for washing with suction, and the obtained product was dried in an oven at 85 ℃ for 12 h.

Figure S1

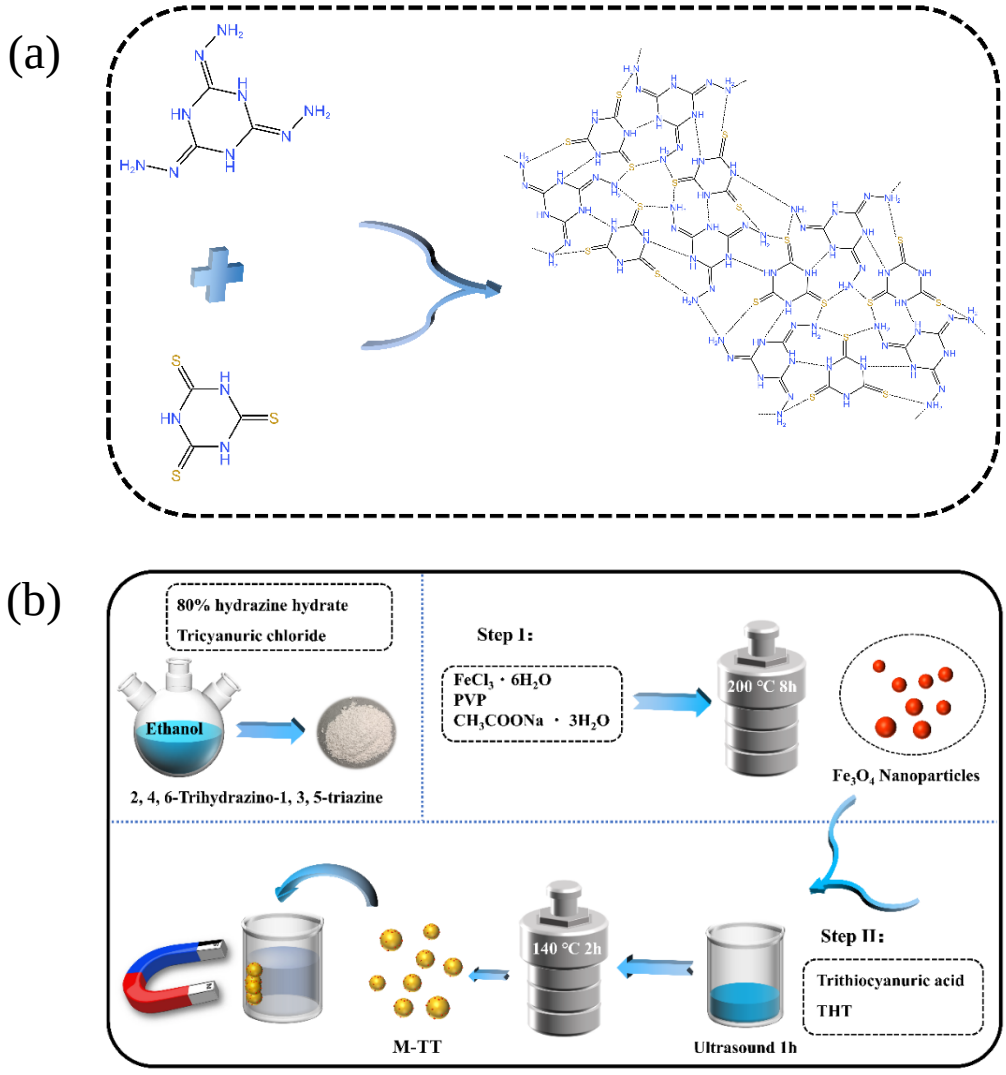

Fig. S1 (a) TT chemical synthesis diagram, (b) M-TT preparation process.

Text S2

Fe_3O_4 nanoparticles were prepared by solvothermal reduction method. Under vigorous stirring, 3 g $FeCl_3 \cdot 6H_2O$, 4 g $CH_3COONa \cdot 3H_2O$ and 2 g polyvinylpyrrolidone (PVP) were dissolved in 60 mL of ethylene glycol. Then, the homogeneous mixture was transferred to a 100 mL stainless steel autoclave lined with Teflon, heated to 200 ℃ and held for 8 h. After that, a black precipitate was obtained by magnetic separation, washed with deionized water and ethanol, and dried in a vacuum oven at 60 ℃ for 12 h.

Figure S2

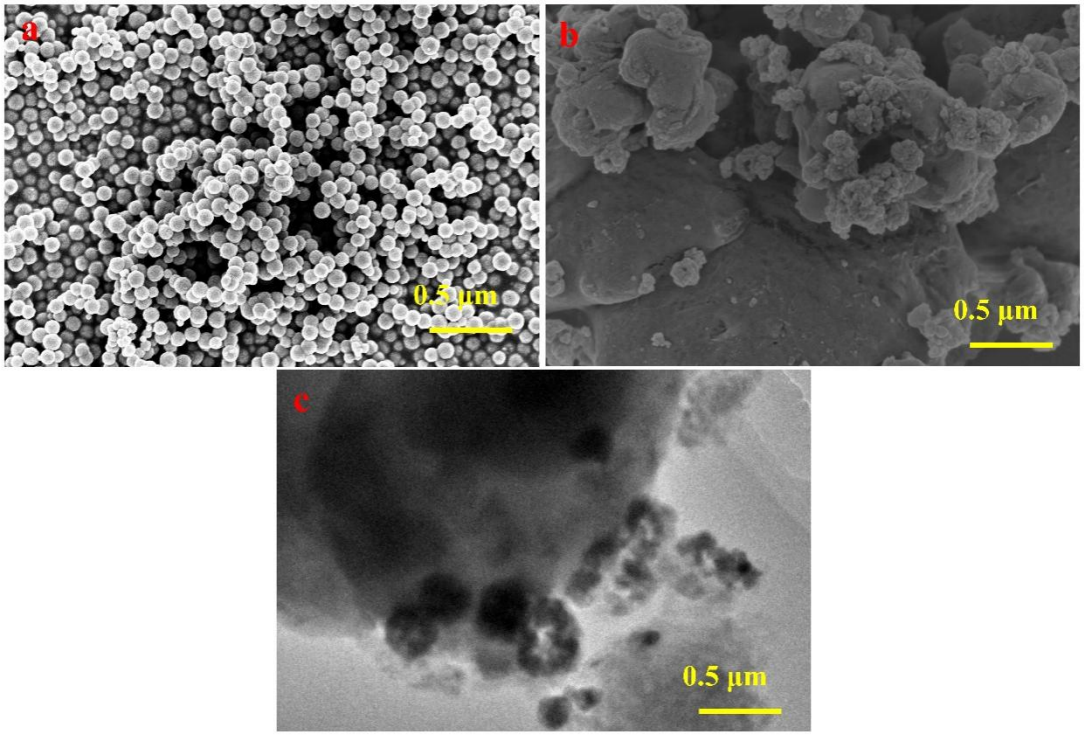

Fig. S2 (a) SEM image of Fe_3O_4, (b) SEM image of M-TT. (c) TEM image of M-TT.

Figure S3

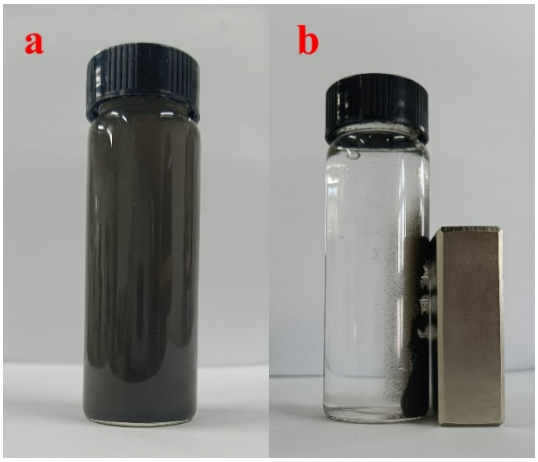

Fig. S3 Comparison of M-TT magnetic separation before (a) and after (b).

Text S3

The specific surface area of M-TT determined by the BET method was about 28.9648 $m^2 \cdot g^{-1}$ (Fig. S4a), and the specific surface area of TT was 39.4639 $m^2 \cdot g^{-1}$. The pore sizes of both M-TT and TT calculated by BJH analysis were in the range of 3-50 nm (Fig. S4b), indicating the presence of

mesopores in the prepared samples. There is clear absorption at higher relative pressures, indicating the existence of mesopores in the material framework. The surface of M-TT material contains very rich adsorption active sites, and the larger pore size can provide more ions with the opportunity to contact the active sites, which is beneficial to enhance its adsorption performance.

Figure S4

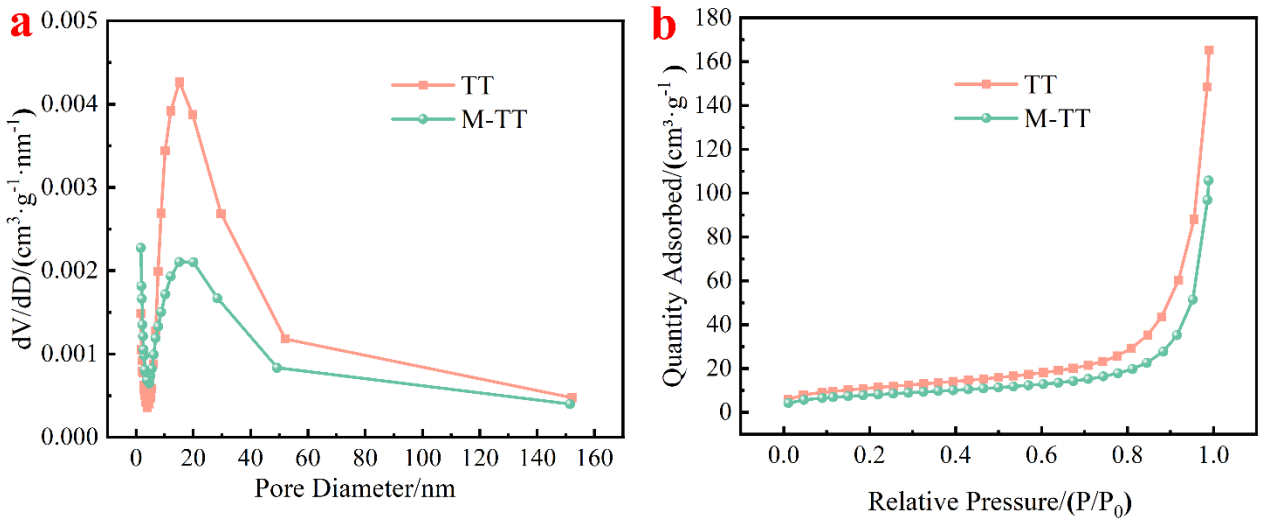

Fig. S4 (a) Distribution of pore diameter; (b) BET analysis of TT and M-TT.

Figure S5

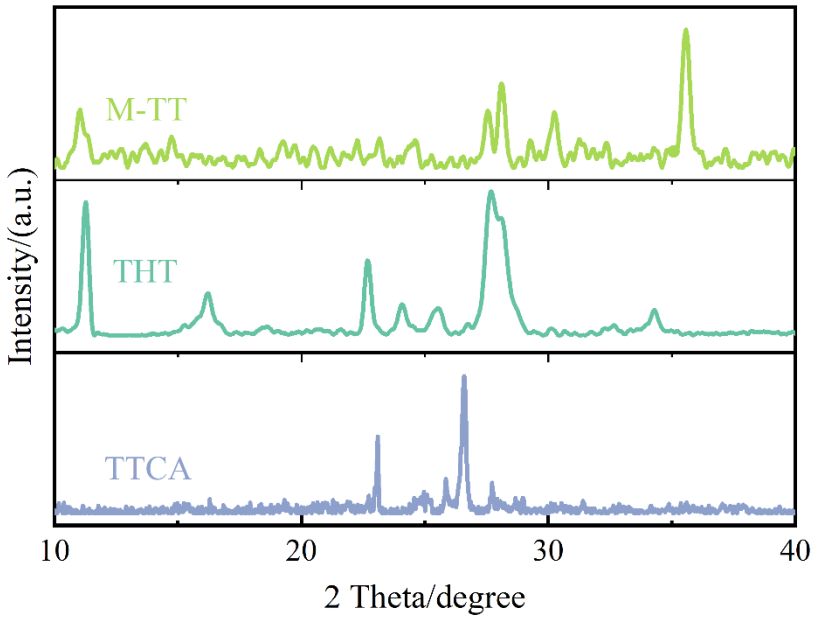

Fig. S5 XRD pattern of raw materials and products.

Figure S6

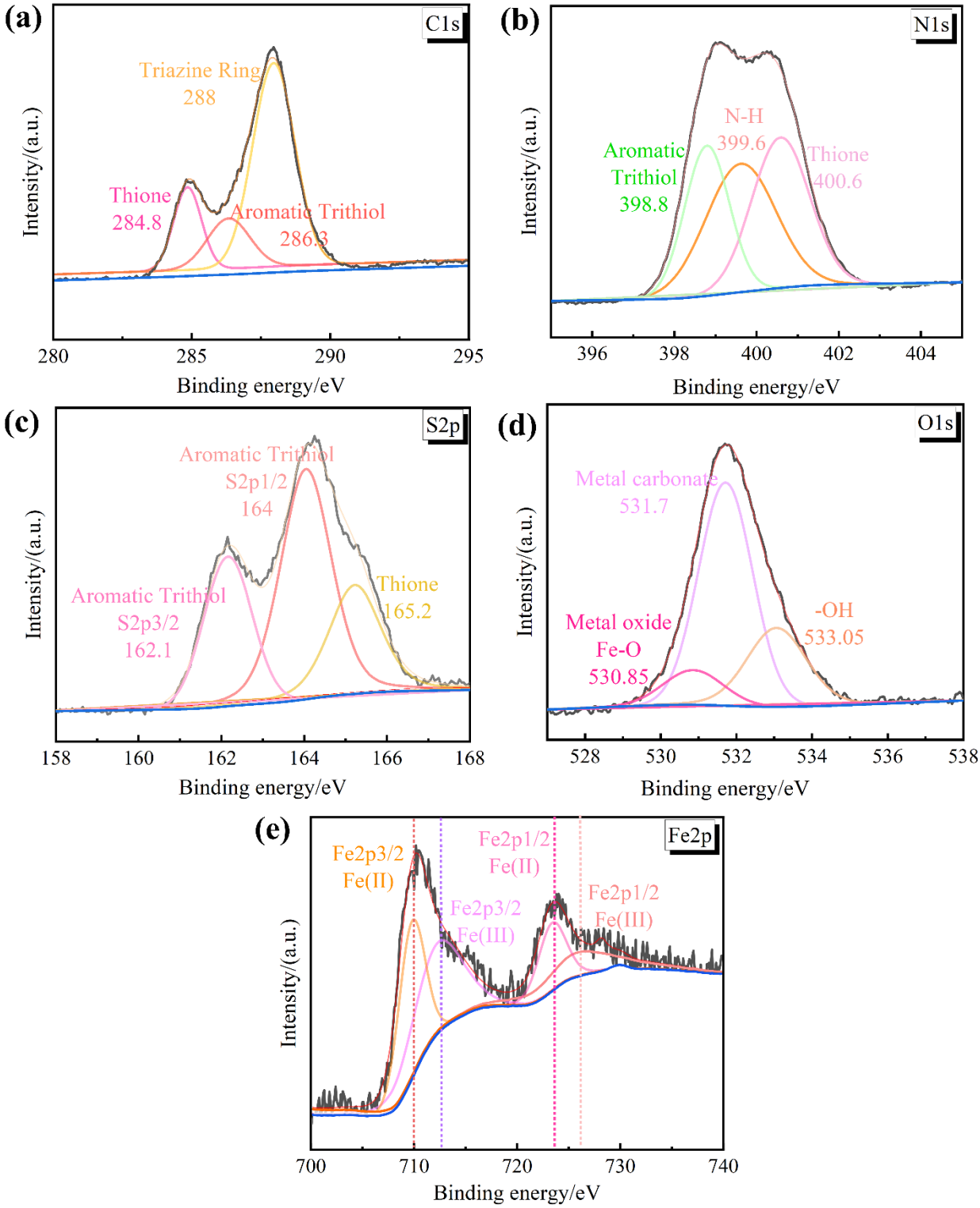

Fig. S6. C1s(a), N1s(b), S2p(c), O1s(d), Fe2p(e)'s XPS high-resolution spectrum.

Text S4

The Langmuir and Freundlich, separation factor (R_L) isotherm model is expressed as the equation

Eq. (1), Eq. (2), Eq. (3):

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m K_L} \quad (1)$$

$$q_e = \frac{1}{n} lnc_e + lnK_F \quad (2)$$

$$R_L = \frac{1}{1+K_L c_0} \quad (3)$$

where q_m (mg·g^{-1}) is the theoretical maximum monolayer adsorption capacity, k_L is the Langmuir constant (L·g^{-1}), k_F is the Freundlich constant (mg/g) (L·mg^{-1})$^{1/n}$, *1/n* represents the heterogeneity factor, C_0 is the initial Cr(VI) concentration, and C_e is the Cr(VI) concentration at equilibrium.

Figure S7

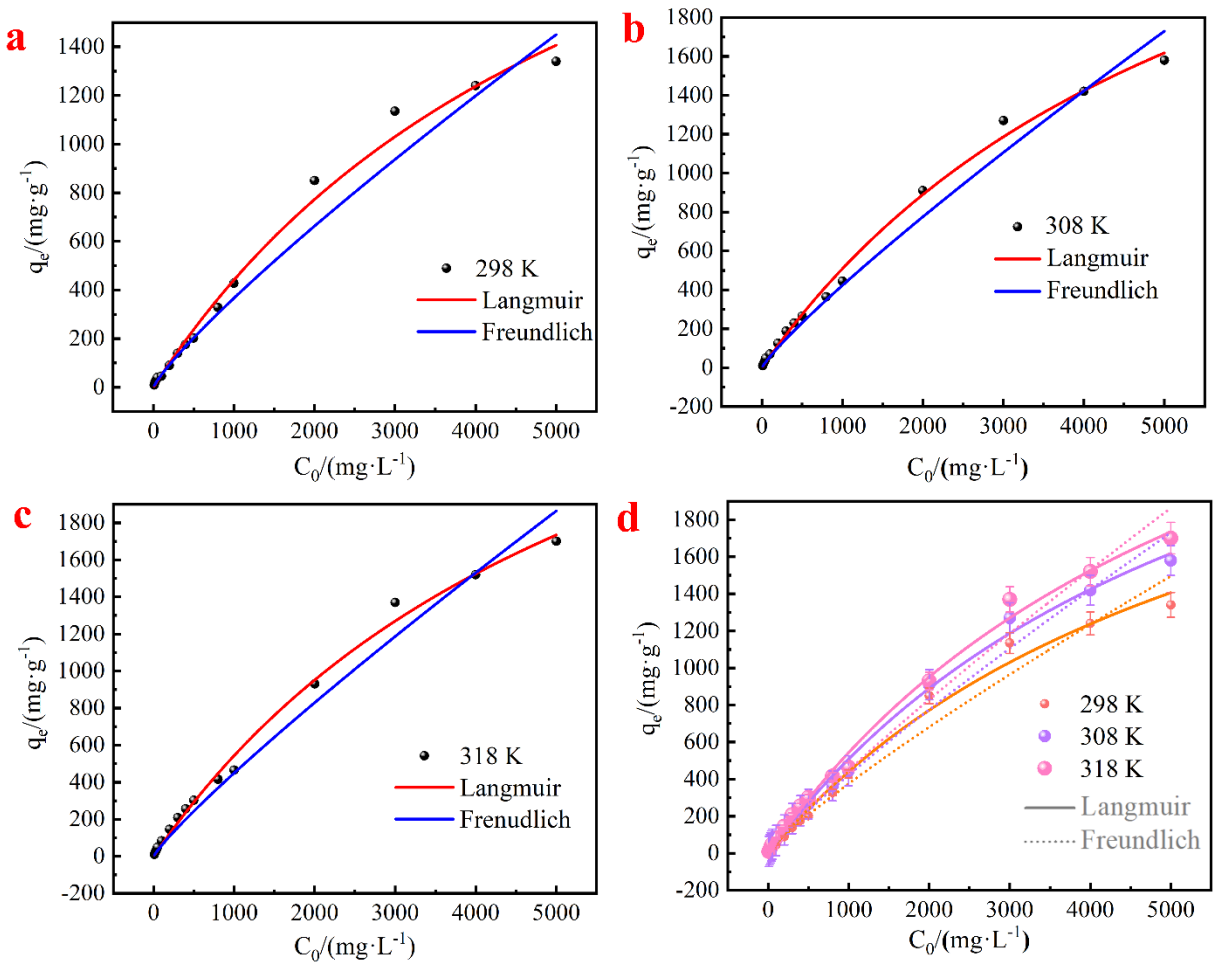

Fig. S7 The Langmuir model and Freundlich isotherm model fitting of Cr(VI) adsorption onto M-TT (pH = 4.4, T = 298 K) (a), onto M-TT (pH = 4.4, T = 308 K) (b) and onto M-TT (pH = 4.4, T = 318 K) (c), and General drawing(pH = 4.4, T = 298 K, T=308 K, T=318 K) (d).

Table S2

Two isotherm parameters for Cr(VI) adsorption onto M-TT (pH = 4.4, T = 298 K).

Samples	Langmuir Model			Freundlich Model		
	q_{max} ($mg \cdot g^{-1}$)	K_L (L/1)	R^2	K_F	n	R^2
M-TT (298 K)	1655	0.00098	0.988	419.59	1.17	0.973
M-TT (308 K)	1666.67	0.00153	0.996	30.47	1.14	0.983
M-TT (318 K)	2000	0.00159	0.966	464	1.13	0.982

Text S5

The pseudo-first-order kinetic model, pseudo-second-order kinetic model, and intraparticle diffusion model are expressed as equations Eq. (4), Eq. (5), Eq. (6):

$$\ln(q_e - q_t) = lnq_e - k_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

$$q_t = k_{id} t^{1/2} + C \quad (6)$$

where q_e and q_t are the amounts of adsorbent Cr(VI) on the M-TT at equilibrium and at time t. k_1 is the pseudo-first-order rate constant (min^{-1}). k_2 is the pseudo-second-order adsorption rate constant. k_{id} is the intra-particle diffusion rate, and constant C is the intercept ($mg \cdot g \cdot min^{1/2}$).

Figure S8

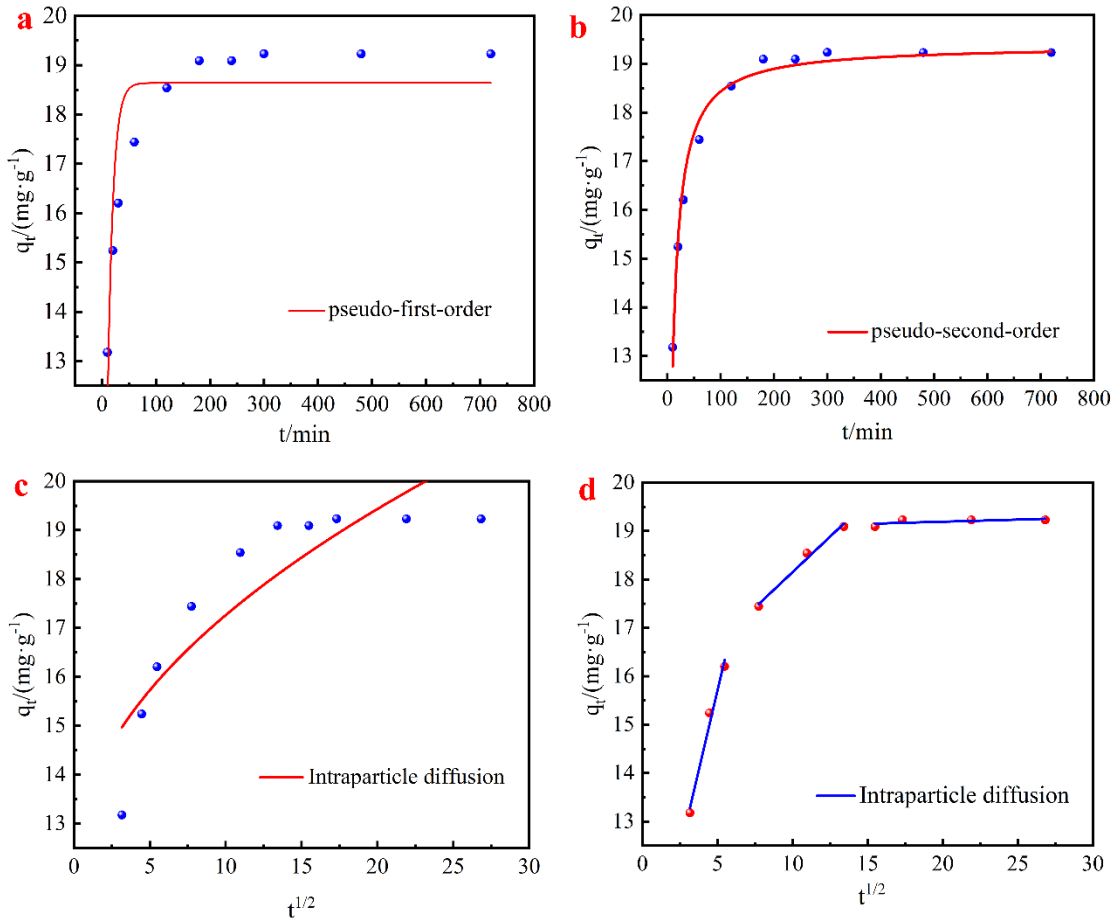

Fig. S8 The fitting of the pseudo-first-order kinetic model (a), the pseudo-second-order (b) and the intra-particle kinetic models (c, d) for Cr(VI) adsorption onto M-TT (pH = 4.4, T = 298 K, C_0 = 20 mg·L^{-1}).

Table S3

Kinetic parameters for Cr(VI) adsorption onto M-TT (pH = 4.4, T = 298 K, C_0 = 20 mg·L^{-1}).

Kinetic model	Parameter	Value	R^2
Pseudo-first-order	k_1 (min^{-1})	0.101	0.817
	q_e (mg·g^{-1})	18.64	
Pseudo-second-order	k_2 (mg·min^{-1}·g^{-1})	0.0104	0.986
	q_e (mg·g^{-1})	19.406	
Intraparticle diffusion	k_{id} (mg·g^{-1})	1.656	0.785
	C (mg·g^{-1}·min^{-1})	12.024	

Text S6

To investigate the effect of temperature on the adsorption capacity of Cr(VI), adsorption experiments were carried out at 298 K, 308 K and 318 K. The relevant thermodynamic parameters

are listed in Table S4, including Gibbs function change ΔG, enthalpy change ΔH, and entropy change ΔS, which are calculated from the following equations Eq. (7), Eq. (8), Eq. (9):

$$lnK_d = \frac{\Delta S}{R} - \frac{\Delta H}{\mathrm{T}} \quad (7)$$

$$\Delta G = \Delta H - \mathrm{T}\Delta S = -\mathrm{RTln}K_d \quad (8)$$

$$K_d = \frac{C_0 - C_e}{C_e} \quad (9)$$

where K_d is the equilibrium constant ($\mathrm{L \cdot g^{-1}}$), T is the temperature (K), and R is the standard gas constant (8.314 $\mathrm{J \cdot mol \cdot K^{-1}}$).

Table S4

Thermodynamic parameters for Cr(VI) adsorption onto M-TT at different temperatures.

K_d (L·g^{-1})			ΔG (kJ mol^{-1})			ΔH	ΔS	R^2
298 K	308 K	318 K	298 K	308 K	318 K	(kJ·mol^{-1})	(J·mol^{-1}·K^{-1})	
2.73	2.16	1.94	-2.49	-1.97	-1.75	334.25	1.13	0.97

Figure S9

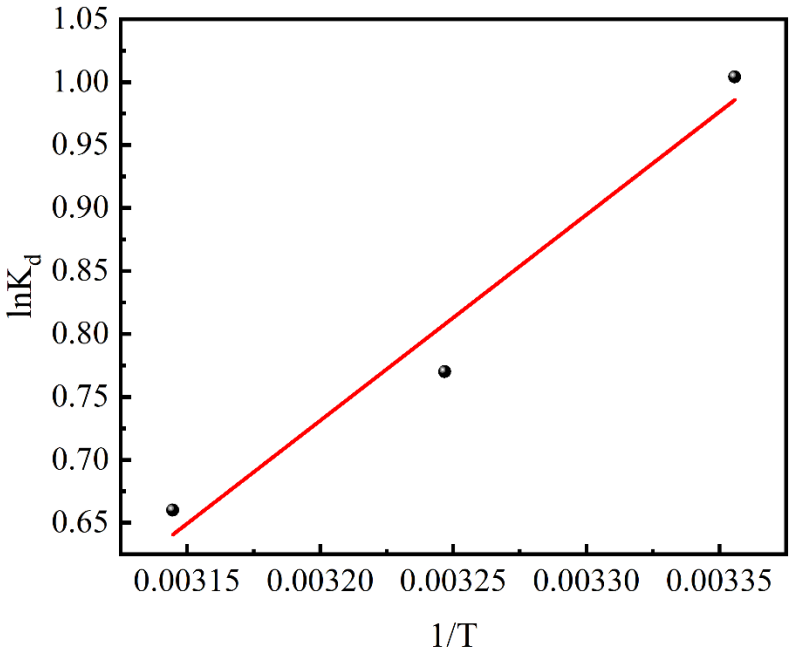

Fig. S9 Thermodynamic curve of Cr(VI) adsorption onto M-TT (pH = 4.4, T = 298 K, C_0 = 20 $\mathrm{mg \cdot L^{-1}}$).

Figure S10

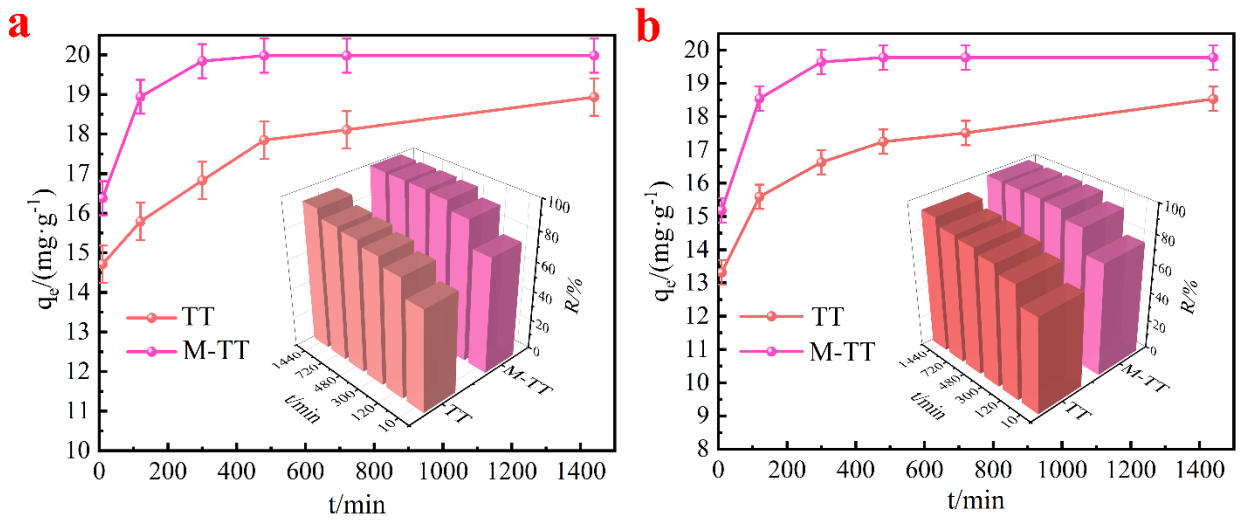

Fig. S10 Removal of Cr(VI) (a) and Cr(III) (b) by TT and M-TT (pH = 4.4, T = 298 K, C_0 = 20 mg·L^{-1}).

Table S5

The calculated adsorption energies of Cr atom on four sites of substrate material.

site	Adsorption energy (eV)
1	-0.193
2	-0.966
3	-1.080
4	-0.999

Table S6

Comparison before and after adsorption of other components in electroplating wastewater.

	Raw effluent	After treatment			
	Concentration (mg/L)	Raw effluent		Adjustive effluent	
		Concentration (mg/L)	R%	Concentration (mg/L)	R%
Cr(VI)	247.6	228.28	7.8	0.32	98.4
Cr(tot)	356.8	350.84	1.67	1.44	92.8
Li	1.17	0.998	15.15	0.026	3.76
Ni	110.25	95.02	13.81	7.16	7.4
Zn	0.46	0.426	7.69	0.04	91.3
Pb	36.6	23.62	35.47	0.44	47.27
Co	17.05	9.597	43.72	0.118	69.58
pH	12.69	12.69		4.4	

*Adjust the concentration of Cr(VI) in the wastewater to 20 $mg \cdot L^{-1}$, the pH value to 4.4, and the dosage to 1 $g \cdot L^{-1}$.