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Supplementary Information

Efficient Identification and Degradation of Tetracycline Hydrochloride from Water by Molecularly Imprinted Core-Shell Structure SiO_2@TiO_2

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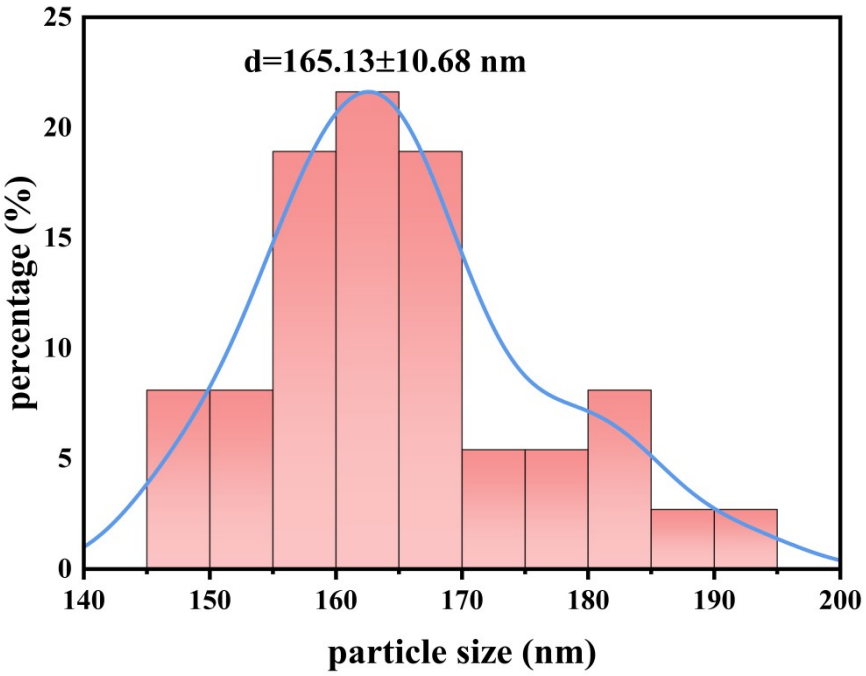

Fig. S1 The particle size distribution of SiO_2 (n=37)

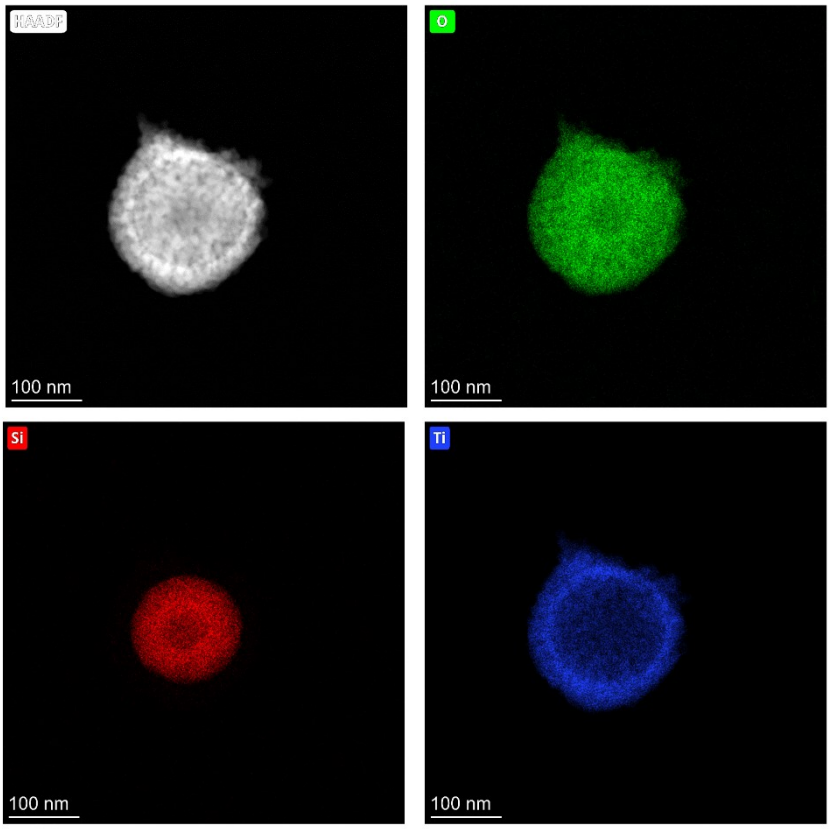

Fig. S2 Mapping of SiO_2@TiO_2@MIPs

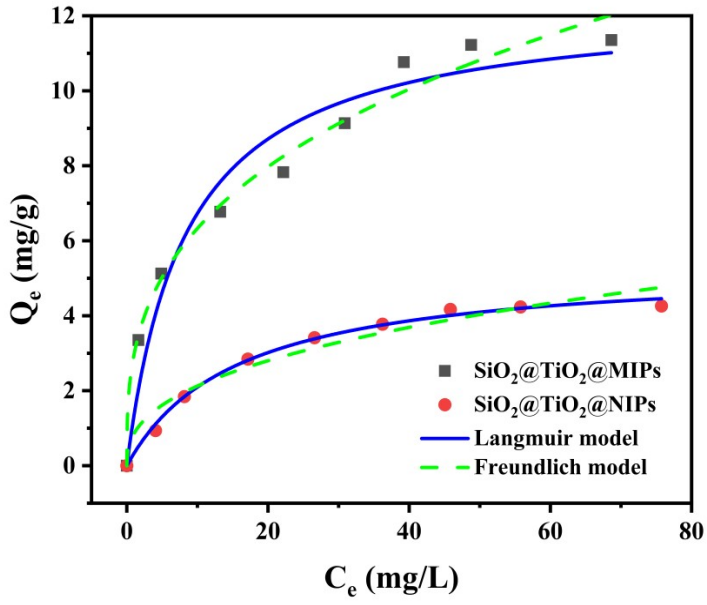

Fig. S3 Langmuir and Freundlich isotherm adsorption models fitting curve of SiO_2@TiO_2@MIPs and SiO_2@TiO_2@NIPs

The adsorption capacity (Q) and imprinting factor (IF) are calculated as follows:

$$Q = \frac{(C_0 - C_t)V}{W}$$

$$IF = \frac{Q_{MIPs}}{Q_{NIPs}}$$

Where C_0(mg/L) is the initial concentration of TC; C_t is the concentration of TC after adsorption equilibrium; V(mL) is the volume of TC solution; W(g) is the mass of photocatalysts, Q_{MIPs}(mg/g) is the adsorption capacity of SiO_2@TiO_2@MIPs; Q_{NIPs}(mg/g) is the adsorption capacity of SiO_2@TiO_2@NIPs

The Langmuir isotherm adsorption models is a single molecular layer adsorption model with the following expressions：

$$Q_e = \frac{k_L Q_{max} C_e}{1 + k_L C_e}$$

Where C_e(mg/L) is the concentration of TC at the equilibrium state of adsorption; Q_e(mg/g) is the adsorption capacity of TC at the equilibrium state; Q_{max}(mg/g) is the theoretical maximum adsorption capacity; and k_L(mg/L) is the Langmuir adsorption constant.

Freundlich isotherm adsorption models is as follows:

$$Q_e = k_F C_e^{\frac{1}{n_F}}$$

Where C_e(mg/L) is the concentration of TC at the equilibrium state of adsorption; n_F and k_F are Freundlich constants.

Table S1 Isotherm parameters of SiO_2@TiO_2@MIPs and SiO_2@TiO_2@NIPs

Photocatalyst	Langmuir isotherm adsorption model			Freundlich isotherm adsorption model		
	Q_{max}(mg·g^{-1})	k_L(mg·L^{-1})	R^2	n_F	k_F	R^2
SiO_2@TiO_2@MIPs	12.358	0.200	0.901	2.940	-0.333	0.985
SiO_2@TiO_2@NIPs	5.375	0.064	0.989	0.851	-0.398	0.953

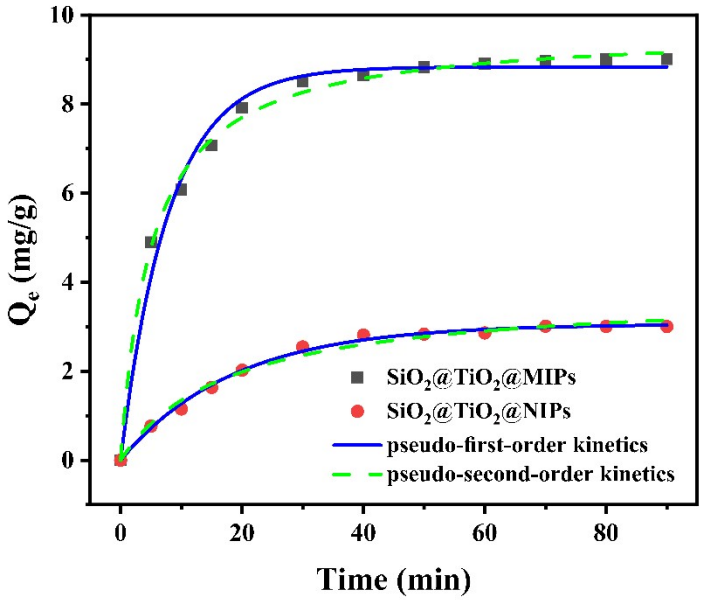

Fig. S4 The pseudo-first-order kinetics and pseudo-second-order kinetics fitting curve of SiO_2@TiO_2@MIPs and SiO_2@TiO_2@NIPs

The pseudo-first-order kinetics equation is expressed as:

$$ln(Q_e - Q_t) = lnQ_e - k_1 t$$

The pseudo-second-order kinetics equation is expressed as:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$

Where Q_e(mg/g) is the amount of adsorbate at equilibrium; Q_t(mg/g) is the amount of adsorbate at any time; t (min) is adsorption time; k_1(min^{-1}) is quasi-first-order kinetic adsorption constant; k_2($g\cdot(mg\cdot min)^{-1}$) is quasi-second-order kinetic adsorption constant.

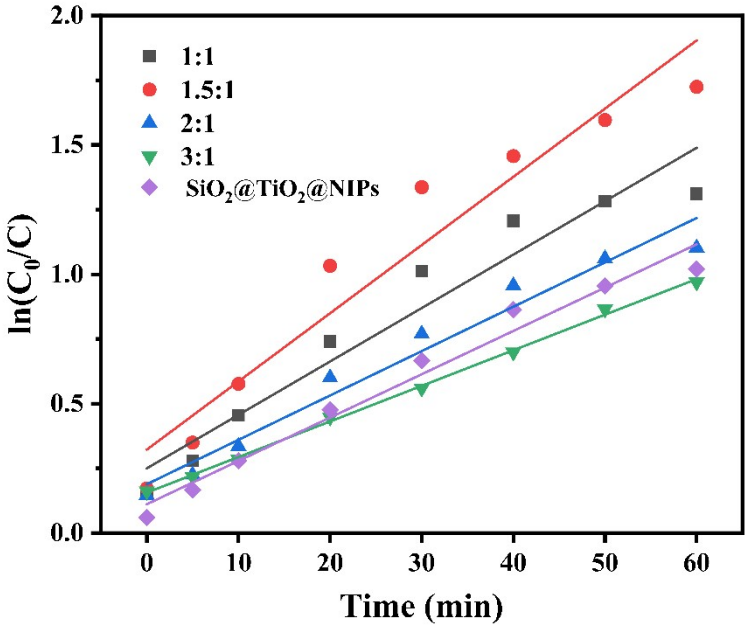

Fig. S5 Reaction kinetics of SiO_2@TiO_2@MIPs with different Ti/Si molar ratios

Table S2 The degradation rate constants of SiO_2@TiO_2@MIPs

Photocatalyst	k (min^{-1})
SiO_2@TiO_2@MIPs-1	0.021
SiO_2@TiO_2@MIPs-1.5	0.026
SiO_2@TiO_2@MIPs-2	0.017
SiO_2@TiO_2@MIPs-3	0.014
SiO_2@TiO_2@NIPs	0.017

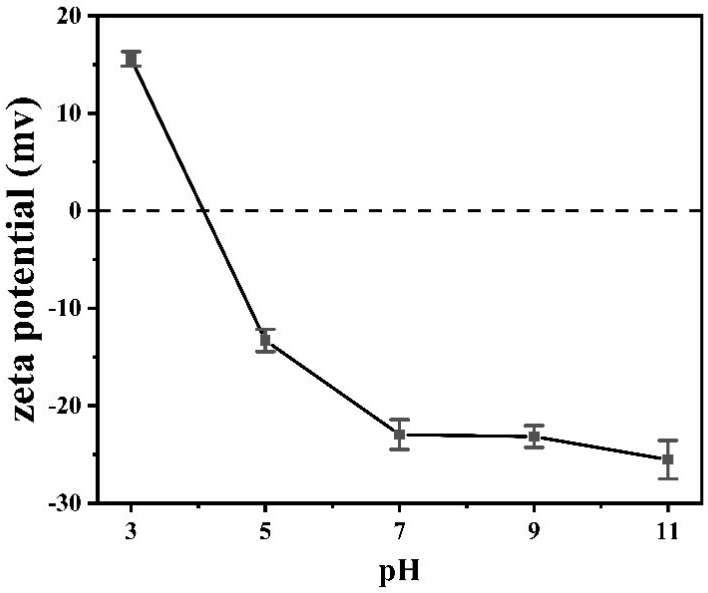

Fig. S5 Zeta potential of SiO_2@TiO_2@MIPs

Table S3 Comparison of MIP-coated photocatalysts for removal of organic pollutant

Material	Templates	Synthesis method	k (min^{-1})	Ref.
TiO_2	2,4-dichlorophenoxyacetic acid	Sol-gel method	0.0036	1
Pr-TiO_2	2-sec-Butyl-4,6-dinitrophenol	Solvothermal method	0.0077	2
S-TiO_2	Salicylic acid	Surface molecular imprinting technique	0.0071	3
NaCl/TiO_2	Ciprofloxacin	Surface molecular imprinting technique	0.0100	4
TiO_2/WO_3	2-nitrophenol	Sol-gel method	0.0037	5
SiO_2@TiO_2	Tetracycline hydrochloride	Sol-gel method	0.026	This work

Table S4 Degradation rates of three antibiotics by SiO_2@TiO_2@MIPs and SiO_2@TiO_2@NIPs in simulated wastewater (n=3)

Antibiotics	Degradation rate (SiO_2@TiO_2@MIPs) (%, average±SD)	RSD (SiO_2@TiO_2@MIPs) (%)	Degradation rate (SiO_2@TiO_2@NIPs) (%, average±SD)	RSD (SiO_2@TiO_2@NIPs) (%)
TC	78.27±1.70	2.17	42.62±1.74	4.08
SMX	18.47±0.76	4.13	25.15±1.13	4.49
DCF	15.57±0.73	4.70	24.27±0.93	3.84

Table S5 Degradation rate of TC by SiO_2@TiO_2@MIPs with the addition of scavenger (n=3)

Scavenger	Degradation rate (%, average±SD)	RSD (%)
No Scavenger	82.17±1.41	1.72
BQ	41.67±1.91	4.58
AO	22.73±1.11	4.88
IPA	59.27±1.40	2.36

Table S6 Degradation rate of TC by SiO_2@TiO_2@MIPs in five cycles (n=3)

Cycles	Degradation rate (%, average±SD)	RSD (%)
1	82.36±1.21	1.47
2	81.28±1.13	1.39
3	80.84±1.29	1.59
4	80.04±1.22	1.52
5	79.15±1.48	1.87

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