Electronic Supporting Information (ESI)

Fabrication of core-shell α-MnO₂@polydopamine nanocomposites

for the efficient and ultra-fast removal of U(VI) from aqueous

solution

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Adsorption kinetics

The pseudo-first-order and pseudo-second-order kinetic were expressed as (S1) and (S2), respectively:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \qquad \text{(S1)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \text{(S2)}$$

where q_t and q_e (mg/g) are the amounts of U(VI) adsorbed at time t (min) and equilibrium time, respectively. k_1 (min^{-1}) and k_2 (g/ (mg min)) are the rate constants of the equation (S1) and (S2), respectively.

Adsorption isotherms

The Langmuir and Freundlich can be expressed by (S3) and (S4), respectively:

$$q_e = \frac{b q_m C_e}{1 + b C_e} \qquad \text{(S3)}$$

$$q_e = K_F C_e^{\frac{1}{n}} \qquad \text{(S4)}$$

where q_e (mg/g) and C_e (mg/L) are the adsorption amount of U(VI) onto adsorbent and the U(VI) equilibrium concentration in supernatant, respectively. q_m (mg/g) is the saturated monolayer adsorption amount. b (L/mg) is the Langmuir constant connected with the energy of adsorbent. K_F (mg/g) is relevant to the adsorption amount, whereas $1/n$ is the Freundlich constant correlated to the adsorption intensity.

The linear form of D-R isotherm is represented by the following equation (S5):

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \qquad \text{(S5)}$$

where β is the constant of the adsorption energy (mol^2/J^2), related to the average energy of adsorption per mole of the U(VI) as it is transferred to the surface of the solid from infinite distance in the solution. ε is Polanyi potential, described as:

$$\varepsilon = RT\left(1 + \frac{1}{C_e}\right) \qquad \text{(S6)}$$

where R is the gas constant (8.314 J/ (mol K)). T is the absolute temperature (K).
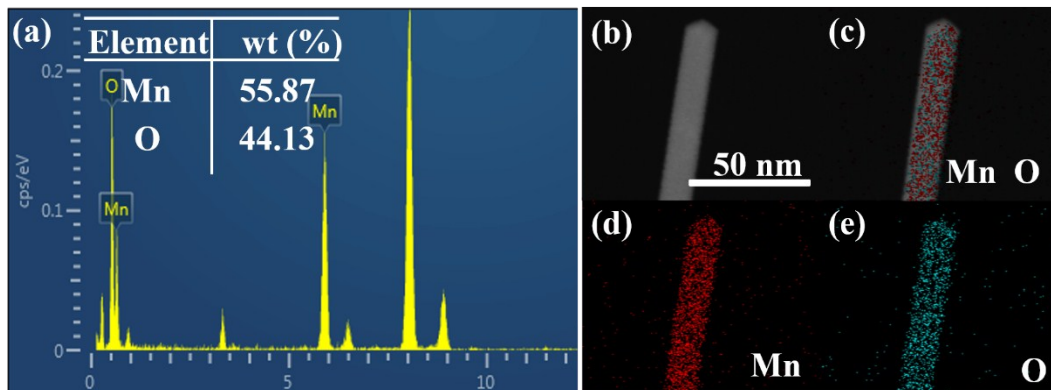

Fig S1 (a) EDX spectrum, (b) TEM and (c-e) the corresponding elemental images of as-prepared α-MnO$_2$ nanowires.
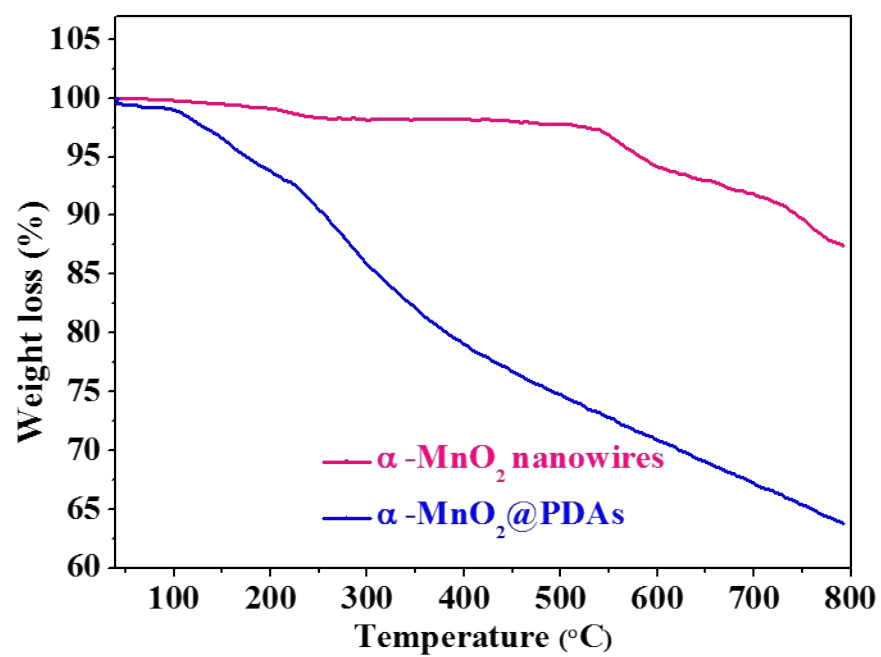
Fig S2 TG curves of α-MnO$_2$ nanowires and α-MnO$_2$@PDAs.
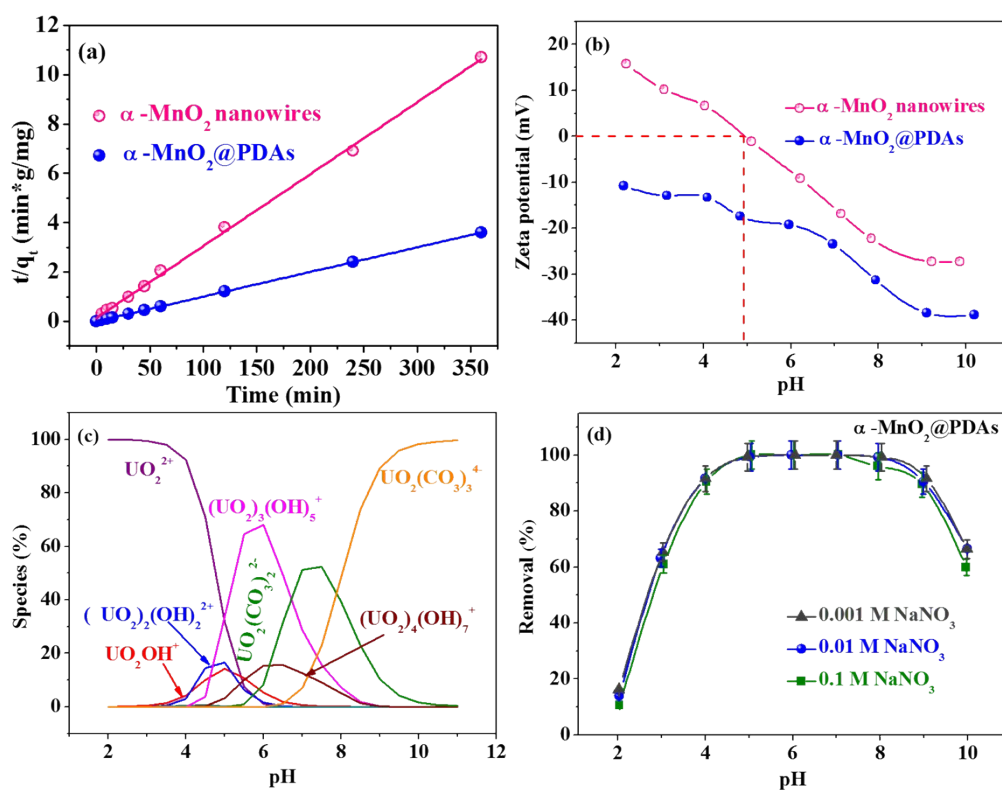
Fig S3 (a) Pseudo-second-order kinetic plots of U(VI) removal on α-MnO$_2$ nanowires and α-MnO$_2$@PDAs, (b) The zeta potential of α-MnO$_2$ nanowires and α-MnO$_2$@PDAs and (c) the relative distribution of U(VI) species in aqueous solution as a function of pH, (d) The effect of ion strength (0.001, 0.01 and 0.1 mol/L NaNO$_3$) on U(VI) adsorption onto α-MnO$_2$@PDAs at T = 298 K, m/V = 0.1 g/L, C_0(U(VI)) = 10 mg/L.
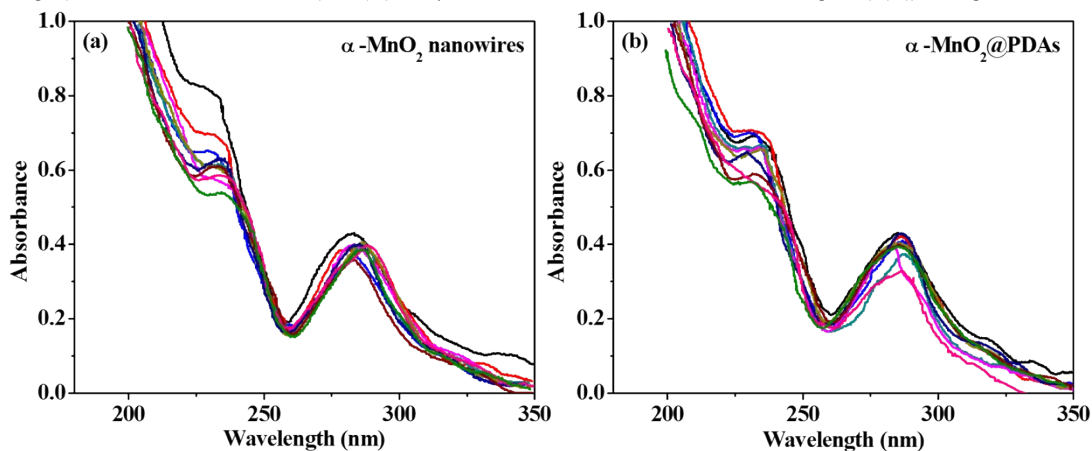

Fig S4 The titration spectra of 0.1 M (a) α-MnO$_2$ nanowires and (b) α-MnO$_2$@PDAs in the pH range 3.36-9.11 at 298 K.
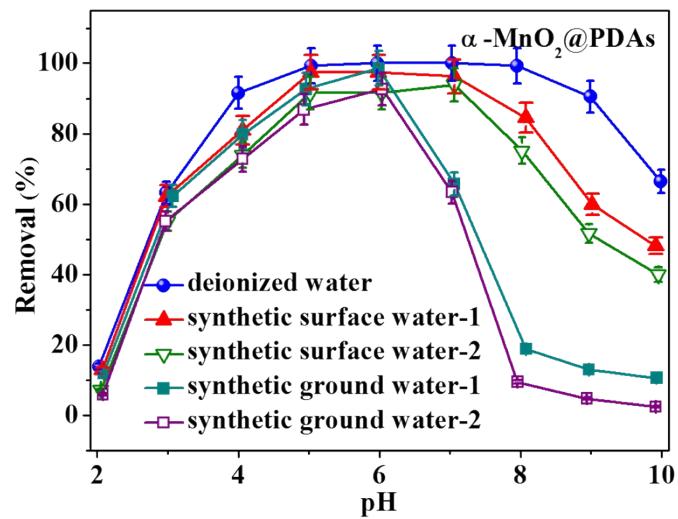
Fig S5 The removal efficiency of U(VI) by α-MnO$_2$@PDAs in deionized water and different imitative uranium-containing wastewater in the pH range of 2.0 – 10.0. m/V = 0.1 g/L, C_0(U(VI)) = 10 mg/L, and T = 298 K.
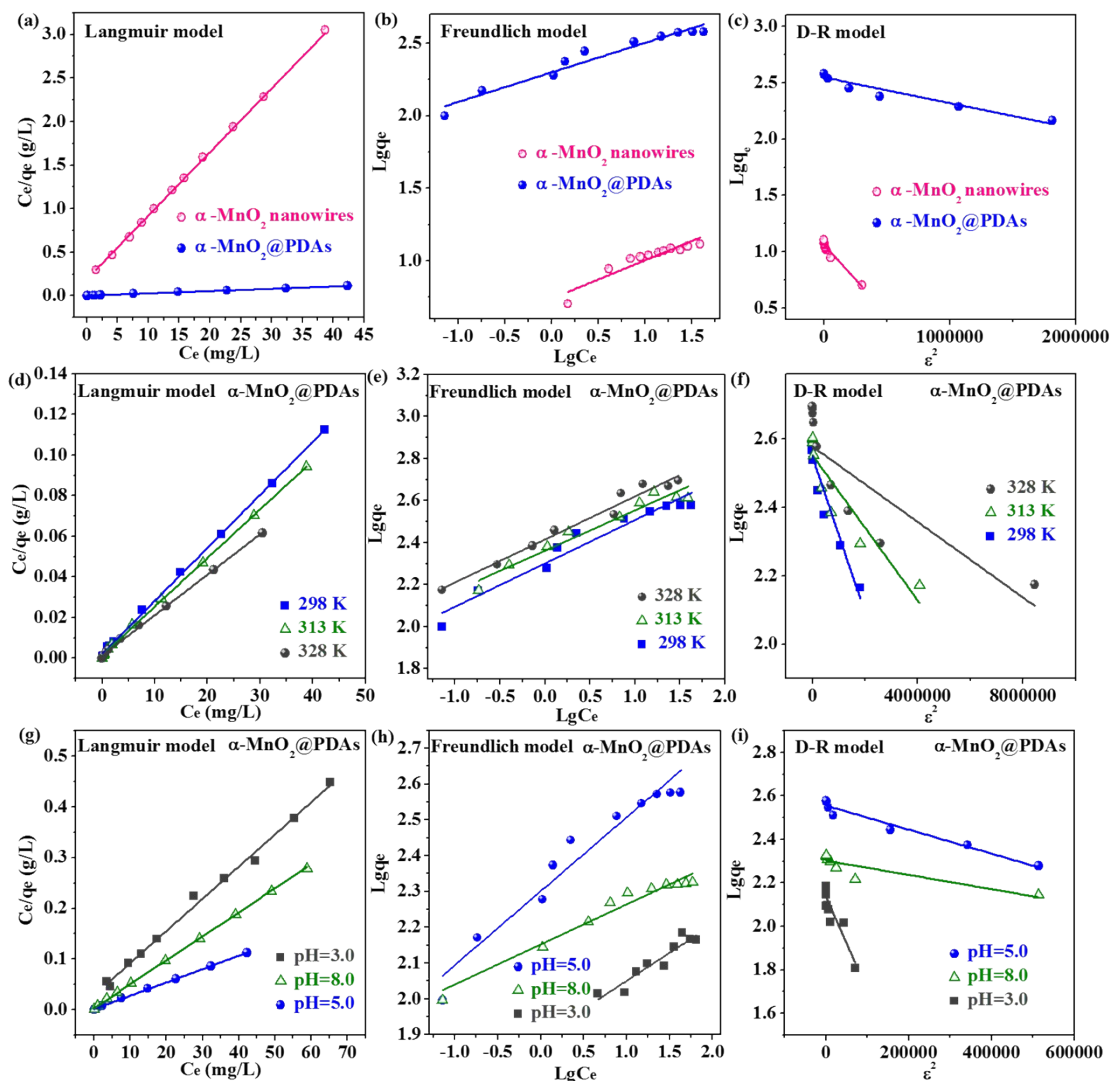
Fig S6 Langmuir, Freundlich and D-R models simulation of (a, b, c) U(VI) adsorption on α-MnO$_2$ nanowires and α-MnO$_2$@PDAs at pH = 5.0 ± 0.05, *T* = 298 K, (d, e, f) U(VI) adsorption on α-MnO$_2$@PDAs at different temperature, and (g, h, i) U(VI) adsorption on α-MnO$_2$@PDAs at three different pH values. All experiments were at *m/V* = 0.1 g/L and *I* = 0.01 M NaNO$_3$.

Fig S7 XPS survey spectra of α-MnO₂@PDAs before and after U(VI) adsorption.

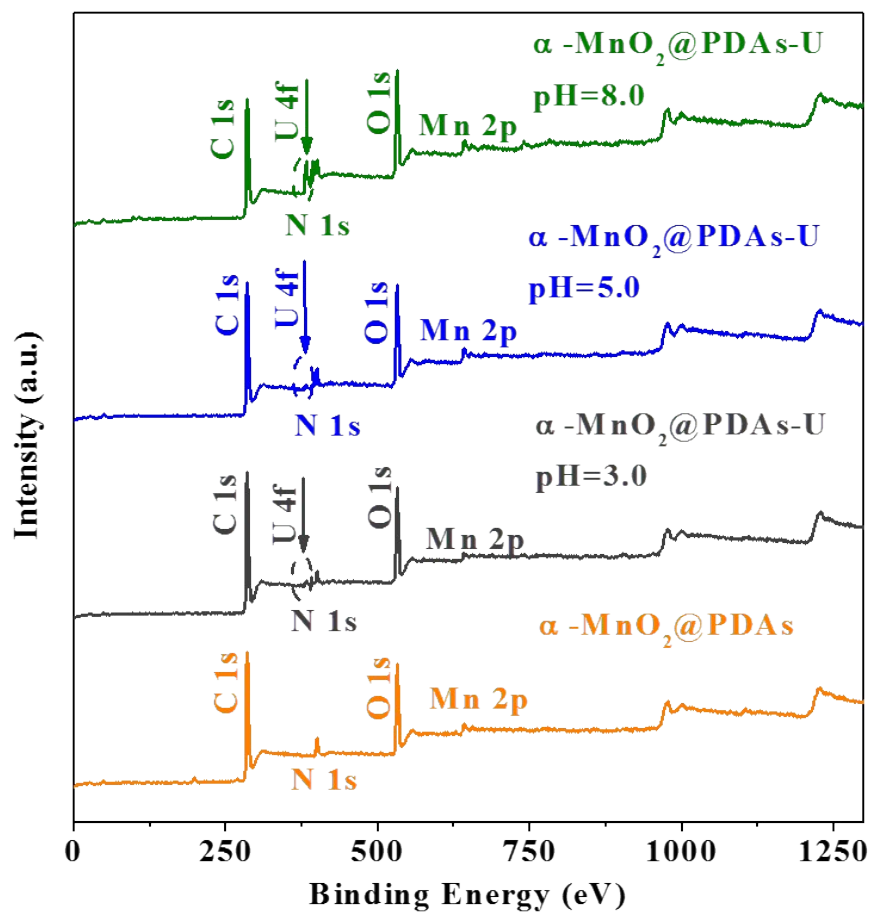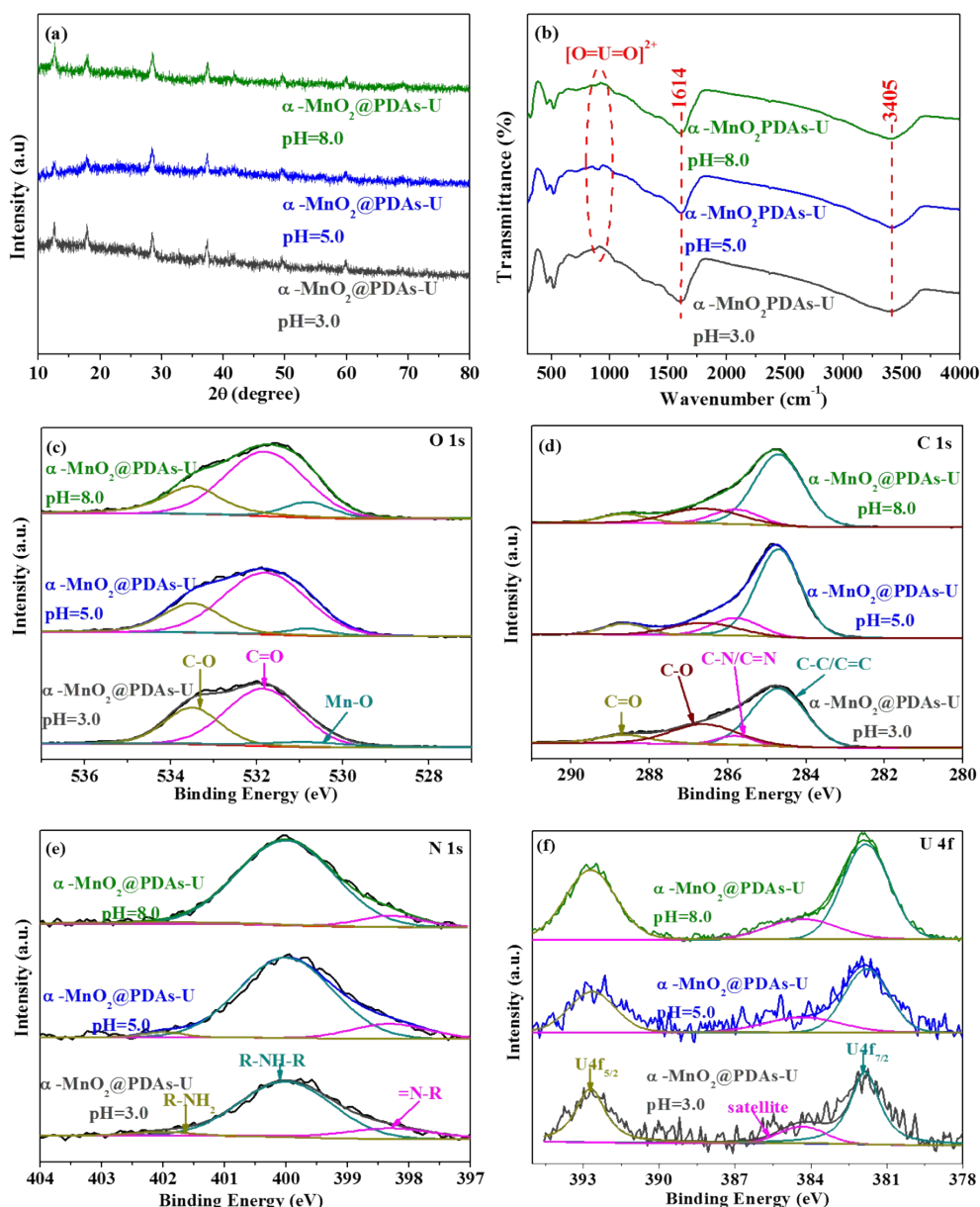**Fig S8** (a) XRD patterns and (b) FT-IR spectra of α-MnO$_2$@PDAs before and after U(VI) adsorption at different pH. High-resolution XPS spectra of (c) O 1s, (d) C 1s, (e) N 1s and (f) U 4f of α-MnO$_2$@PDAs after U(VI) adsorption at different pH.

In Fig S7c, the variable quantity of C-O in diverse pH abided by the order: pH 5.0 (14.65%) > 8.0 (12.52%) > 3.0 (8.19%). Similarly, as shown in Fig S7d, the total content of C-N/C=N and C-O bonds displayed more or less changes whether under acidic or alkaline environment, which changed to lower content from 33.30% to 31.47% (pH 3.0), 26.05% eV (pH 5.0) and 30.02% (pH 8.0), respectively. The above phenomenon was consistent with the adsorption result (Fig 4c), and the trends were attributed to the different amount of the reacted active groups for U(VI) species. As observed in Fig S7f, the presence of U 4f centered at ~281.8 of U 4f$_{7/2}$, ~392.7 of U 4f$_{5/2}$ of U(VI) were observed, respectively.

8

Table S1 The concentrations of different ions in deionized water and different imitative uranium-containing wastewater.

Ions	Synthetic ground water-1 (mM)	Synthetic ground water-2 (mM)	Synthetic surface water-1 (mM)	Synthetic surface water-2 (mM)	Deionized water (M)	Real sea water (mM)
HCO_3^-	0.43	0.43	0.26	0.26	0	-
CO_3^{2-}	0	0.50	0	0.33		
SO_4^{2-}	0.36	0.36	0.07	0.07	0	-
NO_3^-	0.21	0.21	0.12	0.12	0.01	-
Cl^-	0.64	0.64	0.34	0.34	0	-
Ca^{2+}	0.66	0.66	0.33	0.33	0	-
Mg^{2+}	0.24	0.24	0.24	0.24	0	-
Na^+	0.42	0.42	0.23	0.23	0.01	-
K^+	0.20	0.20	0.03	0.03	0	-
pH	6.67	7.43	7.17	7.82	7.03	7.04

Table S2 Structural properties of α-MnO$_2$ nanowires and α-MnO$_2$@PDAs.

Adsorbents	BET surface area (m^2/g)	Maximum pore size (nm)	Pore volume (cm^3/g)	Average pore size (nm)
α-MnO$_2$ nanowires	30.78	99.64	0.12	21.98
α-MnO$_2$@PDAs	22.79	95.48	0.06	12.85

Table S3 Parameters of pseudo-first-order kinetic and pseudo-second-order kinetic models for U(VI) adsorption onto α-MnO$_2$ nanowires and α-MnO$_2$@PDAs.

Adsorbents	Pseudo-first-order			Pseudo-second-order		
	k_1	q_e	R^2	k_2	q_e	R^2
	(1/min)	(mg/g)		(g/ (mg min))	(mg/g)	
α-MnO$_2$ nanowires	0.13	31.98	0.974	0.0060	34.36	0.999
α-MnO$_2$@PDAs	0.94	99.05	0.999	0.0233	100.0	~1

Table S4 Comparisons of U(VI) adsorption capacities of α-MnO$_2$@PDAs with other nanomaterials.

Adsorbents	q_m (mg/g)	Conditions
mSiO$_2$/PDA[1]	286.5	pH = 5.5, T = 298 K
MnO$_2$[2]	39.8	pH = 3.8, T = 298 K
GO/MnO$_2$[2]	185.2	pH = 3.8, T = 298 K
PDA[3]	34.21	pH = 4.0, T = 298 K
PDA/GO[3]	145.39.00	pH = 4.0, T = 298 K
Fe$_3$O$_4$@PDA[4]	71.00	pH = 5.0, T = 293 K
α-MnO$_2$ nanowires (in this work)	13.51	pH = 5.0, T = 298 K
α-MnO$_2$@PDAs (in this work)	383.14	pH = 5.0, T = 298 K

Table S5 Thermodynamic parameters for U(VI) adsorption onto α-MnO$_2$ nanowires and α-MnO$_2$@PDAs.

Adsorbents	q_m (mg/g)	T (K)	pH	ΔH^0 (KJ/mol)	ΔS^0 (J/ (mol K))	ΔG^0 (KJ/mol)
α-MnO$_2$ nanowires	13.51	298	5.0			-2.04
α-MnO$_2$@PDAs	383.14	298	5.0	9.91	78.70	-13.76
	418.41	313	5.0	9.91	78.70	-14.29
	502.51	328	5.0	9.91	78.70	-16.13

Notes and references

1. L. Bai, S. Duan, W. Jiang, M. Liu, S. Wang, M. Sang, X. Gong, J. Li and S. Xuan, *Applied Surface Science*, 2017, **426**, 1121-1132.
2. N. Pan, L. Li, J. Ding, S. Li, R. Wang, Y. Jin, X. Wang and C. Xia, *Journal of Hazard Mater*, 2016, **309**, 107-115.
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4. D. Yang, X. Wang, N. Wang, G. Zhao, G. Song, D. Chen, Y. Liang, T. Wen, H. Wang, T. Hayat, A. Alsaedi, X. Wang and S. Wang, *Journal of Cleaner Production*, 2018, **172**, 2033-2044.