Supporting Information

Tunable Hollow Mesoporous Organosilica for Efficient Adsorption of Heavy Metal Ions from Water

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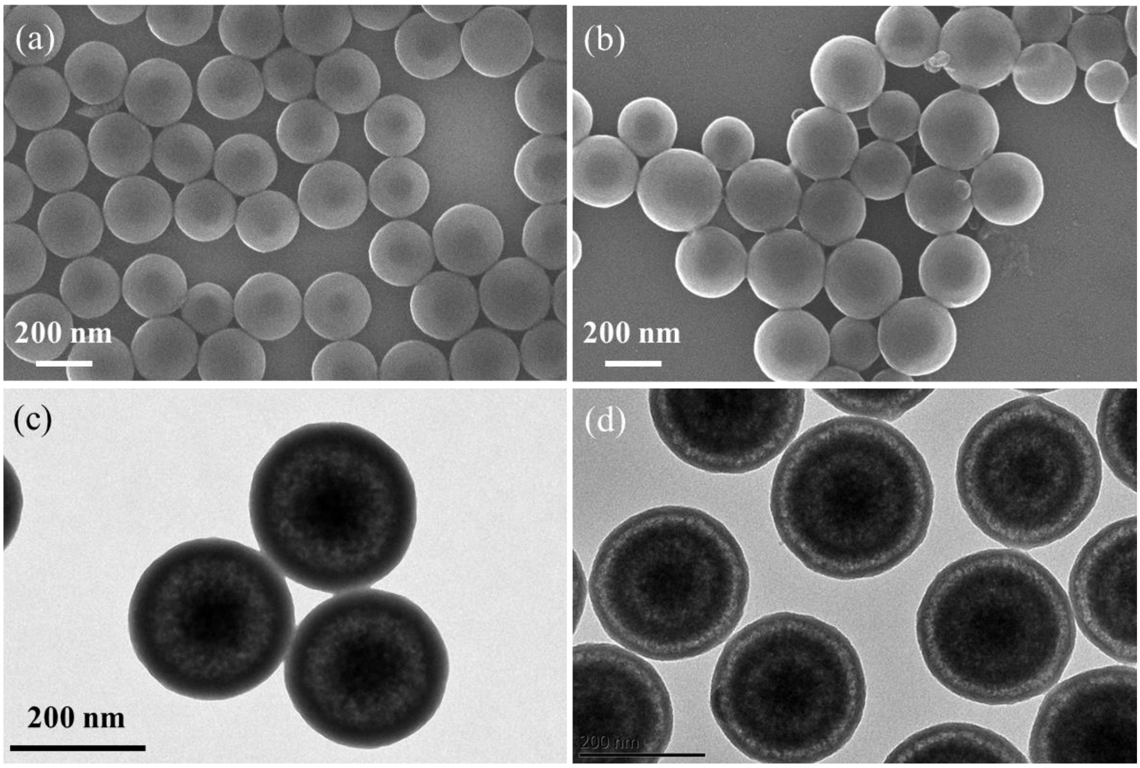

Fig. S1 SEM (a, b) and TEM (c, d) of S-M-HPMO and D-M-HPMO.

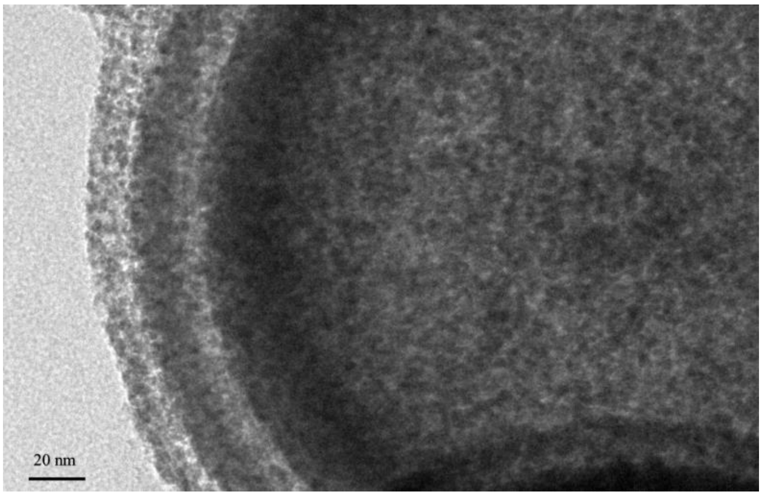

Fig. S2 The high-resolution TEM of T-P-HPMO.

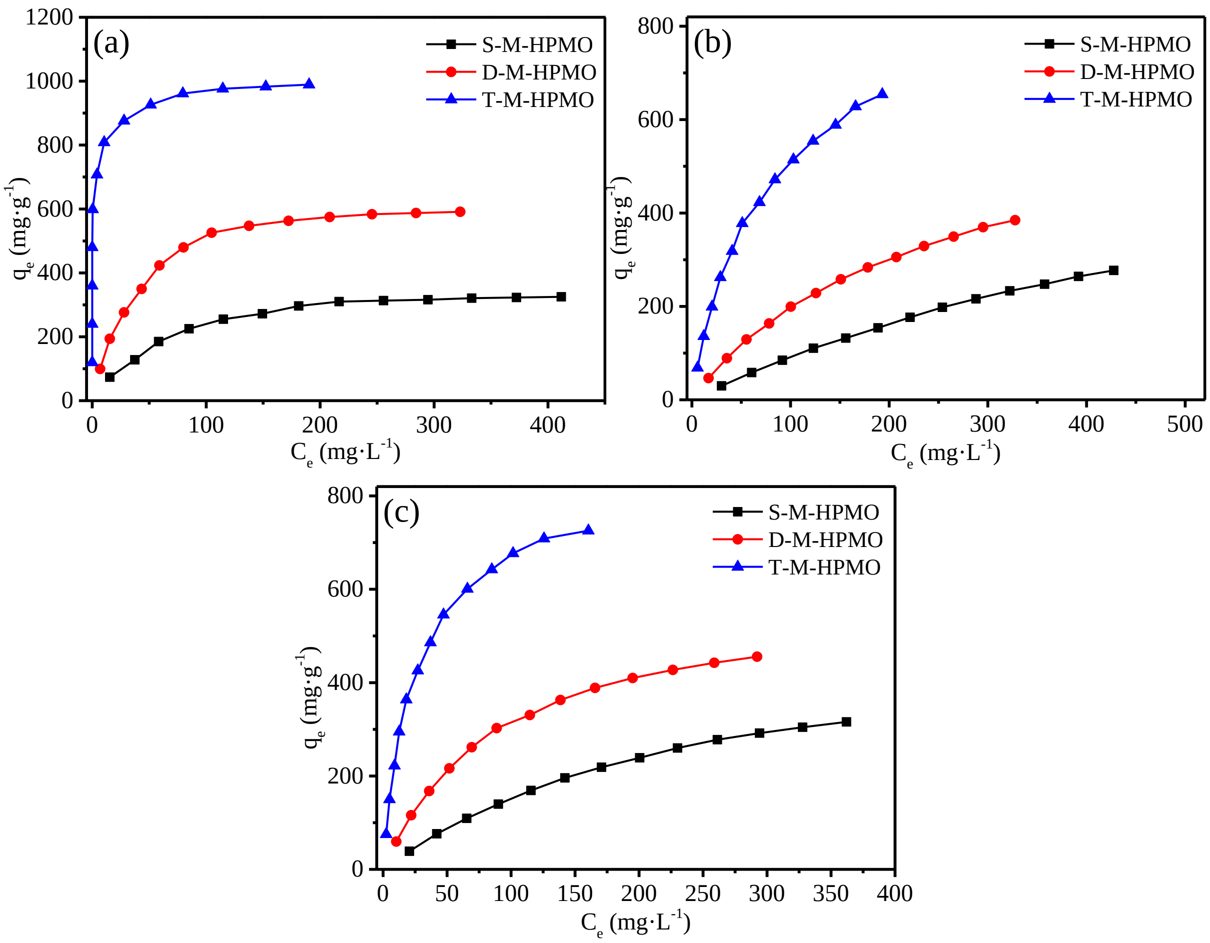

Fig. S3 The adsorption capacity of various organosilica for Hg(II) (a), Cr(VI) (b), and Pb(II) (c).

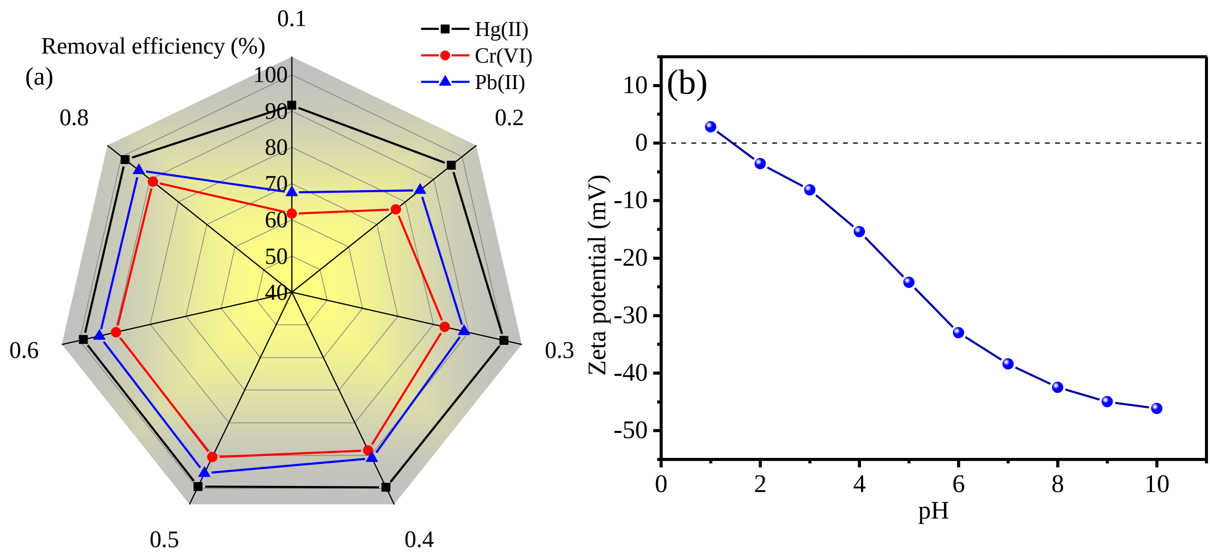

Fig. S4 The relationship between the removal efficiency and T-M-HPMO dosage (a) and the zeta potential of T-M-HPMO under different pH values (b).

Tab. S1 Parameters of adsorption isotherms of Hg(II), Cr(VI), and Pb(II)

Ions	q_m (mg·g^{-1})	b (L·mg^{-1})	R^2
Hg (II)	990.19	0.84	0.9995
Cr (VI)	877.19	0.02	0.9984
Pb (II)	826.45	0.04	0.9987

Tab. S2 Comparison of adsorption performance for Pb (II) between T-M-HPMO and reported adsorbents

Adsorbent	Adsorption capacity		Kinetics		Reference
	q_m (mg·g^{-1})	$R_{S/L}$ (mg·mL^{-1})	Initial concentration (mg·L^{-1})	Equilibrium time (min)	
JUC-505-COOH	559	1/3	100	< 5	[1]
$MnFe_2O_4$@CAC	354	1/2	400	720	[2]
LDH@Fe_2O_3/3DPCNF	426.76	1/2	50	60	[3]
L1@MNP	111.23	1/2.5	200	60	[4]
MKa@CB	90.9	1/0.5	20	60	[5]
Hydrogel/βCB	505.9	1/1	50	75	[6]
MnxLa1-x@HTCC	245.31	1/4	100	60	[7]
CSt-ZnO	256.4	1/4	50	120	[8]
T-M-HPMO	877.19	1/2	320	< 5	**This Work**

Tab. S3 Comparison of adsorption performance for Cr (VI) between T-M-HPMO and reported adsorbents

Adsorbent	Adsorption capacity		Kinetics		Reference
	q_m (mg·g^{-1})	$R_{S/L}$ (mg·mL^{-1})	Initial concentration (mg·L^{-1})	Equilibrium time (min)	
GO-NH_2-AHMT	734.2	1/2	104	100	[9]
CS@BC/S-nZVI	244.07	1/2.5	100	20	[10]
LDH@Fe_2O_3/3DPCNF	400.40	1/2	50	60	[3]
MoS_2@LDC	198.7	1/10	20	40	[11]
PPy/MoS_2	257.73	1/0.33	50	600	[12]
Fe_3O_4/ZIF-67@AmCs	119.05	1/2	50	60	[13]
BM-Fe-HC	48.8	1/2	30	40	[14]
LDH@LDC	274.48	1/10	60	60	[15]
T-M-HPMO	826.45	1/2	320	< 5	**This Work**

Tab. S4 Comparison of adsorption performance for Hg (II) between T-M-HPMO and reported adsorbents

Adsorbent	Adsorption capacity		Kinetics		Reference
	q_m (mg·g^{-1})	$R_{S/L}$ (mg·mL^{-1})	Initial concentration (mg·L^{-1})	Equilibrium time (min)	
MOF-808-SH	977.5	1/5	10	< 5	[16]
PCS-N_2	721	1/4	25	100	[17]
Fe_3O_4@SiO_2-G2-S	605.8	1/0.83	200	150	[18]
UiO-66-DMTD	670.5	1/1.5	200	180	[19]
NHDA	575.17	1/2.5	100	40	[20]
Fe_3O_4@SiO_2@PTL	701.51	1/4	200	10	[21]
MSCTF-2	840.5	1/1.25	300	360	[22]
ZnS-zeolite NaA	553.24	1/2	110	120	[23]
T-M-HPMO	990.19	1/3	320	< 5	**This Work**

Tab. S5 Thermodynamic parameters of Hg(II), Cr(VI), and Pb(II)

Ions	$\triangle G$ (kJ·mol^{-1})			$\triangle H$ (kJ·mol^{-1})	$\triangle S$ (kJ·mol^{-1}·K^{-1})	R^2
	288 K	298 K	308 K			
Hg (II)	-2.82	-3.75	-4.79	30.31	114.94	0.9942
Cr (VI)	-0.87	-2.29	-3.53	39.65	140.64	0.9992
Pb (II)	-1.31	-3.09	-4.57	46.94	167.36	0.9978

Tab. S6 Kinetic parameters of Hg(II), Cr(VI), and Pb(II)

Ions	$q_{e, exp}$ (mg·g^{-1})	q_e (mg·g^{-1})	k (mg·g^{-1}·min^{-1})	R^2	$t_{95\%}$ (min)
Hg (II)	876.93	877.19	0.014	0.9999	2.22
Cr (VI)	479.87	480.77	0.019	0.9999	4.76
Pb (II)	542.9	543.48	0.016	0.9999	4.68

Tab. S7 Adsorption of Hg(II), Cr(VI) and Pb(II) on T-M-HPMO in the presence of interfering ions

Interfering ions	C_0 (mg·L^{-1})	C_e (mg·L^{-1})	Removal efficiency (%)	K_d^M (mL·g^{-1})	*f*
Hg (II)	200	0.42	99.79	1.43×10^6	1
Pb (II)	200	18.16	90.92	3.01×10^4	47.46
Cr (VI)	200	40.81	79.59	1.17×10^4	121.82
Zn (II)	200	196.44	1.78	54.36	2.62×10^4
Cu (II)	200	195.76	2.12	64.98	2.19×10^4
Co (II)	200	196.08	1.96	59.98	2.38×10^4
Ni (II)	200	196.50	1.75	53.43	2.67×10^4
Ca (II)	200	191.48	4.26	133.48	1.07×10^4
Na (I)	200	192.44	3.78	117.85	1.21×10^4
K (I)	200	193.76	3.12	96.61	1.48×10^4
Mg (II)	200	193.84	3.08	95.34	1.50×10^4
Ba (II)	200	196.32	1.84	56.23	2.54×10^4

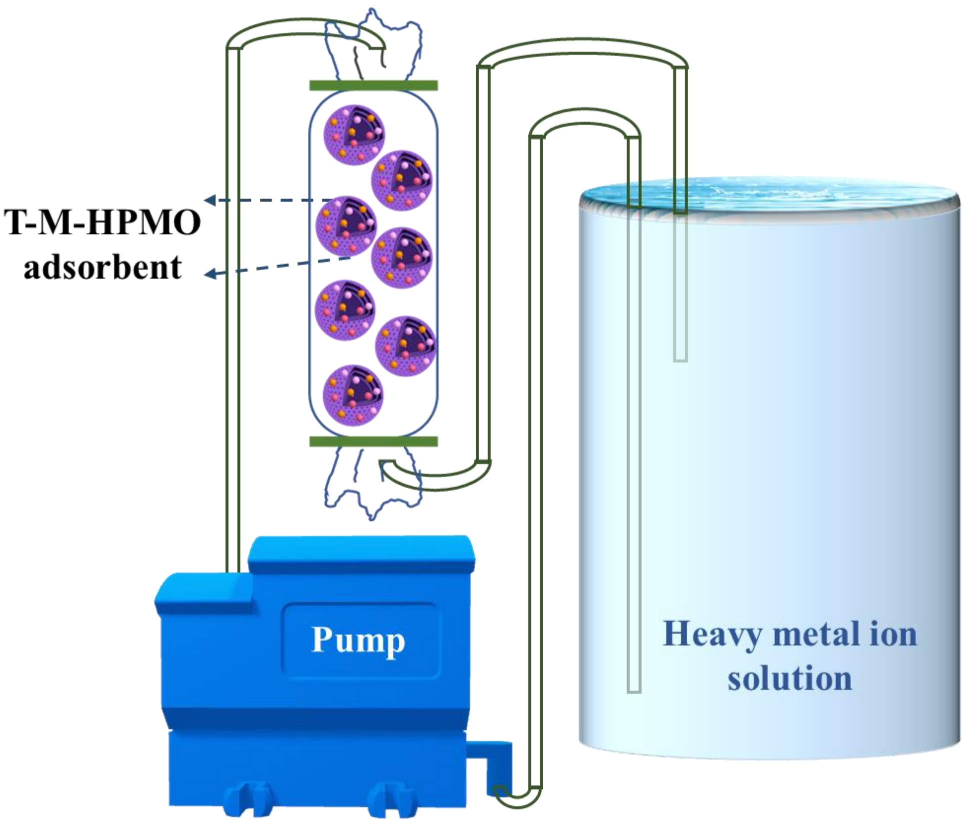

Fig. S5 Equipment applied for removal of trace metal ions.

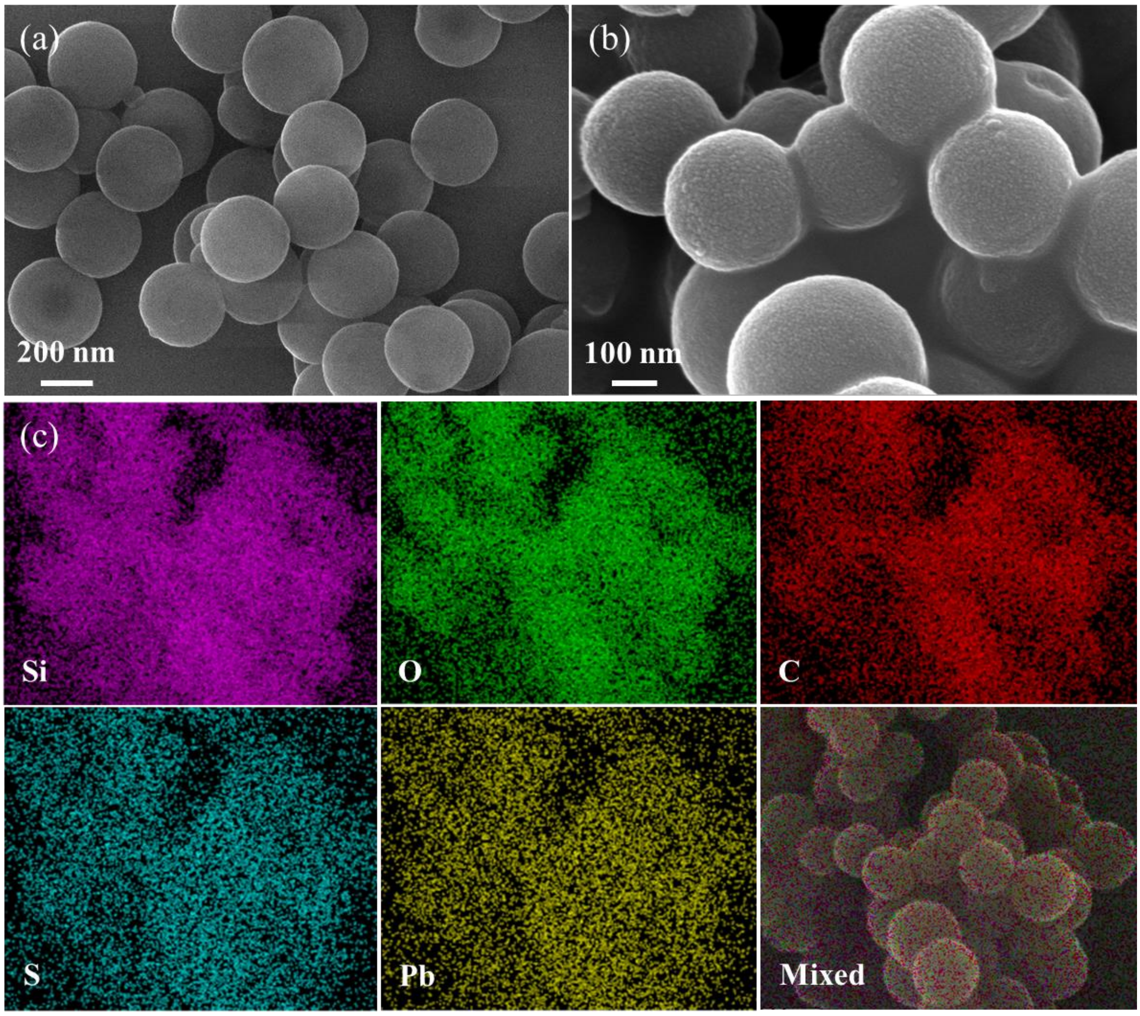

Fig. S6 SEM of T-M-HPMO after adsorption of Pb(II) (a, b), element mapping (c).

Tab. S8 Pore parameters of different organosilica adsorbents before and after adsorption

Sample	BET surface area ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)
S-M-HPMO	428.21	0.40
D-M-HPMO	524.77	0.50
T-M-HPMO	623.36	0.63
T-M-HPMO-Hg	302.34	0.30
T-M-HPMO-Cr	427.13	0.41
T-M-HPMO-Pb	475.46	0.44

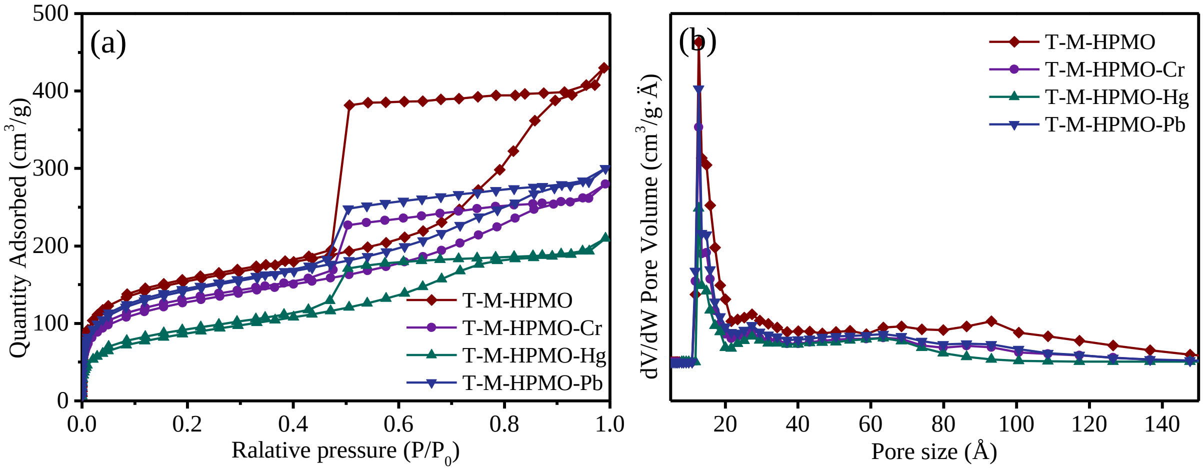

Fig. S7 N_2 adsorption isotherm.

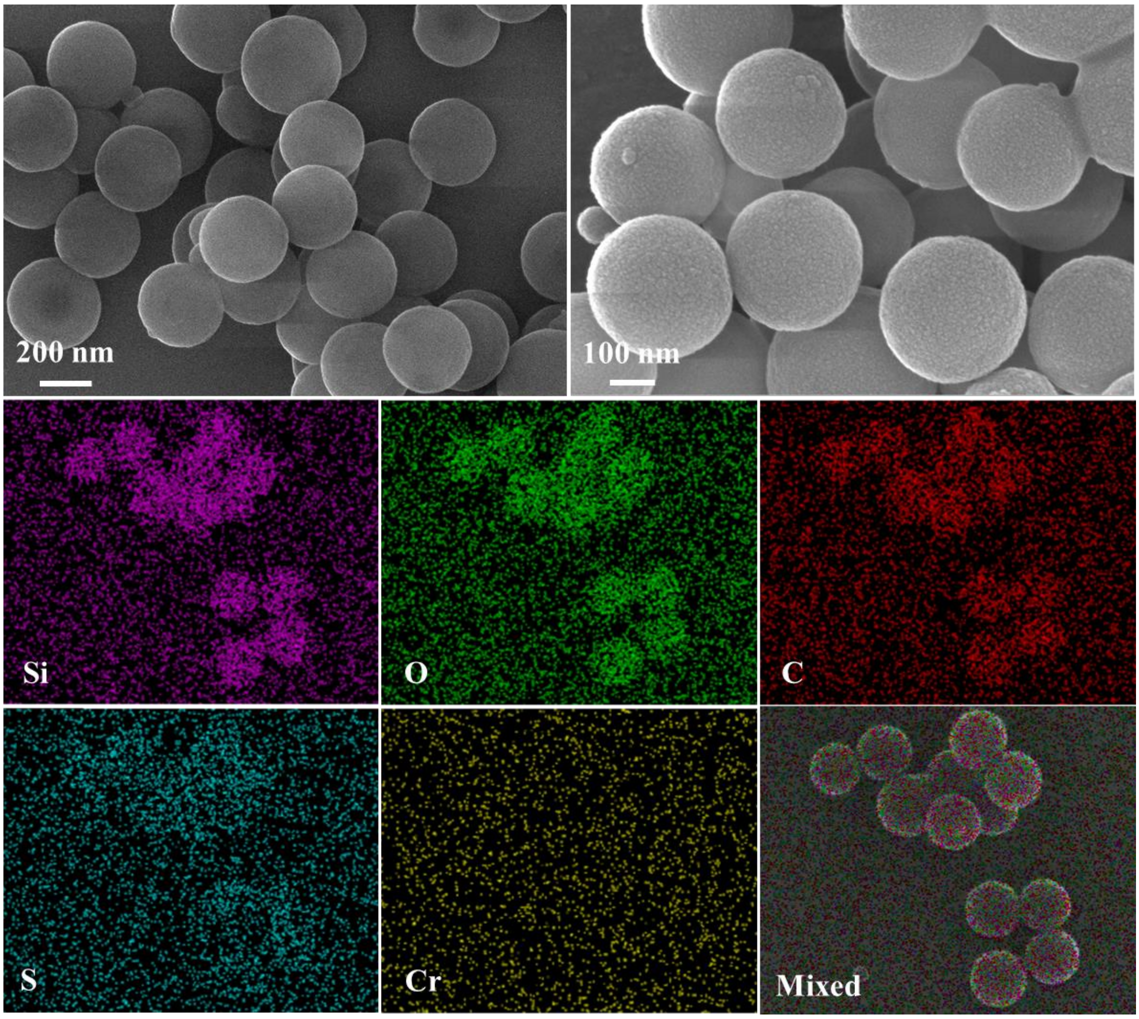

Fig. S8 SEM of T-M-HPMO after adsorption of Cr(VI) (a, b), element mapping (c).

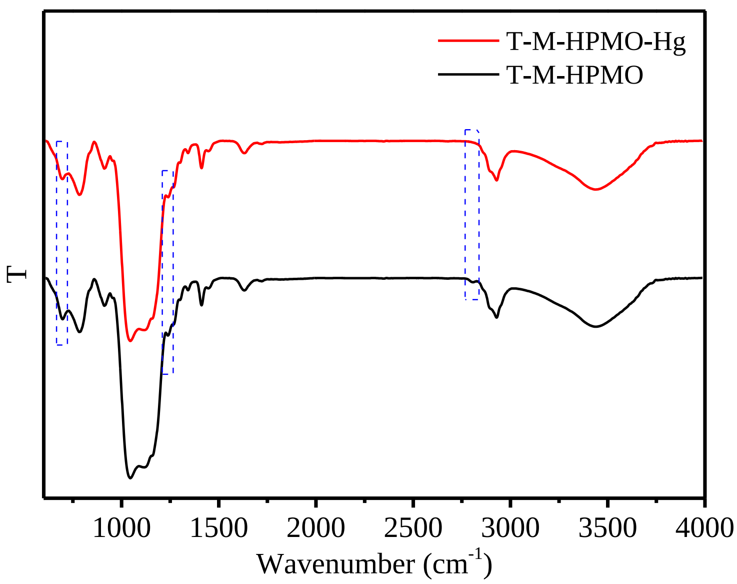

Fig. S9 FTIR of T-M-HPMO and T-M-HPMO-Hg.

References

[1] R. Zhu, P. Zhang, X. Zhang, M. Yang, R. Zhao, W. Liu, Z. Li, Fabrication of synergistic sites on an oxygen-rich covalent organic framework for efficient removal of Cd (II) and Pb (II) from water, Journal of Hazardous Materials 424 (2022) 127301.

[2] Q. Chen, Z. Tang, H. Li, M. Wu, Q. Zhao, B. Pan, An electron-scale comparative study on the adsorption of six divalent heavy metal cations on $MnFe_2O_4$@CAC hybrid: Experimental and DFT investigations, Chemical Engineering Journal 381 (2020) 122656.

[3] M.B. Poudel, G.P. Awasthi, H.J. Kim, Novel insight into the adsorption of Cr (VI) and Pb (II) ions by MOF derived Co-Al layered double hydroxide@ hematite nanorods on 3D porous carbon nanofiber network, Chemical Engineering Journal 417 (2021) 129312.

[4] X. Zhou, C. Jin, G. Liu, G. Wu, S. Huo, Z. Kong, Functionalized lignin-based magnetic adsorbents with tunable structure for the efficient and selective removal of Pb(II) from aqueous solution, Chemical Engineering Journal 420 (2021) 130409.

[5] S.S. Elanchezhiyan, P. Karthikeyan, K. Rathinam, M. Hasmath Farzana, C.M. Park, Magnetic kaolinite immobilized chitosan beads for the removal of Pb(II) and Cd(II) ions from an aqueous environment, Carbohydrate Polymers 261 (2021) 117892.

[6] Z. Wang, T.-T. Li, H.-K. Peng, H.-T. Ren, C.-W. Lou, J.-H. Lin, Low-cost hydrogel adsorbent enhanced by trihydroxy melamine and β-cyclodextrin for the removal of Pb(II) and

Ni(II) in water, Journal of Hazardous Materials 411 (2021) 125029.
[7] Y. Xue, W. Teng, Y. Chen, Q. Ma, X. Chen, Y. Sun, J. Fan, Y. Qiu, R. Fu, Amorphous Mn-La oxides immobilized on carbon sphere for efficient removal of As(V), Cd(II), and Pb(II): Co-adsorption and roles of Mn species, Chemical Engineering Journal 429 (2022) 132262.
[8] M. Naushad, T. Ahamad, K.M. Al-Sheetan, Development of a polymeric nanocomposite as a high performance adsorbent for Pb(II) removal from water medium: Equilibrium, kinetic and antimicrobial activity, Journal of Hazardous Materials 407 (2021) 124816.
[9] S. Bao, Y. Wang, Z. Wei, W. Yang, Y. Yu, Y. Sun, Amino-assisted AHMT anchored on graphene oxide as high performance adsorbent for efficient removal of Cr(VI) and Hg(II) from aqueous solutions under wide pH range, Journal of Hazardous Materials 416 (2021) 125825.
[10] H. Xu, M. Gao, X. Hu, Y. Chen, Y. Li, X. Xu, R. Zhang, X. Yang, C. Tang, X. Hu, A novel preparation of S-nZVI and its high efficient removal of Cr(VI) in aqueous solution, Journal of Hazardous Materials 416 (2021) 125924.
[11] H. Chen, Z. Zhang, X. Zhong, Z. Zhuo, S. Tian, S. Fu, Y. Chen, Y. Liu, Constructing MoS2/Lignin-derived carbon nanocomposites for highly efficient removal of Cr(VI) from aqueous environment, Journal of Hazardous Materials 408 (2021) 124847.
[12] L. Xiang, C.-G. Niu, N. Tang, X.-X. Lv, H. Guo, Z.-W. Li, H.-Y. Liu, L.-S. Lin, Y.-Y. Yang, C. Liang, Polypyrrole coated molybdenum disulfide composites as adsorbent for enhanced removal of Cr(VI) in aqueous solutions by adsorption combined with reduction, Chemical Engineering Journal 408 (2021) 127281.
[13] A.M. Omer, E.M. Abd El-Monaem, M.M. Abd El-Latif, G.M. El-Subruiti, A.S. Eltaweil, Facile fabrication of novel magnetic ZIF-67 MOF@aminated chitosan composite beads for the adsorptive removal of Cr(VI) from aqueous solutions, Carbohydrate Polymers 265 (2021) 118084.
[14] H. Zou, J. Zhao, F. He, Z. Zhong, J. Huang, Y. Zheng, Y. Zhang, Y. Yang, F. Yu, M.A. Bashir, B. Gao, Ball milling biochar iron oxide composites for the removal of chromium (Cr(VI)) from water: Performance and mechanisms, Journal of Hazardous Materials 413 (2021) 125252.
[15] H. Chen, Z. Gong, Z. Zhuo, X. Zhong, M. Zhou, X. Xiang, Z. Zhang, Y. Liu, Y. Chen, Tunning the defects in lignin-derived-carbon and trimetallic layered double hydroxides

composites (LDH@LDC) for efficient removal of U(VI) and Cr(VI) in aquatic environment, Chemical Engineering Journal 428 (2022) 132113.
[16] C. Ji, Y. Ren, H. Yu, M. Hua, L. Lv, W. Zhang, Highly efficient and selective Hg (II) removal from water by thiol-functionalized MOF-808: Kinetic and mechanism study, Chemical Engineering Journal 430 (2022) 132960.
[17] Q. Ge, H. Liu, Tunable amine-functionalized silsesquioxane-based hybrid networks for efficient removal of heavy metal ions and selective adsorption of anionic dyes, Chemical Engineering Journal 428 (2022) 131370.
[18] Y. Zhou, L. Luan, B. Tang, Y. Niu, R. Qu, Y. Liu, W. Xu, Fabrication of Schiff base decorated PAMAM dendrimer/magnetic Fe_3O_4 for selective removal of aqueous Hg (II), Chemical Engineering Journal 398 (2020) 125651.
[19] L. Fu, S. Wang, G. Lin, L. Zhang, Q. Liu, J. Fang, C. Wei, G. Liu, Post-functionalization of UiO-66-NH_2 by 2,5-Dimercapto-1,3,4-thiadiazole for the high efficient removal of Hg(II) in water, Journal of Hazardous Materials 368 (2019) 42-51.
[20] Q. Zeng, L. Hu, H. Zhong, Z. He, W. Sun, D. Xiong, Efficient removal of Hg^{2+} from aqueous solution by a novel composite of nano humboldtine decorated almandine (NHDA): Ion exchange, reducing-oxidation and adsorption, Journal of Hazardous Materials 404 (2021) 124035.
[21] Y. Sun, X. Li, W. Zheng, Facile synthesis of core-shell phase-transited lysozyme coated magnetic nanoparticle as a novel adsorbent for Hg(II) removal in aqueous solutions, Journal of Hazardous Materials 403 (2021) 124012.
[22] Z. Yang, Y. Gu, B. Yuan, Y. Tian, J. Shang, D.C.W. Tsang, M. Liu, L. Gan, S. Mao, L. Li, Thio-groups decorated covalent triazine frameworks for selective mercury removal, Journal of Hazardous Materials 403 (2021) 123702.
[23] Y. Li, L. Yang, X. Li, T. Miki, T. Nagasaka, A composite adsorbent of ZnS nanoclusters grown in zeolite NaA synthesized from fly ash with a high mercury ion removal efficiency in solution, Journal of Hazardous Materials 411 (2021) 125044.