Electronic Supplementary Information

Site-Specific Surface Tailoring for Metal Ion Selectivity via Under-coordinated

Structure Engineering

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Theoretical Calculations

First-principle calculations were performed on the basis of density functional theory (DFT) method. Spin-polarized self-consistent periodic DFT calculations were carried out with the Vienna *ab initio* simulation package (VASP).^{1, 2} The interaction between ionic cores and electrons was described by the projector-augmented wave (PAW) method.^{3, 4} The generalized gradient approximation (GGA) with a Perdew–Burke–Ernzerhof (PBE) functional was used to calculate the exchange-correlation energy.⁵ The kinetic cutoff energy was set at 400 eV to represent the electronic wave functions. The Brillouin zone was sampled using a $3 \times 3 \times 1$ Monkhorst–Pack *k*-point mesh for geometric optimization and $7 \times 7 \times 1$ for electronic calculations.⁶ The Hubbard correction⁷ with $U_{eff} = 4.00$ eV was used in our calculation.⁸ During the DFT calculation, the first three layers of manganese oxides would stop relaxing until the force on each atom less than 0.01 eV/Å, and the energy convergence criteria was 10^{-5} eV.

Note that dissociative chemisorption of water molecules tends to generate OH-terminated metal oxide surfaces.^{9, 10} For simplicity, hydroxylated MnO₂ surface model was used in the calculations, as adsorption is a mainly surface-engaged system. The adsorption processes of Pb(II) and other metal ions (or MeMnO₂ formation) are described by the following reaction:

 $H_2MnO_2 + Me(NO_3)_2 \rightarrow MeMnO_2 + 2 HNO_3$ (Me = Pb, or other metal ions)

The reaction energy for the above reaction is:

$$\Delta E = E_{MeMnO_{2}} + 2E_{HNO_{3}} - (E_{H_{2}MnO_{2}} + E_{Me(NO_{3})_{2}})$$

where E_{MeMnO_2} , E_{HNO_3} , $E_{H_2MnO_2}$ or $E_{Me(NO_3)_2}$ is the total energy of DFT calculation. The more negative of ΔE , then the more strong adsorption of Me ions can be expected.

For accuracy, we use the Gibbs free energy to replace the total energy change, that is

$$\Delta G = G_{MeMnO_2} + 2G_{HNO_3} - (G_{H_2MnO_2} + G_{Me(NO_3)_2})$$

where G_{MeMnO_2} and $G_{H_2MnO_2}$ are gained from the DFT total energy directly; G_{HNO_3} and $G_{Me(NO_3)_2}$ are calculated as

$$G_{HNO_3} = E_{HNO_3} - TS(T, p^{\theta}) + RT \ln \frac{p}{p^{\theta}}$$
$$G_{Me(NO_3)_2} = E_{Me(NO_3)_2} - TS(T, p^{\theta}) + RT \ln \frac{p}{p^{\theta}}$$

where S is the entropy of HNO_3 or $Me(NO_3)_2$.

Supporting Figures and Tables



Fig. S1. Schematic structure of (a) OH-terminated MnO_2 and (b) $MeMnO_2$ (Me = Pb, or other metal ions). (c, d) Projected density of states (PDOS) onto O and Pb(Cu) atoms for Pb/MnO₂ and Cu/MnO₂ systems.

Reaction step	ΔE /eV	∆G/eV
$H_2MnO_2+Pb(NO_3)_2 \rightarrow PbMnO_2+2HNO_3$	0.45	0.13
$H_2MnO_2+Mg(NO_3)_2 \rightarrow MgMnO_2+2HNO_3$	0.72	0.30
$H_2MnO_2+Cu(NO_3)_2 \rightarrow CuMnO_2+2HNO_3$	1.14	0.71
$H_2MnO_2+Ni(NO_3)_2 \rightarrow NiMnO_2+2HNO_3$	1.12	0.66
$H_2MnO_2+Zn(NO_3)_2 \rightarrow ZnMnO_2+2HNO_3$	0.87	0.48
$H_2MnO_2+Cd(NO_3)_2 \rightarrow CdMnO_2+2HNO_3$	0.93	0.59

The adsorption	energy of metal ions o	n OH-terminated M	nO2 at 298 K and 1atm.
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The calculation results reveal metal ions mainly bind to the oxygen atoms at MnO_2 surface with a bond length of ca. 2.0 Å. In particular, the formation of PbMnO₂ shows the relatively low Gibbs free energy (0.13 eV) among all the tested metal ions, indicating a strong adsorption of Pb(II) on manganese oxides. Further electronic analysis gives a distinct overlap between *d*-band of Pb(Cu) and O *2p* band around the Fermi level. In addition, the *d*-band of Pb atom is even separated and spins up and down around the Fermi level, implying a more strong hybridization and interaction between Pb and O atoms in the Pb/MnO₂ system.



Fig. S2. Raman features assigned to MnO₂. The characteristic Raman signal loss of carbon confirms its role as sacrificial templates in the redox-mediated protocol.



Fig. S3. Adsorption assessments in the multiple metal ions coexisting system (all individual metal ions 25 mg L^{-1} , adsorbent dose 0.1 g L^{-1} , initial pH 5.8–6.0).



Fig. S4. The SEM micrograph of Mn_{-C-HAc} reveals agglomerated nanosheets based building blocks.



Fig. S5. FTIR spectra of the synthesized PAA-entangled magnetite (Mag).



Fig. S6. TGA analysis of the as-synthesized samples. According to the TGA curves, the Mag exhibited a significantly stepwise weight loss process, which might be associated with the initial dehydration up to ~180 °C, the subsequent dramatic thermal decomposition of organic ligands at ~200 °C, and the further incineration of the residues at ~250 °C and ~600 °C, respectively. The results distinctly evidenced the surface-coating of ligand layers on Mag. In addition to the similar residual water loss process, Mag-C experienced a mass increase derived from conversion of Fe₃O₄ into Fe₂O₃ in air,¹¹ while a potentially manganese oxide conversion and oxygen release at ~400 °C gave rise to a second weight loss of Mag-Mn.



Fig. S7. Representative elemental mappings of as-synthesized Mag-Mn revealing the homogeneous elemental distributions of Fe, Mn and O.



Fig. S8. Representative SEM and TEM micrographs showing the limited growth of manganese oxide after hydrothermal reaction of 3 d without acetic acid.



Fig. S9. Nitrogen sorption–desorption isotherms collected at 77 K and the derived pore size distributions (inset) of the prepared adsorbents.



Fig. S10. Pb(II) species distribution modeling on MINEQL geochemical program. $c[Pb(II)] = 40 \text{ mg } L^{-1}$ in Pb(NO₃)₂ solution.



Fig. S11. Adsorption assessments of Mag-Mn toward other metal ions (initial concentration 40 mg L^{-1} , adsorbent dose 0.25 g L^{-1}).



Fig. S12. Adsorptive removal of Pb(II) (initial 25 mg L⁻¹) and zeta potentials at different pH.



Fig. S13. Magnetic property investigation. (a) M–H hysteresis loops of the synthesized magnetic composites at 300 K (inset: the magnified view at low magnetic fields) and (b) the corresponding temperature-dependent zero-field-cooled (ZFC) and field-cooled (FC) warming curves with a 100 Oe applied field. (c) Magnetic-responsive retrieval and redispersion of Mag-Mn in aqueous solution under an external magnetic field.

Samples ^b	Carbon (wt %)	Hydrogen (wt %)	Nitrogen (wt %)	Sulfur (wt %) ^c
Mn _{-C} -1	0.108	0.403	0.030	n.d.
Mn _{-C} -2	0.109	0.373	0.030	n.d.
Mn _{-C-HAc} -1	0.444	0.492	0.037	n.d.
Mn _{-C-HAc} -2	0.437	0.485	0.031	n.d.
Mag-1	6.448	1.287	0.039	n.d.
Mag-2	6.864	1.332	0.036	n.d.
Mag-C-1	2.831	0.229	0.031	n.d.
Mag-C-2	2.807	0.222	0.026	n.d.
Mag-Mn-1	0.332	0.983	0.028	n.d.
Mag-Mn-2	0.331	0.957	0.026	n.d.

Table S1. Elemental compositions of different adsorbents^a.

^a Data collected by CHNS elemental analysis.

^b Analysis procedure was repeated twice for each sample.

 c n.d. = not detected.

Table S2. Element analysis of the prepared adsorbent Mag-Mn.

Commute		Element weight perc	cent (%)
Sample	Fe	Mn	Κ
Mag-Mn	45.62	18.68	0.16

Somelas	S_{BET}^{a}	Mesopore diameter ^b	$V_p{}^c$	Mesopore and macropore
Samples	(m^{2}/g)	(nm)	(cm^{3}/g)	volume ^{d} (cm ³ /g)
Mag	134.5	_	0.139	0.117
Mag-C	42.8	18.1	0.147	0.147
Mag-Mn	101.4	5.4	0.183	0.183

Table S3. Specific surface area, pore diameter, and pore volume of the synthesized adsorbents.

^{*a*} Specific surface area calculated using the multipoint Brunauer–Emmett–Teller (BET) method from adsorption data in a relative pressure P/P_o range from 0.05 to 0.30.

^b Mesopore diameter determined based on the local maximum of the Barett–Joyner–Halenda (BJH) pore diameter distribution from the adsorption branch of the isotherms.

^{*c*} Total pore volume (cm³/g) at $P/P_o = 0.99$.

^{*d*} Mesopore and macropore volume obtained from the BJH cumulative adsorption volume of pores with diameters between 1.70 nm and 300.00 nm.

Table S4. Isotherm fitting parameters with Langmuir and Freundlich models for Pb(II) adsorption on the prepared adsorbents.

Isotherm model	Isotherm constants	Mag	Mag-C	Mag-Mn
Langmuir ^a	$Q_m (\mathrm{mg \ g^{-1}})$	51.1	33.9	159.8
$Q_{m} - Q_{m} K_{L} C_{e}$	K_L (L mg ⁻¹)	0.52	0.23	3.10
$Q_e = \frac{1}{1 + K_L C_e}$	r^2	0.906	0.929	0.992
Eroundlich ^b	$K_F ((L mg^{-1}) \cdot 1/n)$	21.7	12.3	83.5
$Q_e = K_F C_e^{1/n}$	п	4.76	4.35	5.26
	r^2	0.929	0.927	0.838

^{*a*} Q_e (mg g⁻¹) represents the quantities of sorbed Pb at equilibrium, C_e (mg L⁻¹) signifies the equilibrium concentration of aqueous Pb, Q_m (mg g⁻¹) stands for the maximum adsorption capacity, K_L (L mg⁻¹) refers to the Langmuir affinity constant associated with adsorption energy.

^b K_F ((L mg⁻¹)•1/n) and *n* denote the Freundlich constants correlated to the adsorption capacity and adsorption intensity, respectively.

Table S5. K⁺ releases and equilibrium pHs in the tested binary metal ions systems.

Binary metal ions	Pb(II)/						
system	Mg(II)	Ca(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
K ⁺ release (mg L ⁻¹)	0.35	0.36	0.27	0.20	0.28	0.21	0.19
Equilibrium pH	4.36	4.18	4.23	4.22	4.38	4.18	4.20

Supplementary References

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