Supporting Information for

Recycling Biowaste Shells to Produce 0D/2D Mn-Ca Nanostructure for Efficient Trace-level Metal Extraction: Confined Growth of Nanosheets and Well Dispersion of Quantum Dots

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Table S1. Parameters of porous structure of the Mn-Ca composite, CaO in ethanol, CaO in water and Pure Mn_3O_4, respectively.

Samples	Specific surface area ($m^2 \cdot g^{-1}$)	Volume of pores ($cm^3 \cdot g^{-1}$)	Average pore size (nm)
Mn-Ca composite	155	0.26	3.21
CaO in ethanol	4.57	0.01	4.82
CaO in water	7.20	0.05	30.6
Pure Mn_3O_4	92.7	0.48	11.7

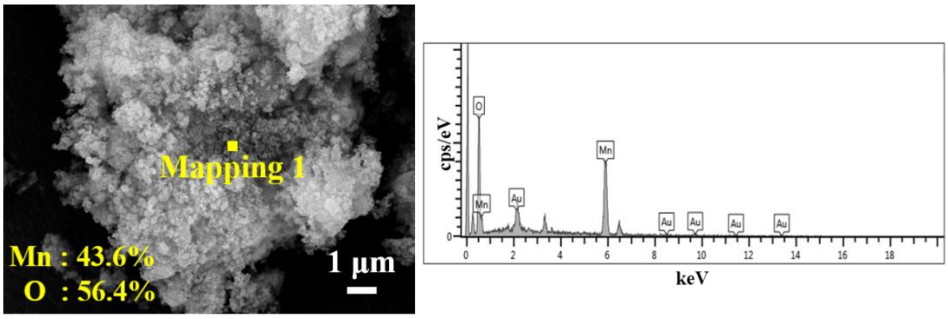

Figure S1. Elemental mapping image of Mn_3O_4 obtained from acid etching of Mn-Ca composite.

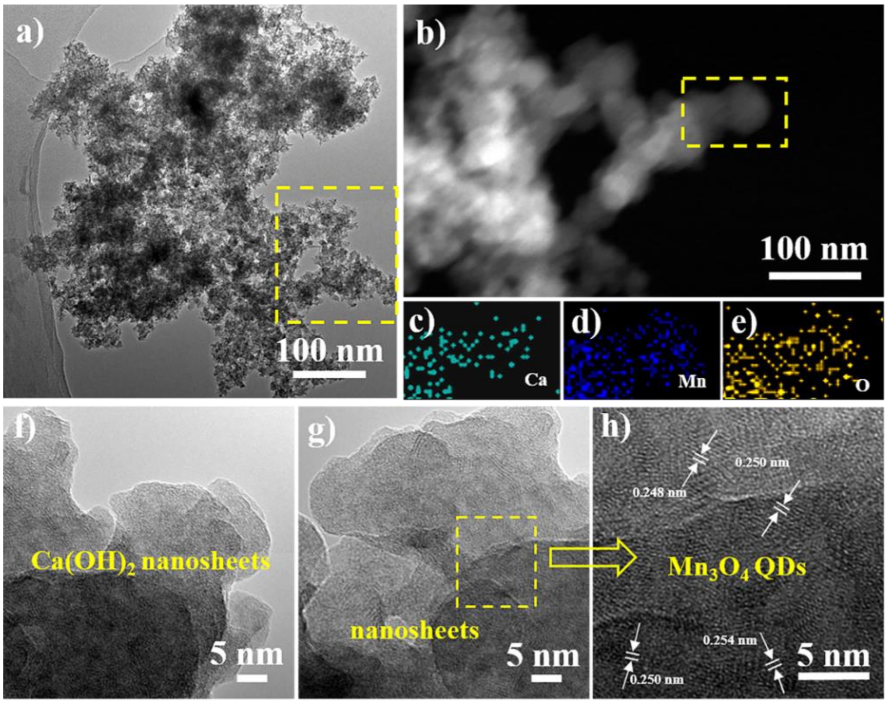

Figure S2. (a) TEM image and (f-h) HRTEM images of the Mn-Ca composite. (b-e) HAADF-STEM image and (c-e) elemental mapping images of the Mn-Ca composite.

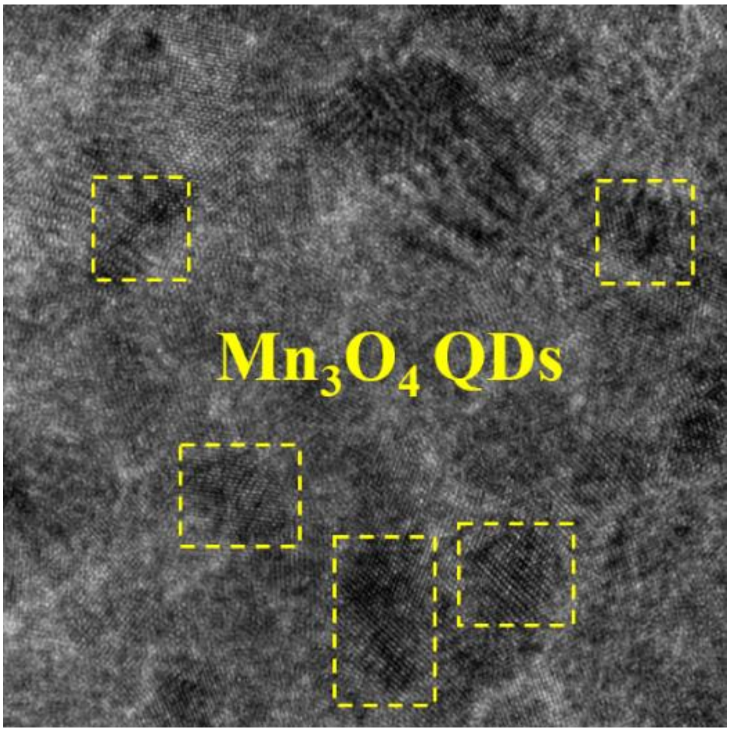

Figure S3. HRTEM image of Mn_3O_4 QDs on the Mn-Ca composite.

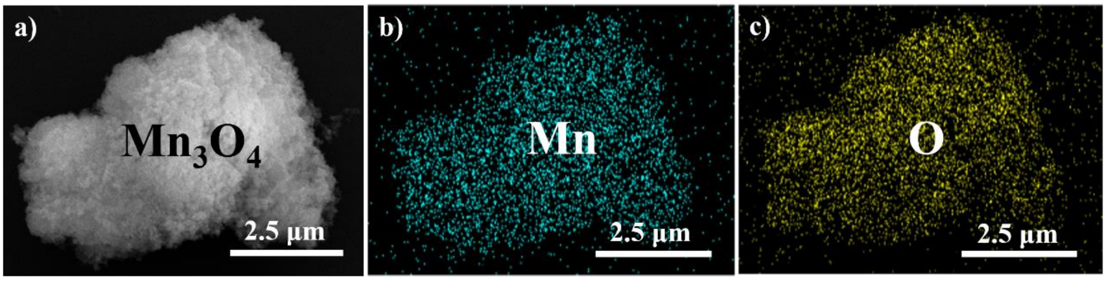

Figure S4. (a) SEM image of pure Mn_3O_4 directly synthesized from the redox reaction of $KMnO_4$ and C_2H_5OH without adding CaO. (b,c) The corresponding elemental mapping images of Mn and O.

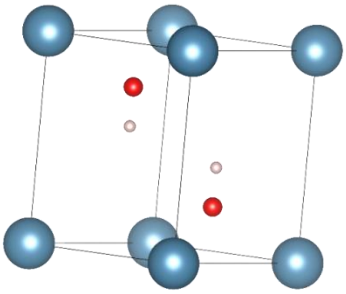

Figure S5. The lattice structure of $Ca(OH)_2$.

I) Adsorption isotherm

Briefly, the Langmuir adsorption equation is expressed as follows[1]:

$$Q_e = Q_m \frac{bC_e}{1+bC_e} \qquad \text{(S1)}$$

where Q_e is the amount adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration (mg/L). Q_m is the maximum amount or the saturated adsorption amount (mg/g). The b is a constant related to the binding strength (L/mg).

The Freundlich adsorption equation is shown as follows[1]:

$$Q_e = k\, C_e^{\,1/n} \qquad \text{(S2)}$$

where k and n are the Freundlich constants, k is roughly an indicator of the adsorption capacity (mg/g), and 1/n is an empirical parameter related to the adsorption intensity.

Figure S6 shows the adsorption isotherms of Pb (II) on Mn-Ca, where Langmuir and Freundlich isotherm models have been employed. The parameters of adsorption fitting are given in Table S2.

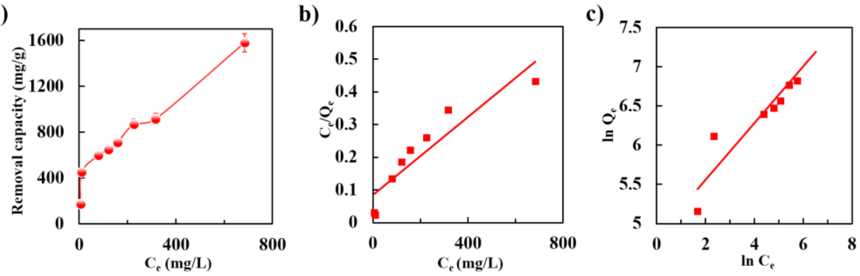

Figure S6. (a) Adsorption isotherm of Mn-Ca for Pb(II) ions (dose: 0.2 g/L, standing, initial concentration: 40-1000 mg/L, initial pH:4.5 ± 0.1, temperature: 25 °C); (b) Linear fitting curves with the Langmuir model for Pb(II) ions; (c) Linear fitting curves with the Freundlich model for Pb(II) ions.

Table S2. Parameters of two kinetic models for the removal of Pb(II) ions over Mn-Ca.

Fitting model	Adsorption constants	Value
Langmuir	Q_m(mg/g)	1675
	b(L/mg)	0.007
	R^2	0.830
Freundlich	k (mg/g)	126.0
	n	2.773
	R^2	0.869

II) Adsorption kinetics

Figure S7 shows adsorption kinetic curves of Pb(II) ions over Mn-Ca composite (dose: 0.2 g/L, standing, initial concentration: 40 mg/L, initial pH: 4.5± 0.1, temperature: 25 °C). Two common kinetic models (pseudo first order equation and pseudo second order equation) were used to fit the experimental data.

Briefly, The pseudo first order equation model is shown as follows[2]:

$$-ln(1-Q_t/Q_e)=k_1t+C \qquad (S3)$$

where Q_t and Q_e are the amounts of the metal ions adsorbed(mg/g) at equilibrium and t time (min), and k_1 (g mg^{-1} min^{-1})is the adsorption rate constant.

The pseudo second order kinetic model is expressed as[3]:

$$\frac{t}{Q_t}=\frac{1}{k_2Q_e^2}+\left(\frac{1}{Q_e}\right)t \qquad (S4)$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo second order adsorption reaction.

The kinetic parameters were summarized in Table S3, and the fitting curves were shown in Figure S7b-c.

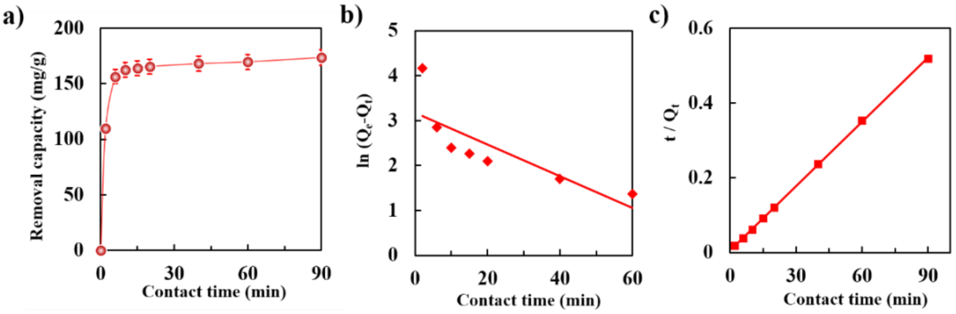

Figure S7. (a) Removal of Pb(II) by the Mn-Ca composite (dose: 0.2 g/L, standing, initial concentration: 40 mg/L, initial pH:4.5 ± 0.1, temperature: 25 °C).(b) the pseudo-first-order kinetics and (c) the pseudo-second-order kinetics.

Table S3. Parameters of two kinetic models for the removal of Pb(II) ions over Mn-Ca

kinetic model	Kinetic constants	Value
pseudo-first-order	k_1 (min^{-1})	0.0353
	Qe (mg/g)	23.9
	R^2	0.5905
pseudo-second-order	k_2(g mg^{-1} min^{-1})	0.005
	Qe(mg/g)	200.0
	R^2	0.9998

III) Supplemental information on the effect of pH value on Pb(II) adsorption

At pH>7, the Pb(II) will be partially precipitated. Despite the difficulty in evaluating the concentration of Pb(II) extracted by adsorbent (i.e., the value of adsorption capacity), the concentration of residual Pb(II) can decrease to a low level (0.36 mg/L) when adding Mn-Ca composite in wastewater. No doubt, the Mn-Ca can efficiently extract the Pb(II) from solutions of a broad pH region (pH >2). In contrast, at pH<2, a reduced adsorption capacity of Pb(II) was found. The reason may lie in that, abundant of $Ca(OH)_2$ nanosheets will be dissolved and become inactive at acid condition.

IV) Discussion on the effect of content of Mn_3O_4 and $Ca(OH)_2$ on Pb(II) adsorption

The content of Mn_3O_4 and $Ca(OH)_2$ in 0D/2D Mn-Ca nanostructure can be tuned, by adjusting the dose of stating precursors (i.e., CaO and $KMnO_4$). As shown in Figure S8, the sample of Mn:Ca=1:1 has the highest efficiency. The reasons may lie in that: 1) With higher amount of $KMnO_4$, the Mn_3O_4 was the dominant phase in 0D/2D Mn-Ca nanostructure. These Mn_3O_4 QDs will be highly aggregated owing to the absence of $Ca(OH)_2$-nanosheets substrate, which results in fast decrease of capacity; 2) With less amount of $KMnO_4$, the hydrolysis and exfoliation of CaO could be prohibited due to limited amount of H_2O, which was released from reaction between $KMnO_4$ and C_2H_5OH. Subsequently, it produced few $Ca(OH)_2$ nanosheets and showed reduced adsorption capacity.

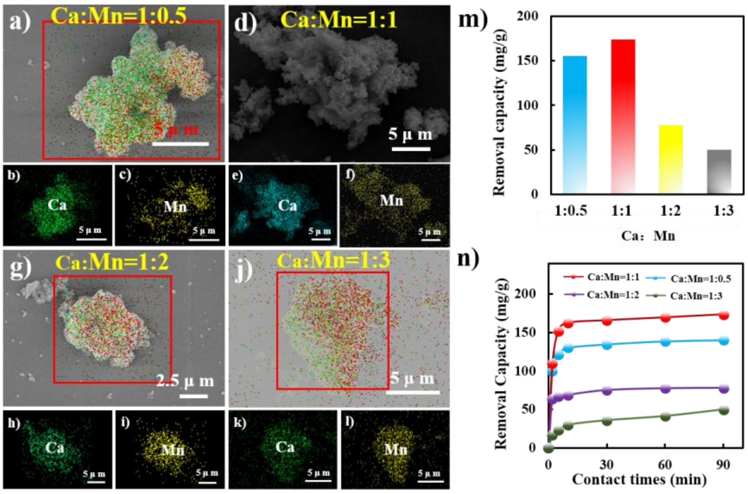

Figure S8. SEM images and elemental mapping of samples prepared from different precursors, with CaO and $KMnO_4$ (denoted as Ca:Mn) ranging from 1:0.5(a-c), 1:1(d–f), 1:2(g-i) to 1:3(j–l), respectively. (m, k) Removal of Pb(II) by the Ca:Mn ranging from 1:0.5, 1:1, 1:2 to 1:3 (dose: 0.2 g/L, standing, initial concentration: 40 mg/L, initial pH: 4.5 ± 0.1, temperature: 25 °C) .

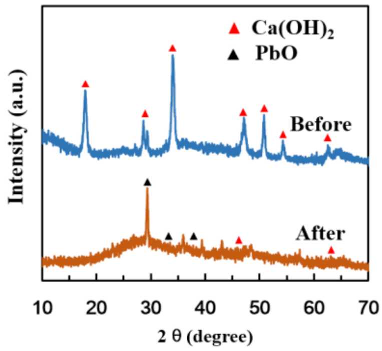

Figure S9. XRD pattern of the Mn-Ca composite before and after extraction of Pb(II).

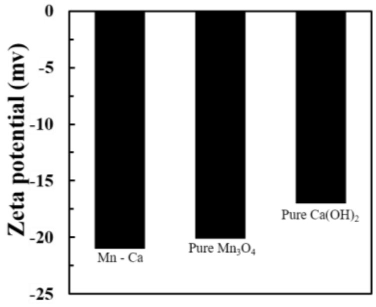

Figure S10. Zeta potential of pure Mn_3O_4, pure $Ca(OH)_2$, and the Mn-Ca composite.

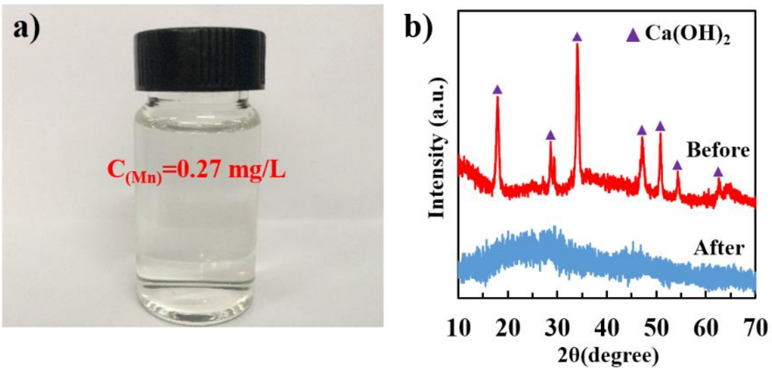

Figure S11. (a) Photograph of the purified solution after removal of Eu(III) by Mn-Ca. (b) XRD pattern of the Mn-Ca composite before and after extraction of Eu(III).

References:

1. V. Gbb, O. A. Oyetade, S. Rana, B. S. Martincigh, S. B. Jonnalagadda and V. O. Nyamori, *Acs Applied Materials & Interfaces*, 2017, **9**, 17290.
2. X. Li, C. Bian, X. Meng and F. S. Xiao, *Journal of Materials Chemistry A*, 2016, **4**, 5999-6005.
3. D. Chen, W. Shen, S. Wu, C. Chen, X. Luo and L. Guo, *Nanoscale*, 2016, **8**, 7172.