Electronic supplementary information(ESI) for

Ultrahigh Aniline-Removal Capacity of Hierarchically Structured Layered Manganese Oxides: Trapping Aniline Between Interlayers

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Experimental details:

Synthesis of α -MnO₂ nanotubes: 0.45 g potassium permanganate (KMnO₄, M=158.0339 g mol⁻¹) was dissolved in 45 mL deionized water. Then 1 mL concentrated HCl (37 wt%, 1.19 g mL⁻¹) was added to the previous solution drop by drop under constant magnetic stirring. The received solution was then transferred to a Teflon-lined stainless steel autoclave with a capacity of 70 mL. The autoclave was then sealed and hydrothermally treated at 140 °C for 12 h. After the autoclave was cooled down to room temperature naturally, the precipitates were collected by centrifugation (9000 rpm) and washed several times by deionized water to remove possible impurities. The as-received brown powders were then dried at 80 °C in air (W. Xiao, D. Wang, X. W. Lou, *J. Phys. Chem. C* 2009, 114, 1694).

Synthesis of Mn₃O₄ octahedra: 0.694 g potassium permanganate was dissolved in 40 mL deionized water. Then 2 mL of ethylene glycol was added to the previous solution drop by drop under constant magnetic stirring for 20 min. The received solution (total 40 mL in volume) was then transferred to a Teflon-lined stainless steel autoclave with a capacity of 70 mL. The autoclave was then sealed and hydrothermally treated at 160 °C for 10 h. After the autoclave was cooled down to room temperature naturally, the precipitates were collected by centrifugation (6000 rpm) and washed several times by deionized water and ethanol to remove possible impurities. The as-received khaki powders were then dried at 80 °C in air (W. Xiao, J. S. Chen, X. W. Lou, *CrystEngComm* 2011, 13, 5685).

Synthesis of $Mn_3O_4@\delta-MnO_2$: The $Mn_3O_4@\delta-MnO_2$ core-shell structures were fabricated by a seed-epitaxial route employing previously synthesized Mn_3O_4 octahedra

as seeds. Typically, 0.10 g of synthesized Mn_3O_4 octahedra seeds, 0.25 g of KMnO₄ and 0.8 mmol of HCl were ultrasonically dispersed into 50 mL of deionized water to form the precursory suspension in a sealed glassy vial. The vial was then heated to 95 °C in an oil bath for 5h under magnetically stirring. After the vial was cooled down naturally to room temperature, brown precipitate was harvested by centrifugation (6000 rpm) and washed with deionized water for 3 times and ethanol once before dry at 80 °C in air (W. Xiao, J. S. Chen, X. W. Lou, *CrystEngComm* 2011, 13, 5685).



Figure S1. Powder XRD patterns of the as-obtained α -MnO₂ nanotubes (a), Mn₃O₄ octahedra (b), Mn₃O₄@ δ -MnO₂ (c) and Mn₃O₄@ δ -MnO₂ after 24h water treatment (d). The miller index shown in black, red and blue represents the characteristic diffraction peaks of tetragonal α -MnO₂ (JCPDS No. 44-0141), tetragonal hausmannite-Mn₃O₄ (JCPDS No. 24-0734) and monoclinic layered birnessite-type manganese oxide (δ -MnO₂, JCPDS No. 80-1098), respectively. The enlarged patterns at (001) diffraction zones of δ -MnO₂ (the dashed zone in the upper) are shown in the lower figure.

Pre-screen of the original waste water:



Figure S2. Q-TOF LC-MS of the simulated water after being diluted by a factor of 1000

Simulated aniline-contained aqueous solution was used in this study (pH=12, initial aniline concentration = 1000.0 mg L⁻¹, NaCl concentration = 2 mol L⁻¹). Before water treatment, the simulated water was prudently screened by Accurate-Mass Quadrupole Time-of-Flight (Q-TOF) Liquid chromatography–mass spectrometry (LC-MS, Agilent 6540, Ion Source: Dual AJS ESI; Scan range of *m/z*: 70-1100; LC column: ZOBRAX SB-C18, 3.5 μ m, 2.1×50 mm; mobile phase: acetonitrile/H₂O mixture(90/10,v/v); 30 °C; injection volume: 0.1µL), to trace the organic species. In particular, the potentially organic species including C₆H₇N, C₆H₄Cl₂N₂O₂, C₆H₅ClO, C₆H₆ClN, C₆H₄ClN₃O₄, C₆H₅ClO, C₆H₆ClN, C₆H₆ClN₂O₂, C₁₂H₁₂O₂, C₁₂H₁₀N₂, and C₄H₄O₄ were traced. As exhibited in Figure S2, only two peaks at 94.0652 and 95.0685 (*m/z*) with intensities of 101715 and 5172 appear in the Q-TOF LC-MS of the original wastewater after being diluted by a factor of 1000. The absence of any peaks with intensity higher than 500 indicates the only organic species in the simulated water is aniline (C₆H₇N, M=93.13 g mol⁻¹).

Determination of aniline concentrations in water:



Figure S3. The standard curve for determination of aniline concentrations in water.

The concentration of aniline was spectrophotometrically determined by measuring the absorbance at 545 nm according to the N-(1-naphthyl) ethylenediamine azo method (GB 11889-89, Standards of China, Anal. Chem., 1982, 54 (4), pp 807-809). The original wastewater and treated water were diluted by a factor of 625. Briefly, 1 mL of the resulting water was sampled out and was further diluted to 10 mL with deionized water. Then some amount (e.g. 50 mg) of KHSO₄ was added to get a pH ranging from 1.5 to 2.0. One drop of NaNO₂ solution (50 g L⁻¹) was added under constant magnetic stirring for 3 min. Afterwards, 0.5 mL of NH₄SO₃NH₂ aqueous solution (25 g L⁻¹) was added under constant magnetic stirring for 3 min. Then 1 mL of N-(1-naphthyl) ethylenediamine dihydrochloride aqueous solution (20 g L⁻¹) was added under constant magnetic stirring for 30 min. The solution was diluted to 25 mL with deionized water. The resulting solution was kept still for 30 min. Finally, UV-visible absorption spectra were recorded on a UV-vis absorption spectroscopy (UV-1700 Pharma. Spec. SHIMADZU). The standard aniline aqueous solutions with specific concentrations were firstly measured to get the standard curve. As shown in Figure S3, the correlation coefficient is extremely high (R²=0.999).

The original water and treated water were also monitored by measuring the total organic carbon (TOC) concentration via a TOC analyzer (Multi1v/C2100, Analytic Jena).



Figure S4. Schematic illustrations on crystal structure of Hausmannite- Mn_3O_4 (derived from ICSD No. 31094), α -MnO₂ (adapted from ICSD No. 20227) and layered-MnO₂ (derived from ICSD No. 68918). The tunnels with size of 0.46 nm in α -MnO₂ and interlayer gaps with size of 0.73 nm in layered-MnO₂ can accommodate cations such as K⁺ and H₃O⁺ which are represented as multiple-color balls. Mn and O atoms are denoted as purple and red balls, respectively.

Determination of Mn²⁺ concentrations in water:



Figure S5. The standard curve for determination of Mn²⁺ concentrations in water.

The Mn²⁺ contents in the original wastewater and treated water were monitored by a UVvis spectrophotometric method (J. Am. Chem. Soc., 1917, 39 (11), pp 2366-2377). Excess amount of sodium periodate was added into the solution to ensure the complete oxidation of Mn^{2+} into MnO_4^{-} . The concentration of Mn^{2+} was spectrophotometrically determined by measuring the characteristic absorbance of MnO₄- at 530 nm. In details, 20 mL of the solution pending for determination was pipette into a beaker with a volume of 200 mL. Then 10 mL of sulphuric acid solution (equal volume between condensed sulphuric acid and deionized water) was added. The solution was then boiled for 3 min. After making up the volume to 60 mL with deionized water, the solution was boiled for 3 min. Then 10 mL of aqueous sodium periodate (50 g L⁻¹) was added. The solution was kept boiling till the appearance of a pink solution. After another boiling for 5 min, the solution was naturally cooled to room temperatures. Then 10 mL of aqueous urea (100 g L⁻¹). Afterwards, the volume of the solution was made up to 100 mL with deionized water. The standard aqueous solutions with specific Mn²⁺ concentrations were firstly measured to get the standard curve. As shown in Figure S5, the correlation coefficient is extremely high (R²=0.9999).



Figure S6. FESEM images of the as-obtained $Mn_3O_4@\delta-MnO_2$ after 24h treatment. After treatment, the sample was collected after thorough rinse in water and vacuum dry at 60 °C.



Figure S7. Fourier-transform infrared spectra (FT-IR) of the as-obtained $Mn_3O_4@\delta$ - MnO_2 before and after 24h treatment. After treatment, the sample was collected after thorough rinse in water and vacuum dry at 60 °C.

As can be seen, the employed $Mn_3O_4@\delta-MnO_2$ shows identical IR spectra before and after water treatment, confirming the absence of polyaniline after water treatment. The band at 520 cm⁻¹ corresponds to the stretching vibration of Mn–O bond in manganese oxides. The band at 880 cm⁻¹ is assigned to the bending vibration of –OH groups located on the [MnO₆] octahedra vacancies. The bands at 1030 cm⁻¹ and 1110 cm⁻¹ are associated with the stretching vibration of the Mn³⁺–O, due to the co-existence of Mn⁴⁺ andMn³⁺ in the obtained Mn₃O₄@ δ -MnO₂. The band at about 1400 cm⁻¹ is ascribed to the bending vibrations of the O–H groups combined with manganese oxides. The peak of 1630 cm⁻¹ is assigned to the bending vibration of H₂O and –OH groups. The band at 2370 cm⁻¹ is due to the stretching vibration of physically adsorbed CO₂ in surface. The broad peak at 3200–3600 cm⁻¹ is assigned to the stretching vibration of H₂O/–OH groups in surface and in the lattice. (*J. Mater. Chem. A*, 2013, 1, 11682–11690).



Figure S8. Energy Dispersive X-ray (EDX) analysis of the as-obtained $Mn_3O_4@\delta-MnO_2$ before and after water treatment. After treatment, the samples were collected directly after vacuum dry at 60 °C (without rinse in water).



Figure S9. Energy Dispersive X-ray (EDX) analysis of the as-obtained $Mn_3O_4@\delta-MnO_2$ after 3h water treatment. After treatment, the sample was collected after thorough rinse in water and vacuum dry at 60 °C. The present Pt element originates from the pre-coated Pt for SEM tests.



Figure S10. Pseudo-second-order kinetics for removal of aniline kinetics on the $Mn_3O_4(a)\delta$ -MnO₂.

The aniline removal kinetics was analyzed by the pseudo-second-order equation shown as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where q_t (mg g⁻¹) is the amount of removed aniline from waste water at any time *t* (min), q_e (mg g⁻¹) is the amount of removed aniline from waste water at equilibrium and k_2 (g mg⁻¹min⁻¹) is the rate constant of second-order sorption.

Upon fitting based on the Pseudo-second-order kinetics model, the obtained correlation coefficient is extremely high (R²=0.99786). The obtained normalized standard deviation S.D. (%) values are 2.41. This indicates that the experimental data agrees well with the pseudo-second-order model. The calculated q_e values obtained from the linear plots is 7151.03 mg g⁻¹.

For comparison, the experimental data was also fitted with the pseudo-first-order equation. A relatively small R^2 value of 0.953 was obtained, with the occurrence of a high normalized standard deviation S.D. (%) value of 23.35. Obviously, the pseudo-second-order equation is better in representing the adsorption kinetics of aniline over $Mn_3O_4@\delta-MnO_2$.



Figure S11. SEM images (a and b), XRD pattern (c) and the corresponding anilineremoval capacity (d) of the prepared microsphere/nanosheet hierarchical birnessite-MnO₂. The XRD pattern can be well indexed to monoclinic layered birnessite-type manganese oxide (δ -MnO₂, JCPDS No. 80-1098). The SEM images exhibit the formation of nanosheets with a thickness ranging from 50 to 80 nm, in which the nanosheets assemble into microspheres. The MO sample was prepared via the same experimental conditions as that of Mn₃O₄@ δ -MnO₂ with the absence of Mn₃O₄. For details, 0.25 g of KMnO₄ and 0.8 mmol of HCl were ultrasonically dispersed into 50 mL of deionized water in a sealed glassy vial. The vial was then heated to 95 °C in an oil bath for 5h under magnetically stirring.

The aniline-removal capability shown in Fig. S11d was performed via the same method as other MOs samples. It is shown that an aniline-removal capacity of 597.6 mg g⁻¹ is achieved over hierarchically structured δ -MnO₂ upon 24h treatment.



Figure S12. Energy Dispersive X-ray (EDX) analysis of the prepared microsphere/nanosheet hierarchical birnessite- MnO_2 before and after 24h water treatment. It is exhibited that the molar K/Mn ratio changes from the initial 0.153 to 0.083 after 24h treatment.