Supplementary Information for "Self-assembled, monodispersed, flowerlike γ-AlOOH hierarchical superstructures for greatly fast removal of heavy metal ions with high efficiency"

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Experimental details

Figures S1 to S4

Experimental

1 Preparation of monodisperse, uniform, flower-like hierarchical structure of γ -AlOOH

All reagents were of analytical grade and used without further purification. In a typical experiment, 1.02g of sodium aluminate (NaAlO₂), 8.67g of urea (H₂NCONH₂) and 0.20 g polyacrylic acid sodium salt (MW $\geq 3.0 \times 10^7$) was dissolved in 30 mL of deionized water under stirring. After being stirred for 30 min, the solution was transferred into a 40 mL Teflon-lined stainless steel autoclave, sealed and maintained at 140 °C for 10 h. After the reaction system was naturally cooled to room temperature, the white precipitates was separated from solution and thoroughly washed several times with deionized water and absolutely ethanol, and then dried in a vacuum oven at 50 °C for 12 h.

2 Characterization

X-Ray scattering patterns were conducted by analyzing the powder samples on a Philips X'Pert Pro X-ray diffractometer (XRD) with Cu Ka radiation (1.5418 Å). Field emission scanning electron microscope (FESEM) images were taken on a FESEM (Quanta 200 FEG) operated at an accelerating voltage of 10.0 kV. Transmission electron microscope (TEM) images were obtained on a JEOL JEM-2010 high resolution transmission electron microscope, equipped with X-ray energy dispersive spectroscopy (EDS) capabilities, working at an acceleration voltage of 200 kV. Fourier transform infrared spectroscopy (FTIR) was performed on a Nicolet iS10 Fourier transform IR (FTIR) spectrometer at room temperature. The samples and KBr crystals were ground together and the mixture pressed into a flake for IR spectroscopy. The photoluminescence (PL) spectrum was

measured by a steady-state/lifetime spectrofluorometer (FLUOROLOG-3-TAU) at room temperature under ambient atmosphere. The γ -AlOOH powders were pressed into the thin slices, and the excitation wavelength was 254 nm. The specific surface areas of the as-prepared products were measured with Micromeritics ASAP 2020 M+C Brunauer-Emmet-Teller (BET) equipment by using nitrogen adsorption and desorption.

3. Removal of heavy metal ions

Solutions containing different concentrations of Pb(II) (10, 20, 78, 157, 216, 316mg/L) and Hg(II) (10, 20, 81, 145, 220, 266mg/L) were prepared using Pb(NO₃)₂ and Hg(NO₃)₂ as the sources of heavy metal ions, respectively. To obtain the adsorption isotherms, 10 mg of the flower-like γ -AlOOH was added to the 10 mL above solution under being shaken at a speed of 100 rpm for 24 hours to establish an adsorption equilibrium at room temperature. Then, the adsorbent was immediately separated from the mixture. And inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Jarrell-Ash, model ICAP 9000) was used to measure the concentration of metal ions in the remaining solution.



Figure. S1 Fourier transform infrared spectroscopy (FTIR) (a) and Room temperature photoluminescence (PL) spectra (excited by $\lambda_{ex} = 254$ nm) of the flower-like γ -AlOOH.

The FTIR spectrum of flower-like γ -AlOOH is shown in Figure. S1a. The intensive bands at 3372 and 3112 cm⁻¹ belong to the v_{as} (Al)O-H and v_s (Al)O-H stretching vibrations. The band at 1068 cm-1 and the shoulder at 1173 cm⁻¹ are assigned to the δ_s Al-O-H and δ_{as} Al-O-H modes of γ -AlOOH, respectively. The three strong bands at 743, 607 and 480 cm⁻¹ are ascribed to the vibration mode of AlO₆. The room temperature photoluminescence (PL) spectrum of the flower-like γ -AlOOH is shown in Figure. S2. The strong and broad emission band at 431 nm for flower-like γ -AlOOH, which differ from the boehmite whiskers prepared by the sol-gel process ¹. The excitation band located at 254 nm was observed at the F⁺-centre excitation ¹. The broad emission band, coming from the cluster of Al³⁺:[O²⁻]₆, can be ascribed to anionic vacancies (F-centre or this type of defects) ². The cluster of Al³⁺:[O²⁻]₆ matches well with the FTIR result.



Figure. S2 XRD patterns of the products prepared at different reaction stages: (a) 0.5h, (b) 1 h and (c) 5 h.

The corresponding XRD patterns of the intermediate products obtained at different reaction times are shown in Figure S2. It is shown that the peaks from γ -AlOOH are weak in the XRD pattern for the reaction of 30min (Figure S2a). The results indicate that the product obtained at the early reaction stage is poorly crystallized. Besides, as shown in Figure S2a, the XRD pattern of the product obtained at the thirtieth minute exhibits some impurity peaks besides those peaks from γ -AlOOH. The impurity peaks are from bayerite with a monoclinic structure (JCPDS 15-0136). From Figure S2b, c and Figure 1g, it can be observed that the products can be assigned to the pure orthorhombic phase of γ -AlOOH (JCPDS 21–1307). Furthermore, the products obtained at different stages displayed the same crystallinity, and there was no physical transformation in the hydrothermal process.



Figure. S3 SEM images of the γ -AlOOH particles synthesized without using PAAS as surfactant.



Figure. S4 SEM images of the products obtained at different temperatures for 10 h: (a) $100 \,^{\circ}$ C, (b) $180 \,^{\circ}$ C, (c) $200 \,^{\circ}$ C. (d) XRD patterns of the products above.

It was found that product morphology is sensitive to the temperature of the reaction

process. To substantially understand the effect of the temperature on morphologies of y-AlOOH architectures, the experiments of the reaction process with different reaction temperature were carried out. As shown in Figure S4a (see the Supplementary Information), the product obtained at 100 °C was spindle-like particles with a size of about 12 µm. From Figure S4b, it is clear that the size of the product obtained increased when the reaction temperature enhanced to 180 °C, in comparison with the product obtained at 140 °C (Figure 1c). Furthermore, the dispersity of the product obtained at 180 $^{\circ}$ C was not good, and most of the flower-like γ -AlOOH architectures adhere to each other. When the temperature was further enhanced to 200 °C (Figure S4c), the size of the product obtained further increased. The boundary between the flower-like y-AlOOH architectures has almost disappeared. Figure S4d shows the corresponding XRD patterns of the products above. In an XRD pattern of the product obtained at 100 °C (curve a), all the diffraction peaks could be easily indexed to the bayerite with a monoclinic structure (JCPDS 15-0136). Curve b and c show the corresponding XRD patterns of the products obtained at 180 °C and 200 °C, respectively, which can be assigned to orthorhombic y-AlOOH (JCPDS 21-1307), indicating that high temperature is beneficial to the preparation of well-crystallized products without changing their crystal phase. Therefore, a proper reaction temperature should have a great influence on the formation of γ -AlOOH architectures, and the well-defined flower-like γ -AlOOH architectures were obtained at 140 °C (Figure 1c).

References

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