New hierarchical zinc silicate nanostructures and their application in lead ion adsorption†

Jin Qu,ab Chang-Yan Cao,a You-Li Hong,bc Chao-Qiu Chen,ab Pei-Ping Zhu,c Wei-Guo Song*a and Zi-Yu Wu cdef

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A low cost and reliable hydrothermal method was developed for the tunable synthesis of flower-like and urchin-like zinc silicate nanostructures. High resolution TEM, XRD, solid state 29Si NMR spectra and X-ray nanotomography revealed new morphologies and crystal structures. Solid state NMR indicated very different silicon bonding patterns between the two materials. For urchin-like zinc silicates, a synchrotron based three dimensional X-ray nanotomography technique provided unprecedented structural details and revealed structural defects during the assembly process. For flower-like zinc silicates, HRTEM images showed that their secondary nanopetals had a clay-like layered structure, resulting in a higher BET surface area of 236 m2 g−1 as well as higher adsorption capacity for lead ions at 210 mg g−1 than reported zinc silicate samples. The adsorption isotherms and mechanism were investigated.

Introduction

Materials with porous nanostructures have shown exciting properties in surface applications such as sensors and adsorption.1,2 Among various functional materials, hierarchical structured silicates, which combine nanoparticles’ high chemical activity and microscale structures’ physical stability, are appealing materials as adsorbents in water treatment and catalyst applications.3,4 Hierarchical structures offer advantages in terms of mechanical stability, allowing water to readily flow through and ease of handling. For example, Wang et al. reported a chemical-template method to fabricated a hollow magnesium silicate as an efficient adsorbent for water treatment.3 Among metal silicates, zinc silicate is a low cost material to adsorb toxic metal ions from water.5 Zinc silicate nanoparticles,6,7 nanowires,8,9 microfibers/microbelts,10 micro/nanowire bundles,11 film,12,13 and nanotubes14 have been reported. Wang et al. reported the structure-related adsorption properties of zinc silicates (hemimorphite, Zn2Si2O7(OH)2·H2O) for Pb2+, Cr3+, Cd2+ and Fe3+. They found that hollow spheres showed higher removal capacity than one dimensional nanowires and two dimensional membranes.5

Crystal structures of metal oxide nanostructures are well characterized. For example, titanium oxide can be produced in different morphologies, but most titanium oxides are either anatase or rutile structures. However, metal silicates have various crystal structures because the metal to silicon ratio can be varied over a wide range. They can be considered as composites of metal oxides and silica. For zinc silicates, most of the reported zinc silicate nanomaterials are composed of highly crystalline hemimorphite or willemite units.5,11-13,19 Fabricating zinc silicate nanomaterials with new structures as well as new morphologies is the rational way to develop better adsorbents. For hierarchical structured zinc silicates, new characterization techniques are needed for better understanding of the structural details.

In this paper, we report the morphology and crystallographic information of two new hierarchical zinc silicate nanomaterials: flower-like and urchin-like zinc silicates. They were produced by a low cost hydrothermal method using low cost sodium silicate as the silicate precursor, and at a relatively mild temperature of 140 °C. No organic surfactants were used. XRD and solid state 29Si NMR spectra of these two materials suggest them to have different crystal structures. For highly crystalline urchin-like zinc
silicates (hemimorphite, Zn₄Si₂O₇(OH)₂·H₂O), three-dimensional X-ray nanotomography provided real time three-dimensional imaging with a 30 nm spatial resolution, showing several misaligned sub-units and providing new insights into how the urchin-like structure was assembled. Such structural information has never been offered by other techniques. HRTEM images showed that the nearly amorphous flower-like zinc silicates’ secondary nanopetals had a layered structure with zinscisilite (Zn₃Si₄O₁₀(OH)₂·nH₂O) layers, which was very different from other hierarchical zinc silicates, whose units were usually made of aggregated nanoparticles or highly crystalline rods. The flower-like zinc silicate had a high BET surface area of 236 m² g⁻¹ as well as high adsorption capacity for lead ions at 210 mg of lead per gram of sorbent.

**Experimental section**

**Materials**

Analytical-grade zinc chloride, zinc acetate, zinc nitrate, ammonia chloride, NH₄F, NH₃·H₂O (28%) and sodium silicate were purchased from Beijing Chemicals Co. (Beijing, China). All chemicals were used without further purification.

**Synthesis of zinc silicates**

In a typical procedure, zinc chloride (0.75 mmol), ammonia chloride (10 mmol) and NH₃·H₂O (1 ml) were dissolved in 30 ml deionized water as solution A. And sodium silicate (1.266 mmol) was dissolved in deionized water (20 ml) as solution B. The above two solutions were mixed and transferred into an autoclave (70 ml) at 140 °C for 12 h. The white product was collected by centrifugation and rinsed with deionized water several times. Finally, the product was dried in an oven at 60 °C overnight. The urchin-like zinc silicate was produced in a similar procedure, except decreasing sodium silicate to 0.375 mmol.

**Characterization**

The microscopic features of the samples were characterized by scanning electron microscopy (SEM, JEOL-6701F) equipped with an energy-dispersive X-ray (EDX) analyzer (Oxford INCA), transmission electron microscopy (TEM, JEOL JEM-1011, 100 kV), and high resolution transmission electron microscopy (HRTEM, JEM 2100F, 200 kV). X-Ray powder diffraction (XRD) patterns were collected on an X-ray diffractometer (Rigaku D/max-2500 diffractometer with Cu-Kα radiation, λ = 1.54056 Å) at 40 kV and 200 mA. The surface area of the products was measured by the Brunauer–Emmett–Teller (BET) method using N₂ adsorption and desorption isotherms on an Autosorb-1 analyzer at 78.3 K. Metal elemental analysis was conducted using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Shimadzu, ICPE-9000). The three dimensional imaging data was collected on a full-field transmission hard X-ray microscopy system installed at the beam line 4W1A in Beijing Synchrotron Radiation Facility (BSRF). Solid-state ²⁹Si NMR spectra were obtained on an AVANCE III 400 spectrometer using a 7 mm rotor spun at 5 kHz.

**Lead ion adsorption experiments**

Lead nitrate solutions of different concentrations were prepared. The adsorption isotherm was obtained using 10 mg zinc silicates mixed with lead nitrate solutions of different concentrations at room temperature, and stirred overnight. Then the zinc silicates were separated by centrifugation, and the solutions were analyzed by ICP-AES.

**Results and discussion**

By changing the mole ratio of Zn to Si, two zinc silicates with flower-like or urchin-like morphology were produced. Besides very different morphologies, these two zinc silicate materials had different crystallographic structures, as revealed by X-ray nanotomography, solid state NMR and high resolution transmission electron microscopy (HRTEM).

The morphologies of the flower-like products were studied by SEM (Fig. 1a). The flower-like spheres had an average diameter of about 600 nm. The entire structure of the architecture was built from twisted nanopetals with a thickness of about 40 nm, which were connected with each other to form the three-dimensional flower-like hierarchical structure by self-assembly (TEM image, Fig. 1b). The EDX analysis of the flower-like zinc silicate indicated the presence of Zn, Si, and O, consistent with the formation of zinc silicate (Fig. S1†). The atomic ratio of zinc and silicon in the whole structure was determined by elemental analysis using ICP-AES, which showed the Zn : Si molar ratio was 0.753, agreeing very well with the crystallographic structure of zinscisilite (Zn₃Si₄O₁₀(OH)₂·nH₂O).

The morphology was very similar to reported flower-like metal oxide nanostructures such as iron oxide and magnesium oxide. However, unlike these flower-like metal oxide nanostructures, whose nanopetals were composed of aggregated
The HRTEM image (Fig. 1c) showed that the flower-like zinc silicates’ nanopetals had a layered structure with an interlamellar spacing of 1.22 nm, as shown in the inset of Fig. 1d. The layered structure of the nanopetals was further confirmed by the low angle XRD pattern (Fig. 1d). There was a strong peak with a 2θ value of 7.22°, corresponding to \( d = 1.22 \) nm, which was exactly the same as what was observed from HRTEM. Such thin and lamellar secondary structures lead to the broad XRD peaks observed on the flower-like zinc silicate (Fig. 3a).\(^8\) The 1.22 nm spacing between the layers allowed the molecules and ions to be able to diffuse into layers, maximizing the adsorption capacity of the materials. As a result, the flower-like zinc silicate showed an excellent adsorption capacity for lead ions, as discussed in detail later. Also, it may serve as a main component or functional filler in hybrid films, or it could be designed for practical applications through covalent modification of interlayer surfaces.\(^18,19\)

Very different from the flower-like zinc silicates, the urchin-like zinc silicate was a sphere with a diameter of about 20 \( \mu m \), and formed by relatively uniform microrods (SEM image in Fig. 2a). The TEM image of the sample showed only a black shadow (inset in Fig. 2a). Because the sample was too thick for the transmission of the TEM electron beam, internal structure was hard to observe using TEM, making it difficult to understand the growth mechanism of the materials, i.e. how the microrods were assembled and connected to form such an urchin-like structure. For a better illustration of the internal structure of the material, a three dimensional imaging of the material was obtained by X-ray nanotomography (Nano CT),\(^20\) which has a spatial resolution of 30 nm using an 8 keV monochromatic synchrotron beam in BSRF.\(^21\) Such spatial resolution is suited for this urchin-like structure.

As shown in Fig. 2b, almost all microrods were assembled in order to point from the center to the outer surface with an urchin-like morphology. For a better visualization of three dimensional structural details, a video clip showing the rotation of the sphere and its reconstructed slice images (Fig. S2\(^\dagger\)) are included in the ESI.\(^\dagger\) Three dimensional images showed new structural details not detectable with other techniques. Though most microrods were aligned in a radial manner nicely, some misaligned microrods could be observed. As shown in Fig. 2b and the supporting video,\(^\dagger\) some microrods were dangling inside the regular microrod array (red square in Fig. 2b). These dangling rods may be broken from the assembly, or they were latecomers that could not be fit into the assembly. Such defects during the assembly became visible with the synchrotron based X-ray nanotomography.

The as-prepared flower-like and urchin-like samples showed very different XRD patterns (Fig. 3a). All the peaks of the urchin-like product could be well indexed to zinc silicate (hemimorphite, \( \text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}, \) JCPDS 05-0555). These sharp peaks indicated that the as-prepared zinc silicate was well crystallized. On the contrary, the flower-like product showed very broad XRD peaks that could be hardly identified.

To investigate how Si atoms were connected with other silicon or zinc atoms, both samples were then characterized using solid state \( ^{29}\text{Si} \) NMR spectroscopy. For urchin-like zinc silicate, a sharp peak at \(-77.6 \text{ ppm}\) was observed, corresponding to \( Q_1 \) groups (\( Q_n \) referred to Si atoms that connected with \( n \) other Si atoms through oxygen bridges, \( n \) can be 0–4). The sharp \( Q_1 \) peak in the urchin-like zinc silicate agreed well with its \( \text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O} \) structure reported by Lippmaa.\(^22\) As shown in Fig. 4, in hemimorphite, silicon atom and zinc atom connect with each other through oxygen bridges in a disilicates structure. The flower-like zinc silicate showed a broad peak at \(-96.9 \text{ ppm}\), corresponding to \( Q_3 \) groups. Such a connected pattern is consistent with a chain branching structure,\(^22,23\) compatible with a talc-like clay structure such as zinsilite (\( \text{Zn}_3\text{Si}_4\text{O}_{10}(\text{OH})_2\cdot n\text{H}_2\text{O} \)),\(^24\) whose Zn to Si molar ratio was confirmed by the ICP-AES result. There were also two weak chemical shifts which were assigned to \( Q_6 \) (\(-70.4 \text{ ppm}\)) for the urchin-like zinc silicate and \( Q_2 \) (\(-87.2 \text{ ppm}\)) for the flower-like zinc silicate, respectively. They were likely due to the defect sites.

Solid state NMR and Nano CT imaging technologies provided new structural information for both flower-like and urchin-like...
structures. Unambiguous bonding information of silicon atoms from solid state NMR helped us to make clear the crystallographic information for the two. And the Nano CT offered a 30 nm spatial resolution to highlight the assembly defect for the urchin-like structures.

The new layer by layer structure of the flower-like zincsilite is quite new for nanostructured zinc silicates. Most of the hierarchical zinc silicate nanomaterials reported are composed of highly crystalline hemimorphite (Zn₄Si₂O₇(OH)₂·H₂O) or willemite (Zn₂SiO₄) units. However, the as-prepared flower-like zinc silicate in the study was assembled from zinsilite (Zn₅Si₄O₁₀(OH)₂·nH₂O) layers. The urchin-like zinc silicate was composed of conventional hemimorphite (Zn₄Si₂O₇(OH)₂·H₂O) nanoparticles. However, the urchin-like morphology was also new; and its images from the Nano CT were very impressive.

Both flower-like and urchin-like zinc silicates were synthesized under identical conditions, except using different molar ratios between silicon and zinc compounds. Apparently, the molar ratio of the Zn to Si precursor was the key factor in determining the morphology of the product. As shown in Fig. 4, when the Zn to Si molar ratio was 2 : 1, two zinc—oxygen or silicon—oxygen tetrahedrons linked with each other by oxygen bridges to form 4-, 6-, and 8-membered rings, with water molecules existing in the resulting pores. It tended to grow along a preferential direction to form a rod like structure, then highly crystalline hemimorphite (Zn₄Si₂O₇(OH)₂·H₂O) was formed, in which Si atoms were in the Q₁ position. When the Zn/Si molar ratio was decreased to 3 : 5, silica tetrahedrons linked with each other to form silica sheets, and the Zn atoms linked to two silica sheets by oxygen bridges to form a sandwich-like three-layer packing pattern, promoting crystal growth along two dimensional planes to form nanopetals, characteristic of clay-type structures in which Si atoms occupied the Q₃ position. At the same time, the hydrogen bonding forces in the system propelled these secondary structures to self-assemble.

Several series of control experiments for flower-like and urchin-like zinc silicates were carried out to investigate the self assembly of the zinc silicate materials for a better understanding of the assembly process.

First, the ZnCl₂ precursor was changed to Zn(NO₃)₂ or Zn(Ac)₂. The same products (flower-like and urchin-like zinc silicate) were obtained as shown in Fig. S3 of the ESI, suggesting that low cost Zn(NO₃)₂ was suitable for this method.

Then the role of ammonia was tested. When the synthesis experiments were carried out without NH₃·H₂O, no flower-like or urchin-like product was obtained. However, the secondary building units, i.e. nanorods and nanopetals were produced, as shown in Fig. S4 of the ESI. Apparently, NH₃·H₂O was a key factor for the self-assembly process. Based on SEM and XRD results (Fig. S4 and S5†), we believe that NH₃·H₂O not only serves as an additional OH⁻ supply to form the hemimorphite crystallographic structure when Zn : Si = 2 : 1, but also induces the self-assembly process under the two different Zn : Si molar ratios. Note that the hydrolysis of sodium silicate could supply enough OH⁻ to form zinsilite.

The synthesis procedures were then carried out without ammonia chloride, and only disordered nanorods or nanosheets were obtained, respectively (Fig. S4b and e†). The nanorods and nanosheets could be considered as the building units of micro-rods and nanopetals. Thus, without ammonia chloride, even secondary building units (microrods and nanopetals) could not form. When NH₄F replaced NH₄Cl, the same three dimensional structures (urchin-like structure and flower-like structure) were produced (Fig. S4c and f†). Results from these control experiments suggest that NH₄Cl acts as the mineralizer in this system. It provides the necessary ionic strength to the aqueous solution.

Silicate materials are efficient adsorbents. For practical usage, the stability of the nanomaterials in acidic and basic solution should be evaluated. Zinc ion concentrations in water were analyzed with ICP-AES at the pH range of 2–11. The data showed that both the zinc silicate nanomaterials were stable within pH 5–11 (Fig. S5†). In our study, the abilities of the zinc silicates to adsorb lead ions from water (pH at 5.26–7.0 depending on the concentrations) were investigated. The adsorption data fitted the Langmuir adsorption isotherm well, as shown in Fig. S7 of the ESI. The fitting parameters are listed in Table 1. Most lead ions could be removed at low initial concentrations, and the maximum adsorption capacity of the flower-like zinc silicate reached 210 mg g⁻¹ for lead ions, which was nearly 2.6 times greater than the urchin-like zinc silicate, which had an adsorption capacity of 81.7 mg g⁻¹ at room temperature. Flower-like zinc silicate had a larger surface area (236 m² g⁻¹) than urchin-like zinc silicate (11 m² g⁻¹), and the large surface area was favorable for adsorption. In addition, the flower-like zinc silicate’s lamellar structure favored the fast diffusion of lead ions. Moreover, the adsorption capacity of the flower-like zinc silicate was higher than several outstanding reports in the literature, such as the sepiolite (Table 2). Meanwhile, as the amount of adsorbed lead ions increased, the concentration of zinc ions in the solution increased. (Fig. S8†)

Table 1 Langmuir equation parameters of the adsorption of Pb²⁺ on flower-like and urchin-like zinc silicate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Qm° (mg g⁻¹)</th>
<th>b</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flower-like</td>
<td>210</td>
<td>0.0855</td>
<td>0.95036</td>
</tr>
<tr>
<td>Urchin-like</td>
<td>81.7</td>
<td>0.40541</td>
<td>0.97578</td>
</tr>
</tbody>
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*Qm: the maximum adsorption capacity of Pb²⁺.*

**Fig. 4** Schematic illustration of the preparation of the zinc silicate nanomaterials.
The molar number of zinc ions in the solution was nearly the same as the molar number of adsorbed lead ions. Thus, we believe that the lead ions were mainly adsorbed by zinc silicate through ion exchange; one lead ion exchanged with a zinc ion during the adsorption process. From such an ion exchange mechanism, zinc ions would be in the treated water. However, the safe concentration for lead and zinc ions in drinking water is 0.01 ppm and 1.0 ppm, respectively. Thus, if the lead ion concentration in water is lower than 3 ppm, which is very high for lead ion polluted drinking water, the zinc ion concentration will be below the limit. In this regard, the zinc silicate is a safe adsorbent for lead ions in water.

However, if the adsorption capacity was evaluated based on the surface area, urchin-like zinc silicate adsorbed much higher adsorption capacity per unit of the surface area. Its 11 m$^2$ g$^{-1}$ surface area and 81.7 mg g$^{-1}$ adsorption capacity resulted in 7.43 mg m$^{-2}$ for lead ions; while for flower-like zinc silicate, such value was 0.89 mg m$^{-2}$. Such a difference indicates that the surface of the hemimorphite structure in the urchin-like material has a much higher affinity for lead ions than the flower-like structure and other zinc silicates in the literature. Thus, if the hemimorphite type material with higher surface area can be produced, it may be an even better lead ion adsorption material than the flower-like structure in this study. Research on such high surface area zinc silicate with hemimorphite crystallographic structure is underway.

For practical usage, the nanostructures were very small and difficult to be separated from water. We used centrifugation for this study, but it is not suitable for practical water treatment application in powder form. Such powders must be processed again to be used in water treatment, while maintaining the surface area of the nanostructures. One option we are working on is to produce millimetre sized pellets.

Conclusions

In summary, we produced two new hierarchical structured zinc silicate nanostructures by a low cost method. One characterized with an urchin-like structure and another with a flower-like structure. New structural information on these two materials was obtained by X-ray nanotomography, HRTEM, XRD and solid state $^{29}$Si NMR. These two materials had very different crystallographic structures according to the X-ray nanotomography and XRD. Flower-like zinc silicate (zincsilite, Zn$_3$Si$_4$O$_9$(OH)$_2\cdot$H$_2$O) had a novel clay-like lamellar structure with most of the silicon atoms being in the Q$_3$ position, while urchin-like zinc silicate (hemimorphite, Zn$_2$Si$_2$O$_7$(OH)$_2\cdot$H$_2$O) was highly crystalline with a hemimorphite structure. Synchrotron based three dimensional X-ray nanotomography imaging showed the urchin-like zinc silicate’s defects during the self-assembly process. The flower-like hierarchical zinc silicates had a large specific surface area (236 m$^2$ g$^{-1}$) and an excellent adsorption capability for lead ions up to 210 mg g$^{-1}$.

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Notes and references