Template-induced synthesis of hierarchical SiO$_2$@γ-AlOOH spheres and their application in Cr(VI) removal

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Abstract
Hierarchical structured SiO$_2$@γ-AlOOH spheres were fabricated in one step by using silica colloidal spheres as a template. Scanning electron microscopy and transmission electron microscopy investigation showed that the shell is composed of large amounts of nanoscale γ-AlOOH lamellas. The growth mechanism was proposed as silica template-induced heterogeneous deposition of γ-AlOOH lamellas. The adsorption properties of hierarchical SiO$_2$@γ-AlOOH spheres annealed at different temperatures were investigated through the removal test of Cr(VI) ions in model wastewater, and the nanostructures annealed at 400 °C showed good adsorption capability of Cr(VI) ions.

S Supplementary data are available from stacks.iop.org/Nano/20/155604

1. Introduction

Recently, hierarchical nanoarchitectures with extremely high surface-to-volume ratios assembled from nanoscale units have stimulated tremendous interest. Preliminary encouraging applications of the hierarchical nanoarchitectures have been demonstrated in new catalysts [1], gas sensors [2] or absorbents [3]. Self-assembly has been proved an important approach for the fabrication of complex architectures, and many hierarchical nanoarchitectures have been successfully synthesized, such as dandelion-like CuO [4] and ZnO [5], feather-like BaWO$_4$ [6], 3D dendritic CuO [7], flower-like iron oxide [3] and γ-AlOOH [8], hierarchical MnO$_2$ [9] and ZnO [10] nanostructures. Lately, the colloidal spheres have been widely used as templates for the synthesis of hierarchical structures. Generally, the surface of colloidal spheres needed to be modified [2]. Developing facile synthetic approaches for building novel hierarchical architectures is still a challenge.

Boehmite (γ-AlOOH) is the precursor of γ-Al$_2$O$_3$, which is widely used as one of the most important industrial catalyst supports. Recently, considerable efforts have been directed towards the γ-AlOOH nanostructures due to their novel uses, such as gas sensors [11] and anion-specific adsorbents [12–14]. Different synthesis strategies have been developed for the fabrication of γ-AlOOH nanostructures with various morphologies, including hollow nanospheres [15], nanococoons [11], nanofibers, nanowires, nanotubes [16–20] and mesoporous structures [21, 22]. Nevertheless, there are few reports on the preparation of hierarchical γ-AlOOH nanostructures, which are expected to exhibit novel properties.

In this paper, we report that silica colloidal spheres can be used to fabricate hierarchical structured SiO$_2$@γ-AlOOH spheres in one step. In the experiment, the dissolution property of silica colloidal spheres in alkaline solution [23] was employed to promote the hydrolysis of precursor sodium aluminate [24] and then induce the formation of lamellar γ-AlOOH and preferential deposition around the silica colloidal spheres. In addition, the capability of the as-prepared hierarchical SiO$_2$@γ-AlOOH spheres annealed at different temperatures to adsorb Cr(VI) ions was investigated in model wastewater.

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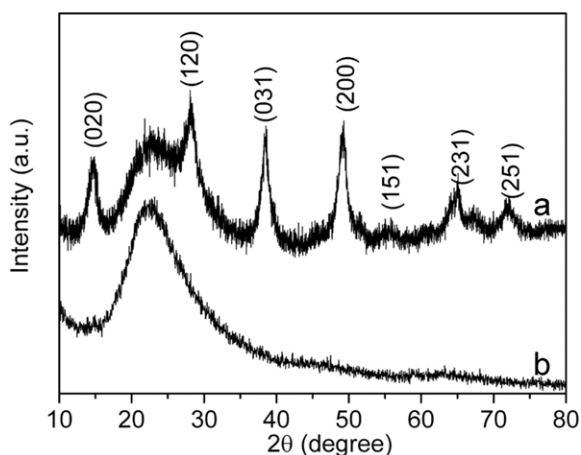
Figure 1. XRD patterns of (a) as-prepared hierarchical $SiO_2@\gamma$-AlOOH spheres and (b) silica colloidal spheres.

Figure 2. SEM images of (a) hierarchical $SiO_2@\gamma$-AlOOH spheres and (b) single $SiO_2@\gamma$-AlOOH spheres; TEM images of (c) hierarchical $SiO_2@\gamma$-AlOOH spheres and (d) partial hierarchical $SiO_2@\gamma$-AlOOH spheres.

2. Experimental details

2.1. Material synthesis

The reagents for this study were used without further purification. Monodisperse silica colloidal spheres were prepared according to the process developed by Stöber *et al* [25]. The synthesis process of hierarchical $SiO_2@\gamma$-AlOOH spheres is described briefly as follows. Silica colloidal spheres (0.13 g) were dispersed in 20 ml deionized water homogeneously. Sodium aluminate (0.17 g, Sinopharm Chemical Reagent Co. Ltd, CP) and urea (0.48 g, Shantou Xilong Chemical Factory, GuangDong, AR) were dissolved in 30 ml deionized water under stirring. The above solutions were mixed homogeneously and transferred into a Teflon autoclave (70 ml) and heated to a temperature of 160 °C for 12 h. After cooling to room temperature, the white precipitate was collected by centrifugation and washed with deionized water, and then the product was dried in a vacuum oven at 60 °C for 12 h. The dried products were annealed at different temperatures (200–700 °C) for investigation of the adsorption ability. In order to understand the growth process of hierarchical $SiO_2@\gamma$-AlOOH spheres, a time-dependent synthesis was also conducted.

2.2. Characterization

The products were analyzed by x-ray diffraction (XRD), in a 2θ range from 10° to 80°, using Cu Kα radiation (Philips X'pert diffractometer). The surface area of the samples was determined by nitrogen adsorption (Micrometrics ASAP 2020) using the five-point Brunauer–Emmet–Teller (BET) isotherm. The morphology of the prepared $SiO_2@\gamma$-AlOOH was studied by field emission scanning electron microscopy (FESEM, Sirion 200 FEG) and field emission transmission electron microscopy (FETEM, JEOL-2010, 200 kV) with an energy-dispersive x-ray spectrometer (EDS, Oxford, Link ISIS). The powders were dispersed in ethanol using ultrasonic vibration. The samples for microscopy studies were prepared by deposition of dispersions of the powder in ethanol directly on the SEM stubs or holey carbon grid for TEM examination.
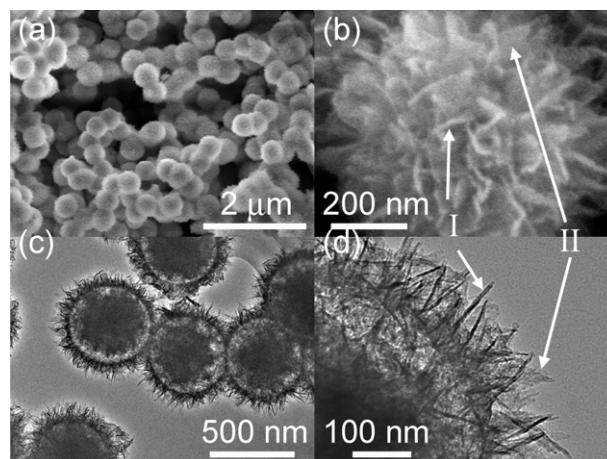
2.3. Cr(VI) removal experiments

$K_2Cr_2O_7$ was used as the source of Cr(VI). The different concentrations of Cr(VI) ions were prepared and the pH value of 3 was adjusted by HCl or NaOH [3]. For each sample, 40 mg adsorbent was added to the above solution. The mixture was stirred for 0.5 h and then kept for 5 h to establish adsorption equilibrium at room temperature. The adsorbent was then separated from the mixture by centrifugation. To determine Cr(VI) ion removal by the adsorbent, the Cr(VI) concentration in the remaining solution was measured by an inductively coupled plasma atomic emission spectrophotometer (ICP-AES Atomscan Advantage). The adsorbents here were the hierarchical $SiO_2@\gamma$-AlOOH spheres annealed at different temperatures (200–700 °C). The adsorption isotherm was obtained by varying the initial Cr(VI) concentration.

3. Results and discussion

The phase of the as-prepared product was examined by XRD, as shown in figure 1(a). The typical peaks can be identified clearly as orthorhombic γ-AlOOH (JCPDS card 21-1307). The broad diffraction peaks around 23° in figures 1(a) and (b) (silica colloidal spheres for comparison) are ascribed to amorphous silica [26]. Figure 2(a) is a typical SEM image of hierarchical $SiO_2@\gamma$-AlOOH spheres, in which the mass production of uniform-sized sphere-like structures can be observed. The surface morphology of a single sphere can be clearly observed in the SEM image with a high magnification, as shown in figure 2(b). The whole surface of the sphere-like structure with a diameter of 700 nm is rough, which is composed of large amount of thin lamellas. The TEM image (figure 2(c)) demonstrates that the as-prepared particles have a core–shell structure and the thickness of the shell is about 100 nm. The shell seems to be composed of many nanowires at first glance, as shown in figure 2(d): however, careful observation found that it was the edge of thin lamellas parallel to the electron beam (see arrow I in figures 2(b) and (d)), and
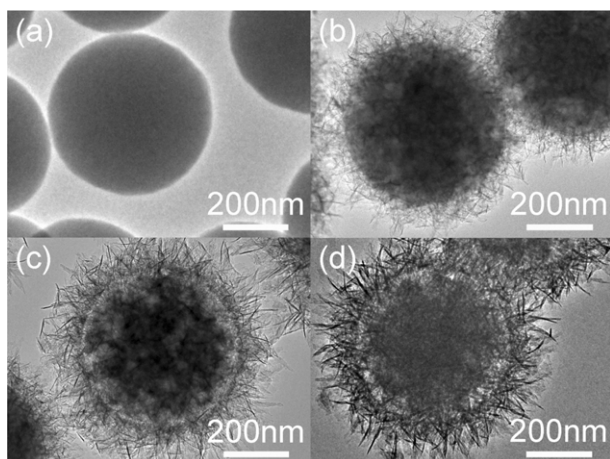
Figure 3. TEM images of products obtained at 160 °C for different reaction times: (a) 0 h, (b) 1 h, (c) 5 h and (d) 12 h.

many lamellar structures with an average thickness of about 5 nm can be observed (see arrow II in figures 2(b) and (d)).

In order to investigate the formation process of the hierarchical structure, experiments with different reaction duration were conducted and the corresponding products were examined using TEM, as shown in figure 3. The silica colloidal spheres in the present experiment are of 500 nm in diameter with a smooth surface, as shown in figure 3(a). After 1 h reaction, as shown in figure 3(b), a hazy layer with a thickness of 30 nm was found on the surface of the silica colloidal sphere; thin lamellas bestrewed around the silica colloidal sphere. When the reaction time was prolonged to 5 h, two obvious changes can be observed in figure 3(c): lamellas of the shell become thicker and denser; meanwhile, a blank boundary was observed between the core and shell. When the reaction was further increased to 12 h (figure 3(d)), the product still exhibited the core–shell structures that were similar to the samples in figure 3(c), but lamellas become much thicker (about 5 nm) and the core–shell becomes clear.

At high temperature, aluminate anions undergo the following chemical reactions:

$$AlO_2^- + 2H_2O \rightleftharpoons Al(OH)_3 + OH^- \qquad (1)$$

$$Al(OH)_3 \rightarrow \gamma\text{-AlOOH} + H_2O. \qquad (2)$$

When the solution was heated at 160 °C, $Al(OH)_3$ colloids would be formed on the basis of the hydrolysis reaction through equation (1); the newly formed $Al(OH)_3$ colloid was active and unstable, which would further dehydrate and convert into γ-AlOOH over 150 °C through equation (2) [11]. The growth process of the γ-AlOOH shell was therefore proposed as follows. As known, the silicon–oxygen bond of silica can be broken by hydroxide ions, thus alkaline solutions like sodium hydroxide are often used to dissolve the silica core in the template synthesis of hollow structures [23, 27]. In the present experiment, the surface silicon–oxygen bonds of silica colloidal spheres would be broken by hydroxide ions, inducing the preferential hydrolysis of aluminate anions around the silica colloidal template. The generated $Al(OH)_3$ colloids were

unstable and would be converted gradually into γ-AlOOH according to equation (2) at 160 °C, which then deposited onto the silica colloidal template. In the following process, hydroxide ions were consumed by silica colloidal spheres, which then promoted the formation of γ-AlOOH. Finally, the gradual deposition of γ-AlOOH made the shell grow thicker. The above reaction went on until all the aluminate anions were used up. Although the silica colloidal spheres were used without prior surface modification in our experiment, no separate irregular particles in the final product were found (shown in figure 2(a)), indicating that almost all generated γ-AlOOH was deposited onto the silica colloidal spheres. The deformation of the silica colloidal sphere in figures 3(c) and (d) indicated that the silica template was indeed partially dissolved by hydroxide ions. In other words, the silica colloidal spheres not only were employed as a template, they also led the hydrolysis of aluminate anions. The generated γ-AlOOH were located around the silica template and preferentially deposited onto the surface of silica colloids. Thus the growth mechanism of the hierarchical SiO$_2$@γ-AlOOH core–shell structure could be proposed as the template-induced deposition.

The shell consists of lamellar γ-AlOOH in the final product in figure 2, which still can be found in high magnification TEM images of intermediate products of 1 and 5 h in figures S3a and S3b (available at stacks.iop.org/Nano/20/155604), while these generated γ-AlOOH lamellas did not scroll into nanowires or nanotubes like other layer materials under elevated temperature and pressure [28–30]. It is known that γ-AlOOH is a layered structure with octahedra range within the lamellae, and hydroxyl ions hold the lamellae together through hydrogen bonding [16]. Under acidic conditions, the solution contains protons which would combine with the hydroxyl oxygen lone pairs to give aqua ligands and destroy the γ-AlOOH layers [31]. Then separated layers subsequently curl into 1D nanostructures via the scrolling-growth route. In reverse, the 2D lamellar nanostructure would be retained in basic solution [32]. In the present experiment, the reaction solutions are weakly basic with a pH of above 8. Thus only lamellar γ-AlOOH was generated, which interweaved with each other and presented the hierarchical surface structure.

The effect of urea was investigated by changing the amount of urea in the reaction system. Urea played an important role in the deposition process, since it could release hydroxide ions through hydrolysis in the solution. When no urea was added, the final product was composed of uniform silica colloidal spherical particles with smooth surfaces and irregular aggregation particles of γ-AlOOH as shown in figure S1a (available at stacks.iop.org/Nano/20/155604). A hierarchical structure was not observed. It indicated that the γ-AlOOH nucleated homogeneously in the solution. When the amount of urea used was up to 0.24 g, the product was composed of the hierarchical structured spherical particles and some irregular aggregation particles, as shown in figure S1b (available at stacks.iop.org/Nano/20/155604). When the amount of urea added was more than or equal to 0.48 g, only uniform hierarchical structured spherical particles were observed, as shown in figure 2(a). These results indicate that
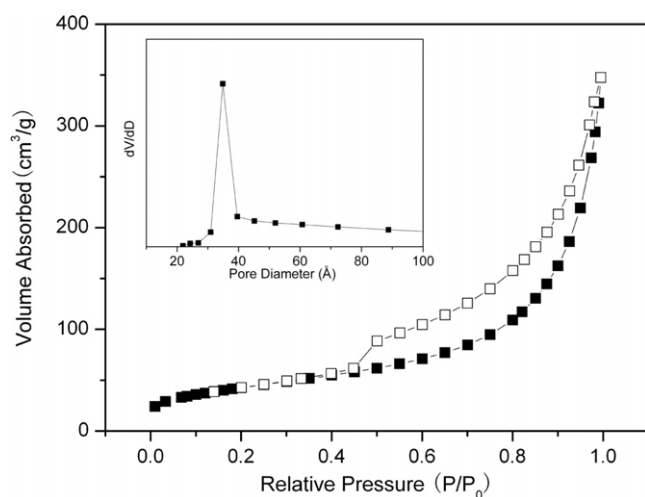
Figure 4. Nitrogen absorption and desorption isotherms and pore size distribution (inset) for hierarchical $SiO_2@\gamma$-AlOOH spheres.

Figure 5. Amount of Cr(VI) ions adsorbed onto the hierarchical $SiO_2@\gamma$-AlOOH spheres annealed at different temperatures (200–700 °C).

hydroxide ions released from the hydrolysis of urea restrained the generation of γ-AlOOH in the solution, and only promised the preferential hydrolysis of aluminate anions around the silica cores to form hierarchical structure. From a serial experiment, 0.48 g urea is enough for the complete deposition of γ-AlOOH. When the silica colloidal spheres were not added and the other condition was unchanged, only irregular particles were obtained, as shown in figure S2 (available at stacks.iop.org/Nano/20/155604). However, the uniform hierarchical structured spherical particles (figure 2(a)) were obtained using the silica colloidal spheres. These results indicated the silica colloidal spheres here played the role as template, which not only induced the preferential generation and deposition of the generated γ-AlOOH on the silica colloidal template, but also avoided agglomeration and growth of γ-AlOOH particles in the solution.

The hierarchical $SiO_2@\gamma$-AlOOH spheres were further characterized by a BET surface area analyzer. The nitrogen adsorption and desorption isotherm and corresponding BET pore size distribution are shown in figure 4. The isotherm is identified as type IV, which is characteristic of mesoporous materials. BET calculation for the pore size distribution, derived from desorption data, reveals a narrow distribution for the hierarchical $SiO_2@\gamma$-AlOOH spheres centered at 3–4 nm (figure 4, inset). The BET specific surface area of the as-prepared $SiO_2@\gamma$-AlOOH spheres calculated from the nitrogen isotherm is about 152 m^2 g^{-1}, larger than 90 m^2 g^{-1} of γ-AlOOH particles shown in figure S2 (available at stacks.iop.org/Nano/20/155604) and also larger than that of the flower-like γ-AlOOH, being composed of nanowires reported previously [8]. The extremely large specific area of the as-obtained hierarchical $SiO_2@\gamma$-AlOOH spheres in the present study could be attributed to the hierarchical surface structure. The $SiO_2@\gamma$-AlOOH spheres annealed at 400 °C were also characterized with a BET surface area as high as 139.5 m^2 g^{-1}, which implied they still kept a high specific surface area even after annealing.

Recently, considerable attention has been paid to the environmental problems involving water treatment. Cr(VI)
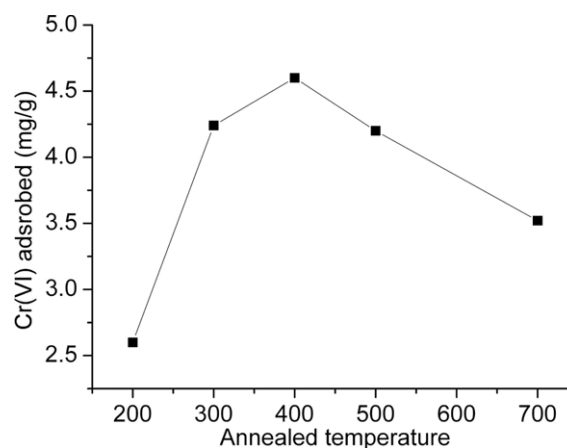
ions are considered as primary highly toxic pollutants in water and their efficient removal from water is of great importance. Nanostructured material based technologies are promising for environmental remediation. Hierarchical nanostructured materials can avoid aggregation and maintain the high specific surface areas which are important in enhancing the accessibility of adsorbates to reactive sites [3]. The annealed γ-AlOOH was often used as adsorbents to remove phosphorus and arsenic ions due to its layered structure and ion exchange ability [13]. Here the as-prepared $SiO_2@\gamma$-AlOOH spheres with hierarchical structure annealed at different temperature were tried to be used as adsorbents to remove Cr(VI) ions from model wastewater, and the silica core here is unnecessary to remove and could accelerate the separation of particles after adsorption [33].

The adsorption capabilities of hierarchical $SiO_2@\gamma$-AlOOH spheres annealed at different temperatures were investigated. The phase γ-AlOOH changed under different annealing temperatures from 200 to 700 °C; the corresponding XRD patterns were shown in figure S4 (available at stacks.iop.org/Nano/20/155604), which is similar to the previous report [13]. The surface morphology of the annealed hierarchical $SiO_2@\gamma$-AlOOH spheres was also studied and it was found that the products annealed even at 700 °C still kept the hierarchical structure shown in figure S5 (available at stacks.iop.org/Nano/20/155604), indicating that annealing temperature had little effect on the morphology change. The adsorption abilities of the annealed hierarchical $SiO_2@\gamma$-AlOOH spheres were investigated in the same condition (40 mg adsorbent dispersed in 20 ml 80 mg l^{-1} Cr(VI) ions solution at a pH of 3). The effect of silica core on the adsorption experiment shows that silica colloidal spheres almost have no adsorption ability on Cr(VI) ions. Figure 5 shows the corresponding adsorption capabilities of hierarchical $SiO_2@\gamma$-AlOOH spheres annealed at different temperatures, and the hierarchical spheres annealed at 400 °C had the highest adsorption ability, the reason for which will be further investigated in our study.

The relationship between the adsorption capability of as-obtained $SiO_2@\gamma$-AlOOH spheres annealed at 400 °C and
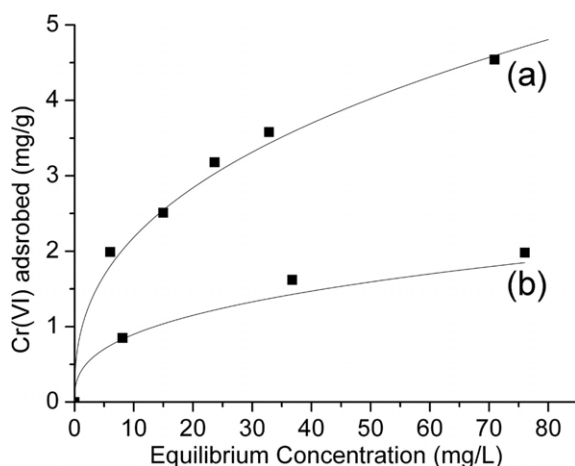
Figure 6. The Cr(VI) ion adsorption isotherm curves of
(a) hierarchical $SiO_2@\gamma$-AlOOH spheres and (b) γ-AlOOH particles
annealed at 400 °C for 4 h.

the equilibrium concentration of Cr(VI) ions in solution was
studied and illustrated by an adsorption isotherm in figure 6(a),
which fitted the Freundlich equation very well [12]. For
comparison, the adsorption capability of γ-AlOOH particles
annealed at 400 °C prepared without using a silica template
was tested (figure 6(b)). From the adsorption curves, the as-
prepared hierarchical $SiO_2@\gamma$-AlOOH spheres exhibit much
higher adsorption capability than that of γ-AlOOH particles,
indicating the superiority of the hierarchical structure of the
as-prepared product. The adsorption mechanism of Cr(VI)
ions can be explained as follows: when the annealed $SiO_2@\gamma$-
AlOOH spheres were suspended in water, a water molecule
was adsorbed and hydroxyl groups were generated on the
surface of the annealed $SiO_2@\gamma$-AlOOH spheres by the
dissociation of water [12, 13]. Also the Cr(VI) ions mainly
existed in the form of $HCrO_4^-$ in acidic conditions [34]. Then
the hydroxyl groups on the surface of the annealed $SiO_2@\gamma$-
AlOOH spheres would ion-exchange with $HCrO_4^-$, which led
to the removal of Cr(VI) ions in the model wastewater. In the
adsorption experiment, the pH of the solution was observed
to increase from 3 to 5.4, thus implying an ion exchange
mechanism [13]. If the sample has more hydroxyl groups, it
will show a higher adsorption capability to remove Cr(VI) ions.
It has been reported that γ-AlOOH annealed at 400 °C had
the highest value of hydroxyl groups in water [12, 13], thus
the $SiO_2@\gamma$-AlOOH spheres annealed at 400 °C presented
the highest adsorption capability as compared with the other
samples annealed at different temperatures (figure 5).

4. Conclusions

In summary, hierarchical $SiO_2@\gamma$-AlOOH spheres were
synthesized by using silica colloidal spheres in one step.
The growth mechanism was proposed as template-induced
heterogeneous deposition, in which the dissolution properties
of silica colloidal spheres in alkaline conditions played the
main role. The hierarchical nanostructures annealed at
different temperatures were investigated, and the product

annealed at 400 °C with high specific area showed the best
adsorption capacity of Cr(VI) ions in model wastewater.
Furthermore, the hierarchical structure was expected to have
other potential applications such as gas sensing or as a catalyst.

Acknowledgments

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