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The mechanical properties of pure synthetic hydroxyapatite and hydroxyapatite-carbon nanotube composites were examined. Vickers microhardness and nanoindentation using a Berkovich tipped indenter were used to determine the hardness, fracture toughness and Young’s modulus of the pure hydroxyapatite matrix and the composite materials.

Preparation of Akaganeite Nanorods and Their Transformation to Sphere Shape Hematite

Akaganeite (β-FeOOH) nanorods were synthesized through hydrolysis of FeCl₃ and FeCl₂ solutions containing urea in the temperature range from 90 to 95 °C under reflux condition for 8 h. The average diameters and lengths of nanorods were impacted by FeCl₃ and urea. Upon heating the solution containing FeCl₃, FeCl₂ and urea, the average diameters were about 80 nm and lengths of nanorods were about 1.2 μm. The morphologies of β-FeOOH nanorods in different growth times were shown by TEM images. β-FeOOH nanorods were calcined and the influence of the calcining temperature and time about the morphology and size of the powder was studied. By heating β-FeOOH nanorods at 800 °C for 6 hours, the hematite in sphere shape was obtained and the forming mechanism was discussed.

Highly Luminescent Inverted ZnS/CdS Core/Shell Quantum Dots

Synthesis of highly luminescent and monochromatic inverted core–shell structures utilizing ZnS/CdS quantum dots (QDs) has been investigated. The core/shell quantum dots have been characterized using grazing angle X-ray diffraction (XRD), Transmission electron microscopy, Optical absorption and luminescence spectroscopy. The results suggested that passivation of surface states along with an increased localization of electrons and holes in CdS shell layer, give rise to increased monochromaticity with higher quantum yield. The possibility of using the inverted core–shell structure as an additional parameter for tuning the color of luminescence has also been discussed.
Preparation of Akaganeite Nanorods and Their Transformation to Sphere Shape Hematite

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Akaganeite (β-FeOOH) nanorods were synthesized through hydrolysis of FeCl₃ and FeCl₂ solutions containing urea in the temperature range from 80 to 95 °C under reflux condition for 8 h. The average diameters and lengths of nanorods were impacted by FeCl₃ and urea. Upon heating the solution containing FeCl₃, FeCl₂ and urea, the average diameters were about 80 nm and lengths of nanorods were about 1.2 μm. The morphologies of β-FeOOH nanorods in different growth times were shown by TEM images. More interestingly, in the growth process of nanorods, they can self-assemble and form cross structure. The ultrasonic might promote effectively the formation of the nano-cross structure. β-FeOOH nanorods were calcined and the influence of the calcining temperature and time about the morphology and size of the powder was studied. By heating β-FeOOH nanorods at 800 °C for 6 hours, the hematite in sphere shape was obtained and the forming mechanism was discussed.

Keywords: Akaganeite, Nanorods, Synthesis, Characterization.

1. INTRODUCTION

Iron oxyhydroxides and oxides can be used as model systems for the study of fundamental colloid and surface properties of metal oxides. These compounds are also of technological importance as catalytic materials, sorbents, pigments, flocculents, coatings, gas sensors, ion exchangers and magnetic carriers for drug targeting. They are also widely used as electrode materials and precursors to phases for information storage media and for lithium batteries.

Akaganeite (β-FeOOH), a natural oxyhydroxide mineral, has a hollandite-like (BaMnO₃) type crystal structure containing tunnel-shaped cavities, running parallel to the c-axis, the sites being bound by double rows of fused octahedral. A certain number of extraframework halide anions are necessary in the structure to balance the extra protonation of oxides in the iron octahedra since akaganeite is synthesized in acidic solutions. This tunnel structure makes β-FeOOH an especially interesting material in the areas of catalysis and ion exchange. Pradel et al. have reported high catalytic activity of akaganeite for the hydrotreatment of coal. The anion exchange of Cl-akaganeite with F⁻, Br⁻, and OH⁻ and some properties of different anion-exchanged akaganeites has been reported. Anion exchange significantly changes the loss of chloride and affects the decomposition of akaganeite upon being heated. Guo and Chen have reported that a new adsorbent, bead cellulose loaded with iron oxyhydroxide (BCF), was prepared and applied for the adsorption and removal of arsenate and arsenite from aqueous systems. Akaganeite, the reactive center of BCF that was stably loaded into the cellulose, had a high sensitivity to arsenite as well as arsenate. Akaganeite was synthesized and used as absorbent to adsorb phosphate ions from phosphate-enriched seawater. Quan and Fu have reported the absorption of fulvic acid on the surface of akaganeite. For these reasons, many scientists investigated the methods for the synthesis of akaganeite.

Akaganeite can be formed from aqueous iron(III) solution under a wide range of hydrolysis conditions, from dilute or concentrated solutions, at room temperature or at elevated temperatures and at pH between 1.2 and 1.9. It has been reported that by adding ammonia to a Fe(NO₃)₃·9H₂O solution, at pH 7.5, a gel was produced. The powder obtained by dehydrating the gel consisted of small particles (2-3 nm in size) with high surface area (about 270 m²·g⁻¹). This product, however, was not identified.

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2.3. Preparation of Akaganeite Nanorods

The aqueous solution of 1.1250 g FeCl₃·6H₂O dissolved in 20 mL water was heated to 90–95 °C to make Fe⁺⁶ hydrolyze for 8 h. Then the yellow product, labeled as p1, was separated from the mother liquor with an ultra-speed centrifuge (operational range up to 8000 rev·min⁻¹) and rinsed with distilled water repeatedly in order to eliminate the remaining chloride ions on the surfaces, and finally dried in a vacuum oven at temperature of 45 °C.

To investigate the effects of urea and FeCl₃ upon the morphology of akaganeite nanorods, in above reaction system, urea, FeCl₃·4H₂O, or both of them were added, respectively. Then the products labeled as p2, p3, and p4, respectively, were obtained in same method. In a separated experiment, the effects of ultrasonic on the morphology of akaganeite nanorods were checked. Here, the mixture of FeCl₃·6H₂O, FeCl₃·4H₂O and urea was heated to 90–95 °C, too. Meanwhile, the mixture was also stirred with ultrasonic for 2 h at the beginning. Then the solution was kept static for another 6 h. It will be found that the morphology of akaganeite nanorods, labeled p5, was affected by the ultrasonic, which will be discussed later.

At last, 500 mg of p3 powder samples were heat-treated in a china crucible for 6 h at 200 °C, 400 °C, 600 °C and 800 °C, in air, and the products of p6, p7, p8 and p9 were obtained, respectively.

3. RESULTS AND DISCUSSION

Figure 1 showed the XRD patterns of the four products. In Figure 1, p1 was the sample prepared without FeCl₃·4H₂O and urea. All the peaks were clearly distinguished.

![XRD patterns of the four products](image)
Fe$^{2+}$ ions for the formation of nanorods and made them longer. If the addition was urea instead of FeCl$_2$, short rods were obtained as shown in Figure 2(c). The length of nanorods did not change and was still ~550 nm, but the diameters of the two ends were increased to 70 nm, which were close to the diameters of middle parts. Urea was decomposed continuously at 90–95 °C in water and the products of decomposition were CO$_2$ and NH$_3$. In the acid condition, CO$_2$ was quickly released from the reaction system. However, NH$_3$ can react with H$^+$, which was the product of the hydrolyzation of Fe$^{2+}$ ions. NH$_3$ may neutralize part of H$^+$ effectively, which facilitated the hydrolyzation of Fe$^{3+}$ ions advantageously. When both FeCl$_3$ and urea were added into the reaction systems, the longer nano-sized akaganeite rods were obtained as shown in Figure 2(d). The length of nanorods grew to 1.2 μm and the diameters of the production p4 were larger than the previous products (p1–p3). This might be the result of the coordinated effect of FeCl$_3$ and urea to the formation of akaganeites. The former provided the Fe$^{3+}$ ions to nanorods sequential growth and the later adjusted pH of the solution and promoted the hydrolyzation of Fe$^{3+}$ ions.

From the above TEM images and explanation, the forming mechanism of β-FeOOH nanorods can be inferred as Eqs. (1)–(5) as follows.

1. Fe$^{3+}$ + 3H$_2$O $\rightarrow$ Fe(OH)$_3$ + 3H$^+$
2. Fe(OH)$_3$ $\rightarrow$ β-FeOOH + H$_2$O
3. 4Fe$^{2+}$ + O$_2$ + 4H$^+$ $\rightarrow$ 4Fe$^{3+}$ + 2H$_2$O
4. (NH$_3$)$_2$CO + H$_2$O $\rightarrow$ 2NH$_3$ + CO$_2$
5. NH$_3$ + H$^+$ $\rightarrow$ NH$_4^+$

The morphology and size of akaganeite nanorods were characterized by transmission electron microscopy (TEM). The images of akaganeite nanorods labeled as p1, p2, p3, and p4 prepared in different reaction systems were shown in Figure 2. As described previously, p1 was the akaganeite nanorods prepared with FeCl$_2$ as the only reactant. As shown in Figure 2(a), p1 looked like spindle. The average length of the rods was about 400 nm and the average diameter of the rods was about 50 nm. The two ends of the rods were slender than the middle. The result was similar to the literature. However, as shown in Figure 2(b), with the addition of FeCl$_3$, the nanorods grew longer and the length reached to ~550 nm, but the shape of akaganeite nanorods still kept spindly. Because of no use of deoxygenated water and no nitrogen protection during the reflux, a little oxygen dissolved into the solution containing Fe$^{2+}$ and Fe$^{3+}$ ions and Fe$^{2+}$ ions was easily oxidized into Fe$^{3+}$ ions in the acid condition. Therefore, Fe$^{2+}$ ions were slowly oxidized into Fe$^{3+}$ ions in the process of growth of the nanorods, which provided the subsequent...
TEM images of β-FeOOH nanorods which were obtained in different growth times were shown in Figure 3. In Figure 3(a), the length of the nanorods was about 100 nm and the diameter was about 35 nm. It can be seen that the most of the nanorods grew side by side, which looked like wooden raft arranged tightly. The two ends of the nanorods presented sawtooth, which showed that the length of nanorods may still extend. After 2 h, the length and the diameter were increased to about 200 nm and about 50 nm, respectively. When the reaction time reached 6 h, the length was extended to 650 nm and the diameter was increased to 60 nm (Fig. 3(c)). The two ends of the nanorods were still coarse, which reflected that the nanorods still possessed of growth room in the one dimension orientation. With the reaction time prolonged, the length and the diameter would increase continuously. After 6 h, the length and the diameter were increased to about 2.2 μm and 80 nm, respectively, which showed no change with the time any more. The two ends of the nanorods turned into smooth and each other of the nanorods didn’t arrange so compactly again (Fig. 3(d)). A serial of lattice in the TEM patterns of the electron diffraction of the β-FeOOH nanorods, shown in illustration of Figure 3(d), indicate that the β-FeOOH nanorods are a kind of single crystal.

There is an interesting phenomenon shown in TEM image (Fig. 4(a)) of the production p4. In the growth process of nanorods, they can self-assemble and form cross structure. Much more interesting, before the encounter of rod A and B the diameter of rod A was 86 nm, the diameter of rod A became smaller and decreased to 60 nm after their encounter, which was the reason that rod B blocked the growth of two edges of rod A when rod A passed through rod B. At the same time, the diameter of rod B showed no change before and after encounter. With the TEM images of the precursors which have many serrations on both ends (Fig. 4(b)), it is possible that during the growth of nanorods the serrations in the precursors intersected and wove together and formed the crosses.

The whole process was similar to weaving. Although this case is a stochastic phenomenon, the nano-cross configuration may be constructed through increasing the collision probability among nanorods. The more frequently the collisions occurred, the more the crosses can be seen at the beginning of the growth. In order to confirm the supposition, the solution containing Fe$^{3+}$, Fe$^{2+}$ ions and urea was treated in an ultrasonic condition for 2 h at the beginning. The ultrasonic may increase the chance of the collision of nanorods and form the much more cross structure in the nanorods. Then the solution was kept static growth for 24 hours. Luckily more cross configuration can be seen in the pane in Figures 5(a) and (b). Even, three rods intersected together and formed star structure. However, it is clear that the length of nanorods had no change with the time prolonging. The ultrasonic may accelerate Fe$^{3+}$ ions oxidized into Fe$^{2+}$ ions, produce much more crystal nuclei and weaken the function of Fe$^{2+}$ ions in the growth process of nanorods. To sum up, the self-assembly cross configuration was a properly significant revelation. We can use one dimension nano-material as basic construction materials through analogous weaving method to self-assemble and form nano-web or nano-cloth, even more complicated nano-structure.

As we know, being similar to the goethite, akaganeite will decompose and form Fe$_2$O$_3$ when it is subject to high temperature. Figure 6 showed the TGA (left axis)/DTA (right axis) data obtained for β-FeOOH powder heated in nitrogen. Prior to this measurement, β-FeOOH powder was heated at 24 °C for 24 h in a vacuum oven. Some features can be found in the figure. An endothermic process accompanying a 17% weight loss was observed at ca. 280 °C. This process was attributed to the dehydration of akaganeites. The experimental value of weight loss was greater than the theoretical value, which was due to a little water molecules removed difficulty by...
the physical drying, remaining in the tunnel-shaped cavities of the nanorods. After 300 °C, there was no change for the weight of β-FeOOH powder, which indicated that β-FeOOH powder was dehydrated completely. However, an exothermic process without weight loss occurred at around 500 °C. This process reflected that the crystal structure of powder changed with the temperature increasing. At 800 °C, another endothermic process without weight loss can be seen in curve (b), which indicated that the crystal structure of powder had changed again.

In order to study the change of the residual structure with the temperature increasing, the β-FeOOH powder (the productions of p3) was calcined at 200 °C, 400 °C, 600 °C and 800 °C for 6 hours, respectively, and the productions were marked p6, p7, p8 and p9. Figure 7 showed the XRD pattern of the production, p9, which came from the productions of p3 calcined at 800 °C for 6 h. In Figure 7, all the peaks were clearly distinguished and matched up to crystal planes of pure hematite (JCD 01-089-8104). The color of the powder turned into red. The XRD pattern of p9 showed that the red powder was pure Fe₂O₃ without β-FeOOH.

The morphology and size of the powder calcined at 200 °C, 400 °C, 600 °C and 800 °C for 6 hours, respectively, were checked using TEM. When the powder was calcined at 200 °C for 6 hours, some nanopores, the diameters were smaller than 5 nm, were observed in the TEM image (Fig. 8(a)). As the calcining temperature was reached at 400 °C, some hollows and disfigurements can be seen obviously in the TEM image (Fig. 8(b)). The anomalous shape of nanorods might be the result of the dehydration of the akaganite. During the dehydration process, water molecular was released from the framework of β-FeOOH nanorods and left a lot of hollows on the surface of nanorods, which led to the framework of β-FeOOH nanorods looseness and collapse. After calcined at 600 °C for 6 hours, small fragments were congregated and fused to form larger network aggregation. After 6 h at

![Fig. 7. XRD pattern of the production p9 (the productions of p3 calcined at 800 °C for 6 h).](image-url)
hematite. The whole procedure of transformation was divided into two steps as illustrated in Figure 10. The first step was the dehydration of \(\beta\)-FeOOH crystals. At 200 °C some smaller nanopores developed inside the acicular \(\beta\)-FeOOH crystals (Fig. 10(b)). With the temperature increasing, more pores appeared throughout the nanorods. After 6 h at 400 °C (Fig. 10(c)), the pores coalesced together and their size was increased. All the \(\beta\)-FeOOH was transformed into hematite, yet the external shape of the crystals is still the acicular shape of the

Fig. 9. TEM images of the production p3 calcined at 800 °C for (a) 20 min, (b) 1 h, (c) 3 h, (d) 6 h.

Fig. 10. Schematic representation of synthetic \(\beta\)-FeOOH dehydration.
original $\beta$-FeOOH crystals. During the dehydration process, water molecular was released from the framework of nanorods and left a lot of hollows on the surface of nanorods, which led to the framework of nanorods incompaction and collapse. The second step was recrystallisation process. When the temperature was increased, nanorods were broken to pieces (Fig. 10(d)). Small fragments were congregated and fused to form larger particles at 600 °C (Fig. 10(e)), which led to the diameter of new crystals increase. After 6 h at 800 °C (Fig. 10(f)), recrystallisation is complete, and all the crystals are isotropic. The diameter was about 450 nm, which attributed to the amalgamation of small fragments. These observations enabled us to underline the main stages of the dehydration and recrystallisation. Therefore, sphere-shape $\text{Fe}_3\text{O}_4$ nanoparticles were prepared by heating $\beta$-FeOOH nanorods.

4. CONCLUSION

Akaganeite ($\beta$-FeOOH) nanorods were synthesized through hydrolysis of $\text{FeCl}_3$ and $\text{FeCl}_2$ solutions containing urea in the temperature range from 90 to 95 °C in reflux condition for 8 h. $\text{FeCl}_2$ and urea may change the shape and increase the length and diameter of $\beta$-FeOOH nanorods. This was the result of the coordinated effect of $\text{FeCl}_3$ and urea to the formation of akaganeites. The former provided the $\text{Fe}^{3+}$ ions to nanorods sequential growth and the later adjusted pH of the solution and promoted the hydrolyzations of $\text{Fe}^{3+}$ ions. In the growth process of nanorods, they can self-assemble and form cross structure. The ultrasonic might promote effectively the formation of nano-cross structure, even start structure. By thermal treatment $\beta$-FeOOH nanorods at 800 °C for 6 hours, the hematite nanoparticles in sphere shape were obtained. The diameter of hematite was about 450 nm, which was much larger than the diameter of $\beta$-FeOOH nanorods. During the forming process of hematite, the dehydration and recrystallisation were the main stages. The dehydration of $\beta$-FeOOH crystals led to the framework of nanorods incompaction and collapse and nanorods were broken to pieces. During recrystallisation process, small fragments were congregated and fused to form larger particles with the temperature increasing.

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References and Notes


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