

## 水热法制备核—壳结构勃姆石超细粉体

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**摘要:** 以硫酸铝水溶液和尿素为原料, 两亲嵌段共聚物聚苯乙烯-嵌段-聚丙烯酸-2-羟基乙酯(P(St)-*b*-P(HEA))为结构引导剂, 通过水热法合成了核壳状勃姆石超细粉体。使用 X-射线衍射技术(XRD), 透射电子显微镜(TEM)和扫描电子显微镜(SEM)对产物进行了表征。并在试验的基础上, 对可能的形成机理进行了讨论。

**关键词:** 水热合成; 核—壳; 勃姆石; 形貌; 形成机理

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## Hydrothermal Synthesis of Core-shell Structured Boehmite Ultra-fine Powders

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**Abstract:** A hydrothermal approach has been developed for the synthesis of core-shell structured boehmite ultra-fine powders by using inexpensive  $\text{Al}_2(\text{SO}_4)_3$  aqueous solution and urea as raw materials, amphiphilic copolymer of Poly(styrene)-block-Poly(2-hydroxyethyl acrylate)(P(St)-*b*-P(HEA)) as structure-directing agents. The hydrothermal product was characterized by techniques of X-ray diffraction(XRD), transmission electronic microscopy(TEM) and scanning electron microscope(SEM). The possible formation mechanism is discussed based on the experimental facts.

**Key words:** hydrothermal synthesis; core-shell; boehmite; morphology; formation mechanism

Core-shell ultra-fine powders are composite materials consisting of a core domain covered by a shell domain, the core and shell domains may be composed of a variety of materials including polymers, inorganic solids, and metals<sup>[1]</sup>. Such composite materials have exhibited improved physical and chemical properties over their single-component counterparts, thus providing a new way to tailor the properties of the ultra-fine powders. And core-shell ultra-fine powders have been the subject of extensive study due to their potential application in many areas<sup>[2]</sup>. Boehmite is the most commonly

used precursor for the preparation of high-purity and high-strength monolithic-alumina ceramics used in a variety of applications, such as substrates for electronic circuits, abrasive grains, high-temperature refractory materials, fibers and thin films. Boehmite is also a crucial precursor for preparation of  $\gamma\text{-Al}_2\text{O}_3$  used as a high-temperature catalyst support and as a membrane due to its high surface area and mesoporous properties<sup>[3]</sup>. Although various morphologies of boehmite, such as nanofibers<sup>[4-6]</sup>, nanowire<sup>[7]</sup>, coral-shape<sup>[8]</sup>, nanofibers and nanorods<sup>[9]</sup>, nanotubes and nanorods<sup>[10]</sup> and flowerlike

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boehmite<sup>[11]</sup> have been successfully prepared, and some other core-shell ultra-fine powders have also been successfully fabricated, such as polymer microspheres<sup>[1]</sup>, metal/semiconductor<sup>[2]</sup>, CdS and ZnS<sup>[12]</sup>, carbon<sup>[13]</sup>, it still remains a great challenge to fabricate core-shell structured boehmite ultra-fine powders. However, to the best of our knowledge, there has been no report on the synthesis of the core-shell structured boehmite ultra-fine powders by a hydrothermal approach.

Here we report a hydrothermal method for synthesizing core-shell structured boehmite ultra-fine powders by using inexpensive  $\text{Al}_2(\text{SO}_4)_3$  aqueous solution and urea as raw materials, and amphiphilic copolymer of Poly(styrene)-block-Poly(2-hydroxy-ethylacrylate) (P(St)-*b*-P(HEA))<sup>[14]</sup> as structure directing agents.

## 1 Experimental

In a typical hydrothermal synthesis process, 10 mL of  $0.1 \text{ mol} \cdot \text{L}^{-1}$   $\text{Al}_2(\text{SO}_4)_3$  aqueous solution and 2 mL of  $2.5 \text{ mmol} \cdot \text{L}^{-1}$  P(St)-*b*-P(HEA)/THF solution was added to a Teflon-lined stainless steel autoclave of 50 mL capacity, the molar ratio of  $\text{Al}^{3+}$  and P(St)-*b*-P(HEA) was 400:1. Then, 28 mL distilled water was added to fill the autoclave up to 80% of the total volume. After adding 0.164 g urea (accounted for 90% theoretical dosage), the autoclave was sealed and maintained at  $150^\circ\text{C}$  for different hours, without shaking or stirring, then cooled to room temperature naturally. The as-synthesized precursor was collected by centrifugation and washed with distilled water for several times until free from  $\text{SO}_4^{2-}$  ions, subsequently, absolute ethanol was used to wash the precursor for three times. The precursor was dried at room temperature in air.

The phase purity and phase structure of the final hydrothermal product (24 h reaction time) was characterized by X-ray powder diffraction (XRD) using Japan Rigaku D/max r-B X-ray diffractometer (40 kV, 60 mA) equipped with graphite monochromatized Cu  $K\alpha$  radiation ( $\lambda=0.15418 \text{ nm}$ ). The step size of  $0.02^\circ$  and scan rate of  $4^\circ \cdot \text{min}^{-1}$  was applied, the patterns were recorded in the  $2\theta$  range of  $10^\circ \sim 80^\circ$ . The microstructure and morphologies of the samples were analyzed with a JEOL Model JEM-100CX transmission electronic microscopy

(TEM) with an accelerating voltage of 160 kV. The samples for TEM observation were dispersed in anhydrous ethanol under ultrasonication, and a drop of solution was deposited onto a carbon-coated copper grid before evaporating naturally. Scanning electron microscope (SEM) images were obtained on JEOL Model JSM6700F and JSM-6390LV instruments operating at 8~10 kV.

## 2 Results and discussion

### 2.1 XRD pattern of final hydrothermal product

As shown in Fig.1, diffraction peaks corresponding to boehmite (PDF No. 21-1307) have been found for the final hydrothermal product<sup>[6,10,11]</sup>. No obvious XRD peaks arising from other phases of alumina are found, indicating pure  $\gamma\text{-AlOOH}$  phase in the hydrothermal product.

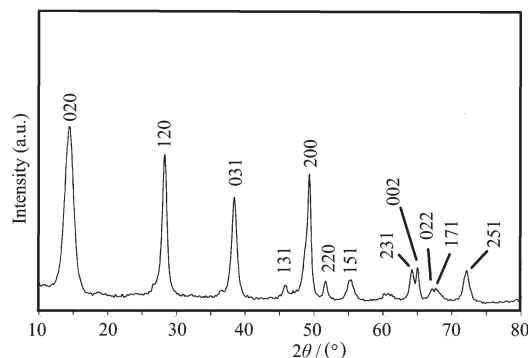


Fig.1 XRD pattern of hydrothermal product

### 2.2 TEM and SEM images of the final hydrothermal product

Fig.2 is the TEM images for the final hydrothermal product (24 h reaction time). The distinct dark and light contradistinction in TEM images indicate the existence

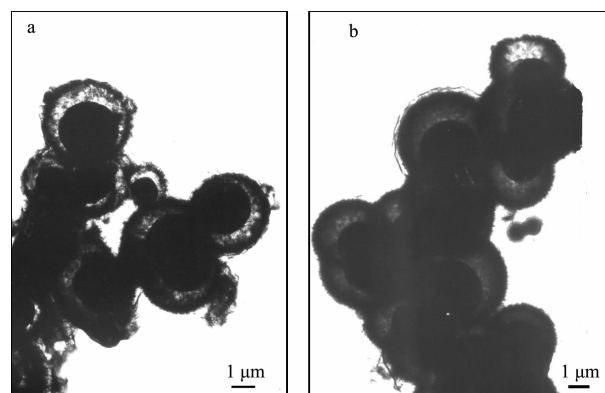


Fig.2 TEM images of the final hydrothermal product

of core-shell structure. Xie et al.<sup>[12]</sup> prepared CdS and ZnS ultra-fine powders with similar morphology by using in-situ source-template interface-reaction route and called it as peanut-like ultra-fine powders.

The SEM images of the final hydrothermal product (24 h reaction time) are shown Fig.3. Fig.3a shows the general view of core-shell morphology of boehmite. The distinct gaps between the core and shell can be ob-

served clearly from the amplified images of Fig.3b. Fig.3c is the amplified image of a broken up core-shell structured boehmite ultra-fine particles. We can observe clearly that the spherical kernel part is composed of boehmite particles and the shell part is composed of laminar morphology boehmite. The microscope analysis reveals that the core is around 3~4  $\mu\text{m}$  and the shell is about 7~8  $\mu\text{m}$  in diameter, respectively.

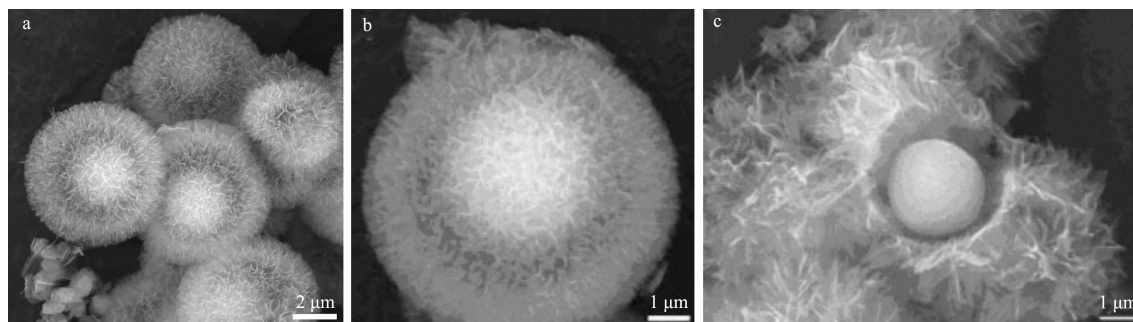
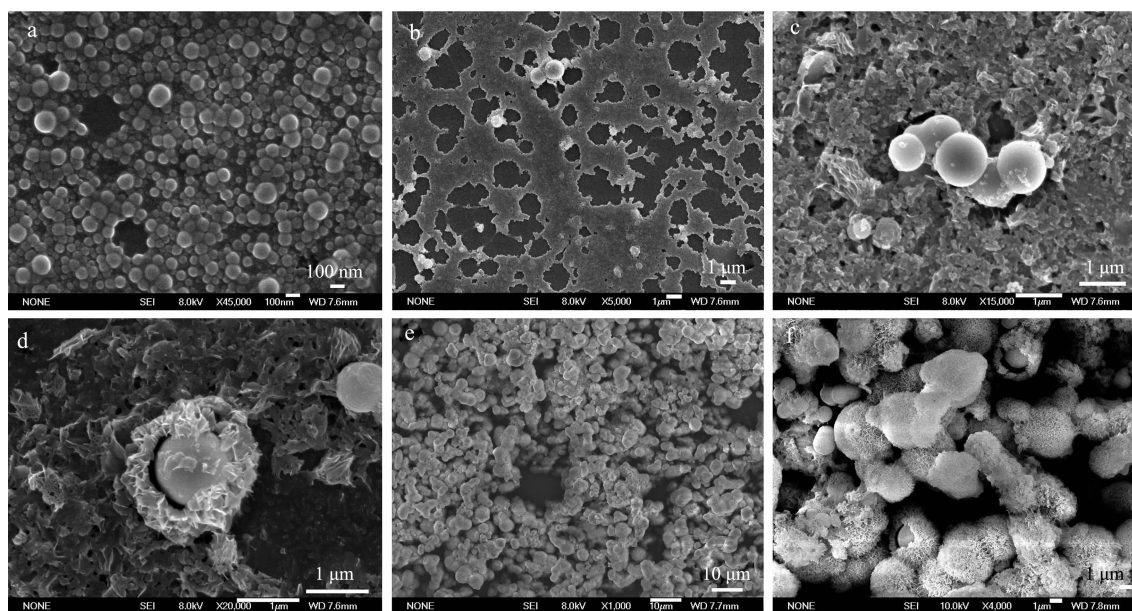


Fig.3 SEM images of the final hydrothermal product

### 2.3 SEM images of the hydrothermal product with different reaction time

To investigate the formation process of the core-shell structured boehmite ultra-fine powders, samples subjected to different reaction durations were studied

by SEM. Fig.4 is the SEM images of the hydrothermal product with different reaction time. It reveals the self-assembly evolution process of the core-shell structured boehmite ultra-fine powders. The pH value of reaction solution with different reaction time is shown in Table 1.



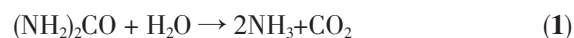
(a) 1 h, (b) 2 h, (c) 4 h, (d) 6 h, (e) 10 h, (f) 24 h

Fig.4 SEM images of hydrothermal product with different reaction time

Table 1 pH values of reaction solution with different reaction time

Reaction time / h	1	2	4	6	10	24
pH value	2.85	3.42	5.73	5.71	5.14	3.55

Based on the experimental results, the reactions and equilibria in the system are shown as follows<sup>[15]</sup>:





Three obvious evolutionary stages can be clearly observed and are shown in Fig.4. we could suggest the formation process of core-shell boehmite product as follows: In the first step of reaction, urea hydrolyses into carbon dioxide and ammonia and yields carbonate and hydroxide as the major ligands in water at about 353 K and above<sup>[16,17]</sup>. Precipitates will be formed when the concentration of both metal and hydroxyl ions are momentarily higher than those permitted by the solubility product<sup>[17]</sup>. In response to the initial step, there is a low pH value reaction system (pH=2.85, as shown in Table 1), Ramanathan et al.<sup>[16]</sup> indicated that the lower pH favored a high rate of nucleation, while the growth was a much slower process compared to the hydrolysis of urea. After 1h reaction, as shown in Fig.4a, we can see a large amount of spherical nanoparticles with 50~200 nm in diameter. It is usual, because the nanoparticles have large surface area, they tend to assemble into spherical shape of particles and aggregate to minimize their total surface energy<sup>[18]</sup>. In conclusion, we call the first step of reaction as the formation process of the original particles.

We call the second step of reaction as the originally formation process of the core-shell structured boehmite particles. As temperature is increased and the existence of comparatively large amount of urea, more and more hydroxide is produced from urea and the reaction equilibrium shifts towards the higher pH value, and there is a change from the nucleation to growth region<sup>[17]</sup>.

According to the study of Ramanathan et al.<sup>[16]</sup>, the original precipitates is amorphous aluminum hydroxide and the nuclei of boehmite are entrapped inside the powder formed, it is the prolonged refluxing at the reaction temperature with the mother liquor that leads to the orderly polymerization which results in the formation of more boehmite nuclei. The increase in the average crystal size of the boehmite nuclei is due to an Ostwald ripening process, in which larger crystallites grow at the expense of dissolving smaller crystallites driven by a reduction in surface energy<sup>[4-6]</sup>. It is also reported that the fresh aluminum hydrate precipitate possibly contains various species or as a result of its unstable state,

some of the small particles are dissolved and redeposited onto the existing nuclei of boehmite (>363 K) leading to their growth<sup>[5,16]</sup>. Fig.4b shows this Ostwald ripening process clearly, we can find that the majority of the small spherical nanoparticles are dissolved away and transformed into laminar products. A very small quantity of much larger spherical particles appears simultaneously. These large spherical particles will act as the core of the final core-shell structured boehmite ultra-fine powders.

Fig.4c shows that a large amount of laminar particles congeries appears at the top pH value of reaction solution (pH=5.73) after 4 h. It is well known that the boehmite has a lamellar structure characteristics, hydroxyl ions hold the lamellae together through hydrogen bonding. Because of the presence of weak hydrogen bonds and the interaction between the solvent molecules and the surface OH<sup>-</sup> groups via hydrogen bonds, this weak and asymmetric hydrogen bonding gives these minerals perfect cleavage parallel to the lamellae to gain laminar boehmite particles<sup>[10]</sup>. At elevated temperature and pressure, layered boehmite tends to curl, leading to the formation of one-dimensional boehmite nanowires<sup>[7]</sup>, nanorods<sup>[11]</sup> via a rolling mechanism.

Literatures indicate that a high pH value (under our experimental conditions, pH value raised from 3.42 to 5.73) is beneficial for the formation of laminar or fibrous boehmite in a hydrothermal synthesis procedure<sup>[3,18,19]</sup>. The possible reason why we only gain laminar boehmite particles might be that the dosage of urea we used is insufficient, the somewhat insufficient amount of urea terminates the increase trend of pH value, so we could not gain the fibrous boehmite which needs a higher pH value<sup>[3,18,19]</sup>.

Fig.4d reveals that these laminar particles congeries subsequently attempt self-assemble around the large spherical particles which act as the core to form the shell of the core-shell structured boehmite ultra-fine powders. This is a typical self-assembly evolution process attributed to the use of amphiphilic copolymer of P(St)-*b*-P(HEA). Amphiphilic copolymer is widely used as the template or directing agent for the effective control of morphology and structure of inorganic

crystals<sup>[4,20]</sup>. When it exists in the solution, the surface tension is reduced, which facilitates the formation of a new phase<sup>[6]</sup>. On the other hand, the amphiphilic copolymer of P(St)-*b*-P(HEA) has a long hydrophobic chain with a large numbers of hydroxyl on it, so that the P(St)-*b*-P(HEA) can form intermediate state by the inter-reaction of the surfactant micelles with the boehmite crystallite surface<sup>[4]</sup>. Because this inter-reaction is hydrogen bonding in nature, it seems not to be sufficiently high to alter the intrinsic structure of boehmite crystallites according to the study of Zhu et al.<sup>[4]</sup>, but it indeed results in changes in the growth and assembly of boehmite crystallites. As discussed above, the growth mechanism of boehmite is not a direct crystal growth mechanism, but a particle coagulation mechanism which can be easily influenced by the pH value and surfactants, thus may form particles of variable morphologies<sup>[3]</sup>.

It is found that under our reaction conditions, without P(St)-*b*-P(HEA), ordinary hydrothermal synthesis can only get irregular particles, so the amphiphilic copolymers of P(St)-*b*-P(HEA) might act as structure-directing agent and might also show space blocking roles, like some PEO-based amphiphilic copolymers<sup>[19,21]</sup>.

We call the last step of reaction as the largely forming process of the core-shell structured boehmite particles. As can be observed from Fig.4e, after 10 h, the core-shell structured ultra-fine powders have almost completely formed. The particles shown in Fig.4e have almost the same morphology with Fig.4f(24 h reaction time). Because the formation of boehmite nuclei, growth of laminar boehmite particles and the formation of core-shell structured boehmite ultra-fine powders by self-assembly evolution process all need adequate time, so it is usual that long reaction time is in favor of the production of fine particles<sup>[4,5,16]</sup>. Park et al.<sup>[22]</sup> reported that without stirring, the phase of the as-synthesized product was found to be pure boehmite and had clear fibrous structure morphology.

### 3 Conclusions

Core-shell structured boehmite ultra-fine powders were synthesized by a convenient hydrothermal route. The usage of P(St)-*b*-P(HEA) as structure-directing agents and somewhat insufficient dosage of urea might

be the two main influence factors. The evolution process of the morphology and nanocrystals phase structure is a very complex process including nucleation, growth, coagulation and self-assembly, all these steps might be influenced significantly by the experimental conditions<sup>[4,6]</sup>.

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