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Influence of Different Surfactants on Morphology of Single Crystal $\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ and Formation Mechanism

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Three kinds of ultra-fine $\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ powders with different morphologies were prepared by adding CTAB, PEG19000 and OP-10 to a solution of $\text{Ce}_2\text{O}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and urea according to the principle and the characteristics of the homogeneous precipitation method. The products were characterized by TEM and XRD. The results showed that the precursor was a single crystal, and that different surfactants had different influences on the morphology of the products. The cationic surfactant CTAB had little effect on crystal morphology merely reducing its size. Nonionic surfactants PEG19000 and OP-10 are both able to change the crystal morphology to a much greater extent. Adding PEG19000 produces an array of rod-like particles with ordered formation and uniform dimension. Meanwhile, in the system of OP-10, a sort of flower-like pattern with a dispersed center can be prepared. The formations of ultra-fine $\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ powders with different morphologies occurred because of the mechanism of formation and grain growth.

Key words: Surfactant, Homogeneous precipitation, Single crystal, Morphology, Mechanism

I. INTRODUCTION

Rare earth elements are identified in part IIIB of the periodic table. IIIB lists fifteen elements in all. They can also be referred to as lanthanides. Their valence electrons are found in 4f orbits which can be screened by bigger shield, as a result, they have unique characteristics not found in transition metals, such a lack of bond strength leading to a lack of interaction between rare metals and ligand orbits. They have larger ionic radii and higher coordinate numbers (4-12), therefore these compounds do not readily attain coordinate saturation. The chemical properties of these elements are very active and similar to alkaline metals and alkaline earth metals, and they are easy to be ionization and combine with oxygen, so that they have a very strong trait of ion and philic-oxygen. During the synthesis and reaction of the rare earth compounds, although the interaction between metals and ligand orbit is not significant, they are very easy to reset the ligand and change the coordinate space if electric charge and space request are satisfied [1,2].

Recently, many researchers have been investigating the influence of surfactants on particle size and morphology. We have referenced some of the related research [3-7]. There have been few reports about the influence of different surfactants on the morphology of the precursor ($\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$). In this work, ultra-fine $\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ powders, with three different morphologies, were prepared according to the principles

and characteristics of the homogeneous precipitation method using urea as a raw material.

II. EXPERIMENTAL SECTION

The precursor ($\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$) powders were synthesized by precipitation. Three isometric solutions of $\text{Ce}(\text{NO}_3)_3$ and urea were prepared. The mole ratio between $\text{Ce}(\text{NO}_3)_3$ and urea was 1:40. Then the surfactants cetyltrimethylammonium bromide (CTAB), polyethylene glycol 19000 (PEG19000), and nonyl phenol polyethyleneoxy ether (OP-10) were each added at a ratio of 0.6% (*w/w*). The mixed solutions were heated in a water bath at 85 °C with strong stirring for 4 h. The precipitates were collected by centrifugation and then washed, four times with distilled water, and once with isopropyl alcohol. Finally, the precipitates were dried in desiccators at room temperature for 24 h to obtain white powders.

The morphology of the samples was characterized by TEM (Type 2010, JEOL, Japan). The samples were dispersed in pure alcohol and evaporated on a grid at room temperature. XRD analysis (D8 advance-XRD, BRUKER, Germany) was used to determine the phase composition and structure of the products.

III. RESULTS AND DISCUSSION

A. The influence of surfactants on the morphology of precursors

Because of the high surface energy, the particles ($\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$) prepared by our precipitation

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method are easy to aggregate. TEM showed that the morphology of the products was spindle-like. The scale was micron grade and the size of the product was not uniform. SAED indicated that the products were in a single crystal form (Fig.1).

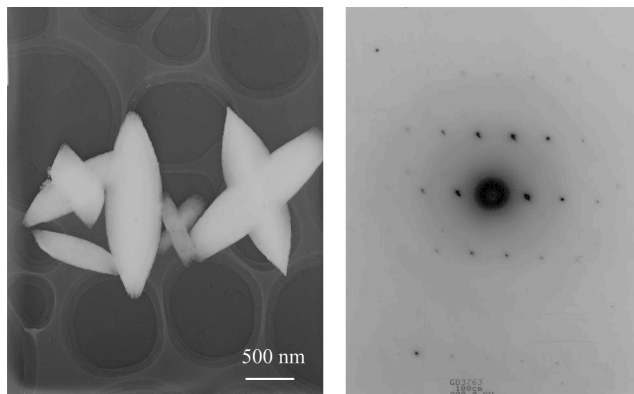


FIG. 1 TEM and SAED photos of the products without surfactant.

Adding different surfactants not only resulted in a steric hindrance effect, but also prevented the particles from reuniting effectively. Due to the different constructions and capabilities of the surfactants, they could be adsorbed by the surface of crystal and interacted with the crystal interface easily. Accordingly, the formation mechanism and the growth rate of $\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ were changed. Finally, a crystal with a different morphology formed [8,9].

Three different morphologies of the CeO_2 precursor ($\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$) detected by TEM, resulted from adding different surfactants (see Fig.2). When the cationic surfactant CTAB was added, there was little change in the morphology. However the scale became uniform and its size was reduced. On the contrary, if nonionic surfactants PEG19000 and OP-10 were added, the crystal morphology was changed markedly. An array of rod-like particulates with ordered formations, uniform sizes, and flower-like patterns with dispersed centers were produced.

B. The mechanism of surfactants affecting the morphology of the precursors

1. The effect of CTAB ($\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Br}$)

According to our experiments, spindle-like carbonic acid oxygen cerium ($\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$) prepared by the homogeneous precipitation method followed Lamer theories [10,11]. Urea was hydrolyzed and the CO_3^{2-} was created in both neutral and alkaline environments [11]. Concentration of the CO_3^{2-} was increased gradually along with the hydrolyzation reaction and as the

CO_3^{2-} reached the supersaturated level, crystal nuclei were formed instantly. Next, CO_3^{2-} of the solution diffused into the crystal nucleus, making the crystal's nucleus grow gradually. Finally, the whole system reached equilibrium and the crystal stopped growing.

If no surfactants were added, the initial particles would aggregate together very easily because of the high surface energy. Because of its high surface activity, when cationic surfactant CTAB was added, it could not only diminish the Vander Waals energy, but also it was adsorbed on the crystal's surface. This changed the growth mechanism of the crystal grains. When the concentration of this critical micelle was reached, an electrostatic repulsive force resulted, retarding the aggregation of crystal nuclei and contraining $\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ particles' arrival on the surface of crystal nuclei to the diffusion function (i.e. particle growth relied solely on the diffusion mechanism [3]). Therefore, the scale of the particles became smaller and more uniform (see Fig.2(a)).

2. The effect of PEG19000

Polyethylene glycol 19000 is a nonionic surfactant. Its molecular formula is $\text{H}-(\text{O}-\text{CH}_2-\text{CH}_2)_n-\text{OH}$. The polyether segment lies in the center with the alcohol hydroxyl group at one end. This type of surfactant has a long molecular chain with tooth shape in anhydrous elements, but its configuration can twist when dissolved in water. Hydrophilic oxygen atoms are extracted by water molecules located outside the chain, whereas lipophilic methylene ($-\text{CH}_2-$) is located inside (Fig.3). As a result, the chains combined with water turned easy. So PEG molecules took root in the solution and combined with product particles easily; its interaction force significantly exceeding the electrostatic force adsorbed by the surface. At the beginning of precipitation, PEG was adsorbed on the surface of the precursor $\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$, which weakened the linkage between hydroxyl and the particle surface. Therefore, the surface tension of the particle interface was reduced, and growth of the particles was limited [3]. The concentration of precipitate was increased with the reaction. The hydroxyl on the surface of the particles and the hydrate film formed by PEG made colloid particles combined. At that stage, PEG played an important role by stepping into the particles [4]. Moreover, the like charges adsorbed on the surfaces of the hydrophilic group repulsed each other. The adsorbing layer was composed of a double-electricity layer construction, hence the potential of the surface repulsion force was enhanced. An ordered array of rod-like particulates appeared as products (Fig.2(b)).

3. The effect of OP-10

OP-10 is a nonionic surfactant with polyethylene oxide chains (POE). Its structure is shown in Fig.4. Due

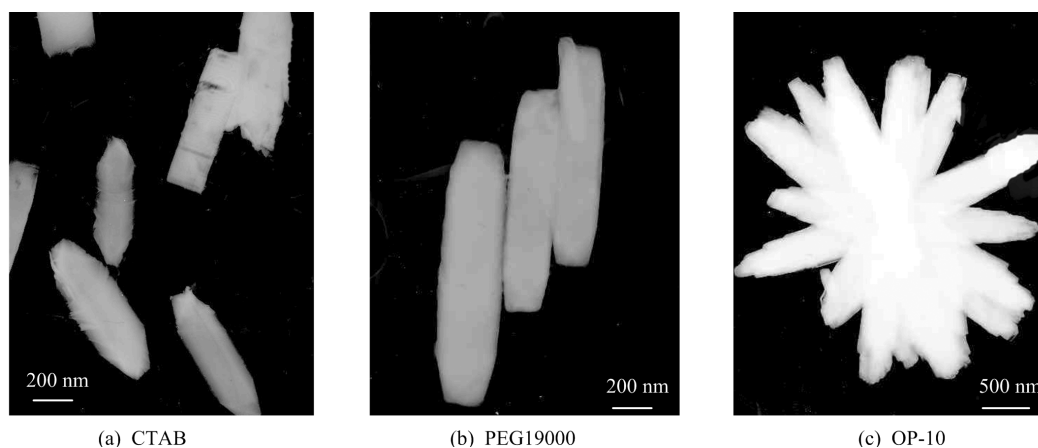


FIG. 2 TEM photos of the products with different surfactants.

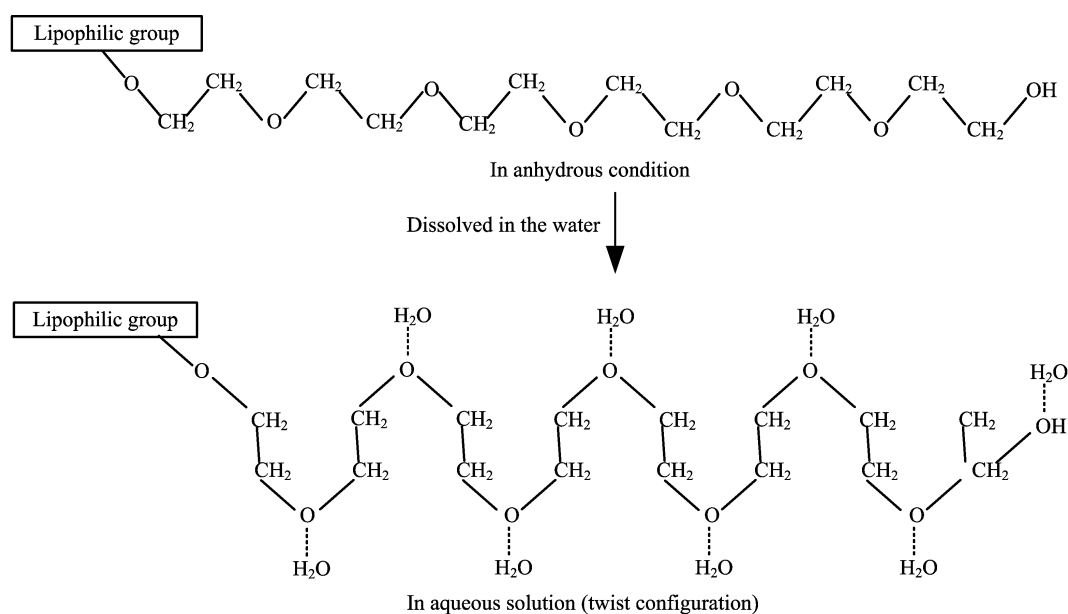


FIG. 3 Chain varieties of PEG.

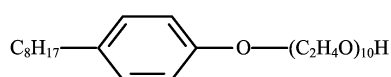


FIG. 4 The structure of OP-10.

to POE nonionic surfactant with the hydrophilic groups (such as ether group $-\text{O}-$) and the lipophilic groups (such as poly ethylene oxide group), OP-10 has high stability and good dissolving ability both in water and organic dissolvent. The stable benzene ring with a π -bond was connected with the ether group. The other end of the molecule was a long chain polyethylene oxide group with many electrons. Because the metal ions have empty orbits, which can accept lone-pair electrons, the

interaction of two sets of lone-pair electrons with the oxygen atom was easy to coordinate. If OP-10 is involved in particle formation at this stage, a crystal with a combined center will result. Although the mechanism of this process is still not clear, this kind of flower-like construction, with a dispersed center, could confirm the above theory (shown in Fig.2(c)).

C. XRD analysis of orthorhombic $\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$

In order to verify the structure and phase constitution of the products, the product powders were dried at room temperature and analyzed by X-ray diffraction. The analysis indicated that the spectra of the CeO_2 precursors were nearly identical (see Fig.5). The patterns

of spectrum peaks revealed by XRD of the products without surfactants, were consistent with the JCPDS cards. This indicated that the products' crystallization degree can be increased by the addition of surfactants examined in this study.

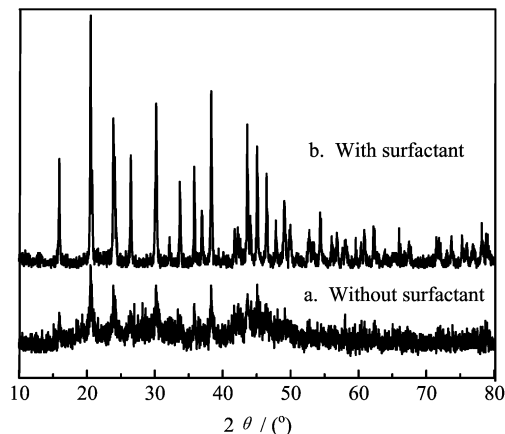


FIG. 5 XRD patterns of the product.

IV. CONCLUSIONS

The product, made without surfactants, was large and asymmetric, and there was evidence of melting among the particles. Surfactants can improve the products' crystallization degree.

Surfactants had an important influence on the size and morphology of the products. Cationic surfactant CTAB had little influence on the morphology of $\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ crystalline, only reducing its size. Nonionic surfactants PEG19000 and OP-10 can change the crystal morphology much more. Adding PEG19000

can yield an array of rod-like particulates with ordered formation and uniform sizes. Meanwhile in the system of OP-10, a kind of flower-like crystal with a dispersed center can be prepared.

The morphology of the prepared products was affected not only by internal construction of the crystal, but also by outside factors, such as surfactants. A change in crystal growth environment would change the final morphology of the crystal. Adding surfactants could change the environment of crystal growth to a certain extent, thus powder particles with different morphologies were formed.

- [1] X. Z. You, Q. J. Meng and W. S. Han, *Progress in Coordination Chemistry*, Beijing: Higher Education Press, 108 (2000).
- [2] H. L. Fan, M. H. Cao, Y. J. Qi, *et al.* *Chem. J. Chin. Univ.* **25**, 1419 (2004).
- [3] X. Zhang, Y. Zhao and C. B. Zhang, *Chin. J. Chem. Phys.* **17**, 613 (2004).
- [4] X. L. Jia and X. H. Zhong, *Chin. Powder Technol.* **5**, 12 (2004).
- [5] L. L. Li, Y. Liu and Y. Chu, *J. Mol. Sci.* **21**, 16 (2005).
- [6] X. L. Hu, D. D. Chen, X. H. Hu and H. Yin, *China Ceramic Industry* **10**, 25 (2003).
- [7] Q. L. He, P. Li, H. L. Zhao, *et al.* *J. Hebei Normal Univ.* **28**, 488 (2004).
- [8] A. S. Michaels and F. W. Tausch, *J. Phys. Chem.* **65**(10), 1730 (1961).
- [9] A. Janekovic and E. Matijevic, *J. Colloid Interface Sci.* **103**, 436 (1985).
- [10] A. Muramatsu and T. Sugimoto, *J. Colloid Interface Sci.* **189**, 167 (1997).
- [11] T. Sugimoto, *Adv. Colloid Interface Sci.* **28**, 65 (1987).