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Synthesis of CeF_3 nanoparticles from water-in-oil microemulsions

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Abstract

The paper presents the synthesis of CeF_3 nanoparticles from polyisobutene-butanediimede (T154)/cyclohexane/water microemulsions. The CeF_3 nanoparticles were characterized by transmission electron microscopy (TEM), X-ray diffractometer (XRD) and dynamic laser light scattering (DLS). The results showed that the nanoparticles in shape, size and size distribution were strongly affected by water content and precursor concentration. With increasing water content and precursor concentration, the size and polydispersity of particles increased and the morphology of the particles was converted from the mixtures of spherical and cylindrical particles to the mixtures of cylindrical and polygonal particles. The crystal structure of nanoparticles was a face-centered cubic lattice.

Keywords: CeF_3; Nanoparticle; Microemulsion

1. Introduction

Nanometer-sized particles have attracted great interest in recent years because of their unique properties in physics and chemistry as well as their potential application in industry [1–7]. Various types of nanoparticles can be synthesized by many methods such as gas evaporation, laser vaporization, ionized beam deposition, sol–gel processing, freeze drying, etc. [8–13]. However, their properties were greatly affected by the synthesis methods. Compared with other techniques, microemulsions as microreactors to prepare nano-sized particles have two marked features. One is the well-controlled particle size and the other is good monodispersity of the resulting particles. Therefore, many investigators have paid more attention to it as a main method to synthesize nanoparticles, e.g., Cu, Fe, etc. [14–18]. CeF_3 is a good solid lubricant because of its layered structure, whereas no report about preparation of its nanoparticles has been published so far.

The microemulsions composed of polyisobutene-butanediimede (hereafter abbreviated as T154), cyclohexane and water were developed as reactors and CeF_3 nanoparticles were synthesized in our laboratory. Nanoparticles were characterized by transmission electron microscopy (TEM), X-ray diffractometer (XRD) and dynamic laser light scattering (DLS).

2. Experimental details

T154 was produced by Jingzhou Petroleum Processing factory. Its chemical structure was shown in Fig. 1 and its average molecular weight is about 2320. A microemulsion system with T154 as the surfactant, cyclohexane as the continuous oil phase, and salt solution as the dispersed aqueous phase was developed as a microreactor to synthesize CeF_3 nanoparticles. The weight ratio of T154/cyclohexane was 1/200. The concentration of NH_4F aqueous solution was three times that of the $Ce(NO_3)_3$ aqueous solution. T154, cyclohexane and salt solution were blended in a given weight ratio and the mixture was ultrasonicated until it reached the stable state of microemulsion. Two microemulsions with the same volume but containing $Ce(NO_3)_3$ and NH_4F, respectively, were prepared first. The microemulsion containing $Ce(NO_3)_3$

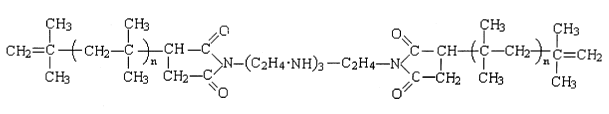

Fig. 1. The chemical structure of polyisobutene-butanediimede (T154).

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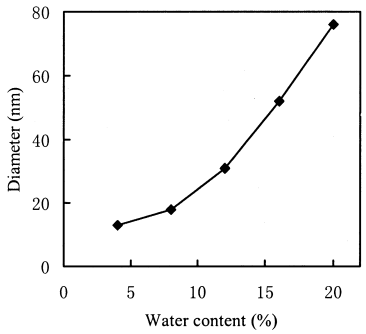

Fig. 2. Variation of the diameter of microemulsion droplets with water content.

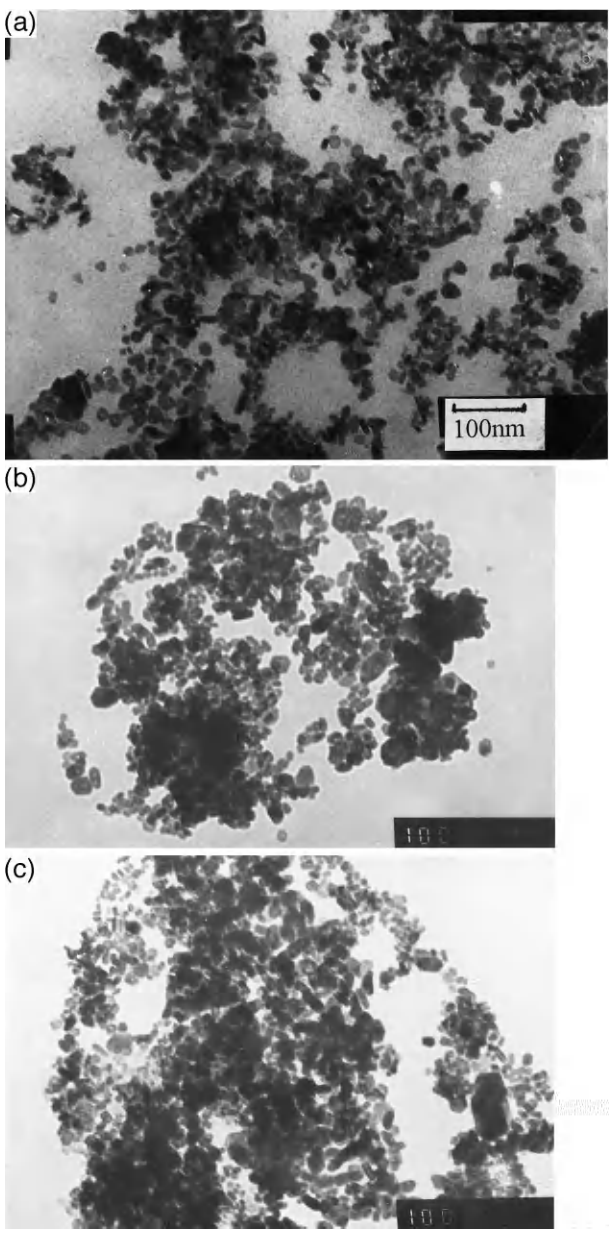

Fig. 3. The TEM micrographs of CeF_3 nanoparticles with different water contents ($[Ce^{3+}] = 0.1000$ mol l^{-1}): (a) 4%; (b) 8%; (c) 12%.

was then added all at once to that containing NH_4F. The resultant CeF_3 nanoparticles can be obtained by centrifugation and washing with acetone and ethanol. The characteristics of CeF_3 nanoparticles were estimated by TEM, XRD and DLS.

3. Results and discussion

3.1. Characteristics of microemulsion system

The microemulsion composed of T154/cyclohexane/water has good stability. The water droplet size was detected by DLS as shown in Fig. 2. It can be seen that the size of water droplets is gradually increased with water content at water content below 8%, but the droplet size is sharply raised with water content above 8%. These indi-

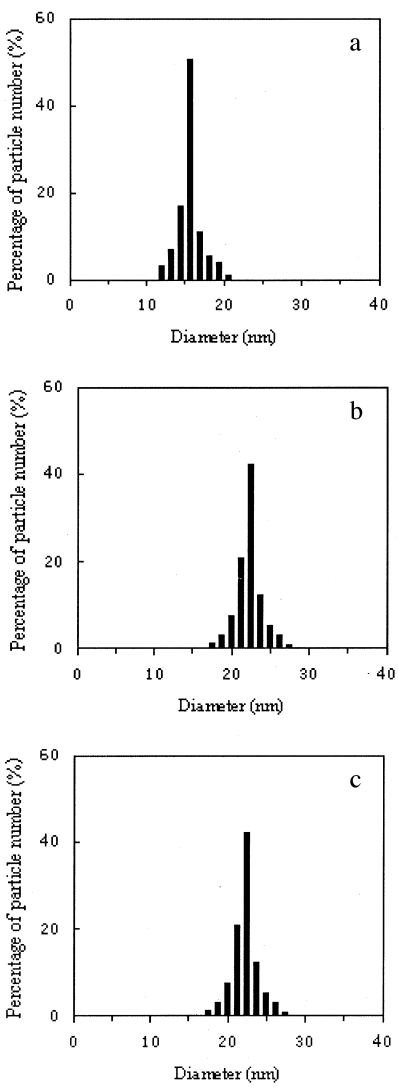

Fig. 4. Variation of the size distribution of CeF_3 nanoparticles with water content (a, b and c same as Fig. 3).

cate that the water molecules in the water core of the microemulsions are relatively immobilized and bound to the hydrophilic portion of the amphiphile (T154) via hydrogen bond at water content below 8%, but free water or unbound water molecules exist at water content above 8%. Hence, as compared with water content above 8%, the interfacial rigidity of water core is better and the droplet size is smaller at water content below 8%.

3.2. Effect of water content

The effects of water content on nanoparticle morphology, size (detected by TEM) and size distribution (detected by DLS) are shown in Figs. 3 and 4, respectively. From Fig. 3, it is clear that CeF_3 nanoparticles are spherical and cylindrical in shape and the number of spherical particles is more than that of cylindrical particles at 4% water content. When water content is 8%, polygonal nanoparticles appear in addition to spherical and cylindrical particles. If water content is increased further, the number of spherical particles becomes fewer, and most of nanoparticles are cylindrical or polygonal in shape, and the size becomes larger. From Fig. 4, it can be seen that the size distribution of particles is markedly affected by water content. The size distribution of particles is widened as water content increases. When water content is 4%, the size is varied in the range of 12–21 nm, but at 12% water content, the size distribution is broadened in the range of 17–36 nm. Hence, water content should be controlled below 8% in order to prepare nanoparticles with small size and good monodispersity.

The reason may be that at higher water content, there are more free water molecules in microemulsions and the interfacial rigidity is poorer as compared with at lower water content. These lead to enhance the exchange rate of reactants among micelles and produce more polygonal particles and widen the particle size distribution. So, it can be rationalized that the presence of free water in the microemulsions provides morphological tailoring of particles and is disadvantageous to the formation of spherical particles.

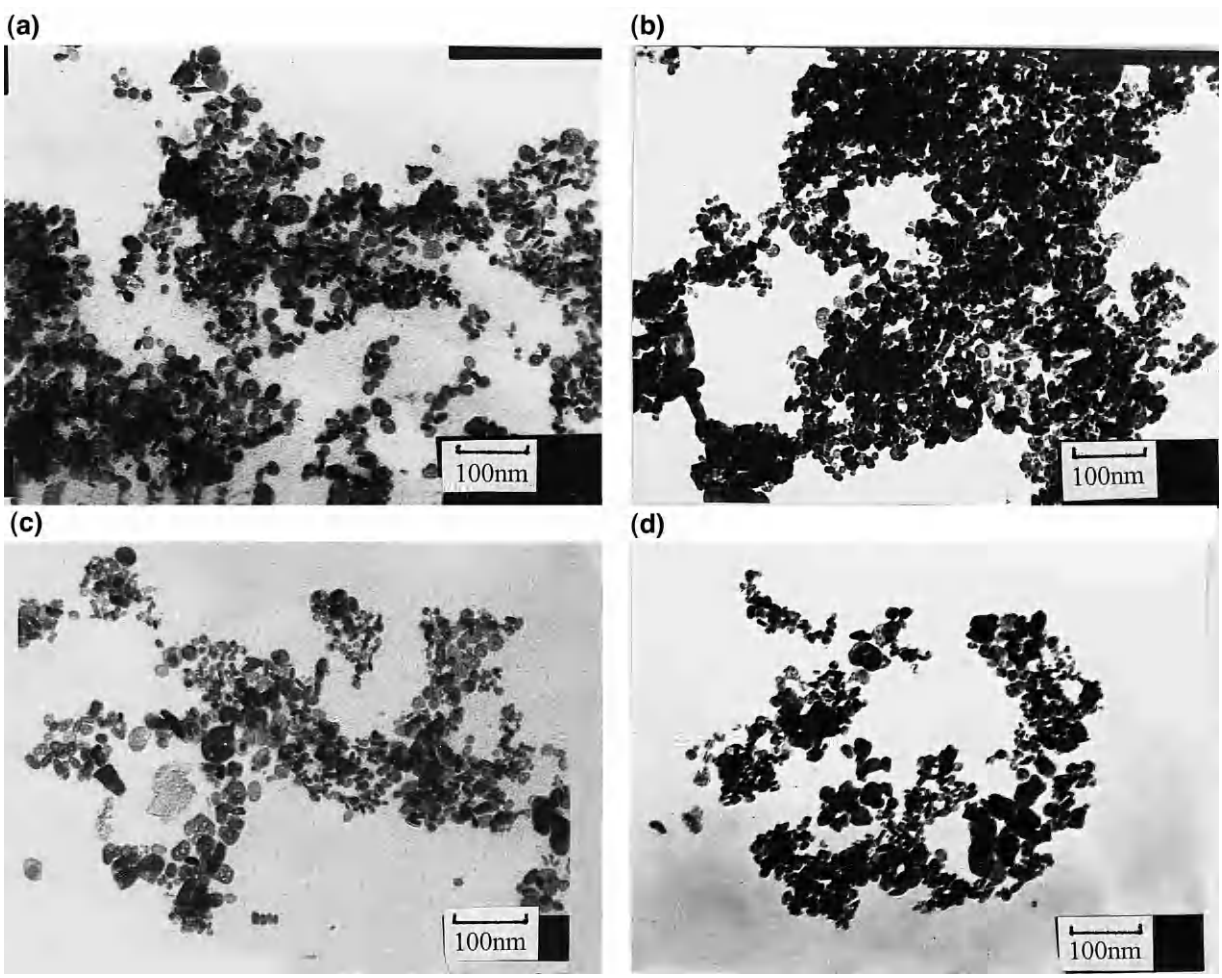

Fig. 5. The TEM micrographs of CeF_3 nanoparticles with different $[Ce^{3+}]$ (water content: 4%): (a) 0.05000 mol l^{-1}; (b) 0.2000 mol l^{-1}; (c) 0.3000 mol l^{-1}; (d) 0.5000 mol l^{-1}.

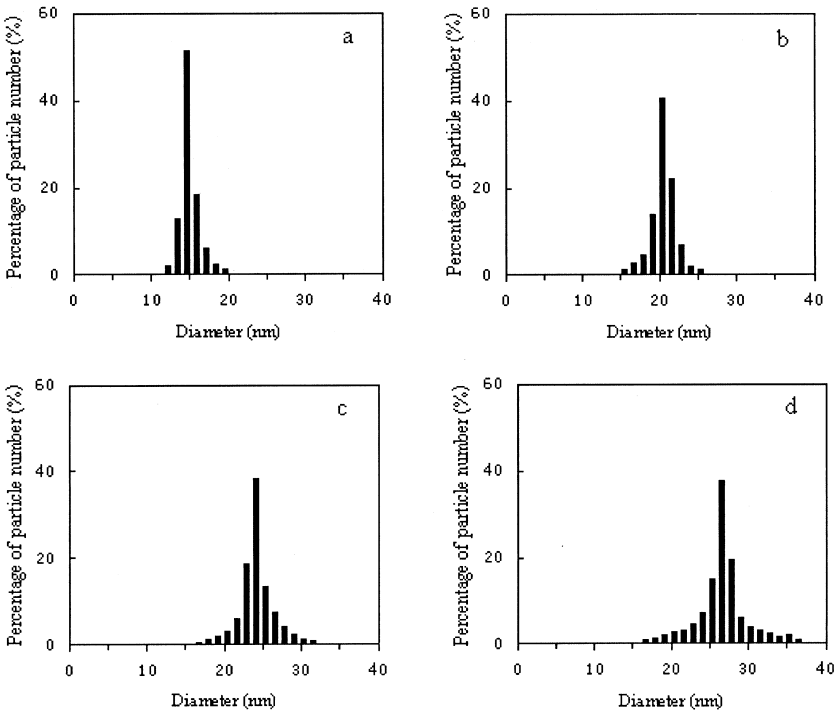

Fig. 6. Variation of the size distribution of CeF_3 nanoparticles with $[Ce^{3+}]$ (a, b, c and d same as Fig. 5).

3.3. Effect of precursor concentration

The morphology, size and size distribution of the nanoparticles are not only dependent on the water content, but also strongly affected by the precursor concentration as shown in Figs. 5 and 6. From Fig. 5, it can be seen that the size of CeF_3 nanoparticles increased with precursor concentration and the morphology was converted from spherical and cylindrical to cylindrical and polygonal. The spherical particles almost disappeared when the Ce^{3+} concentration was above 0.2000 mol l^{-1} and were replaced by polygonal particles. From Fig. 6, we can find that the polydispersity of particles was increased with the concentration of precursors. The size distribution of particles was apparently broadened at $[Ce^{3+}] = 0.2000$ mol l^{-1}. These results indicate that the aggregation of nuclei and primary particles takes place seriously via the intermicellar interaction, leading to form larger particles, and the particles exhibit a broad size distribution and polygonal shape at the higher precursor concentration. Therefore, Ce^{3+} concentration should not be over 0.2000 mol l^{-1} in order to synthesize the nanoparticles with small size and good monodispersity.

3.4. Structure of CeF_3 nanoparticles

CeF_3 nanoparticles were examined by XRD and the pattern is shown in Fig. 7. From Fig. 7, it is found that the positions and the intensities of the peaks are consistent with those for the CeF_3 crystal, which appeared in JCPDS card no. 8-45. This means that the crystal structure of CeF_3 nanoparticles is a face-centered cubic lattice.

3.5. The formation mechanism of CeF_3 nanoparticles

The mechanism for the formation of CeF_3 nanoparticles in microemulsions is shown in Fig. 8. The exchange of reactants among droplets is very frequent because of the huge micelle surface area and the CeF_3 nuclei will form quickly. After a stable nucleus is formed, it grows by the following processes: (1) incorporation of ions and monomers in solution into already formed nuclei; and (2) aggregation of primary particles or nuclei to form bigger particles. When the particle size reaches the droplet, the surfactant will cap the surface of nanoparticles and hinder further particle growth. If the growth occurs through the intramicellar interaction, the size of particle can be well-controlled by the inner core. On the other hand, the particle size may be over the diameter of water core if the growth occurs through the intermicellar interaction. How-

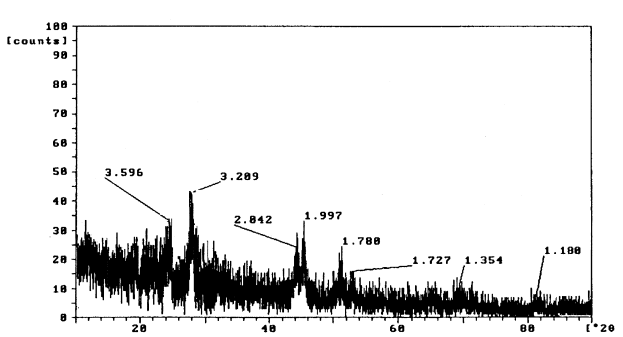

Fig. 7. The XRD pattern of CeF_3 nanoparticles produced at $[Ce^{3+}] = 0.1000$ mol l^{-1} and water content: 4%.

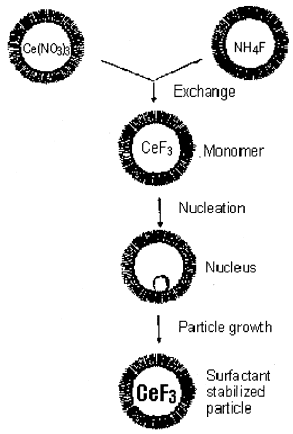

Fig. 8. Model illustrating the formation of CeF_3 nanoparticles in microemulsions.

ever, in the discussed situations, the initial growth of particle through intermicellar interaction predominated over intramicellar interaction, e.g., by collision, fusion, and splitting of inverse micelles. So, the particle size is generally slightly larger than that of water droplet. Because the interfacial rigidity of water core decreases with increasing water content, the aggregating phenomena of nuclei and primary particles by intermicellar interaction occur more strongly at higher water content and higher precursor concentration, resulting in the appearance of polygonal particles besides spherical particles and decrease of the nanoparticle monodispersity.

4. Conclusions

The microemulsion system composed of polyisobutene-butanediimede, cyclohexane and water was developed as a microreactor to synthesize CeF_3 nanoparticles. With increasing water content and precursor concentration, the particle size and polydispersity rose and the morphology of the particles was converted from the mixtures of spherical and cylindrical particles to the mixtures of cylindrical and polygonal particles. When water content and Ce^{3+} concentration were below 8% and 0.2000 mol l^{-1}, respectively, the CeF_3 nanoparticles with small size and good monodispersity were obtained. The crystal structure of nanoparticles is a face-centered cubic lattice.

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