

Synthesis of dysprosium oxide by homogeneous precipitation

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Abstract Nanocrystals of uniform dysprosium oxide (Dy_2O_3) particles have been prepared by homogeneous precipitation technique. The particles were produced by aging DyCl_3 solution in presence of urea at elevated temperature. The particles were characterized with respect to their size, shape, and thermal decomposition behavior. It was found that the precipitated particles were spherical, uniform in size, and amorphous in nature. Upon heating in air, these particles decomposed into oxide and no change in morphology was observed. The dysprosium ion concentration was found to have significant effect on the particle size and its distribution.

Keywords Nanoparticles · Dysprosium oxide · Homogeneous precipitation

1 Introduction

Recent advances in synthesizing and characterizing nanomaterials in the range of 1–100 nm have enabled the first tentative steps in the synthesis of a wide range of new materials from nanoscale particles. Interest in these materials is motivated by their interesting electronic, optical, magnetic, mechanical, and chemical properties, which are totally different from those of their bulk counterparts [1]. The oxides of rare earths such as dysprosium, samarium, erbium, yttrium, europium, and lutetium have many important applications, such as dielectric formulation for multilayer ceramic

capacitors (MLCC) application, high efficiency phosphor, and catalysis [2–4]. In most of these applications, the properties of the materials could be altered by doping them with another constituent to form a solid solution system. Therefore, it is of no surprise that preparation of single and mixed component solid with well defined shape and uniformity in particle size is a great challenge.

Homogeneous precipitation by urea has been recognized as one of the methods to synthesize nanometer sizes of rare earth oxide particles [5–7]. It is a relatively simple, reproducible, and economically feasible method for its potential large scale production. Yet, the formation of nanoparticles by urea precipitation in aqueous solution process and its processing conditions are not fully understood, which is essentially important to obtain particles with desired morphology and narrow size distribution. Therefore, it is the aim of this paper to study the effect of metal cation concentration as one of important factor to the size and size distribution of the resulting particles.

2 Experimental details

In this study, dysprosium (III) oxide (99.99%), hydrochloric acid, and urea (98%) were used as starting materials. The dysprosium oxide was prepared by AMR Technologies Inc. The hydrochloric acid and urea were procured from Sigma Aldrich and used without any further purification.

Aqueous dysprosium chloride solution was prepared by dissolving the oxide powder in appropriate amount of hydrochloric acid. The aqueous urea solution was prepared by dissolving urea in deionized water, after which mixed with appropriate amount of dysprosium chloride, and stirred homogeneously in a glass beaker. This mixture of solution was then placed into a water bath, where it was heated up to

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90°C and stirred for additional 90 min after the first sign of turbidity was observed. After cooling down, the precipitates were centrifuged and washed thoroughly with deionized water and ethanol. The precipitates were dried in drying oven at 75°C for 18 h. Dried precipitates were calcined in air at different temperatures up to 700°C for 2 h. In this study, the metal cation concentration ($[Dy^{3+}]$) was varied from 0.005 M to 0.1 M with constant urea concentration of 1.0 M, aging temperature of 90°C, and 90 min aging after the turbidity sign.

The morphology, particle size, and particle size distribution of the Dy_2O_3 particles were examined using transmission electron microscopy (TEM–JEOL 2010) and field emission scanning electron microscopy (FE–SEM–JSM 6340F). Simultaneous differential thermal and thermogravimetric analysis (DTA–TGA) was carried out in flowing air at normal atmosphere by a Netzsch thermal analyzer (STA449C). The sample was prepared by weighing 100 mg of precipitated powder and poured into an alumina DTA crucible. The temperature was ramped at a rate of $5^\circ C \cdot min^{-1}$ from ambient temperature to 1000°C. X-ray analysis was performed using a Shimadzu XRD-6000 diffractometer, using $Cu K\alpha$ -radiation ($\lambda = 1.5418 \text{ \AA}$). Using Bragg–Brentano focusing, the diffraction patterns were recorded with a scanning speed of $2\theta = 2^\circ \cdot min^{-1}$ for a range of $2\theta = 10^\circ$ – 100° . The sample was prepared by placing the powder into the XRD sample holder and pressed to obtain flat surface.

3 Results and discussions

Simultaneous thermogravimetric and differential thermal analysis (TGA/DTA) traces of the dried dysprosium precipitates are shown in Fig. 1. There is continuous weight loss during heating from room temperature to $\sim 750^\circ C$, with no stepwise reaction being indicated. No further weight loss is

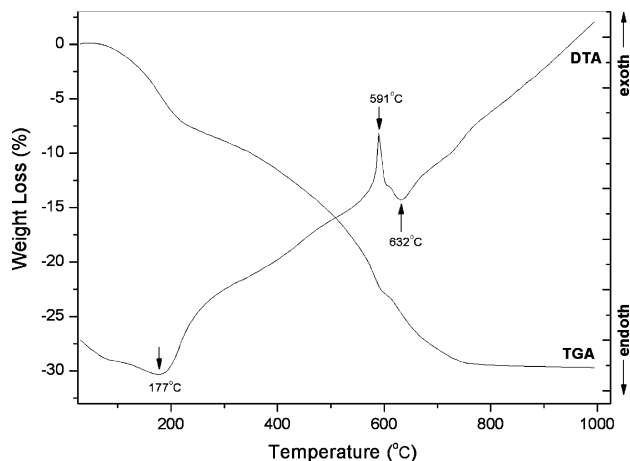


Fig. 1 TGA/DTA curves of the dried precipitates

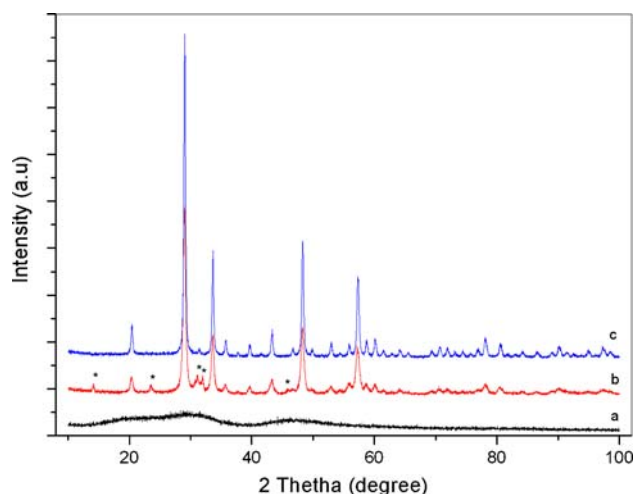


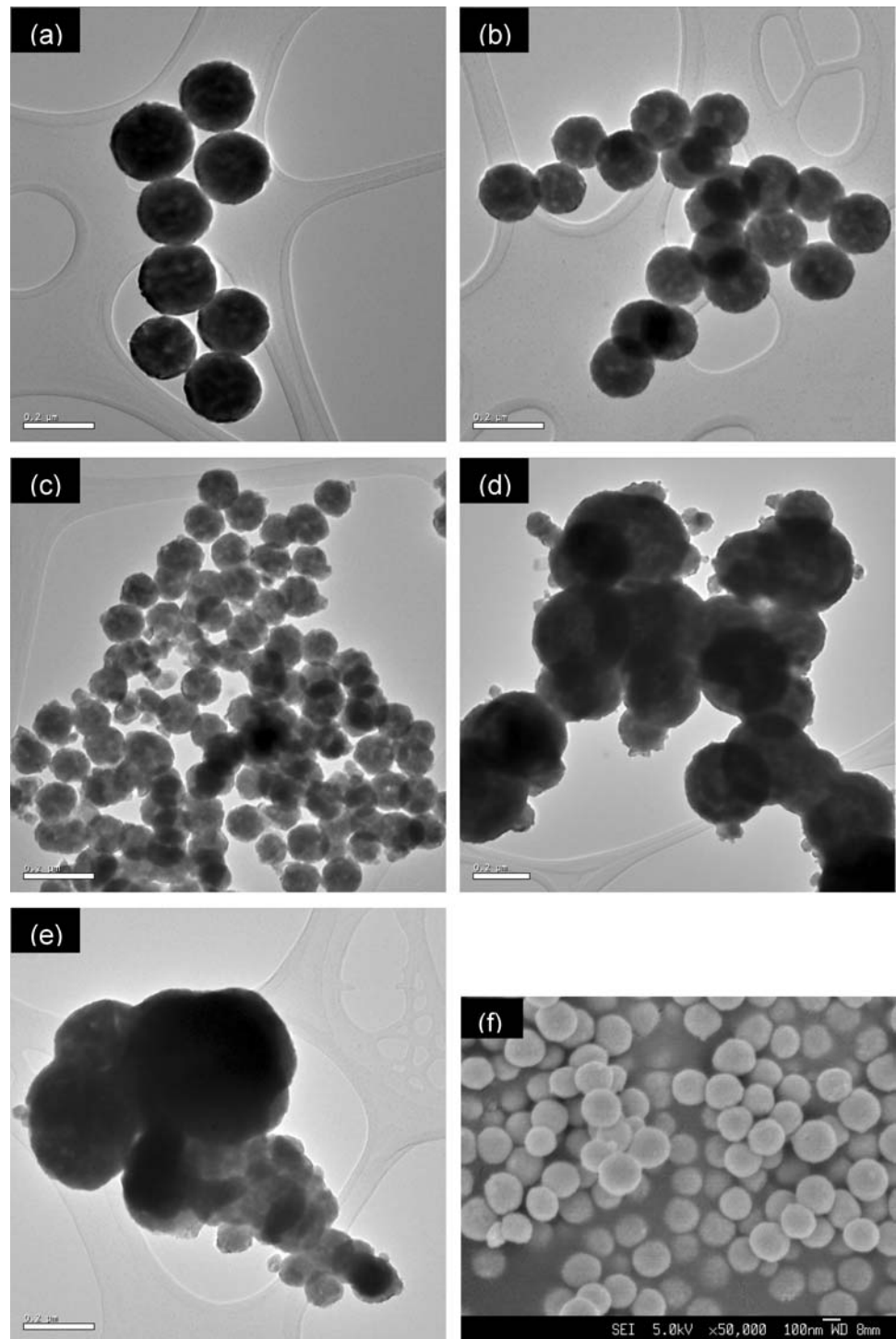
Fig. 2 X-ray diffraction patterns of the samples calcined at different temperatures for 2 h (a) 250°C (b) 500°C (c) 700°C

observed upon heating further to 1000°C. The DTA trace indicates a rather broad endothermic peak around 177°C with a shoulder around 100°C. It has been reported previously [5, 6] that the weight loss at 100°C is due to the evaporation of the adsorbed water and the endothermic peak was due to decomposition of hydroxycarbonate to oxycarbonate. With further heating up to 600°C, the weight loss continues and is accompanied by appearance of exothermic peak, which later one may correspond to crystallization of oxycarbonate. An endothermic peak around 632°C is detected, which is believed to represent the conversion of oxycarbonate to oxide.

Figure 2 illustrates the XRD patterns of the samples calcined at different temperatures. The precipitates after heat treatment at 250°C have an amorphous microstructure as indicated by broad humps in the patterns in Fig. 2(a). Annealing the samples at 500°C results in formation of two crystalline phases, namely dysprosium oxide and an additional compound (indicated by * in the pattern of Fig. 2(b)). The later one is possibly one form of dysprosium oxide carbonate, whereby in present case, the exact composition may deviate from stoichiometry formula in database, $Dy_2O_2CO_3$. The dysprosium oxide in the pattern corresponds to cubic structure, ICSD #962080. Pure dysprosium oxide with a crystallites size of approximately 30 nm can be obtained by annealing the precipitates at 700°C.

Few investigations have been done on the effect of metal cation concentration on particle formation by urea precipitation, yet with contradictory results [8, 9]. Transmission electron micrographs in Fig. 3 show an interesting particle size dependency on dysprosium ion concentration. Secondary electron micrograph is also included in this picture to show that the particles observed morphology in TEM are representative for the sample. Initially, as the dysprosium ion concentration increases from 0.005 M to 0.02 M, while retaining its spherical morphology, the average particle size

Fig. 3 Transmission electron micrographs of Dy_2O_3 particles precipitated at constant urea concentration of 1.0 M; aging temperature of 90°C and aging duration 90 min for different dysprosium ion concentration (a) $[\text{Dy}^{3+}] = 0.005 \text{ M}$ (b) $[\text{Dy}^{3+}] = 0.010 \text{ M}$ (c) $[\text{Dy}^{3+}] = 0.020 \text{ M}$ (d) $[\text{Dy}^{3+}] = 0.050 \text{ M}$ (e) $[\text{Dy}^{3+}] = 0.100 \text{ M}$ (f) secondary electron images of Dy_2O_3 particles precipitated at $[\text{Dy}^{3+}] = 0.005 \text{ M}$



decreased from 205 nm to 105 nm; with narrow particle size distribution for all three concentrations. However, as the concentration increases further, from 0.02 M to 0.100 M, though retaining the spherical morphology in general, the particles are agglomerated to one another, as can be observed in Fig. 3(d) and (e), such it is difficult to distinguish one particle from each other. This agglomeration trend is also accompa-

nied by an increase average particle size and widening of particle size distribution. In conclusion, this trend in particle size, which initially decreases and then increases as the dysprosium ion concentration increases, can be related to how these particles grow during the aging process.

In previous works [5, 6, 8], the short nucleation time model of LaMer [10] has been used to describe the urea

precipitation process. In this model, nuclei are formed homogeneously from solution when the reactive species in the solution reach supersaturation. Afterwards, the particles grow via diffusion molecular addition. However, this model alone cannot justify the observation of some perfectly spherical particles which consist of much smaller crystalline subunits [11, 12]. In recent years, it has been found that using homogeneous precipitation by urea resulted in particles with smaller sub-units in different materials [13, 14]. Therefore, based on these findings, it is believed that the growth mechanism by urea precipitation can be described better by an aggregation mechanism.

In aggregation model, the process is started by the growth of nuclei by molecular addition mechanism to form small particles, which can be called as primary particles. Once these primary particles have been formed, they will aggregate with one another to form larger particles. This aggregation process will stop once a stable size of particles has been reached. The aggregation process could be facilitated by Brownian motion, Van der Waals forces, or change in the pH of the solution such that the surface potential of primary particles approaches its isoelectric point. Such growth mechanism has also been observed for preparation of monodispersed silica [15] and gold particles [16].

As mentioned previously, the size of the particles changes with dysprosium ion concentration, which suggests that there is a size selection process during the aging. The size selection mechanism by this model involves how the primary particles interact with one another and the stability of the formed particles. The stability of the particles can be related to its surface potential such there is electrostatic barrier to prevent further attachment of primary particles. In our system, there is strong relationship between the surface potential and dysprosium ion concentration. Rare earth carbonate particles precipitated by urea has an isoelectric point (IEP) about pH 7.2 [8]. In our precipitation, the dysprosium particles were precipitated at pH 4.0–5.5, which suggest that the particles were positively charged in this pH range. Since dysprosium ions have a positive charge, it appears that the surface potential of the particles increased with increases in dysprosium ion concentration from 0.005 M to 0.020 M, which in turn led to smaller particle size.

However, the importance of the surface potential, since the growth by aggregation mechanism is also determined by primary particle interactions or collisions. As dysprosium ion concentration increases further from 0.020 M to 0.100 M, the effect of primary particle collisions is larger than increase in the surface potential, such the particles grow to larger size at higher dysprosium ion concentration. One could also observe effect of particle collisions in a stronger agglomeration of the particles in Fig. 3(d) and (e). Therefore, in conclusion, there

should be a balance between primary particles collision process and stabilization process of the resulting particles during precipitation, such one can retain spherical morphology, small particle size, and narrow particle size distribution.

4 Conclusion

In this paper, homogeneous precipitation technique using urea was reported for preparing Dy₂O₃ nanoscale particles at low processing temperatures at large (liters) lab scale. The as-precipitated particles have an amorphous microstructure, which can be converted into pure cubic dysprosium oxide by heating in air at 700°C for 2 h without further particle growth. Dysprosium ions concentration was shown to have a significant effect on size and size distribution of the particles. This effect could be related to their growth mechanism, namely the aggregation mechanism. Depending on the dysprosium ion concentration, uniform particles with a size ranging from 100–200 nm were successfully synthesized.

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