

Structural and Optical properties of CTAB assisted Dy₂O₃ nanoparticles prepared by co-precipitation route

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Abstract

CTAB assisted Dy₂O₃ nanoparticles were prepared by co-precipitation route and the sample was calcined to 500°C. The calcined nanoparticles were investigated under structural and optical property studies. XRD results confirmed the phase pure cubic formation of Dy₂O₃ nanoparticles. TEM images showed the calcined nanoparticles were in nano regime. The composition and functionalization of the samples were traced using FTIR studies. The role of starting material and surfactant on the formation of Dy₂O₃ nanoparticles was discussed. The calcined nanoparticles showed strong UV absorption properties below 400nm which could be a promising candidate for UV blocking materials.

Keywords: nanoparticles, CTAB, Dy₂O₃, structural, optical

1. Introduction

Dy₂O₃ is considered as one of the stable binary rare earth oxides in which the rare earth ions hold typically a trivalent state. As it is insoluble and thermally stable, it is one of the promising materials to be used for optical and laser related applications [1–3]. In addition to that, Dy₂O₃ is known for its structural and optical properties raised because of its 4f electrons.

Numerous attempts were made on synthesizing and characterizing Dy₂O₃ nanoparticles and nanostructures to reveal its functional properties. Xu et al. have successfully prepared Dy(OH)₃ and Dy₂O₃ nanotubes by hydrothermal method[4]. Sonochemical route is employed by M. Salavati-Niasari et al. for the preparation of Dy₂(CO₃)₃ nanoparticles followed by the conversion Dy(OH)₃ nanotubes to Dy₂O₃ nanoparticles [5]. Apart from nitrates and chlorides, Song et al. adopted soft chemical route to synthesize dysprosium hydroxide and oxide nanorods from bulk Dy₂O₃ [6]. We have already reported the structural and photoluminescence property changes happening on HMT passivated Dy₂O₃ nanoparticles treated upto 600°C [7]. All these methods yield the less quantity of the product and take a lot of time.

The present investigation details about the preparation of Dy₂O₃ nanoparticles by coprecipitation route from bulk dysprosium oxide and sodium hydroxide as starting materials and Cetyl trimethyl ammonium bromide (CTAB) as surfactant. The prepared Dy₂O₃ nanoparticles were subjected to calcine to 500°C and the sample was characterized with structural and optical property studies.

2. Headings and Footnotes

2.1 Materials synthesis

Dysprosium nitrate solution was prepared by treating bulk Dy₂O₃ particles with concentrated nitric acid (5mL). 0.14g of Sodium hydroxide (NaOH) was dissolved in 100ml of deionized water with CTAB (0.01M) under constant stirring. The latter solution was added drop wise to the dysprosium nitrate solution, till the solution started precipitated under vigorous stirring. The precipitate was washed multiple times with distilled water and ethanol, dried at 70°C for 8 h.

2.1 Materials characterization

XRD pattern was recorded using a Bruker D8 Advance X-ray diffractometer using Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range from 20° to 70°. JOEL JEM-200CX was used to record TEM images operated at 200 kV. Perkin-Elmer spectrum spectrometer was used to study FTIR spectrum in the range 500–4000 cm⁻¹. PG Instruments Inc. T90+ spectrophotometer was used to record UV-vis absorption spectrum in the range between 200 and 500 nm. Perkin-Elmer spectrophotometer was used to carry out photoluminescence studies in the range of 525 to 650 nm.

3. Results and Discussion

3.1 Structural

The XRD pattern for 500°C calcined Dy₂O₃ nanoparticles is depicted in Figure 1. The XRD pattern confirms the formation of Dy₂O₃ with phase pure cubic structure (JCPDS # 86-1327). The XRD peak broadening in all the lattice planes is broad, indicating that the calcined particles are in nano regime. The average crystalline size of the calcined Dy₂O₃ is calculated as 12 nm using Debye Scherer equation.

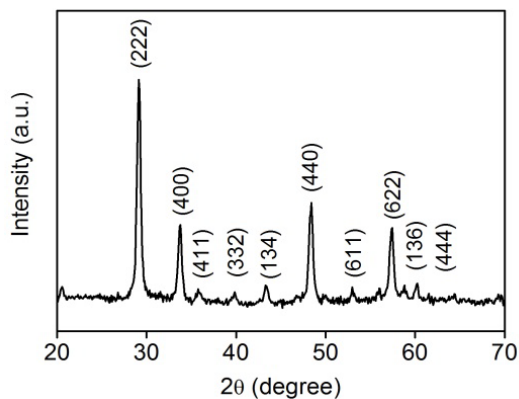


Figure 1 (a) XRD pattern of 500°C calcined Dy₂O₃ nanoparticles.

3.2 Morphological

TEM images of Dy₂O₃ nanoparticles calcined at 500°C are shown in Figure 2. From the images (a) and (b), it is observed that the particles are solid, spherical and identical in shape with narrow size distribution. The particle size estimated from TEM images are larger than the crystallite sized obtained from X-ray peak-broadening analysis.

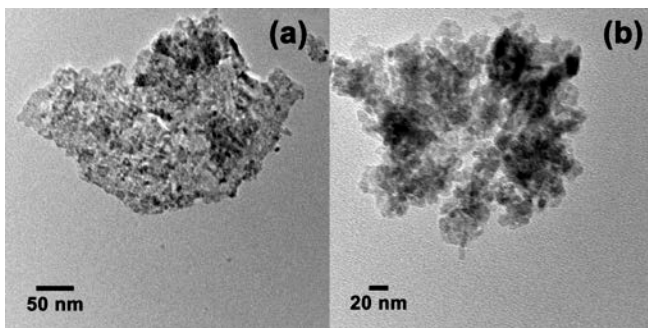
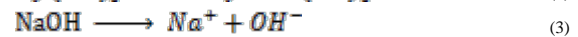
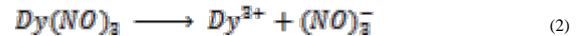
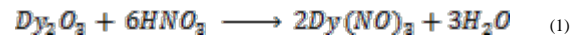


Figure 2 (a) and (b) TEM images of 500°C calcined Dy₂O₃ nanoparticles.

3.3 Formation Mechanism

By considering the characterization results, a possible reaction mechanism is detailed. When the bulk Dy₂O₃ is treated in Conc. Nitric acid, Dy₂O₃ is decomposed in to Dy³⁺ and reacts with NO³⁻ and forms Dy(NO)₃.



Upon calcining the sample at 500°C, the phase transformation occurred from Dy(OH)₃ to Dy₂O₃ as per the following equation:



The CTAB won't participate in the reaction but acts as template in the coprecipitation process.

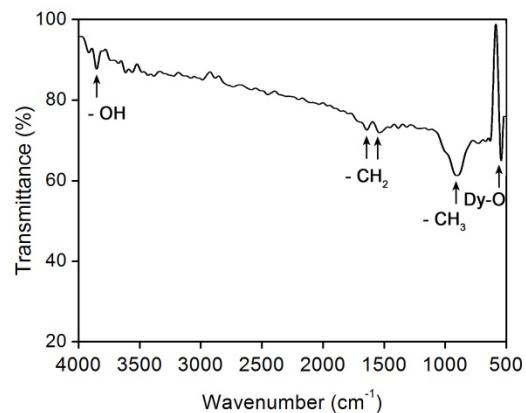


Figure 3 (a) FTIR spectrum of 500°C calcined Dy₂O₃ nanoparticles.

3.4 FTIR

FTIR spectrum (Figure 3) of Dy₂O₃ samples calcined at 500°C shows the traces of peak at 3858 cm⁻¹ is corresponding to the bending and stretching vibration of O-H bond. It is attributed due to the physically absorbed water molecules on the calcined sample. The peaks at 1640 and 1536 cm⁻¹ are attributed due to the deformation of –CH₂ and –CH₃ symmetric stretching vibrations of the surfactant. The methylene chains present in CTAB are the reasons for the appearance of doublet peaks at 1045 and

900 cm^{-1} [9]. The spectrum also exhibits a broad band at 536 cm^{-1} which is due to the Dy–O mode.

3.5 UV-vis absorption

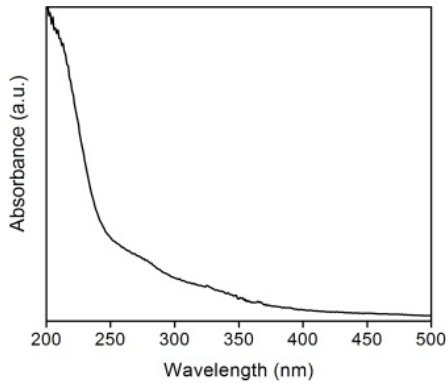


Figure 4 UV-vis absorption spectrum of 500°C calcined Dy_2O_3 nanoparticles.

From the Figure 4, an intense absorbance peaks positioned well-below in the ultraviolet region is obtained for 500°C calcined Dy_2O_3 nanoparticles. The spectrum shows a strong blue shift with respect to the bulk Dy_2O_3 which is also clear evidence that the particles are in nano regime. Since the entire absorbance of the sample happens within 400nm of ultraviolet region, the calcined Dy_2O_3 sample could be a promising candidate for UV blocking materials.

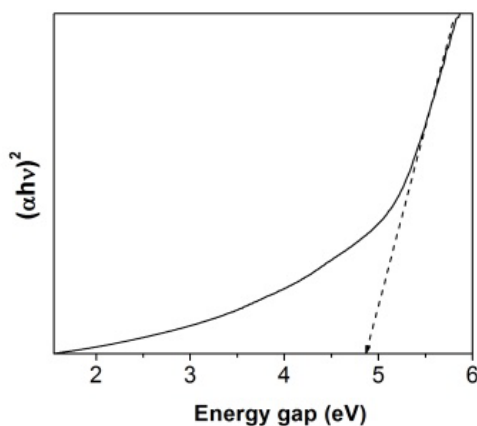
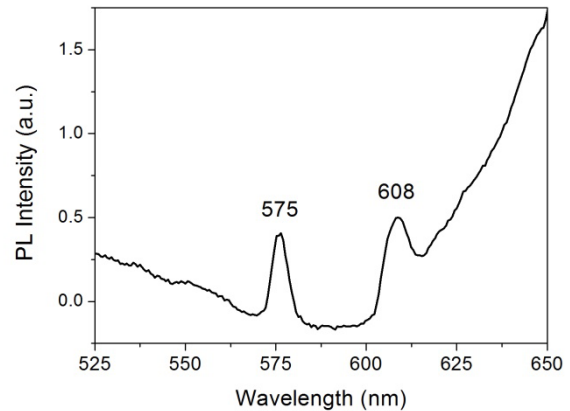


Figure 5 plot of $(\alpha h\nu)^2$ versus eV of 500°C calcined Dy_2O_3 nanoparticles.

In the Figure 5, the plot of $(\alpha h\nu)^2$ versus energy gap shows that the bandgap 4.9 eV is larger than the bulk Dy_2O_3 , which is attributed to the Dy_2O_3 particles in nano regime.

Figure 6 PL spectrum of 500°C calcined Dy_2O_3



nanoparticles.

3.6 Photoluminescence

Among the rare earth element series, Dy^{3+} is known for its white light emission. It is originated from the electron transition happening within the 4f shell. The PL spectrum (Figure 6) for calcined sample at 500°C show two distinct emissions at 575 nm (yellow) and at 608 nm (red). These two emissions are attributed to the intraband transition happened within Dy^{3+} energy bands which are originated from the same excitation wavelength of 450 nm [10].

4. Conclusions

Coprecipitation route was employed for the preparation of Dy_2O_3 nanoparticles using CTAB as template. The sample attained its phase pure cubic crystallinity on calcining at 500°C which was confirmed from XRD results. The average particle size calculated from the peak broadening pattern of calcined sample is ~ 12 nm. FTIR results confirmed the material formation of Dy_2O_3 nanoparticles along with the traces of CTAB as template. The optical property studies showed the size dependent property by means of blue-shifted UV absorption peak towards shorter wavelength. Since the UV absorption of the sample fell below UV range, it could be used as UV blocking materials. The two distinct white light emissions at 575 and 608 nm show that it could be a promising material as a white light phosphor.

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