Facile hydrothermal and novel preparation of nanostructured Ho_2O_3 for photodegradation of eriochrome black T dye as water pollutant

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Abstract

$\text{Ho}(\text{OH})_3$ nanostructures were synthesized via a new facile hydrothermal reaction between $\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and tetraethylenepentamine (tepa) as novel precipitator in presence of bis-(2-hydroxy-1-naphthaldehyde)-o-phenylenediamine Schiff base compound as new capping agent. Pure Ho_2O_3 nanostructures were prepared by thermal conversion of $\text{Ho}(\text{OH})_3$ nanostructures in air at 600°C for 4h. The as-obtained nanostructured samples were characterized by field emission scanning electron microscopy (FESEM), energy dispersive X-ray microanalysis (EDX), X-ray diffraction (XRD), transmission electron microscopy (TEM), UV–vis diffuse reflectance spectroscopy, and Fourier transform infrared (FT-IR) spectroscopy. Effects of reaction temperature, reaction duration and Schiff base compound as new capping agent on the shape and particle size of the final samples were studied. It was found that the particle size and shape of the samples could be controlled by setting these factors. The photocatalytic behavior of as-obtained Ho_2O_3 nanostructures was also examined by photodegradation of eriochrome black T dye as water pollutant.

Keywords: Nanostructures; Electron Microscopy; Optical Properties; Ho_2O_3 ; Photocatalytic properties

1. Introduction

The preparation and characterization of the nanoscale materials has been the focus of new scientific and industrial research because of their excellent and unique characteristics [1-4]. Among these nanoscale materials, Ho_2O_3 as a significant rare earth metal oxide exhibit noteworthy and attractive electrical and optical characteristics and have found excellent and unique usages in the field of pyrolysis catalysts as well as wavelength-calibration instruments [5,6]. Until now, thermal decomposition way has been introduced to synthesize Ho_2O_3 [7-10]. Control over particle size and morphology of the nanoscale materials is a novel challenge in the scientific and industrial research [11-14]. Among the various procedures developed for the preparation of the nanoscale materials, hydrothermal process has been proven to be a simple and reliable route, particularly to control the particle size and morphology of the nanoscale materials.

Herein, we report a new facile hydrothermal approach to prepare $\text{Ho}(\text{OH})_3$ nanostructures from the reaction between $\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and tetraethylenepentamine (tepa) as novel precipitator in presence of 2-hydroxy-1-naphthaldehyde)-o-phenylenediamine Schiff base compound as new capping agent. Moreover, Ho_2O_3 nanostructures can be prepared by calcination of as-synthesized $\text{Ho}(\text{OH})_3$ nanostructures at 600 °C. This is first attempt on the hydrothermal preparation of $\text{Ho}(\text{OH})_3$ and Ho_2O_3 nanostructures using tepa as novel precipitator in presence of bis-(2-hydroxy-1-naphthaldehyde)-o-phenylenediamine Schiff base compound as new capping agent. Utilizing of the new compounds may be beneficial and open a novel route for size and shape-controlled preparing of the nanoscale materials. This approach is cost-effective and facile; and suggests a reproducible route to the preparation of other rare earth metal hydroxides and oxides. We have examined the influences of reaction temperature, reaction duration and Schiff base compound as new capping agent on the shape and particle size of the final samples.

2. Materials and methods

2.1. Materials and characterization

All the chemicals employed for the preparation of $\text{Ho}(\text{OH})_3$ and Ho_2O_3 nanostructures including holmium nitrate ($\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), liquor ammonia solution containing 25% ammonia, methanol, tetraethylenepentamine (tepa), 2-Hydroxy-1-naphthaldehyde, o-phenylenediamine were purchased from Merck Company and were employed as received. The UV-vis diffuse reflectance spectrum of the as-synthesized Ho_2O_3 nanostructures was obtained on a UV-vis spectrophotometer (Shimadzu, UV-2550, Japan). Powder X-ray diffraction (XRD) patterns of as-produced $\text{Ho}(\text{OH})_3$ and Ho_2O_3 nanostructures were collected from a Philips diffractometer employing X'PertPro and the monochromatized Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). Morphological characteristics of the $\text{Ho}(\text{OH})_3$ and Ho_2O_3 samples were examined by a Tescan mira3 microscope (FESEM). GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. Thermogravimetric-differential thermal analysis (TG-DTA) was performed by a thermal gravimetric analysis instrument (Shimadzu TGA-50H) with a heating rate of $10^\circ \text{C min}^{-1}$ and flow rate of 20.0 ml min^{-1} . Fourier transform infrared spectra of the as-prepared samples were obtained employing KBr pellets on an FT-IR spectrometer (Magna-IR, 550 Nicolet) in the $400\text{--}4000 \text{ cm}^{-1}$ range. The energy dispersive spectrometry (EDS) analysis was examined by Tescan mira3 microscope. TEM micrographs of as-obtained Ho_2O_3 nanostructures were obtained on a JEM-2100 with an accelerating voltage of 200 kV equipped with a high resolution CCD Camera.

2.2. Preparation of bis-(2-hydroxy-1-naphthaldehyde)-o-phenylenediamine Schiff base compound

In order to synthesize the Schiff base compound, 0.1 mol of 2-Hydroxy-1-naphthaldehyde dissolved in methanol (50 ml) was added drop-wise to the o-phenylenediamine solution (0.05 mol in 50 ml of methanol). The precipitate of the Schiff base compound was prepared after refluxing the mixture for 3 h, separating by filtering, washing and air-drying. It was ultimately recrystallized from methanol.

2.3. Preparation of $\text{Ho}(\text{OH})_3$ and Ho_2O_3 nanostructures

Ho(OH)₃ and Ho₂O₃ nanostructures were prepared by a new facile hydrothermal approach. To synthesize Ho(OH)₃, in a typical experiment, 0.1 g of Ho(NO₃)₃.6H₂O was dissolved in 25 ml distilled water. The pH of the Ho(NO₃)₃.6H₂O solution was adjusted to 12 by drop-wise adding tepa solution under constant stirring. After 1/4 h stirring the resultant solution was transferred in a 200 mL Teflon-lined stainless steel autoclave and maintained at 160 °C for 12 h. The final precipitate was filtered, washed out with ethanol and distilled water for three times, air-dried (sample no. 1). For examining the influence of the capping agent, a certain quantity of the capping agent was dissolved in 5 ml methanol and added to Ho(NO₃)₃.6H₂O solution before adding tepa solution. The influence of the reaction temperature, reaction duration and Schiff base compound as new capping agent on the particle size and shape of the samples were also investigated (Table 1). To prepare Ho₂O₃ nanostructures, the as-obtained Ho(OH)₃ nanostructures (sample no. 6) was calcined at 600 °C for 4 h. Schematic diagram of the synthesis of Ho(OH)₃ and Ho₂O₃ nanostructures (sample nos. 6 and 8) is demonstrated in Scheme 1.

2.4. Photocatalytic experiment

The photocatalytic behavior of as-prepared Ho₂O₃ nanostructures (sample no. 8) was examined by applying eriochrome black T dye solution. The solution containing 1 mg of the eriochrome black T and 40 mg of the as-synthesized Ho₂O₃ nanostructures in the quartz reactor was applied to carry out the photocatalytic experiment. After aerating for 1/2 h, the mixture was subjected to the irradiation of the UV light from the 400 W mercury lamps. The quantity of eriochrome black T dye was checked on the basis of its UV–visible absorption value.

3. Results and discussion

In order to determine the synthesis of the bis-(2-hydroxy-1-naphthaldehyde)-o-phenylenediamine Schiff base compound as new capping agent, FT-IR analysis was performed. Fig. 1a exhibits the infrared spectrum of the capping agent. The bands located at 1615 and 1321 cm⁻¹ in the FT-IR spectrum of the capping agent (Fig 1a) are attributable to the ν(C=N) of the azomethines and ν(Ar-O) of the phenolic hydroxyl substituent, respectively,

which proves the synthesis of the capping agent [15]. As mentioned before, in this research $\text{Ho}(\text{OH})_3$ nanostructures were prepared via a novel facile hydrothermal reaction between $\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and tetraethylenepentamine (tepa) as new precipitator in presence of bis-(2-hydroxy-1-naphthaldehyde)-o-phenylenediamine Schiff base compound as novel capping agent. Pure Ho_2O_3 nanostructures were synthesized by thermal conversion of $\text{Ho}(\text{OH})_3$ nanostructures in air at 600°C for 4h. In this hydrothermal approach, the employed Schiff base compound with high steric hindrance influence plays capping agent role to control the grain size and shape. Synthesis of $\text{Ho}(\text{OH})_3$ at 160°C for 12 h has been selected as a basic reaction in this study and the influences of the reaction temperature, reaction duration and Schiff base compound as new capping agent on the grain size and shape of the samples have been evaluated by FESEM technique. The reaction duration effect on the shape and grain size of the $\text{Ho}(\text{OH})_3$ was investigated. For this aim, three reactions were performed during 12, 16 and 20 h (sample nos. 1-3). The FESEM images indicate that the relatively homogeneous spherical nanoparticles, less uniform spherical nanostructures and not uniform spherical nanostructures with large particle size are prepared at 12, 16 and 20 h, respectively. It can be observed that the size becomes larger and the quantity of homogeneous $\text{Ho}(\text{OH})_3$ nanostructures decreases by prolonging the reaction duration from 12 to 20 h (Fig. 2a-c). This occurred enhancement in grain size can be corresponding to the Ostwald ripening process. Results of FESEM indicate that 12 h is the most favorable reaction duration for preparing nanoparticles with relatively homogeneous spherical shape (Fig. 2a), hence other samples were synthesized at this reaction duration.

Furthermore, the reaction temperature effect on the particle size and shape of the $\text{Ho}(\text{OH})_3$ was examined. The reaction temperature was changed to 120 and 200°C and the samples were synthesized at 12 h (sample nos. 4 and 5). FESEM images of the $\text{Ho}(\text{OH})_3$ samples obtained at 120 and 200°C were taken and depicted in Fig. 3a and b. As depicted in Fig. 3a and b, when the reaction temperature was changed to 120 and 200°C , not uniform spherical nanostructures and irregular sphere-like nanostructures with large particle size were prepared, respectively. It seems that at 120°C temperature, nucleation stage overcome to growth stage because this

temperature for growth don't suitable and not uniform spherical nanostructures were achieved. It seems that when reaction temperature altered from 160 to 200 °C, the relatively homogeneous spherical $\text{Ho}(\text{OH})_3$ nanoparticles with small size which were prepared at 160 °C, agglomerated and fused to each other and thus the size enhances. According to the FESEM results, 160 °C is the best reaction temperature for relatively homogeneous spherical shape with small grain size (Fig. 2a).

The effect of the bis-(2-hydroxy-1-naphthaldehyde)-o-phenylenediamine Schiff base compound as new capping agent on the shape and grain size of the $\text{Ho}(\text{OH})_3$ was also studied. FESEM image of the $\text{Ho}(\text{OH})_3$ (sample no. 6) prepared by applying the new capping agent was taken and depicted in Fig. 4a. By applying the bis-(2-hydroxy-1-naphthaldehyde)-o-phenylenediamine, very uniform sphere-like nanoparticles are synthesized (Fig. 4a). Schiff base compound with high steric hindrance effect can act as a capping agent and limit the size of the $\text{Ho}(\text{OH})_3$ nanoparticles by protecting them from additional aggregation (Scheme. 1). It can be clearly seen that applying bis-(2-hydroxy-1-naphthaldehyde)-o-phenylenediamine as a capping agent results in very uniform spherical nanoparticles formation (Fig. 2a and 4a). Hence, an excellence of utilizing bis-(2-hydroxy-1-naphthaldehyde)-o-phenylenediamine in presence of tepa is that it leads to synthesize nanostructured $\text{Ho}(\text{OH})_3$.

The influence of the tepa on the shape and size of the $\text{Ho}(\text{OH})_3$ was evaluated. FESEM image of the $\text{Ho}(\text{OH})_3$ (sample no. 7) as blank sample synthesized by applying NH_4OH in the presence of bis-(2-hydroxy-1-naphthaldehyde)-o-phenylenediamine as a capping agent was taken and illustrated in Fig. 4b. Fig. 4b depicts the high agglomerated particle-like structures. The tepa as precipitator that has high steric hindrance influence can play co-capping agent role to control the shape and size by hindering the aggregation of the $\text{Ho}(\text{OH})_3$ nanoparticles (Scheme. 1). It is apparent that the applying tepa in presence of bis-(2-hydroxy-1-naphthaldehyde)-o-phenylenediamine brings about $\text{Ho}(\text{OH})_3$ nanoparticles with homogeneous spherical shape are prepared (Fig. 4a).

According to the FESEM results, applying tetraethylenepentamine (tepa) as novel precipitator in presence of bis-(2-hydroxy-1-naphthaldehyde)-o-phenylenediamine Schiff base compound as new capping agent, reaction duration = 12 h and reaction temperature = 160 °C are the optimum condition for homogeneous spherical $\text{Ho}(\text{OH})_3$ nanoparticles with small grain size (Fig. 4a). To prepare Ho_2O_3 nanostructures (sample no. 8), the as-prepared $\text{Ho}(\text{OH})_3$ nanostructures in the optimum condition (sample no. 6) was calcined at 600 °C for 4 h. Fig. 4c depicts FESEM image of the Ho_2O_3 nanostructures (sample no. 8). The sample no. 8 reveals very uniform sphere-like Ho_2O_3 nanoparticles.

In order to evaluate the detailed morphological features of the as-prepared Ho_2O_3 sample (sample no. 8) TEM images were taken. Fig 5a-c depicts TEM images of Ho_2O_3 sample is prepared by calcining $\text{Ho}(\text{OH})_3$ nanostructures (sample no. 6), demonstrating quasi-spherical shape with size in the range of 12-35 nm.

Fig. 1b and c exhibits the infrared spectra of the as-prepared $\text{Ho}(\text{OH})_3$ (sample no. 6) and Ho_2O_3 nanostructures (sample no. 8), respectively. FT-IR spectrum of the $\text{Ho}(\text{OH})_3$ nanostructures (sample no. 6) is seen in Fig 1b. The bands appear at 3606 and 678 cm^{-1} in Fig 1b are attributable to the O–H stretching vibration of $\text{Ho}(\text{OH})_3$ and the O–H bending vibration of Ho–O–H, respectively [16]. The (C-H) bending vibration peak at 1383 cm^{-1} in Fig 1b illustrates the presence of tepa (Fig. 1b). Besides the peaks centered at 836, 992, and 1505 cm^{-1} can be ascribed to carbonate group [17]. It seems that the $\text{Ho}(\text{OH})_3$ formed at the hydrothermal approach has high affinity to the atmospheric CO_2 , hence transforming to the hydroxy-carbonate phase during washing stages and very small amount of the hydroxy-carbonate phase forms. In the case Ho_2O_3 nanostructures (sample no. 8), the peak located at 3433 cm^{-1} is corresponding to the $\nu(\text{OH})$ stretching of the surface adsorbed water molecules [2]. The absorption peak at 1527 cm^{-1} is attributed to the ν_3 mode of CO_3^{2-} [19]. The characteristic peaks of the Ho_2O_3 centered at 560 and 500 cm^{-1} [18] (Fig. 1c).

Thermal gravimetric analysis (TGA) was carried out to examine the thermal stability of the as-synthesized $\text{Ho}(\text{OH})_3$ nanostructures (sample no. 6). The TGA curve of the as-obtained $\text{Ho}(\text{OH})_3$ nanostructures is indicated in Fig. 6. It can be seen that one mass loss step happened in the 25–600 °C (indicating 11.53 % mass loss) possibly corresponds to the chemical conversion: $2 \text{Ho}(\text{OH})_3 \rightarrow \text{Ho}_2\text{O}_3 + 3 \text{H}_2\text{O}$ [16] and the formation of Ho_2O_3 .

In order to characterize the crystalline structure of the as-prepared $\text{Ho}(\text{OH})_3$ (sample no. 6) and Ho_2O_3 nanostructures (sample no. 8), XRD patterns were taken and indicated in Fig. 7a and b. As seen in XRD pattern $\text{Ho}(\text{OH})_3$ (sample no. 6), all the diffraction peaks can be readily indexed to pure hexagonal $\text{Ho}(\text{OH})_3$ with P63/m space group (JCPDS 83-2040). All the diffraction peaks illustrated in Fig. 7b are well-matched to pure cubic Ho_2O_3 (JCPDS card 83-0932). The mean crystallite size of the as-prepared Ho_2O_3 nanostructures (sample no. 8) determined by the Scherrer formula [14] is 12 nm.

To determine the purity level and chemical composition of the as-produced Ho_2O_3 nanostructures (sample no. 8), EDS analysis was carried out. Fig. 8 reveals the EDS spectrum of the sample no. 8 (the position in which the EDS is detected on the FESEM image (Fig. 4c) using the yellow vector is shown). The EDS spectrum demonstrates that this produced sample containing Ho and O elements (Si and C signals are from the substrate). Hence, the obtained XRD, FT-IR, and EDS results indicate the high purity of the prepared Ho_2O_3 nanostructures in this research. The obtained FESEM, XRD and EDS results indicated that pure Ho_2O_3 nanoparticles with very uniform sphere-like were prepared via the new facile hydrothermal approach.

To evaluate the optical features and band gap (E_g) of as-synthesized Ho_2O_3 sample (sample no. 8), UV–vis diffuse reflectance spectrum was taken. Fig. 9a reveals the UV–vis diffuse reflectance spectrum of the Ho_2O_3 sample. The absorption bands at 292, 325, 419, 435, 493, 529, 561, 615 and 721 nm are observed in Fig. 9a. The E_g can be determined based on the absorption spectrum by employing Tauc's equation [4]. The E_g of the Ho_2O_3 sample (sample no. 8) can be calculated by extrapolating $(ah\nu)^2$ against $h\nu$ at $(ah\nu)^2 = 0$ [12,13] (Fig. 9b). The

energy gap value of the Ho_2O_3 sample (sample no. 8) determined to be 4.14 eV. According to the determined E_g value, the as-produced Ho_2O_3 sample can be employed as the photocatalyst material.

In this research, photooxidation of the eriochrome black T (anionic dye) as water contaminant under UV light was applied to evaluate the photocatalytic behavior of the as-obtained Ho_2O_3 sample (sample no. 8). Before starting the irradiation, the suspension was stirred vigorously for 30 min in dark to achieve adsorption/desorption equilibrium. Fig. 9c exhibits the result of the photocatalytic experiment. No eriochrome black T dye was practically broken down after 100 min in absence of the UV light or as-produced Ho_2O_3 sample (sample no. 8). According to this observed result, it can be deduced that the contribution of self-degradation was insignificant.

The possible mechanism of the photooxidation of eriochrome black T can be assumed as:

The percentage of eriochrome black T degradation was calculated as follows:

$$D.P.(t) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_0 and A_t are the absorbance quantity of eriochrome black T dye solution at before and after degradation by a UV–vis spectrometer, respectively. The eriochrome black T dye degradation was about 80% after 100 min illumination of UV light and the as-produced Ho_2O_3 sample (sample no. 8) indicated very good photocatalytic behavior. In the heterogeneous photocatalytic processes, there are the diffusion, adsorption and reaction stages. It has been shown that photocatalytic performance depends predominantly on the number of active sites available for the adsorption of contaminant molecules on the photocatalyst surface, the diffusion of reactants and products, and thus appropriate distribution of the pore. It seems that the very good photocatalytic behavior of the as-produced Ho_2O_3 sample (sample no. 8) can be owing to high number of active sites on the photocatalyst surface, appropriate distribution of the pore, very good hydroxyl amount and high separation rate of charge carriers [20, 21] (Scheme 1).

4. Conclusions

$\text{Ho}(\text{OH})_3$ nanostructures have been prepared through a new simple hydrothermal reaction between $\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and tetraethylenepentamine (tepa) as novel precipitator in presence of bis-(2-hydroxy-1-naphthaldehyde)-o-phenylenediamine Schiff base compound as new capping agent. Pure Ho_2O_3 nanostructures were prepared by thermal conversion of $\text{Ho}(\text{OH})_3$ nanostructures in air at 600°C for 4h. This investigation illustrates that the reaction temperature, reaction duration and Schiff base compound as new capping agent have a great influence on the shape and particle size of the final samples. In comparison to other similar studies, the current approach is novel, facile and is of low cost. When as-produced Ho_2O_3 was applied as photocatalyst, the percentage of the eriochrome black T dye degradation was about 80 after 100 min irradiation of UV light. This result suggests as-obtained Ho_2O_3 as desirable and noteworthy candidate for photocatalytic utilizations under UV light.

Acknowledgements

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Table 1 The synthesis conditions of the $\text{Ho}(\text{OH})_3$ and Ho_2O_3 nanostructures.

Sample No.	Reaction temperature (°C)	Reaction duration (h)	Capping agent	Precipitator	Figure of SEM images
1	160	12	-	Tepa	2a
2	160	16	-	Tepa	2b
3	160	20	-	Tepa	2c
4	120	12	-	Tepa	3a
5	200	12	-	Tepa	3b
6	160	12	+	Tepa	4a
7	160	12	+	NH_3	4b
^a 8	160	12	+	Tepa	4c

^a After calcination at 600 °C

Figure Captions:

Figure 1. FT-IR spectra of the capping agent (a), as-prepared $\text{Ho}(\text{OH})_3$ (sample no. 6) (b) and Ho_2O_3 nanostructures (sample no. 8) (c).

Figure 2. FESEM images of the $\text{Ho}(\text{OH})_3$ samples prepared at 160°C for (a) 12, (b) 16 and (c) 20 h.

Figure 3. FESEM images of the $\text{Ho}(\text{OH})_3$ samples synthesized at (a) 120°C and (b) 200°C for 12 h.

Figure 4. FESEM images of the $\text{Ho}(\text{OH})_3$ samples synthesized by applying the new capping agent in presence of tepa (a) and NH_3 (b) and FESEM image of the as-prepared Ho_2O_3 nanostructures (sample no. 8) (c).

Figure 5. (a-c) TEM images of the as-obtained Ho_2O_3 nanostructures (sample no. 8) at different scales.

Figure 6. TGA of the as-prepared $\text{Ho}(\text{OH})_3$ (sample no. 6).

Figure 7. XRD patterns of the as-prepared $\text{Ho}(\text{OH})_3$ (sample no. 6) (a) and Ho_2O_3 nanostructures (sample no. 8) (b).

Figure 8. EDS pattern of the as-prepared Ho_2O_3 nanostructures (sample no. 8).

Figure 9. UV-vis diffuse reflectance spectrum (a), plot to determine the band gap (b) of the Ho_2O_3 nanostructures (sample no. 8) and photocatalytic anionic dye (eriochrome black T) degradation of the sample no. 8 (c).

Scheme 1. Schematic diagram of the synthesis of $\text{Ho}(\text{OH})_3$ and Ho_2O_3 nanostructures (a) and reaction mechanism of eriochrome black T photodegradation over Ho_2O_3 nanostructures under UV light illumination (b).

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