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

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$Ho(OH)_3$ nanostructures were synthesized via a new facile hydrothermal reaction between $Ho(NO_3)_3{\cdot}6H_2O$ 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 $Ho(OH)_3$ nanostructures in air at 600 °C for 4 h. 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.

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 $Ho(OH)_3$ nanostructures from the reaction between $Ho(NO_3)_3{\cdot}6H_2O$ and tetraethylenepentamine (tepa) as novel precipitator in presence of 2-hydroxy-1-naphthaldehyde)-o-phenylene diamine Schiff base compound as new capping agent. Moreover, Ho_2O_3 nanostructures can be prepared by calcination of as-synthesized $Ho(OH)_3$ nanostructures at 600 °C. This is first attempt on the hydrothermal preparation of $Ho(OH)_3$ and Ho_2O_3 nanostructures using tepa as novel precipitator in presence of bis-(2-hydro xy-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 $Ho(OH)_3$ and Ho_2O_3 nanostructures including holmium nitrate ($Ho(NO_3)_3{\cdot}6H_2O$), liquor ammonia solution containing 25% ammonia, methanol, tetraethylenepentamine (tepa), 2-Hydroxy-1-naphthaldehyde, o-phenylenediamine were purchased from Merck Company and

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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 $Ho(OH)_3$ and Ho_2O_3 nanostructures were collected from a Philips diffractometer employing X'PertPro and the monochromatized Cu Ka radiation (l = 1.54 Å). Morphological characteristics of the $Ho(OH)_3$ 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 °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 400–4000 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 $Ho(OH)_3$ and Ho_2O_3 nanostructures

$Ho(OH)_3$ and Ho_2O_3 nanostructures were prepared by a new facile hydrothermal approach. To synthesize $Ho(OH)_3$, in a typical experiment, 0.1 g of $Ho(NO_3)_3{\cdot}6H_2O$ was dissolved in 25 ml distilled water. The pH of the $Ho(NO_3)_3{\cdot}6H_2O$ 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 $Ho(NO_3)_3{\cdot}6H_2O$ 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 Ho_2O_3 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 Ho_2O_3 nanostructures (sample nos. 6 and 8) is demonstrated in Scheme 1.

2.4. Photocatalytic experiment

The photocatalytic behavior of as-prepared Ho_2O_3 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 Ho_2O_3 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 $Ho(OH)_3$ nanostructures were prepared via a novel facile hydrothermal reaction between $Ho(NO_3)_3{\cdot}6H_2O$ 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 $Ho(OH)_3$ nanostructures in air at 600 °C for 4 h. 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 $Ho(OH)_3$ 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 $Ho(OH)_3$ 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 $Ho(OH)_3$ 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

Table 1
The synthesis conditions of the $Ho(OH)_3$ 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.

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