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Facile synthesis and enhanced photocatalytic activity of Sm(OH)$_3$ nanorods

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Abstract: Samarium hydroxide (Sm(OH)$_3$) nanorods with the enhanced photocatalytic activity to degrade RhB were prepared by a facile precipitation method. The phase composition, morphology and optical properties of the as-prepared sample were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and UV–vis diffuse reflectance spectroscopy. Results show that the as-prepared Sm(OH)$_3$ nanocrystallites are hexagonal phase with the rod-like microstructure, which exhibit strong absorption ability of UV light. Moreover, the low temperature precipitation synthesis introduced an amorphous layer on the Sm(OH)$_3$ nanorods. The amorphous surface layer was confirmed to have a positive impact on improving the photocatalytic activity of Sm(OH)$_3$ nanorods.

Keywords: Samarium hydroxide; Nanocrystalline materials; Microstructure; Photocatalytic activity

1. Introduction

Lanthanide compounds have aroused considerable interest over the past several years because of their novel optical [1], electronic [2] and chemical [3] properties arising from their 4f electrons. Lanthanide hydroxides as a kind of typical functional lanthanide compounds have caused the growing exploration [4–5]. A number of synthesis techniques have been developed to prepare 1D nano/microsized inorganic materials, such as hydrothermal technique [6], sol–gel route [7] and chemical conversion method [8]. Moreover, hydrothermal process [9] and homogeneous precipitation method [10] were widely used to prepare 1D lanthanide hydroxides, which may be due to their facile,

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high efficiency and low cost. Sm(OH)$_3$ as one of the promising lanthanide hydroxides materials, the hexagonal prism–like Sm(OH)$_3$ nanocrystallites have been prepared for the photocatalytic degradation of Rhodamine B (RhB) by hydrothermal process [11], in our previous research. To deep investigate the property of Sm(OH)$_3$ nanocrystallites, the facile and controllable synthesis methods will play an important role in it.

In the present work, a low–temperature precipitation method was proposed to prepare Sm(OH)$_3$ nanorods efficiently. Firstly, the phase composition and microstructure of the as–prepared sample were investigated. Secondly, the enhanced photocatalytic activity of the sample was successfully achieved. Finally, the reason for the enhanced photocatalytic activity of the as–prepared sample was analyzed.

2. Experiment

Sm(NO$_3$)$_3$·6H$_2$O and diethylenetriamine (DETA) were of analytical reagent (A.R.) grade and used without further purification. First, 1.5 mmol Sm(NO$_3$)$_3$·6H$_2$O was dissolved in 60 ml distilled water, then 0.28 ml DETA was added dropwise with magnetic stirring to form the precursor solution. The precursor solution was transferred to a 100 ml flask and thermal aging in 60 °C water–bath for 2 h after stirring for 1 h. Subsequently, the product was centrifuged and washed with distilled water and anhydrous ethanol for several times, finally dried in the vacuum drying oven at 60 °C for 3 h. The weight of the dried product was measured through a precision balance with sensitivity of ± 0.1 mg. The reaction yield was calculated to be 84.85% by Eq.(1), which means the raw materials can be fully utilized in the reaction.

\[ \text{Reaction yield} (\%) = \left( \frac{m}{m_0} \right) \times 100\% \]  

Where $m$ represents actual yield and $m_0$ represents theoretical yield.

The crystalline microstructure of the as–prepared powder was characterized by a powder X–ray diffraction (XRD, Rigaku D/max–2000) with Cu Kα radiation ($\lambda$=0.15406 nm) at 40 kV and 40 mA in the 2θ range of 10°–60°. The morphology of the sample was observed by field emission scanning electron microscopy (FE-SEM, Hitachi S–4800, Acceleration voltage: 3 kV). High–resolution transmission electron microscopy (HRTEM operated at 200 kV) was taken by field emission...
transmission electron microscopy (FE–TEM, American FEI Tecnai G² F 20 S–TWIN). UV–vis diffuse reflectance spectrum of the sample was measured by Shimadzu UV–2450 UV–vis spectrophotometer.

Photocatalytic activities of the prepared Sm(OH)$_3$ nanorods were evaluated by photocatalytic degradation of 5 mg·L$^{-1}$ Rhodamine B, Methyl orange and Neutral red aqueous solution. The photocatalytic activity tests were carried out by employing a BL–GHX–V photocatalytic reactor (Xi’an, BILOBN, Co. Ltd.) with a 500 W mercury lamp as UV light source. The loading amount of catalysts was 1.0 g·L$^{-1}$. Before illumination, the suspensions of dyes with catalysts were magnetically stirred in the dark for 30 min, after dispersing in an ultrasonic bath for 5 min, to ensure the establishment of an adsorption–desorption equilibrium between catalysts and dyes. Then, the solution was exposed to a 500 W mercury lamp under magnetic stirring. By the irradiation time prolong, 6 ml of the solution was collected by centrifugation each 5 min. The concentrations of the remnant dyes in the collected solution were monitored by UV–vis spectroscopy (Unico UV–2600) at 553 nm [11]. In the process of photocatalytic reaction, the degradation efficiency of dyes was calculated by Eq. (2):

$$\text{Degradation efficiency} = \left(1 - \frac{C_t}{C_0}\right) \times 100\%$$  \hspace{1cm} (2)

Where $C_0$ represents the initial concentration of dye aqueous solution and $C_t$ represents the concentration of dye aqueous solution after different minutes of UV irradiation.

3. Results and discuss

3.1. Phase analysis

![Fig.1. XRD pattern of the as–prepared Sm(OH)$_3$ nanocrystallites](image-url)
The XRD pattern of the sample prepared by a facile precipitation method is shown in Fig.1. The XRD peaks of the as-prepared sample can be finely indexed to the hexagonal Sm(OH)$_3$ (JCPDS No.83–2036). No characteristic peaks of impurities can be detected, indicating that the pure phase of Sm(OH)$_3$ was achieved under the current synthetic condition.

3.2. Morphological analysis

Fig.2 (a) shows the SEM image of the Sm(OH)$_3$ nanocrystallites prepared by a facile precipitation method. It can be obviously observed that the microstructure of the prepared sample is rod-like and the average length of the nanorods is about 300 nm. Fig.2 (b) exhibits the high magnification TEM image of an individual Sm(OH)$_3$ nanorod. The lattice spacing of $d_{(200)} = 0.276$ nm and $d_{(110)} = 0.318$ nm were clearly observed from Fig.2 (b), which means that the prepared Sm(OH)$_3$ nanorods are polycrystal. The Sm(OH)$_3$ nanorods may be composed by numerous Sm(OH)$_3$ crystalline subunits with various orientations. Moreover, the high magnification TEM image of an individual Sm(OH)$_3$ nanorod shows that the prepared Sm(OH)$_3$ nanorods were wrapped with a layer of amorphous particles. The layer of amorphous particles was only found on the Sm(OH)$_3$ nanorods prepared by precipitation method, by comparing with the high-resolution TEM image (Fig.S1b) of the well crystallized Sm(OH)$_3$ nanorods prepared by hydrothermal method.

3.3. Optical and photocatalytic properties

UV–vis diffuse spectroscopy was used to characterize the optical absorbance of the as-prepared Sm(OH)$_3$ nanorods. Fig.3 presents the direct band-gap energy estimated from a plot of $(\alpha h\nu)^2$ vs. photo
energy ($h\nu$) according to the K–M model. The optical band–gap of Sm(OH)₃ nanorods is calculated to be 4.25 eV. Moreover, the UV–vis diffuse spectroscopy of the as–prepared Sm(OH)₃ nanorods is shown in Fig.3 (Inset), in which Sm(OH)₃ nanorods exhibit the strong band edge absorption in the region between 200–300 nm. Combine the good ultraviolet absorbing property and the unique properties of lanthanide compounds [1–3], the photocatalytic activity of Sm(OH)₃ nanorods was investigated [12].

![Graph showing the relationship between $(ah\nu)^2$ and photon energy](image)

**Fig.3.** The relationship between $(ah\nu)^2$ and photon energy (Inset: UV–vis diffuse reflectance spectrum of Sm(OH)₃ nanorods)

The degradation of Rhodamine B (RhB), Methyl orange (MO), Neutral red (NR) were used to evaluate the photocatalytic activity of the as–prepared Sm(OH)₃ nanorods, corresponding photocatalytic results were shown in Fig.4(a). The photocatalytic results exhibit that Sm(OH)₃ nanorods can mainly degrade RhB and Neutral red in only 30 min, which degradation efficiency reaches 94.3% and 97.3%, respectively. This means the prepared Sm(OH)₃ nanorods have good responsiveness to the cationic (RhB) and neutral (Neutral red) dyes. However, the degradation of Neutral red is also very quick without photocatalysts, which affect the proper evaluation of the as–prepared Sm(OH)₃ nanorods. Therefore, the degradation of RhB was used to compare the photocatalytic activity of the as–prepared Sm(OH)₃ nanorods with other products.
The photocatalytic results of RhB degraded by different kinds of photocatalysts were shown in Fig. 4(b). The adsorption test shows that the adsorption–desorption equilibrium between Sm(OH)₃ nanorods and RhB was achieved after the dark stirring for 30 min. The blank test demonstrates that the degradation of RhB is very slow without photocatalysts. When the prepared Sm(OH)₃ nanorods were used as photocatalyst, the RhB absorption peak decreases quickly (Fig.S2.) as irradiation time prolongs. The photocatalytic results exhibit that the as–prepared Sm(OH)₃ nanorods can mainly degrade RhB in only 30 min with the degradation efficiency reaches 94.3%. Whereas, the degradation efficiency of the fully crystallized Sm(OH)₃ nanocrystallites prepared by hydrothermal process only reaches 76.5%. These results show that the Sm(OH)₃ nanorods prepared by precipitation method exhibit enhanced photocatalytic activity to degrade RhB.

![Fig. 4. (a) Photocatalytic results of RhB, MO and NR degraded by Sm(OH)₃ nanorods](image)

(b) Photocatalytic results of RhB degraded by different kinds of photocatalysts

The microstructures and sizes of the precipitation and hydrothermal products are similar (Fig.S3.). The better photocatalytic activity of the Sm(OH)₃ nanorods prepared by precipitation method may be due to the amorphous particles wrapped on the Sm(OH)₃ nanorods. The functionalized surface seems to enhance the adsorption amount of dissolved oxygen and RhB molecules. This made the life–time of the photogenerated holes prolong, which can participate in the degradation process by the formation of reactive radicals or by the direct oxidation of the pollutant, so as to promote the photocatalytic reaction efficiency [13]. Moreover, the degradation efficiency of RhB can reach 97.9% when the well known commercial photocatalyst P25 was used as catalyst. This means that the photocatalytic activity of the
prepared Sm(OH)\(_3\) nanorods is still needs to be improved in the further exploration. The small gap
between the prepared Sm(OH)\(_3\) nanorods and the well known commercial photocatalyst P25 suggests
that the improved Sm(OH)\(_3\) nanocrystallites have potential to be used as photocatalyst or co-catalyst
materials in the future.

4. Conclusion

In summary, pure hexagonal phase Sm(OH)\(_3\) nanorods have been successfully prepared by a facile
and efficient precipitation method at 60 °C for 2 h using Sm(NO\(_3\))\(_3\) · 6H\(_2\)O and DETA as raw materials.
The prepared sample exhibits high photocatalytic activity to degrade RhB, which degradation
efficiency reaches 94.3% under UV irradiation for 30 min. The enhanced photocatalytic activity of
Sm(OH)\(_3\) nanorods is attributed to the presence of the amorphous surface layer. The further research
about the photocatalytic mechanism of Sm(OH)\(_3\) nanocrystallites will be made in the future.

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