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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 explore enthusiasm in the synthesis of one–dimensional (1D) nanostructure with the properties 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 Rhdamine 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

$Sm(NO_3)_3 \cdot 6H_2O$ and diethylenetriamine (DETA) were of analytical reagent (A.R.) grade and used without further purification. First, 1.5 mmol $Sm(NO_3)_3 \cdot 6H_2O$ 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.

$$\text{Reaction yield}(\%) = (m/m_0) * 100\% \quad (1)$$

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 (λ=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 G^2 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 $mg \cdot L^{-1}$ Rhdamine 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 $g \cdot L^{-1}$. 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):

$$\text{Degradation efficiency } (\%) = (1 - C_t/C_0) * 100\% \quad (2)$$

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

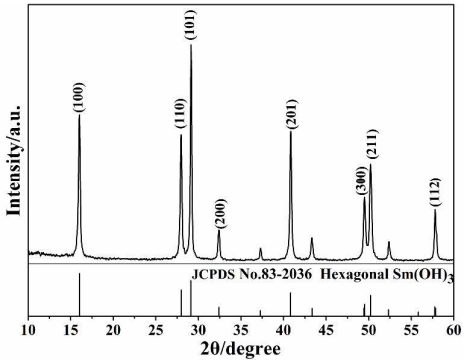

Fig.1. XRD pattern of the as–prepared $Sm(OH)_3$ nanocrystallites

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.

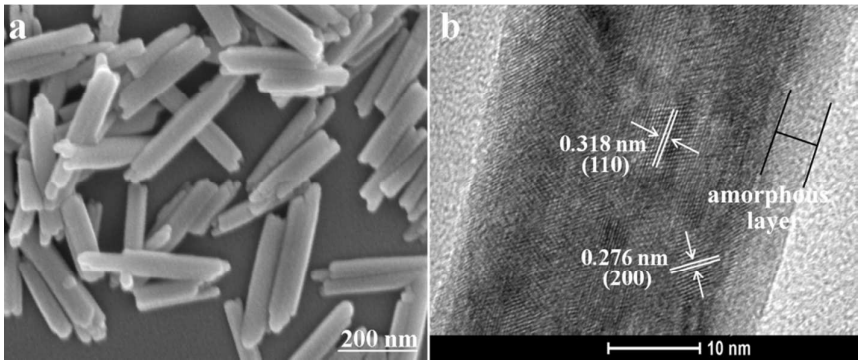

Fig.2. SEM (a) and HRTEM (b) image of the as–prepared $Sm(OH)_3$ nanocrystallites

3.3. Optical and photocatalytical 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 $(\alpha hv)^2$ vs. photo

energy (*hv*) 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].

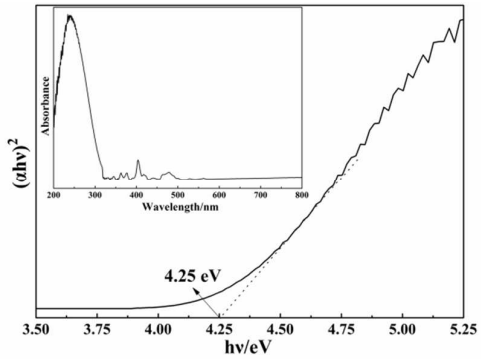

Fig.3. The relationship between $(\alpha hv)^2$ and photonenergy (Inset: UV–vis diffuse reflectance spectrum of $Sm(OH)_3$ nanorods)

The degradation of Rhdamine 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.

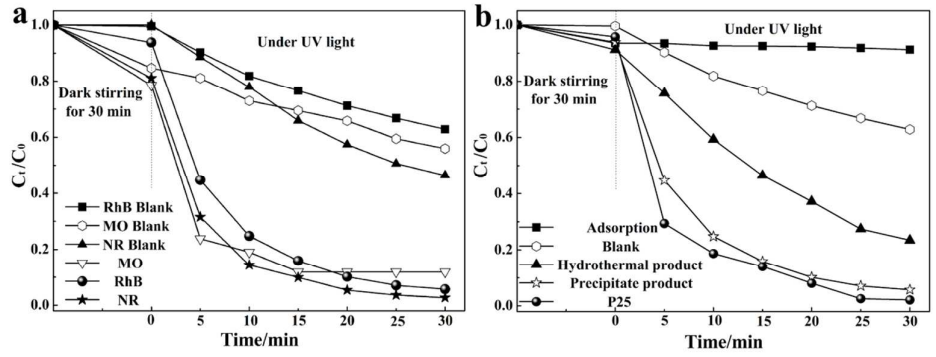

Fig.4. (a) Photocatalytic results of RhB, MO and NR degraded by $Sm(OH)_3$ nanorods

(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 $Sm(NO_3)_3 \cdot 6H_2O$ 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 $Sm(OH)_3$ nanrods 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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References

[1] Wang GF, Peng Q, Li YD. Acc Chem Res 2011; 44: 322–332.

[2] Djerdj I, Garnweitner G, Su DS, Markus N. J Solid State Chem 2007; 180: 2154–2165.

[3] Van Der Kolk E, Dorenbos P. Chem Mater 2006; 18: 3458–3462.

[4] Xie JS, Wu QS, Zhang D, Ding YP. Cryst Growth Des 2009; 9: 3889–3897.

[5] Mu QY, Wang Y D. J Alloys Compd 2011; 509: 396–401.

[6] Zhu YC, Mei T, Wang Y, Qian YT. J Mater Chem 2011; 21: 11457–11463.

[7] Kuang Q, Lin ZW, Lian W, Jiang ZY, Xie ZX, et al. J Solid State Chem 2007; 180: 1236–1242.

[8] Jia G, You HP, Song YH, Jia JJ, Zheng YH, et al. Inorg Chem 2009; 48: 10193–10201.

[9] Wang X, Li YD. Chem-Eur J 2003; 9: 5627–5635.

156 [10] Zhang N, Yi R, Zhou LB, Gao GH, Shi RG, et al. Mater Chem Phys 2009; 114: 160–167.

157 [11] Wang D, Huang JF, Yin LX, Cao LY, Ouyang HB, et al. Mater Lett 2014; 116: 393–395.

158 [12] Huang JF, Wang D, Yin LX, Cao LY, Ouyang HB, et al. J Alloys Compd 2014; 612: 233–238.

159 [13] Krivec M, Segundo RA, Faria JL, Silva AMT, et al. Appl Catal B: Environ 2013; 140–141: 9–15.

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