Optical Materials 38 (2014) 193–197

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Controllable synthesis and luminescence properties of TiO_2:Eu^{3+} nanorods, nanoparticles and submicrospheres by hydrothermal method

Xiaofei Qi [a], Yanhua Song [a], Ye Sheng [a], Hongguang Zhang [a], Huan Zhao [a], Zhan Shi [b], Haifeng Zou [a,*]

[a] College of Chemistry, Jilin University, Changchun 130012, PR China
[b] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China

ARTICLE INFO

Article history:
Received 19 June 2014
Received in revised form 10 October 2014
Accepted 12 October 2014
Available online 31 October 2014

Keywords:
TiO_2:Eu^{3+}
Hydrothermal method
Different morphologies
Optical properties

ABSTRACT

Eu^{3+}-doped TiO_2 nanocrystals with three kinds of morphologies (nanorods, nanoparticles, and submicrospheres) have been successfully fabricated in cetyltrimethylammonium bromide (CTAB)/water/cyclohexane/*n*-pentanol reverse micelle by hydrothermal method for the first time and their photoluminescence (PL) properties have also been studied. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), FT-IR, and PL spectra were used to characterize the samples. The acidic and alkaline conditions of the microemulsion play an important role in determining the geometric morphologies of the final products. TiO_2:Eu^{3+} with three different morphologies all exist only in anatase phase and show high luminescence intensity without further calcinations, which show its advantages of energy saving. The shape of emission spectra was independent of the morphologies of the products but the luminescence intensity of the TiO_2:Eu^{3+} materials is strongly dependent on their morphology. The results show that TiO_2:Eu^{3+} nanorods possess the strongest luminescence intensity among the three nanostructured samples.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Compounds doped with rare earth ions have received considerable interest in both fundamental and application studies due to their significant technological importance, and are used as high-performance luminescent devices [1], solar cells [2], solid-state lasers [3], time-resolved fluorescence labels for biological detection [4], and other functional materials. As a host material, TiO_2 is considered as a promising semiconductor with outstanding optical properties [5–7]. Inorganic particles often show unique size- and shape-dependent properties, thus a lot of investigations are focused on the controllable synthesis of rare earth ions doped TiO_2 luminescent materials. Up to now, various morphologies of TiO_2 have been fabricated via different methods. For example, TiO_2 nanofibers through electrospinning technique [8], TiO_2 nanoparticles prepared by sol–gel method [9], and TiO_2 nanowire arrays by hydrothermal technique [10] have been reported. Among these synthesis methods, hydrothermal technique is the most popularly used one because it can provide several adjustable parameters such as pH value, reaction temperature, ripening time, and solution concentration and thereby the size, morphology, and structure of the synthesized materials can be effectively controlled.

In recent years, soft templates, such as microemulsions or reverse micelles, have been widely used as an ideal media to prepare inorganic nanomaterials [11]. Microemulsion method promises to be a highly useful route due to its advantages in controllable synthesis methodology. Within water-in-oil (W/O) microemulsion, spherical reverse micelles, which have minimum surface energy, are the most common form. The nanosized water pools inside these spherical micelles offer ideal microreactors for the formation of nanoparticles, and therefore spherical nanoparticles easily form. Further growth and aggregation of the primary nanoparticles can result in different nanostructures [12].

TiO_2:Eu^{3+} nanocrystals exhibit good luminescence efficiency, color purity, and stability. The composition and microstructure of the host play an important role in controlling the optical properties of these rare earth ions doped nanomaterials [13,14]. The luminescence signal from these materials provides fixed lines of the rare earth ions, which is almost independent of the host matrix. However, the width and relative intensity of those lines are usually affected by the nature of the host matrix. A major motivation for this research has been the goal of creating materials exhibiting unique optical properties, which are dependent not only on size but also on shape.

In this paper, we first report the synthesis of TiO_2:Eu^{3+} nanostructures with different morphologies (nanorods, nanoparticles, and submicrospheres) in a cetyltrimethylammonium bromide

* Corresponding author. Tel./fax: +86 431 85155275.
E-mail address: zouhf@jlu.edu.cn (H. Zou).

http://dx.doi.org/10.1016/j.optmat.2014.10.026
0925-3467/© 2014 Elsevier B.V. All rights reserved.

(CTAB)/water/cyclohexane/*n*-pentanol microemulsion system under hydrothermal conditions. By carefully controlling fundamental experimental parameters, such as the acidic and alkaline conditions of the microemulsion, we realize the controllable synthesis of TiO_2:Eu^{3+} materials. Without further calcinations, samples with three different morphologies all show high luminescence intensity. The shape-dependent luminescence properties of the TiO_2:Eu^{3+} samples were studied.

2. Experimental details

2.1. Materials

CTAB, cyclohexane, *n*-pentanol, rare earth oxide (99.9%), $NH_3{\cdot}H_2O$, HNO_3, TBOT, and absolute ethanol were purchased from Beijing Chemical Co. All chemicals were analytical grade reagents and used directly without further purification. $Eu(NO_3)_3$ aqueous solution were obtained by dissolving Eu_2O_3 (99.99%) in dilute HNO_3 solution under heating with ceaseless agitation.

2.2. Preparation

In a typical procedure, 1.0 g CTAB and 1.5 mL of *n*-pentanol was dissolved in 30 mL of cyclohexane. The mixing solution was stirred for 20 min. Then a certain volume of 2 M $Eu(NO_3)_3$ aqueous solution (the doping content of Eu^{3+} is 3 mol%) and 2.5 mL $NH_3{\cdot}H_2O$ solution were dropped to the solution, separately. The solution was further stirred for another 10 min. Then 1.7 mL TBOT was added dropwise to the solution under continuous stirring. Then the transparent feedstock was transferred to a 50 mL teflon-lined stainless steel autoclave and maintained at 180 °C for 48 h. Then the autoclave was cooled to room temperature naturally. The products were separated by centrifugation, washing with ethanol and distilled water for several times, and drying in an air atmosphere at 60 °C for 4 h. If we replace $NH_3{\cdot}H_2O$ by 1.3 mL HNO_3 or without adding any acid or base, different morphologies will form.

2.3. Characterization

X-ray diffraction (XRD) analyses were carried out using a XRD-6000 X-ray diffractometer from Shimadzu with Cu Kα radiation (λ = 0.15405 nm). The morphology of the samples was examined with scanning electron microscope (SEM, s-4800, Hitachi) and transmission electron microscopy (TEM) (JEM-2000EX). Energy dispersive X-ray (EDX) spectroscopy analysis was performed with an IXRF SDD2910 EDS system attached to the SEM microscope. FT-IR spectra were measured with the Nicolette 5PC FT-IR spectrophotometer with the KBr pellet technique. Photoluminescence (PL) excitation and emission spectra were recorded with a Jobin Yvon FluoroMax-4 equipped with a 150 W xenon lamp as the excitation source. All the measurements were performed at room temperature.

3. Results and discussion

Fig. 1 represents the typical XRD patterns of the Eu^{3+}-doped TiO_2 nanorods, nanoparticles, and submicrospheres through the hydrothermal process. The titania samples with different morphologies all exist only in anatase phase with distinctive peaks centered at 2θ = 25.14°, 37.88°, 47.73°, 53.93°, 62.44°, which correspond to the anatase (101), (103, 004, and 112), (200), (105 and 211), (204) crystalline planes (JCPDS: 21-1272). No peaks of any other phases or impurities are detected. The phase structure and crystallinity of TiO_2 play an important role in luminescence intensity. Among these XRD patterns, the diffraction peaks of nanorods are

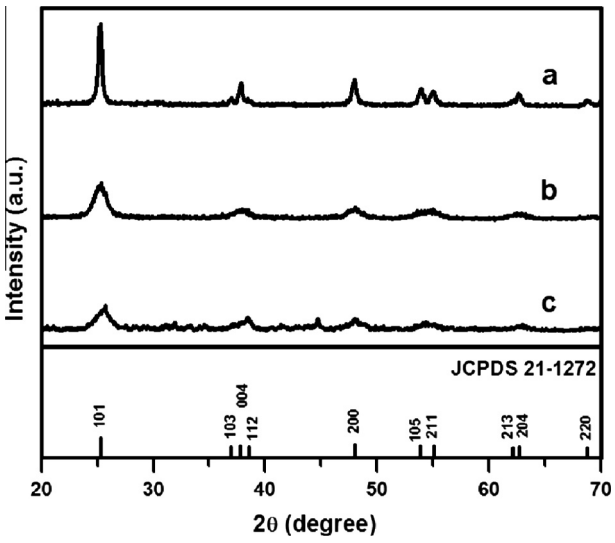

Fig. 1. XRD patterns of TiO_2:Eu^{3+} nanorods (a), nanoparticles (b), and submicrospheres (c) with 3 mol% Eu^{3+} concentration.

the strongest which indicates the good crystallinity of the nanorods. This is important for phosphors because high crystallinity generally means fewer traps and stronger luminescence.

Fig. 2 shows SEM and TEM images of the as-obtained TiO_2 samples. TiO_2 products with different morphologies and sizes were synthesized in the microemulsion with different acidic and alkaline conditions. Fig. 2a and b shows the SEM and TEM images of the Eu^{3+}-doped TiO_2 nanorods, respectively. As can be seen from the pictures, when $NH_3{\cdot}H_2O$ aqueous was added into the microemulsion, nanorods with very smooth surface formed. The diameters of the nanorods are in the range of 15–20 nm and the length are in the range of 20–50 nm. It is clearly seen from Fig. 2c and d that when no acid or base was added into the microemulsion, the strongly agglomerated particles with non-defined shape were obtained. And the average size is about 5 nm. Fig. 2e and f presents the typical images of submicrospheres which were fabricated by the addition of HNO_3 aqueous, from which it can be seen that their average diameter is about 150 nm. The images show that there are many particles grown on the surface of the spheres, which sustains the fact that the TiO_2 spheres are the aggregation of small particles or crystallites.

As a result, the acidic and alkaline conditions played an important role in the formation of TiO_2:Eu^{3+} materials with different morphologies. In the first step, solutes are formed to yield a supersaturated solution, leading to nucleation which was taken place in the water pools of the microemulsion system. The small sized and fairly distributed water pools limited the formation space and shape of the nuclei. The nuclei then grow by a diffusive mechanism to form crystalline subunits. Further growth and aggregation of the primary nanoparticles can result in different nanostructures. Under alkaline condition, which has been reported tending to result in short rod-like nanocrystals [15], the crystalline subunits grow along certain directions to form nanorods. While under acidic condition (HCl), the formation mechanism belongs to an aggregation growing process [11], and those crystal nucleus aggregated to form spheres (composed of nanoparticles) in order to find a place to minimize the surface energy [16]. When no acid or base was added to the microemulsion, high reaction rate will cause fast growing rate and uncontrolled severe agglomeration of the resulting particles. Different acidic and alkaline conditions of the microemulsion could affect the electric charge distributing on the surface of the nanoparticles thus leading to different growth or aggregation forms of the nanoparticles. Then the final products with morphologies changing

Download English Version:

https://daneshyari.com/en/article/1494031

Download Persian Version:

https://daneshyari.com/article/1494031

Daneshyari.com