



Contents lists available at ScienceDirect

Particuology

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

Facile room-temperature coprecipitation of uniform barium chlorapatite nanoassemblies as a host photoluminescent material

Peiyan Zhai, Xiuping Chen, Zhaoqiang Zhang, Lin Zhu, Heng Zhang, Wancheng Zhu*

Department of Chemical Engineering, Qufu Normal University, Shandong 273165, China

ARTICLE INFO

Article history:

Received 4 April 2017

Received in revised form 13 May 2017

Accepted 18 May 2017

Available online xxx

Keywords:

Barium chlorapatite

Nanoassemblies

Phosphors

Luminescence

Room-temperature coprecipitation

ABSTRACT

As an emerging host phosphor material, barium chlorapatite ($\text{Ba}_5(\text{PO}_4)_3\text{Cl}$), is attracting growing attention. However, rare earth-doped $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$ phosphors have mainly been obtained via high temperature-based, energy-consuming techniques. In this contribution, we developed a straightforward, facile room-temperature coprecipitation method in the presence of a specific amount of ethylenediaminetetraacetic acid disodium salt that provided $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$ nanoparticles self-assembled to construct uniform $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$ nanoassemblies (diameter: 80–120 nm) as well as rare earth Tb^{3+} -doped $\text{Ba}_5(\text{PO}_4)_3\text{Cl}:\text{xTb}^{3+}$ nanophosphors. The nanoassemblies were transparent within the ultraviolet and visible spectral range. The $\text{Ba}_5(\text{PO}_4)_3\text{Cl}:\text{xTb}^{3+}$ nanophosphors exhibited four emission peaks under 228-nm excitation, and the optimal doping amount of Tb^{3+} was 4.0%. In contrast to traditional energy-consuming, high-temperature techniques, the facile room-temperature coprecipitation method developed here represents an attractive alternative route to obtain uniform $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$ nanoassemblies and $\text{Ba}_5(\text{PO}_4)_3\text{Cl}:\text{xTb}^{3+}$ nanophosphors that are candidate luminescent hosts.

© 2017 Chinese Society of Particuology and Institute of Process Engineering, Chinese Academy of Sciences. Published by Elsevier B.V. All rights reserved.

Introduction

Nanostructured phosphates are rich in P–O coordination polyhedra, possess an open frame structure, and have been widely used as drug delivery agents (Yang, Hao, Zhao, Du, & Wang, 2013), catalysts (Sreenivasulu, Pendemb, & Viswanadham, 2014), electrode materials (Dimesso et al., 2012), and luminescent materials (Yue et al., 2014). In particular, chlorophosphates are drawing increasing research interest because of their good luminescence performance when doped with just a few mole percent of a rare earth element (Dong, Lin, Yu, & Zhang, 2014; Ju, Hu, Chen, & Wang, 2012; Li et al., 2011; Noginov et al., 2000; Sato, Tanaka, & Ohta, 1994; Shang et al., 2013; Yoo, Vaidyanathan, Kim, & Jeon, 2009). Recently, many researchers have synthesized rare earth element-doped alkaline earth metal chlorophosphates ($\text{M}_5(\text{PO}_4)_3\text{Cl}:\text{M}$, M = Ca, Sr, and Ba) because of their excellent performance when used as phosphors (Shang et al., 2013), among which barium chlorapatite ($\text{Ba}_5(\text{PO}_4)_3\text{Cl}$) has attracted particular attention. $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$ has been obtained through solid-state reactions using BaHPO_4 , BaCO_3 , and BaCl_2 as raw materials, and then activated by adding Eu^{2+} to

the mixture and heating at 1100 °C (Sato et al., 1994). $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$ can also be doped with Nd^{3+} via sintering at 900 °C (Noginov et al., 2000) or Yb^{2+} by solid-state reaction at 900–1300 °C (Yoo et al., 2009). In addition, $\text{Ce}^{3+}/\text{Eu}^{2+}$ co-doped $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$ with high fluorescence intensity has also been reported (Ju et al., 2012). Most of the above rare earth element-doped $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$ phosphors were obtained via solid-state reactions (Ju et al., 2012; Sato et al., 1994; Yoo et al., 2009) or other high-temperature techniques (Noginov et al., 2000). These approaches are limited by their high energy consumption, difficulty controlling product size and morphology, tendency of the products to agglomerate, and sub-optimal product fluorescent intensity and lifetime.

As alternatives to high-temperature techniques, wet chemistry-based strategies have emerged as attractive routes to synthesize rare earth-doped $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$ phosphors. In addition, nanophosphors show promise as luminescent materials (Takeshita, Isobe, & Niikura, 2008). Consequently, it is important to obtain rare earth-doped $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$ nanophosphors with uniform morphology and a narrow size distribution. Self-assembled nanoarchitectures have been produced by surfactant-assisted (Chen, Zhang, Zhang, Zhu, & Zhu, 2015; Zhu et al., 2012), bubble-induced (Li et al., 2017), and ionothermal-confined (Zhang et al., 2014) hydrothermal syntheses, and hydrothermal treatment without any surfactant (Zhang, Wang, & Zhu, 2016). However, it is still challenging to synthesize

* Corresponding author.

E-mail address: zhuwancheng@tsinghua.org.cn (W. Zhu).

<http://dx.doi.org/10.1016/j.partic.2017.05.010>

1674–2001/© 2017 Chinese Society of Particuology and Institute of Process Engineering, Chinese Academy of Sciences. Published by Elsevier B.V. All rights reserved.

Ba₅(PO₄)₃Cl nanophosphors evenly doped with rare earth elements using wet chemistry-based methods.

In this contribution, Ba₅(PO₄)₃Cl nanoparticles (NPs) are constructed to form uniform nanoassemblies with a diameter of 80–120 nm through a facile room-temperature coprecipitation process in the presence of ethylenediaminetetraacetic acid disodium salt (EDTA-2Na). A possible formation mechanism for the nanoassemblies is proposed. Additionally, Tb³⁺-doped Ba₅(PO₄)₃Cl:xTb³⁺ nanophosphors are also acquired via the same room-temperature coprecipitation process in the presence of Tb³⁺.

Experimental

Synthesis

All reagents were of analytical grade and used directly without further purification. BaCl₂·2H₂O was obtained received from Jinan institute of chemical industry. NaH₂PO₄ was bought from Damao Chemical Reagent Tianjin Co., Ltd. (China) and EDTA-2Na was obtained from Guangcheng Chemical Reagent Tianjin Co., Ltd. (China). In a typical room-temperature coprecipitation reaction to obtain Ba₅(PO₄)₃Cl nanoassemblies, a transparent solution (15 mL) containing BaCl₂·2H₂O (1.8320 g, 7.4996 mmol) and EDTA-2Na (0.1567 g, 0.4633 mmol) was dropped from a syringe into NaH₂PO₄ solution (0.2 mol/L, 15 mL) under vigorous magnetic stirring at room temperature. The molar ratio of Ba²⁺:PO₄³⁻ was 5:2. A freshly prepared NaOH solution (1.0 mol/L) was added dropwise to adjust the pH of the mixture to ca. 11.5. Deionized (DI) water was as the solvent for all of the solution. The mixture was stirred for 12.0 h at room temperature. The resultant white slurry was washed with deionized (DI) water, vacuum filtered, rinsed with ethanol three times, and then dried at 60 °C for 24.0 h to give the product. To synthesize Ba₅(PO₄)₃Cl:xTb³⁺ nanophosphors (*x* = 0.2%, 1.0%, 2.0%, 4.0%, 6.0%, and 8.0%), specific amounts of Tb(NO₃)₃·6H₂O were added to the solution of BaCl₂ and EDTA-2Na; the molar percentage of Tb³⁺ to Ba²⁺ was kept within the range of 0.2%–8.0%. The as-obtained solution was added dropwise to the NaH₂PO₄ solution following the same process described above for the Ba₅(PO₄)₃Cl nanoassemblies.

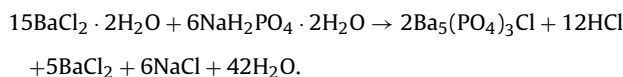
Characterization

Sample composition and structure were identified by powder X-ray diffraction (XRD; MiniFlex600, Rigaku, Japan). Sample morphology and microstructure were examined by field-emission scanning electron microscopy (SEM; JSM7401F, JEOL, Japan) and high-resolution transmission electron microscopy (TEM; JEM-2010, JEOL, Japan). The size distribution of the as-synthesized nanoassemblies was estimated by directly measuring the sizes of about 50 typical particles in SEM images. N₂ adsorption–desorption isotherms were measured at 77 K using a chemisorption–physisorption analyzer (Autosorb-IQ2-MP, Quantachrome, USA) after the samples were degassed at 300 °C for 1.0 h. Specific surface areas were calculated from adsorption branches in the relative pressure range of 0.05–0.30 using the multipoint Brunauer–Emmett–Teller (BET) method, and pore size distributions were evaluated from N₂ desorption isotherms using the Barrett–Joyner–Halenda (BJH) model. Chemical bonds in the molecules of the products were investigated by Fourier transform infrared (FT-IR) spectroscopy (Nexus 470, Nicolet, USA). Optical properties were examined with an ultraviolet–visible (UV–vis) spectrophotometer (UV-756 CRT, Shanghai Yoke Instrument and Meter Co., Ltd., China) using DI water as the dispersive medium. Photoluminescence (PL) measurements were recorded with a fluorescence spectrophotometer (F-4600, Hitachi, Japan).

Results and discussion

Structure and morphology of the Ba₅(PO₄)₃Cl nanoassemblies

An XRD pattern, SEM image, and TEM images of the Ba₅(PO₄)₃Cl nanoassemblies are illustrated in Fig. 1. As shown in Fig. 1(a), all the diffraction peaks of the sample were readily indexed to those of standard alforsite (Ba₅(PO₄)₃Cl, JCPDS No.70-2318). The overall chemical reaction in the coprecipitation process could thus be written as follows:



SEM analysis confirmed that the as-synthesized product consisted of uniform nanoassemblies with spherical or quasi-spherical morphology (Fig. 1(b)), and 74% of the nanoassemblies had a diameter within the range of 80–120 nm (Fig. 1(b₁)). The TEM image further confirmed that the as-obtained nanoassemblies had a quasi-spherical profile, and consisted of aggregations of NPs with an average diameter of 10–20 nm (Fig. 1(c)). The interplanar spacing of 0.299 nm determined from the lattice fringes (Fig. 1(c₁)) was quite similar to the standard value of the (112) plane of hexagonal alforsite (0.307 nm), revealing the high crystallinity of the as-synthesized Ba₅(PO₄)₃Cl nanoassemblies. These results show that we have developed a straightforward, facile room-temperature coprecipitation method to synthesize Ba₅(PO₄)₃Cl, which is has obvious advantages over the traditional high temperature-based techniques (Dong et al., 2014; Ju et al., 2012; Noginov et al., 2000; Sato et al., 1994; Yoo et al., 2009).

To obtain deeper insight into the Ba₅(PO₄)₃Cl nanoassemblies, their N₂ adsorption–desorption isotherms were recorded, and their pore size distributions were also evaluated (Fig. 1(d)). The sorption isotherms of the Ba₅(PO₄)₃Cl nanoassemblies displayed typical type-IV characteristics (Zhang, Zhang, Zhu, Zhang, & Zhu, 2016) and their specific surface area was about 51 m²/g. In Fig. 1(d₁), the sharp peak at about 3.7 nm was weak because of the tensile strength effect, according to the BJH model (Groen, Peffer, & Rérez-Ramírez, 2003). The pore diameter was within the range of 5–100 nm, which is attributed to the presence of mesopores within the bulk of the Ba₅(PO₄)₃Cl nanoassemblies as well as macropores between the nanoassemblies.

Effect of EDTA-2Na and other process parameters on nanoassembly formation

As the surfactant, EDTA-2Na played a crucial role in the formation of the Ba₅(PO₄)₃Cl NPs and their aggregation to form nanoassemblies. As shown in Fig. 2(a₁), the room-temperature coprecipitation reaction without EDTA-2Na gave the two phases Ba₅(PO₄)₃Cl (JCPDS No. 70-2318) and BaHPO₄ (JCPDS No. 44-0743). In contrast, the introduction of 0.006 mol/L (Fig. 2(a₂)) and 0.012 mol/L (Fig. 1(a)) of EDTA-2Na into the transparent BaCl₂ solution led to higher purity and pure Ba₅(PO₄)₃Cl, respectively. Notably, a trace amount of BaHPO₄ formed when too much EDTA-2Na was added (0.024 mol/L), as illustrated in Fig. 2(a₃). When EDTA-2Na was omitted, the resulting product contained Ba₅(PO₄)₃Cl NPs and large BaHPO₄ plates (Fig. 2(b)). Introduction of EDTA-2Na gave Ba₅(PO₄)₃Cl NPs accompanied by small blocks (Fig. 2(c)), and uniform nanoassemblies (Fig. 1(b)). However, excess EDTA-2Na resulted in irregular NPs with a broad size distribution (Fig. 2(d)). The variation of the composition and morphology of the product with the amount of EDTA-2Na used can be attributed to the interaction between EDTA²⁻ and Ba²⁺ to form the EDTA–Ba chelate complex (Geng, Jiang, Lu, & Zhu, 2011). In addition, the concentra-

Download English Version:

<https://daneshyari.com/en/article/7061616>

Download Persian Version:

<https://daneshyari.com/article/7061616>

[Daneshyari.com](https://daneshyari.com)