Synthesis and Enhanced Photoluminescence of Surface-Modified Barium Borate Nanorods

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Well-dispersed barium borate nanorods with uniform diameters were synthesized successfully, using Na₂B₄O₇·10H₂O and Ba(NO₃)₂ as raw materials and oleic acid as a modifying agent. Oleic acid was used to modify the surface property of nanorods prepared from the precipitation reaction. TEM images confirmed that the synthesized sample presented nanorod morphology with a length of about 200–400 nm and an average diameter of 20 nm. Moreover, the photoluminescence properties of both pure and modified BaB₂O₄ nanorods were tested. After the surfaces of the nanorods were modified with oleic acid, the visible light emission of the sample centered at 380 and 400 nm became more intensive. It was discussed that the enhancement of the luminescence intensity was attributed to the formation of surface BaB₂O₄/oleic acid complexes.

Keywords: Nanorods, Surface Modification, Luminescence.

1. INTRODUCTION

Synthesis of hybrid organic–inorganic composites with narrow size distribution and high luminescence efficiency has attracted intensive interest in the past decade due to their wide applications in various fields. A number of borate materials, especially barium borate crystals have been studied extensively due to their unique combination of large electronic bandgaps, environmental stability, and strong non-linear optics applications. To date, many considerable methods such as sol–gel, hydrothermal, and precipitation have been explored for the synthesis of barium borate nanocrystals. However, with these methods, barium borate nanocrystals tend to aggregate severely, owing to their high surface energy. As a result, such nanocrystals were unstable in aqueous solution, which led to agglomeration and hindered the application of barium borate nanocrystals in the domain of optics.

Today, with the development of optical materials for biological fluorescence labeling, much attention has to be paid to preparing stable BaB₂O₄ nanocrystals with high quantum efficiency. Meanwhile, some kinds of BaB₂O₄ nanocrystals doped with different luminescent materials have been synthesized. In this paper, we focus on modifying the surface of barium borate nanorods for enhanced photoluminescence.

Since the surface modification has significantly impacted various properties of BaB₂O₄ nanocrystals, it is more attractive to design and control the surface chemistry. Herein, we present a simple solution route in which Na₂B₄O₇·10H₂O and Ba(NO₃)₂ are used as raw materials and oleic acid is used as a modifying agent. Oleic acid seems to be crucial for the surface and luminescence properties of the BaB₂O₄ nanorods. After modification, more intensive emission bands centered at 380 and 400 nm were observed.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation

In a typical procedure, a 50 ml of 0.1 mol·dm⁻³ Na₂B₄O₇·10H₂O aqueous solution, 10 ml of absolute ethanol, and a certain amount of oleic acid (OA) were placed in a three-necked flask and vigorously stirred at 70 °C. A solution of 50 ml Ba(NO₃)₂ of 0.2 mol·dm⁻³ was added dropwise to the first solution while being stirred for a period of about 0.5 h. After the addition was complete, the mixture was continuously heated for another 6 h. Subsequently, the resulting white BaB₂O₄ precipitate was filtered, washed with distilled water and absolute ethanol several times to remove unreacted reactants, oleic acid, and by-products, then dried in the oven at 80 °C to obtain the modified...
white BaB$_2$O$_4$ powders. A non-modified BaB$_2$O$_4$ sample was also synthesized without the addition of OA while keeping all the other processes the same.

2.2. Characterization

The crystalline structures of BaB$_2$O$_4$ powders were examined by X-ray powder diffraction (XRD) (SHIMADZUXRD-6000 diffractometer employing Cu K$_\alpha$ radiation, with a scanning rate of 6°/min with 2θ in a range of 10–75°). The morphology and size of the samples were observed using a Hitachi H-800 transmission electron microscope (TEM), at an accelerator voltage of 200 kV. The samples used for TEM characterization were dispersed in absolute ethanol and ultrasonicated before observation. IR spectroscopy of the samples as powder-pressed KBr pellets were examined in the wave number range from 4000 to 500 cm$^{-1}$ at a resolution of 4 cm$^{-1}$ using a JIR-5500 (JEOL) spectrophotometer at room temperature. The luminescence spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer at room temperature using 350 and 380 nm as the excitation and detection wavelengths, respectively.

3. RESULTS AND DISCUSSION

Typical XRD patterns of samples (a) and (b) are shown in Figure 1. The X-ray diffraction peaks can fit with the data in the standard card (JCPDS files No. 06-0220) well, which indicates that both pure and modified samples contain BaB$_2$O$_4$ crystals.
Figure 2 shows the infrared spectra (range 4000–500 cm$^{-1}$) of pure BaB$_2$O$_4$ particles and modified BaB$_2$O$_4$ nanorods. In blank BaB$_2$O$_4$ samples, the band at 3420 cm$^{-1}$ is attributed to the stretching vibration of $\text{–OH}$, and the absorption band at 1650 cm$^{-1}$ is assigned to the H–O–H bending mode. The bands at 1346 and 991 cm$^{-1}$ are assigned to the asymmetric stretching of B–O. The bands at 721 cm$^{-1}$ arise from the complex of surface-bonded OA and Na$_2$B$_4$O$_7$·10H$_2$O and Ba(NO$_3$)$_2$ as raw materials, using OA as a modifying agent. Non-modified BaB$_2$O$_4$ nanorods were also prepared without OA for comparison. It is clear that OA helps to form well-dispersed BaB$_2$O$_4$ nanorods successfully, and PL properties of BaB$_2$O$_4$ nanorods have been investigated. The results show that the modified BaB$_2$O$_4$ nanorods have relatively higher luminescence efficiency compared to the non-modified ones, and it has been discussed that the difference in PL results between the modified BaB$_2$O$_4$ nanorods and non-modified ones is due to the formation of surface-bonded molecules of OA. Such surface-modified BaB$_2$O$_4$ nanorods with stable and intense visible light fluorescence are expected to be used for further processing, assembly, or practical applications.

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**References and Notes**


**4. CONCLUSION**

Surface modified BaB$_2$O$_4$ nanorods were synthesized by Na$_2$B$_4$O$_7$·10H$_2$O and Ba(NO$_3$)$_2$ as raw materials, using OA as a modifying agent. Non-modified BaB$_2$O$_4$ nanorods were also prepared without OA for comparison. It is clear that OA helps to form well-dispersed BaB$_2$O$_4$ nanorods successfully, and PL properties of BaB$_2$O$_4$ nanorods have been investigated. The results show that the modified BaB$_2$O$_4$ nanorods have relatively higher luminescence efficiency compared to the non-modified ones, and it has been discussed that the difference in PL results between the modified BaB$_2$O$_4$ nanorods and non-modified ones is due to the formation of surface-bonded molecules of OA. Such surface-modified BaB$_2$O$_4$ nanorods with stable and intense visible light fluorescence are expected to be used for further processing, assembly, or practical applications.

**Fig. 4.** PL spectra of (a) pure BaB$_2$O$_4$ particles and (b) modified BaB$_2$O$_4$ nanorods at room-temperature.
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