Fabrication of TbPO$_4$·H$_2$O nanorods/nanowires by the microwave technique and their characterization

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Abstract

This report presents the results of the fabrication of luminescent terbium orthophosphate monohydrate (TbPO$_4$·H$_2$O) nanomaterials prepared by the microwave synthesis method and their characterization. The effects of synthesis conditions such as microwave irradiated powers, pH values and reaction temperature on properties of nanomaterials are also investigated to obtain controllable size, morphology and strong luminescence. The structure, morphology and optical properties of the nanomaterials have been characterized by x-ray diffraction, field-emission electron scanning microscopy and fluorescence spectroscopy, respectively. The results showed that TbPO$_4$·H$_2$O nanowires/nanorods have been successfully synthesized by using microwave heating of an aqueous solution of terbium nitrate and NH$_4$H$_2$PO$_4$ with pH values ranging from 2 to 10. The length and width of these nanowires/nanorods are 150–350 nm and 5–10 nm, respectively.

Keywords: microwave-assisted synthesis technique, nanowires/nanorods, fluorescence

Classification numbers: 4.00, 4.06, 4.08

1. Introduction

Recently, numerous methods for the synthesis of nanoparticles [1–6], nanotubes [7–9], nanowires [10, 11] and nanorods [12, 13] with desired particle sizes and controlled morphology have been developed. These nanomaterials with different shapes have recently gained interest and become more and more important due to their novel properties associated with their reduced dimensionality and their potential applications in nanotechnologies, especially in nanobiophotonics [14].

Rare-earth compounds have been widely used in high-performance luminescent devices, magnets, catalysts and other functional materials owing to the numerous well-defined transition modes involving the 4f shell of their ions. Recently, increasing interest has been focused on the synthesis and photoluminescence of rare-earth orthophosphates with nanosized scale for their potential application in optoelectronic devices and biomedical fluorescence labeling [15–18]. These rare-earth orthophosphates (LnPO$_4$ with Ln: Y, Sc and La–Lu) nanomaterials exhibit fascinating properties such as very high thermal stability, low water solubility, high refractive index and a high concentration of lasing ions. Possessing these properties, LnPO$_4$ can be used in various applications, such as luminescent or laser materials, magnets, ceramics, catalysts, proton conductors moisture-sensitive sensors, heat-resistant materials, hosts for radioactive nuclear waste, biochemical probes and medical diagnostics [19–21].

In this work TbPO$_4$·H$_2$O nanorods/nanowires have been prepared by microwave (MW) heating and characterized by field-emission scanning electron microscopy (FE-SEM) and x-ray diffraction (XRD). The microwave-assisted synthesis technique is employed for the reasons of its high possibility of providing low dimensional nanomaterials, and that it is simple, very fast, clean, efficient, economical, non-toxic and eco-friendly [19]. The microwave reflexing...
apparatus was used with maximum power as high as 1000 W. The photoluminescence (PL) spectra under 370 nm excitation wavelength of TbPO$_4$·H$_2$O nanorods/nanowires were measured in the wavelength range of 450–650 nm. The photoluminescence excitation (PLE) spectra monitored at 542 nm emission line were recorded in the wavelength range of 300–525 nm. The effects of the microwave irradiated power on crystalline structure, nanostructures and the photoluminescence properties of prepared samples were also discussed for the first time.

2. Experimental

Terbium(III) nitrate and NH$_4$H$_2$PO$_4$ with 99% purity were purchased from Aldrich Co. and used as-received without further purification. TbPO$_4$·H$_2$O nanomaterials were prepared by microwave heating of an aqueous solution containing Tb(NO$_3$)$_3$ and NH$_4$H$_2$PO$_4$ at atmospheric pressure in an open system. In a typical synthesis, 20 ml of aqueous 0.25 M NH$_4$H$_2$PO$_4$ solution was added into a 50 ml round-bottomed flask containing 20 ml of a 0.25 M aqueous solution of Tb(NO$_3$)$_3$. A colloidal suspension, without any special morphology of particles, was obtained upon the addition of NH$_4$H$_2$PO$_4$ into Tb(NO$_3$)$_3$ solution. Different pH values of the reacting solution were intentionally selected in the range of 2–10 by using 0.05 M NH$_4$OH solution. At each selected pH value, this reacting solution was then irradiated using a MAS-II microwave synthesis extraction workstation, Sineo Co., for 30 min with different irradiated powers ranging from 300 to 900 W. From the investigation of the effects of pH value of reaction suspension on structure and the photoluminescence properties, which will be reported in detail elsewhere [22], the optimized pH value of 2 was determined. The resulting products were collected, centrifuged at 5600 rpm, and washed several times using ethanol and distilled water. The final products were dried at 60 °C for 24 h in air. The above experiments were repeated several times and showed good reproductivity. The crystalline phase identification of the as-synthesized samples was carried out by XRD analysis with a Siemens D5000 diffractometer (using CuK$_\alpha$ radiation with $\lambda$ = 1.5406 Å). The morphology of the products was characterized by using a field emission scanning electron microscope, Hitachi, S-4800. The excitation and emission (fluorescence) spectra of studied samples were recorded on a Cary eclipse fluorescence spectrometer and a luminescence spectrophotometer system, Horiba Jobin Yvon IHR 550, respectively.

3. Results and discussion

FE-SEM images of TbPO$_4$·H$_2$O samples synthesized by using microwave heating of an aqueous solution containing Tb(NO$_3$)$_3$ and NH$_4$H$_2$PO$_4$ at pH = 2 with various microwave irradiated powers ranging from 300 to 900 W were shown in figure 1.

The nanorods/nanowires are uniformly distributed with diameters in the range of 5–10 nm and lengths ranging from 150 to 350 nm (figures 1(a) and (b)). There exists a critical value of irradiated power of 500 W for these
nanorods/nanowires tending to bunch with the further increase of microwave irradiated powers as shown in figure 1(c), for example.

XRD patterns of the as-synthesized TbPO$_4$·H$_2$O nanorods/nanowires indicate that only single crystalline phase of TbPO$_4$·H$_2$O existed in the obtained samples (figure 2). All diffraction peaks can be distinctly indexed to a rhabdophane-type pure hexagonal phase. These results are the same as those reported previously [19]. Qualitatively, as shown in figure 2, the switching of microwave irradiated power causes no change in crystalline phase composition or crystallinity of the prepared samples. This implies that, by using microwave synthesis apparatus and an aqueous solution containing Tb(NO$_3$)$_3$ and NH$_4$H$_2$PO$_4$ at a suitable pH = 2 of starting solution, the hydrated terbium orthophosphate, TbPO$_4$·H$_2$O, was always obtained as a unique product instead of anhydrous TbPO$_4$. In the crystal structure of this monohydrate salt [19], each Tb$^{3+}$ cation is not only coordinated by oxygen atoms which reside at two different crystallographic sites, O1 and O2, of PO$_4^{3-}$ anions as observed in the case of TbPO$_4$ [23], but is also connected to oxygen atoms (O3w) of two hydrate water molecules (figure 3). The interatomic distances between Tb$^{3+}$ cation and oxygen atoms of two hydrate water molecules of about 2.6 Å are significantly longer than those of Tb$^{3+}$ cation and oxygen atoms of PO$_4^{3-}$ anions (about 2.3 Å). As a result, it is quite reasonable to expect that TbPO$_4$·H$_2$O nanomaterials exhibit higher hydrophilicity and more chemical activities in water medium than those of TbPO$_4$. It is really a perspective result regarding to biomedical fluorescence labeling application, which required high hydrophilicity of luminescent nanomaterials.

PLE spectra of TbPO$_4$·H$_2$O nanorods/nanowires were recorded on the Cary eclipse fluorescence spectrometer. Excitation bands at 310, 350, 370 and 480 nm were observed in PLE spectra monitored at 542 nm emission line for all measured samples. The PLE spectra of the as-synthesized TbPO$_4$·H$_2$O sample at 400 and 600 W power are shown in figure 4. The peak in PLE spectra at 480 nm is due to the spin allowed $^7F_{6}$$^\rightarrow$$^5D_{3}$ transition of the Tb$^{3+}$ ions. The other peaks at 350, 370 and 310 nm are assigned to the intra $4f^8$ transitions between the $^7F_{6}$$^\rightarrow$$^7L_{6-7}$ and $^7F_{6}$$^\rightarrow$$^5H_{7-4}$, respectively [15]. It can be concluded that the excitation spectra of TbPO$_4$·H$_2$O nanorods/nanowires arose from the transitions in trivalent terbium ion Tb(III).

Figure 5 showed the PL spectra under 370 nm excitation of TbPO$_4$·H$_2$O nanowires synthesized by using microwave heating of an aqueous solution containing Tb(NO$_3$)$_3$ and NH$_4$H$_2$PO$_4$ at pH = 2 with different irradiated powers. Obviously, the emission intensity varied as a function of irradiated power and reached a maximum value with 500 W.

With a higher value of irradiated power the formation of TbPO$_4$·H$_2$O nanobunches might be a reason for the reduction in emission intensity. For prepared TbPO$_4$·H$_2$O nanorods/nanowires, the emission bands centered at 488, 542,
Figure 5. PL spectra under 370 nm excitation of TbPO$_4$·H$_2$O nanowires synthesized by using microwave heating of an aqueous solution containing Tb(NO$_3$)$_3$ and NH$_4$H$_2$PO$_4$ at pH = 2 with irradiated power of: (1) 300 W, (2) 400 W, (3) 500 W, (4) 600 W, (5) 700 W, (6) 800 W and (7) 900 W.

584, 620 nm are assigned to $^5$D$_{4} \rightarrow ^7$F$_{J}$ transitions ($J = 6, 5, 4, 3$), respectively. The maximum emission peak is found at value 542 nm of wavelength corresponding to $^5$D$_{4} \rightarrow ^7$F$_{3}$ transition.

4. Conclusion

Nanorods/nanowires of TbPO$_4$·H$_2$O have been successfully fabricated using microwave technique. The length and width of these nanowires/nanorods are 150–350 nm and 5–10 nm, respectively. These TbPO$_4$·H$_2$O nanomaterials possess rhabdophane-type pure hexagonal structure. The microwave irradiated power clearly affects the intensity of photoluminescence spectra of prepared samples. TbPO$_4$·H$_2$O nanowires/nanorods exhibit the characteristic narrow emission peaks of trivalent terbium ion. The fluorescent intensity reaches a maximum value with 500 W of irradiated power.

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