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Chemical synthesis and functional properties of monodispersed lanthanum phosphate nanorods

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ABSTRACT

Monodispersed $LaPO_4$ nanorods were synthesized by wet chemical method without the aid of organic additives. The effect of concentration of the precursors on the formation of nanorods was investigated. XRD studies revealed the formation of monoclinic phased $LaPO_4$ nanorods. The effect of concentration of the precursor on the electronic state of $LaPO_4$ nanorods was studied by XPS analysis. TEM analysis confirmed the monodispersed $LaPO_4$ nanorods with an average diameter of 10 nm and length of 150 nm. HRTEM analysis revealed the higher crystallinity of the synthesized $LaPO_4$ nanorods. The obtained results demonstrated that the monodispersed nanorods with dominant luminescence properties were obtained for the precursor ratio of 1:2 (lanthanum nitrate:phosphoric acid).

1. Introduction

In recent years, rare earth doped nanostructures have been greatly focused owing to their high luminescent nature. Among the various rare earth elements, lanthanide receives a special attention due to its unique electron configuration (4f electrons) and other optical and magnetic properties [1,2]. Lanthanide nanocrystals have various applications such as solid-state lasers, luminescent markers, bio-labels and displays [3–5]. On the other hand, there were number of host materials available; in which phosphate provides some advantages of having high quality fluorescent lighting due to its quantum fluorescent lighting and it retains the stability at higher temperature [6,7]. Therefore, lanthanum phosphate ($LaPO_4$) has been highly investigated to fabricate the luminescent devices. However, the size confinement and dimensionality are considered to be an important key factor which governs the properties of the nanomaterials owing to their unique optical, thermal, electronic and chemical properties. The one-dimensional (1D) structures [8–12] like nanowires, nanorods, nanotubes, nanobelts were expected to be more efficient comparing to zero-dimensional (0D) structures. Various methods have been adopted for the synthesis of $LaPO_4$ nanostructures such as hydrothermal, wet chemical method, etc. [13–16]. Kai et al. prepared the $LaPO_4$ nanorods by water and ethylene glycol mixed solvothermal route. They observed that the increase in the ratio of ethylene glycol favors the formation of nanorods [17]. Shankar et al. synthesized the $LaPO_4$ nanorods by sol–gel method and the aligned nanorods with size of 25–100 nm and average length of about 50 nm were obtained [18]. Ekthammathat group synthesized the nanorods in de-ionized water by microwave irradiation. $LaPO_4$ nanorods were obtained with the average length of 600–1000 nm and 20–40 nm in diameter [19]. Xiajuan et al. prepared $LaPO_4$ nanorods with the dimensions of 8 nm in diameter and 80 nm in length by oil bath method at 100 °C [20]. Among these methods, wet chemical method is considered to be simple and inexpensive route. However, the excess amount of organic additives during the chemical synthesis of the inorganic material results the quenching of luminescence and increase of defect level emission [21]. Since, there are no reports on the organic additives free wet chemical synthesis of well-defined monodispersed $LaPO_4$ nanorods. It is very important to optimize the growth parameters to obtain the monodispersed $LaPO_4$ nanorods.

In this paper we report the synthesis of $LaPO_4$ nanorods by wet chemical method. The effect of precursor concentration on the formation of nanorods and functional properties were investigated. The possible growth mechanism of the $LaPO_4$ nanorods is discussed.

2. Experimental

All the chemicals were purchased from Aldrich Company and used without further purification. In a typical procedure 0.1 mol of lanthanum nitrate $(LaNO_3)_3$ and 0.1 mol of phosphoric acid

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(H_3PO_4) were added to the 50 ml of de-ionized water. The mixture of the solution was allowed to stir for 5 h. Then the resultant solution was annealed at 200 °C for 3 h. Finally, the samples were dried at 90 °C for 12 h and collected; this sample was labeled as A. The similar procedure was followed for sample B with the variation of $LaNO_3$ from 0.1 to 0.2 mol, whereas the H_3PO_4 was fixed at 0.1 mol. For sample C the $LaNO_3$ concentration was fixed at 0.1 mol and the concentration of H_3PO_4 was varied from 0.1 to 0.2 mol.

XRD pattern was recorded using a Rigaku (Japan) X-ray diffractometer (RINT-2200, Cu Kα radiation) at 0.02 deg/s as the step interval. UV–visible analysis was performed by a Shimadzu (Japan) 3100 PC spectrophotometer using ethanol as a dispersing medium. The analysis of X-ray photoelectron spectroscopy (XPS) was performed via a Shimadzu ESCA 3100. The transmission electron microscope (TEM) images were recorded by a JEOL JEM 2100F microscope at an accelerating voltage of 200 kV. Photoluminescence spectra were recorded using a spectrometer (Hamamatsu Photonics) with 325-nm He–Cd laser excitation.

3. Results and discussion

Fig. 1 shows the XRD pattern of the samples. All the diffraction peaks of $LaPO_4$ can be indexed as the monoclinic phase of $LaPO_4$ with the lattice constants of $a=6.84$, $b=7.07$, $c=6.54$ Å and $\beta=10.85°$. It has good agreement with the JCPDS card no. 35-0731. No other peak related to the secondary phase of impurity was detected. Fig. 2 shows the XPS spectra of monoclinic $LaPO_4$ 1D nanorods. In Fig. 2(a) two strong peaks locating at 835.5 eV and 855.5 eV can be assigned to the binding energy of (La $3d_{5/2}$). All three samples exhibited similar peak position for the La $3d_{5/2}$. The peaks observed at 534 eV (Fig. 2(b)) and 285.5 eV (Fig. 2(c)) correspond to the binding energies of (O1s) and (P2s) core level respectively. There was no shift in the peak position of O1s and P2s states of sample A and B. Whereas, sample C showed slight shifts in the O1s and P2s state. This can be attributed to the presence of more amounts of O and P from the PO_4 group.

Fig. 3(a), (c), and (e) represents the TEM images of $LaPO_4$ in the ratio of (1:1), (2:1) and (1:2) respectively. When $La(NO_3)_3$:H_3PO_4 was in equal ratio, $LaPO_4$ indicated rod-like morphology with the average length of 100–150 nm with the diameter of 10–20 nm. Fig. 3(a) shows that the nanorods are not well defined and not uniform. It indicates the initial stage for the formation of nanorods

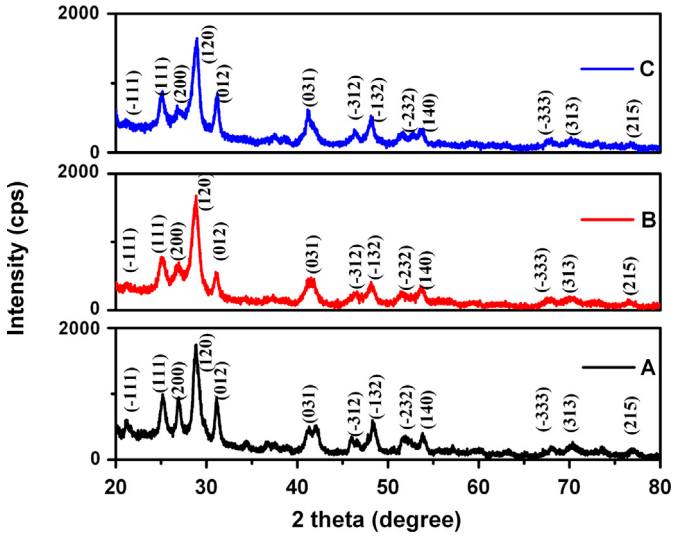

Fig. 1. XRD patterns of samples A, B and C.

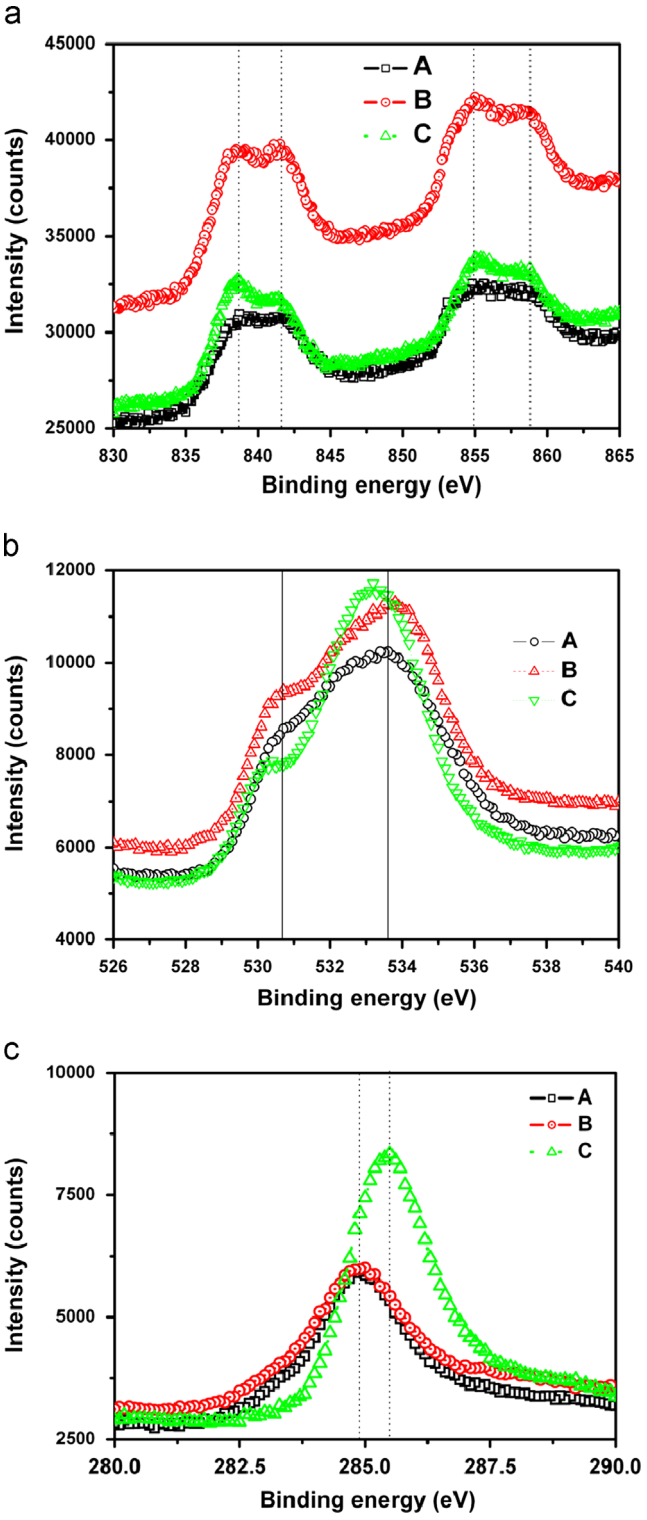

Fig. 2. XPS analysis of (a) La state, (b) O state and (c) P state of samples A, B and C.

by the primary crystals attaching with its neighboring crystal by oriented attachment mechanism. When the ratio of $La(NO_3)_3$:H_3PO_4 was 2:1. There was a monodispersed formation of $LaPO_4$ nanorods with the average length of 100–150 nm and the diameter of 15–20 nm as shown in Fig. 3(c). Moreover, when the ratio of $La(NO_3)_3$:H_3PO_4 is 1:2. The rod shape got ruined and somewhat agglomerated irregular structure was observed. The magnified TEM images were shown in Fig. 3(b), (d), and (f) for sample A, B and C, respectively. HRTEM images were shown as inset.