Room-temperature synthesis and photoluminescence of hexagonal CePO$_4$ nanorods

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Abstract. Hexagonal CePO$_4$ nanorods were synthesized via a simple chemical precipitation route at room-temperature without the presence of surfactants and then characterized by powder X-ray diffraction (XRD), energy-dispersive X-ray (EDX) spectrometry, scanning electron microscopy (SEM), transmission electron microscopy (TEM), ultraviolet-visible (UV–vis) absorption and photoluminescence (PL) spectroscopy. Hexagonal CePO$_4$ nanorods exhibit strong ultraviolet absorption and ultraviolet luminescence, which correspond to the electronic transitions between 4$f$ and 5$d$ state of Ce$^{3+}$ ions.

1. Introduction

Rare earth phosphate nanomaterials have been extensively reported due to their high-performance photoluminescence [1, 2]. Especially, pure and rare-earth ion doped CePO$_4$ nanomaterials have received a lot of research interest [3-6]. CePO$_4$ possesses two common crystallographic structures: monoclinic and hexagonal [7]. Recently, the monoclinic phase was prepared by reflux method [8], hydrothermal synthesis [9] and microwave radiation [10] et al., and the hexagonal phase was synthesized in a sequential, aqueous procedure under continuous flow using a rotating tube processor and a narrow channel reactor by Fang and co-workers [11]. To the best of our knowledge, most of available open literatures focus on the hydrothermal synthesis of pure and rare-earth ion doped CePO$_4$ nanomaterials with different crystallographic structures. However, chemical precipitation, as an important one of chemical synthesis routes, is rarely used for the preparation of rare earth phosphate nanomaterials. There are not reported yet for room-temperature chemical precipitation of CePO$_4$ nanomaterials. So we intend to explore the feasibility of room-temperature precipitation synthesis for rare earth phosphate nanomaterials.

In this work, we synthesized CePO$_4$ nanorods with hexagonal structure by a simple chemical precipitation route at room-temperature without using any surfactant. The product was characterized by XRD, EDX, SEM and TEM. Moreover, luminescent properties of the product were investigated.

2. Experimental section

2.1. Synthesis

All of the chemicals were purchased from Aladdin Chemistry Co. Ltd and used as received without further purification. 5 mmol Ce(NO$_3$)$_3$·6H$_2$O and 5 mmol Na$_3$PO$_4$·12H$_2$O were dissolved in 10 ml deionized water to produce precipitation. Subsequently, the precipitation disappeared when the pH value of the solution was carefully adjusted to 1 with a given concentrated HNO$_3$ solution under
vigorous stirring. The solution was transferred into a sealed beaker and preserved at room temperature. After 20 days, the as-synthesized precipitate was separated by centrifugation and washed five times with deionized water. Finally, the products were dried at 60 °C in air for further characterization.

2.2. Characterization
The powder X-ray diffraction (XRD) pattern of the as-synthesized sample was determined on a RIGAKU DMAX-3B diffractometer with CuKα radiation (λ = 1.54056 Å). The operation voltage and current were maintained at 40 KV and 40 mA, respectively. The sample was scanned from 10 to 90° (2θ) at a scanning rate of 0.02° s-1. Scanning electron microscopy (SEM) images and element analysis were obtained with a FEI QUANTA200 microscope operated at an accelerating voltage of 30 kV. Transmission electron microscopy (TEM) patterns were taken on a JEOL JEM-2100 microscope under a working voltage of 200 kV. The samples for TEM measurement were supported on carbon-coated copper grids by dropping the ethanol suspension containing uniformly dispersed powder. The ultraviolet-visible (UV–vis) absorption spectrum was recorded on a HITACHI U-4100 UV/VIS/NIR spectrophotometer. The photoluminescence (PL) measurement was carried out on a HITACHI F-4500 fluorescence spectrophotometer using Xe lamp as the excitation source at room temperature.

3. Results and discussion

3.1. Phase identification
The crystalline phase and elemental composition of as-synthesized CePO₄ sample have been identified by powder XRD and EDX measurements, as shown in figure 1. All diffraction peaks can be easily indexed with respect to the hexagonal CePO₄ (space group: P6222 (180) with cell parameters: a₁ = 7.055 Å and c = 6.439 Å (JCPDS 34-1380), suggesting that no secondary phase co-exists. Moreover, the EDX analysis (the inset of figure 1) confirms the presence of Cerium (Ce), phosphorus (P) and oxygen (O) in the product, which can effectively support the XRD result. All above analysis means that the as-synthesized sample have the nature of high purity in our synthesis route.

![Figure 1. XRD pattern of CePO₄ sample (EDX image as inset).](image)

It is with regret that the crystallinity of the sample prepared at room-temperature is poor. The observed broad reflection peaks should be attributed to the small size of the sample and the distribution in particle sizes, as revealed by the below SEM and TEM images (figure 2).

3.2. Morphology
The typical low-magnification SEM image of the as-prepared pure hexagonal CePO₄ sample is displayed in figure 2a, from which nanosized-structure morphology with serious aggregation is
detected. The morphology and microstructure of the sample was further characterized by TEM and HRTEM. The typical TEM and HRTEM images of hexagonal CePO₄ sample are shown in figure 2b and figure 2c, respectively. Nanorods with a diameter of 7–10 nm and length of 60–150 nm are demonstrated, suggesting a high growth rate and single growth direction along the axial direction of CePO₄ crystal. The TEM image (figure 2b) clearly unfolds the form of the bundle that is composed of some neighbouring nanorods. The interaction among these nanorods might arise from the synergic effects of chemical binding and physical attachment. The high density of nanorods is representative of the high yield, which may result from this simple room-temperature preparation approach. The HRTEM image (figure 2c) shows that the nanorod is structurally uniform with the interplanar spacing of 0.30 nm, which corresponds to the standard value of d₂₀₀ spacing in hexagonal CePO₄ (JCPDS: 34-1380), meaning that the growing [001] direction of the hexagonal CePO₄ nanorods is parallel to the (200) lattice plane. This result is in good correlation with the anisotropic character of the (200) peak in the XRD pattern (figure 1).

Based on our experimental results, from a structural point of view, the growth mechanism of these nanorods is analyzed. In the crystal structure of hexagonal CePO₄ [12], there are infinite linear chains which are alternating CeO₈ polyhedra and PO₄ tetrahedra along the c axis. Wong et al. [3] claimed that the bonding between these chains is considerably weaker than that within the chains from a thermodynamic perspective, meaning that the activation energy for the c axis direction of growth of hexagonal CePO₄ is lower than that for a growth direction perpendicular to the c-axis itself. Hence, this analysis result indicates a higher growth rate along the c axis. In other hexagonal rare earth phosphate nanomaterials [13, 14], the same preferential growth along the c axis is also observed. Therefore, the hexagonal crystal structure of rare earth phosphate should be responsible for the anisotropic growth of CePO₄, leading to the observed rod-like morphology with high aspect ratio.

**Figure 2.** SEM (a), TEM (b) and HRTEM (c) images of CePO₄ nanorods.

### 3.3. Optical properties

Figure 3a shows the UV-vis spectrum of the as-prepared hexagonal CePO₄ nanorods from the ultraviolet to visible region, from which a strong ultraviolet absorption peak at around 275 nm is observed. According to the previous related literatures [10, 15], the optical absorption of CePO₄ has two electron transition modes (f–f and f–d) of Ce³⁺ ions in IR region and ultraviolet region. So the ultraviolet absorption peak is attributed to the 4f⁽⁷F₅/₂⁾–5d⁽³D₅/₂⁾ electron transition of Ce³⁺ ions. The absorption cutoff wavelength is about 389 nm, indicating the hexagonal CePO₄ nanorods have a wider ultraviolet absorption range with the optical band gap of 3.19 eV than hydrothermally synthesized monoclinic CePO₄ nanorods (the optical band gap of 4.1 eV) [10] due to the effect of the crystal structure and surface area. This result implies the potential applicability of hexagonal CePO₄ nanomaterials as UV absorber, making it a promising material for personal care products [16]. The emission spectrum of hexagonal CePO₄ nanorods monitored at 293 nm is illustrated in figure 3b. The photoluminescence curve exhibits a strong ultraviolet broad emission band centered at 356 nm, which may be linked with the electronic transitions from 5d excited state to ²F ground state. Similar broadening optical transitions are observed in the early reports [7].
4. Conclusions
The present work describes a method for preparing hexagonal CePO$_4$ nanorods by a simple chemical precipitation route at room-temperature without the presence of surfactants. This is the first report on the room-temperature precipitation synthesis of hexagonal CePO$_4$ nanomaterials. Powder XRD and EDX measurement confirm the purity and crystalline phase of CePO$_4$ nanorods with hexagonal P6$_3$22 structure. According to SEM and TEM observations, the hexagonal CePO$_4$ sample is composed of uniform nanorods with a diameter of 7–10 nm and length of 60–150 nm. The formation of rod-like morphology results from the anisotropic growth along the [001] direction. Hexagonal CePO$_4$ nanorods exhibit strong ultraviolet absorption (the optical band gap of 3.19 eV) and ultraviolet luminescence, which correspond to the electronic transitions between 4f and 5d state of Ce$^{3+}$ ions.

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