Epitaxial Synthesis of Uniform Cerium Phosphate One-Dimensional Nanocable Heterostructures with Improved Luminescence

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Uniform CePO₄@LaPO₄ and CePO₄:Tb³⁺@LaPO₄ one-dimensional single-crystalline nanocable heterostructures with highly enhanced photoluminescent emission have been synthesized via a mild and simple hydrothermal approach. The resulting one-dimensional single-crystalline nanocable heterostructures have smooth and uniform LaPO₄ sheaths, which is of great significance in effectively eliminating surface trap-states and suppressing the energy quenching in energy-transfer processes. The photoluminescence results for these onedimensional nanocable heterostructures illustrate that the uniform LaPO₄ sheaths remarkably increase the luminescent efficiency.

Introduction

Nowadays, inorganic luminescent materials with nanometer dimensions have become an important field of modern nanoscale science and technology, which could find many attractive applications, such as in optoelectronic devices and biological fluorescence labeling.¹⁻³ In particular, one-dimensional (1D) luminescent nanostructures with size-dependent optical and electronic properties are motivated by their potential applications as interconnectors and active components in fabricating the optoelectronic nanodevices,⁴⁻⁶ provided that their photoluminescence is highly efficient. Unfortunately, the luminescent efficiency of nanostructures is usually lower than that of the corresponding bulk material, which is due to the nonradiative decay channels originating from surface electronic states in the nanostructures. In recent years, much progress has been made to significantly increase the luminescent efficiency of nanostructures by suppressing energy-loss processes in the energytransfer processes.^{7–10} Of these strategies, coating the surface of the nanocrystals with a suitable inorganic material to form the core@shell heterostructures has been regarded as an effective strategy to improve luminescent efficiency.¹¹⁻¹⁴ Since the pioneering work by Iijima and co-workers,15 several research groups have achieved 1D nanocable heterostructures based on different material systems,16-19 particularly, the preeminent research of Bando's group on the coaxial nanocable heterostructures.^{20–24} However, very few reports on photoluminescent (PL) properties could be found for these 1D nanocable heterostructures, which is important for the application in future optoelectronic nanodevices, so it is still a challenge to seek a facile and high yield synthetic method to fabricate highly efficient luminescent 1D nanocable heterostructures.

As a consequence of the numerous well-defined transition modes involving the 4f shell of their ions, rare earth compounds have been extensively used in high-performance luminescent devices, magnets, catalysts, and other functional materials.^{25,26} Very recently, more and more attention has been focused on the synthesis and PL properties of lanthanide orthophosphate

(LnPO₄) and lanthanide(III)-doped lanthanide orthophosphate (LnPO₄:Ln³⁺) nanostructured materials²⁷⁻³¹ for their potential applications in the domain of optoelectronic devices. Of particular importance in this respect is that LnPO₄ and LnPO₄: Ln³⁺ single-crystalline nanowires have also been successfully prepared by the hydrothermal method.³²⁻³⁴ However, the luminescent efficiency of these 1D nanostructures is usually far away from the demand for the practical application.^{32,34} The relatively low efficiency can be attributed to the numerous defects existing on the surface of nanostructural materials. Therefore, epitaxially coating the surface of LnPO₄ and LnPO₄: Ln³⁺ single-crystalline nanowires with a coherent LaPO₄ crystalline shell to form 1D nanocable heterostructures would significantly eliminate the defects and increase the luminescent efficiency. In accordance with crystal lattice matching theory, effective epitaxial growth of LaPO₄ on the surface of LnPO₄ should be possible because of the identical hexagonal crystal structures and very close lattice constants in the LnPO₄ family. In this contribution, we report the first example of the successful synthesis of very uniform CePO₄@LaPO₄ and CePO₄:Tb³⁺@ LaPO₄ 1D nanocable heterostructures via a facile, hydrothermal method with high yield in 1D core-shell structures and their excellent PL properties. In the synthesis, CePO₄ or CePO₄:Tb³⁺ single-crystalline nanowires with a narrow distribution of diameters obtained by surfactant-assisted synthesis were used as cores for the epitaxial growth of LaPO₄ sheaths.

Experimental Section

CePO₄ and CePO₄:Tb³⁺ single-crystalline nanowires used as the core in the process were prepared according to the reported procedure.^{33,34} In a typical synthesis of uniform CePO₄ singlecrystalline nanowires, 25 mL of Na₃PO₄ aqueous solution (0.8 M) was added into 25 mL of Ce(NO₃)₃ aqueous solution (0.8 M) under vigorous stirring for 30 min. Then the pH value of the solution was adjusted to below pH 1 using 0.1 M HCl under stirring. After that, Pluronic P123 (EO₂₀PO₇₀EO₂₀, $M_{av} = 5800$, Aldrich) (2.0 g, 0.4 mmol) was added into the resulting suspension under stirring at 35–40 °C, and the solution was further stirred for 2 h. The above solution was poured into a Teflon-lined autoclave and was heated subsequently to 100 °C

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Figure 1. XRD patterns of (a) CePO₄ nanowires and (b) CePO₄@LaPO₄ 1D nanocable heterostructures.

for 12 h. Afterward, the autoclave was allowed to cool to room temperature. Subsequently, half of the precipitate was then filtered, washed with absolute ethan distilled water several times, and dried at room temperature for further characterization. The remaining half of the precipitate was used for the preparation of CePO₄@LaPO₄ 1D nanocable heterostructures. CePO₄:Tb³⁺ single-crystalline nanowires were prepared according to the same method.

For the synthesis of CePO₄@LaPO₄ and CePO₄:Tb³⁺@LaPO₄ 1D nanocable heterostructures, the remaining half of the precipitate was highly dispersed in methanol (25 wt %) in 30 mL of distilled water, and then 12.5 mL of La(NO₃)₃ aqueous solution (0.8 M) was added into the resulting colloidal solutions under vigorous stirring for 30 min. After that, 12.5 mL of Na₃PO₄ aqueous solution (0.8 M) was added into the resulting colloidal solutions, with additional stirring for 2 h. The resulting suspension was poured into a Teflon-lined autoclave. The autoclave was sealed and maintained at 100 °C for 12 h and then air cooled to room temperature. The resulting precipitate was then filtered, washed with absolute ethanol and distilled water several times, and dried at room temperature for further characterization.

X-ray powder diffraction (XRD) patterns were obtained on a Rigaku D/Max-II X-ray diffractometer with graphite-monochromatized Cu Ka radiation. Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopic (HRTEM) images, and the selected area electron diffraction (SAED) patterns were recorded on a JEOL200CX microscope with an accelerating voltage of 200 kV. Energydispersive X-ray spectroscopy (EDS) was obtained from an attached Oxford Link ISIS energy-dispersive spectrometer fixed on a JEM-2010 electron microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed in a VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh-vacuum (UHV) chambers. All binding energies were referenced to the C1s peak at 284.8 eV of the surface adventitious carbon. Transparent and scatter-free colloidal solutions were obtained by dispersing the powders in methanol containing a few drops of a solution of tetra-n-butylammonium hydroxide in methanol (25 wt %).¹⁴ The luminescence spectra of dilute colloidal solutions were recorded in cuvettes (1 cm path length) on a RF-5301PC spectrometer. PL quantum yields of colloidal solutions were measured by comparing the emission of the colloidal solution with that of a Rhodamin 6G solution (Lambda Physik, laser grade; solution in spectroscopic grade absolute ethanol; quantum yield 95%,35) of identical optical density at the excitation wavelength.

Results and Discussion

Figure 1a shows a typical XRD pattern for CePO₄ nanowires before being coated with a LaPO₄ shell, which reveals that all



Figure 2. Typical TEM images of (a) CePO₄ nanowires and (b) CePO₄@LaPO₄ 1D nanocable heterostructures. (c) TEM image of a CePO₄@LaPO₄ 1D nanocable heterostructure. (d) HRTEM image of the single 1D nanocable heterostructure in part c and its SAED pattern (inset) obtained from the same 1D nanocable heterostructure.

of the diffraction peaks can be readily indexed to a pure hexagonal phase of CePO₄ [space group: $P3_121(152)$] with lattice constants highly comparable to the values in JCPDS card. No impurity phases could be found from the XRD pattern in the synthesized products. After the nanowires were coated with a LaPO₄ shell, the diffraction peaks shift very little toward smaller *d*-spacings (Figure 1b). The peaks of CePO₄@LaPO₄ core—shell nanostructures become sharper as compared to the XRD patterns of the CePO₄ core, and no additional peaks are present. This indicates the better crystallinity of CePO₄ nanowires coated with LaPO₄ sheaths.

The morphology and microstructural details of the assynthesized samples were further investigated with TEM, SAED, and HRTEM. Representative TEM images of CePO₄ nanowires and CePO₄@LaPO₄ 1D nanocable heterostructures are presented in Figure 2, parts a and b, respectively. Figure 2a reveals that CePO₄ nanowires synthesized via the surfactant-assisted (Pluronic P123) hydrothermal approach are composed of welldefined nanowires, and these nanowires are straight and highly uniform in morphology with an average diameter of 10 nm and a length up to several micrometers. Of particular interest in this synthetic method is the ability to obtain much more uniform morphology, especially in diameter along the entire lengths, than previously reported.³²

These CePO₄ nanowires with uniform morphology were used as one-dimensional cores for epitaxial growth of nanocrystalline LaPO₄ sheaths under subsequent hydrothermal treatment, which led to the formation of the CePO₄@LaPO₄ 1D nanocable heterostructure with similarly uniform morphology, as shown in Figure 2b. The mean diameter increases from 10 nm for the CePO₄ 1D core nanostructures to 20 nm for the CePO₄@LaPO₄ 1D nanocable heterostructure. Figure 2c shows a smooth surface morphology of a single CePO₄@LaPO₄ 1D nanocable heterostructure with well-defined facets and uniform diameter along



Figure 3. EDS spectrum of the CePO₄@LaPO₄ nanocable heterostructures.

the nanowire. Herein, it is important to note that separate cores of CePO₄ nanowires were not observed via TEM in all of our samples (Figure 2b), which indicates that the LaPO₄ shell growth has been uniform and epitaxial, completely coating the CePO₄ cores. As is well-known, the interfacial strain is a very important factor that must be considered during the process of growing for 1D nanocable heterostructures.¹² In our experiment, this problem is well solved by choosing a suitable LaPO₄ shell with the least lattice mismatch between CePO4 and LaPO4 that could induce diminished strain on the CePO₄ crystalline structure. HRTEM analysis provides more detailed structural information on these 1D nanocable heterostructures. Figure 2d shows the HRTEM micrograph of the same single nanowire in Figure 2c, which shows that the 1D nanocable heterostructure is structurally single crystalline without detectable stacking faults, defects, or dislocations. The calculated periodic fringe spacings were 0.61 nm along the longitudinal axis of the nanocable, which are continuous through both the core and the shell, implying effective epitaxial growth of the LaPO₄ shells on the surface of CePO₄ cores. Although the core and the shell of these 1D nanocable heterostructures cannot be distinguished in the TEM and HRTEM images due to the lattice coherence between the LaPO₄ shell and the CePO₄ core, the well-defined epitaxial relationship ([001]LaPO₄//[001]CePO₄) is clear (see the arrow in Figure 2d) and can be attributed to the identical crystalline structure and the almost identical lattice constants between the hexagonal phases of CePO₄ and LaPO₄. The SAED pattern (inset in Figure 2d) taken from the same single nanowires in Figure 2c demonstrates that the as-prepared 1D nanocable heterostructures are single-crystalline, which is in good agreement with the HRTEM result. The EDS results of these 1D nanocable heterostructures reveal the presence of La and Ce in the corresponding nanocable heterostructures with an approximate atomic ratio of 1.02:0.98 (Figure 3), as was designed in the synthesis.

To provide further evidence that as-synthesized CePO₄@LaPO₄ 1D materials are of nanocable heterostructures (i.e., 1D coreshell heterostructures) and are not a mechanical mixing of CePO₄ and LaPO₄, the products were further examined by XPS to investigate the elementary states on the surfaces. If the shell is thicker than the detection limit of XPS in depth, only the elementary peak in the shell can be detected. The thickness of the LaPO₄ shell for the as-synthesized CePO₄@LaPO₄ 1D nanocable heterostructures is 5-6 nm (Figure 2c), thicker than the detection limit of XPS. Figure 4 shows the XPS spectra of the hexagonal CePO₄@LaPO₄ 1D heterostructures and CePO₄: La³⁺ nanowires. The XPS spectrum for CePO₄:La³⁺ nanowires shows the presences of visible Ce 3d and La 3d peaks; however, only La 3d peaks exist in the XPS spectrum for CePO₄@LaPO₄ 1D heterostructures (inset in Figure 4). This indicates that the LaPO₄ shell has completely covered the CePO₄ nanowire core



Figure 4. XPS spectra of the 50% La^{3+} doped CePO₄ nanowires (a) and the CePO₄@LaPO₄ nanocable heterostructures (b). Inset: the XPS spectra in the range 800–1000 eV.



Figure 5. Luminescence emission ($\lambda_{exc} = 280 \text{ nm}$) spectra of the dilute colloidal solutions of the CePO₄ nanowires and CePO₄@LaPO₄ 1D nanocable heterostructures.

and the CePO₄@LaPO₄ 1D nanocable heterostructure, rather than a solid solution of (Ce,La)PO₄, has formed.

Figure 5 shows the luminescent spectra of dilute colloidal solutions of CePO₄ nanowires and CePO₄@LaPO₄ 1D nanocable heterostructures under identical optical densities at the excitation wavelength ($\lambda_{\text{exc}} = 280$ nm). The spectra exhibit a strong ultraviolet PL emission centered at 345 nm and a weak band in the visible region, which correspond to the d-f transitions of the Ce³⁺ ions.^{33,34} From the emission spectra, the relatively low photoluminescence is clearly observed in CePO₄ single-crystalline nanowires before being coated with the LaPO₄ shell, while the CePO₄@LaPO₄ 1D nanocable heterostructures show dramatically increased intensity of the ultraviolet PL emission due to the shielding effect of LaPO₄ sheaths. This can be explained by the fact that a significant amount of nonradiative centers exist on the surface of CePO₄ single-crystalline nanowires which absorb the energy of the electron but give no light emissions. When coated with LaPO₄, the crystallinity of CePO₄ singlecrystalline nanowires should be increased by LaPO₄ sheaths, which could be proved in XRD patterns (Figure 1). Thus, the LaPO₄ sheaths in CePO₄@LaPO₄ 1D nanocable heterostructures can eliminate surface trap-states and suppress the energy quenching in energy-transfer processes. In addition, the enhanced luminescent efficiency could be the result of the suppression of solvent quenching by the LaPO₄ shell. The PL spectra of CePO₄ and CePO₄@LaPO₄ were measured in methanol with tetra-n-butylammonium hydroxide. The C-H and O-H stretches of the solvent can quench surface luminescent centers. If LaPO₄ can be epitaxially grown on the CePO₄ surface, the surface luminescent centers of CePO₄ are protected from the solvents, so the enhancement of the total emission can be expected. In this way, the PL quantum yield is enhanced from 8% for the CePO₄ single-crystalline nanowires up to 19% for CePO₄@LaPO₄ 1D nanocable heterostructures. Figure 6 shows



Figure 6. Luminescence emission ($\lambda_{exc} = 278$ nm) spectra of the dilute colloidal solutions of the Ce_{0.9}Tb_{0.1}PO₄ 1D nanostructures (dashed line) and the Ce_{0.9}Tb_{0.1}PO₄@LaPO₄ 1D nanocable heterostructures (solid line).

another example for Tb³⁺ doped CePO₄ with and without the LaPO₄ sheaths. The PL quantum yield of Ce_{0.9}Tb_{0.1}PO₄ 1D nanostructures is 31% for the terbium emission (40% if the cerium emission is taken into account),³³ and the PL quantum yield of the terbium emission in Ce_{0.9}Tb_{0.1}PO₄@LaPO₄ 1D nanocable heterostructures with 5–6 nm of LaPO₄ sheaths increases to 67% (Figure 6). If the cerium emission is included, the total quantum yield is as high as 75%, which, to our knowledge, is the first report for the excellent green-emitting CePO₄:Tb³⁺@LaPO₄ 1D nanocable heterostructures with 75% PL quantum yield.

Conclusions

In summary, we demonstrated that uniform $CePO_4@LaPO_4$ and $CePO_4:Tb^{3+}@LaPO_4$ 1D single-crystalline nanocable heterostructures could be successfully prepared via a facile, hydrothermal method. The resulting 1D single-crystalline nanocable heterostructures have smooth and uniform LaPO_4 sheaths, which is of great significance to highly enhance luminescent efficiency. Ongoing efforts are being directed to resolve the details of this PL enhancement mechanism for the 1D nanocable heterostructures, and to extend this system to other 1D nanocable heterostructures with high luminescence efficiency.

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