Hydrothermal Synthesis of Ultraviolet-emitting Cerium Phosphate Single-crystal Nanowires

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Cerium phosphate single-crystalline nanowires with a narrow distribution of diameters have been successfully synthesized by a mild and simple hydrothermal approach. Photoluminescence of cerium phosphate single-crystalline nanowires show that these nanowires can emit ultraviolet laser light.

Nanostructured materials have attracted much attention in recent years and been expected to play a crucial role in the future nanotechnological advance in electronics, optoelectronics, and memory devices.[1] In particular, 1D nanostructures have become a class of attractive materials for both fundamental research and technological applications because of their unique chemical and physical properties, which can be attributed to their dimensional anisotropy.[2] During the past decade, considerable research efforts have been directed toward the preparation of carbon nanotubes[3] and semiconductor,[4] metallic[5] binary oxide nanowires,[6] and ternary metal oxide nanorods.[7] However, few reports can be found concerning phosphate single-crystalline nanowires.[8] Since phosphate represents a big branch of many important and interesting materials, development of straightforward and controllable methods to construct phosphate single-crystalline nanowires is of importance to nanotechnology and still remains a key research challenge.

Among various phosphates, rare earth phosphates are particularly suitable for applications as light emitters owing to their well-defined transitions within the 4f shell.[9] Very recently, the cerium phosphate 1D nanostructures have been reported.[8] However, some limitations such as broad distribution of diameters (5–100 nm) and special conditions should be circumvented for practical utilities.[8] Furthermore, to the best of our knowledge, the reports on photoluminescence of cerium phosphate nanowires have not been found up to now. In this letter, we report a facile, surfactant-directed hydrothermal approach to fabricate cerium phosphate single-crystalline nanowires at low temperature with a narrow size distribution (10–12 nm) and its photoluminescence properties. The availability of cerium phosphate nanowires with narrow size distribution should enhance the photoluminescence.

In a typical procedure for the synthesis of single-crystalline $CePO_4$ nanowires, 7.45 g $CeCl_3 \cdot 7H_2O$ and 7.6 g $Na_3PO_4 \cdot 12H_2O$ were dissolved in 80-g distilled water, respectively, and then were mixed, stirring for about 20 min. The resulting precipitate was recovered by centrifugation and washed with distilled water. The precipitate was added into a mixture of nonionic pluronic amphiphilic triblock copolymers (P123, 2 g), H_3PO_4 (30 mL, 2 M), and deionized water (30 g) under stirring at 35–40 °C. The resulting solution was stirred for 2 h and then sealed in a stainless steel autoclave with a Teflon liner. This autoclave was maintained at 100 °C for 12 h. Subsequently, the autoclave was allowed to cool to room temperature. The precipitate was filtered, and washed with absolute alcohol, and distilled water several times. The final products were dried at room temperature.

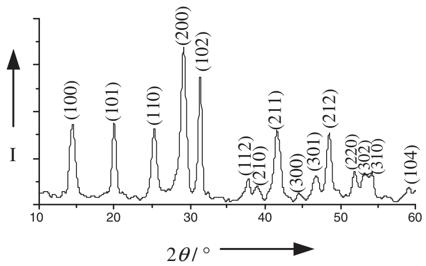

Figure 1. X-ray diffraction pattern of $CePO_4$ nanowires.

The crystal structure and phase purity of the $CePO_4$ samples was examined by X-ray diffraction (XRD) technique (Figure 1). All diffraction peaks can be perfectly indexed as the hexagonal cell of $CePO_4$ [space group: $P6_222$ (180)] with lattice constants comparable to the values in JCPDS card 31-1380, and no impurities can be detected, which indicates that the nanowires obtained by our current synthetic methods consist of a pure hexagonal $CePO_4$ phase.

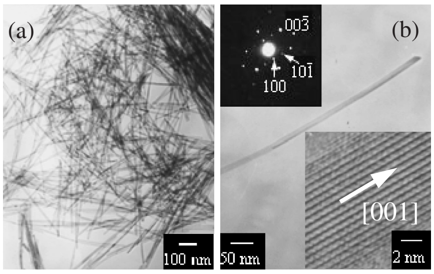

Figure 2. (a) TEM image of $CePO_4$ nanowires; (b) TEM image of an 11-nm diameter $CePO_4$ nanowire. Left inset: selected area electron-diffraction (SAED) pattern obtained from the same nanowire. Right inset: A high-resolution TEM image of the nanowire that shows lattice fringes perpendicular to the [001] direction.

The morphology and microstructure of the products were further investigated with transmission electron microscopy (TEM), selected area electron diffraction (SAED), and high resolution transmission electron microscopy (HRTEM), accompanied by energy dispersive X-ray spectroscopy (EDS). Representative TEM images (Figure 2a) show that the products obtained at 100 °C for 12 h are composed of nanowires in high yield, and these nanowires are straight with an average diameter of 10–12 nm and the length up to several micrometers, which is much more uniform, especially in diameter, than the previously reported ones.[8] Figure 2b shows a typical $CePO_4$ nanowire. Its corresponding SAED pattern at the top left corner of Figure 2b reveals that the nanowire exhibits sharp diffraction spots characteristic of a single-crystalline $CePO_4$, in agreement with X-ray diffraction results. Moreover, the SAED patterns taken from the different nanowires were found to be identical within experimental accuracy, indicating that all $CePO_4$ nanowires synthesized by current synthetic methods are single crystalline. Representative HRTEM image of corresponding nanowire (inset in Figure 2b) showed that the nanowire is highly crystalline without defects or dislocations, which provides another evidences that these nanowires are single crystalline. The calculated interplannar distance of 0.61 nm corresponds to the *d* spacing of (100) crystal planes, consistent with the SAED pattern. The (100) crystal planes are parallel to the long axis of the nanowire, that is, the preferred growth direction is [001]. Both the SAED pattern and the HRTEM image in Figure 2b showed that the *c* axes of the $CePO_4$ unit cells are aligned along the nanowire axis. The chemical stoichiometry of $CePO_4$ nanowires was investigated with energy dispersive spectrometry (EDS), which gave the molar ratio of Ce, P, and O close to the stoichiometric proportions of the formula $CePO_4$. It is also interesting to note that $CePO_4$ single-crystalline nanowires, synthesized by the current approach, have much narrower distribution of diameters (10–12 nm) than that in previous works (5–50 nm, 20–100 nm).[8] Apparently, the P123 had the crucial effect on the size distribution of $CePO_4$ nanowires as compared to that with the absence of P123.[8] Further investigations into the effect of P123 on the size distribution of $CePO_4$ nanowires are in progress.

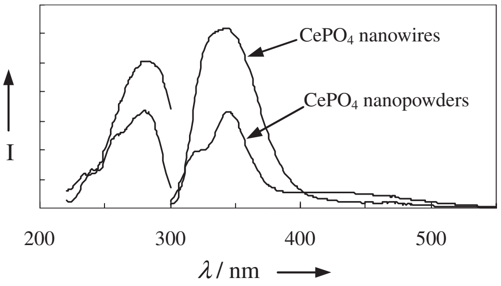

Figure 3. Excitation (200–300 nm, $\lambda_{obs} = 345$ nm) and emission (300–550 nm, $\lambda_{exc} = 280$ nm) spectra of the $CePO_4$ nanowires and $CePO_4$ nanopowders.

No reports have been found about the photoluminescence of $CePO_4$ single-crystalline nanowires. Figure 3 shows the room temperature PL emission and excitation spectra of the $CePO_4$ nanowires/nanopowders. The spectra of the $CePO_4$ nanowires exhibited a strong ultraviolet PL emission peak centered at around 345 nm and one excitation peak at 284 nm (strongest). The excitation spectrum, monitored at the emission wavelength of 345 nm, consists of two broad peaks at 236 and 284 nm, respectively, which corresponds to the transitions from the ground state $^2F_{5/2}$ of Ce^{3+} to the different components of the excited Ce^{3+} 5d states split by the crystal field.[10] However, the characteristic feature of the emission band is the absence of the expected doublet peaks arising from 5d → $^2F_{5/2}$ and 5d → $^2F_{7/2}$ transitions due to spin orbit splitting of the $4f^1$ ground state of Ce^{3+} ions as showed in $CePO_4$ nanopowders (Figure 3, dashed line), which may be attributed to the nearly equal transition probability between 5d to $^2F_{5/2}$ and 5d to $^2F_{7/2}$. The luminescent properties of Ce^{3+} ions imply that a relationship between the product morphology and its optical properties should exist. Systematic and further investigations in this area are in progress.

In summary, we have demonstrated that cerium phosphate single-crystalline nanowires with a narrow distribution of diameters, synthesized by a mild and simple hydrothermal approach, can emit ultraviolet laser light. We consider this work as a preliminary and important step towards the development of lanthanide phosphate based 1D nanostructures with potential luminescent and catalytic application.

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References

1 Y. Cui and C. M. Lieber, *Science*, **291**, 851 (2001); A. P. Alivisatos, *Science*, **271**, 933 (1996); S. Sun, C. B. Murray, D. Weller, L. Folks, and A. Moser, *Science*, **287**, 1989 (2000).

2 A. M. Rao, E. Richter, S. Bandow, B. Chase, P. C. Eklund, K. A. Williams, S. Fang, K. R. Subbaswamy, M. Menon, A. Thess, R. E. Smalley, G. Dresselhaus, and M. S. Dresselhaus, *Science*, **275**, 187 (1997).

3 T. W. Odom, J. l. Huang, P. Kim, and C. M. Lieber, *J. Phys. Chem. B*, **104**, 2794 (2000); M. Bockrath, W. Liang, D. Bozovic, J. H. Hafner, C. M. Lieber, M. Tinkham, and H. Park, *Science*, **291**, 283 (2001); W. Liang, M. Bockrath, D. Bozovic, J. H. Hafner, M. Tinkham, and H. Park, *Nature*, **411**, 665 (2001).

4 X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich, and A. P. Alivisatos, *Nature*, **404**, 59 (2000); A. M. Morales and C. M. Lieber, *Science*, **279**, 208 (1998); L. Manna, E. C. Sher, and A. P. Alivisatos, *J. Am. Chem. Soc.*, **122**, 12700 (2000); J. D. Holmes, K. P. Johnston, R. C. Doty, and B. A. Korgel, *Science*, **287**, 1471 (2000).

5 S. J. Park, S. Kim, S. Lee, Z. G. Khim, K. Char, and T. Hyeon, *J. Am. Chem. Soc.*, **122**, 8581 (2000); V. F. Puntes, K. M. Krishnan, and A. P. Alivisatos, *Science*, **291**, 2115 (2001); T. Thurn-Albrecht, J. Schotter, G. A. Kästle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C. T. Black, M. T. Tuominen, and T. P. Russell, *Science*, **290**, 2126 (2000).

6 M. H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber, and P. D. Yang, *Adv. Mater.*, **13**, 113 (2001); Y. Lei, L. D. Zhang, and J. C. Fan, *Chem. Phys. Lett.*, **338**, 231 (2001).

7 M. Li, H. Schnablegger, and S. Mann, *Nature*, **402**, 393 (1999); S. Kwan, F. Kim, J. Akana, and P. D. Yang, *Chem. Commun.*, **2001**, 447; S. J. Limmer, S. Seraji, M. J. Forbess, Y. Wu, T. P. Chou, C. Nguyen, and G. Cao, *Adv. Mater.*, **13**, 1269 (2001); J. J. Urban, W. S. Yun, Q. Gu, and H. Park, *J. Am. Chem. Soc.*, **124**, 1186 (2002); J. A. Nelson and M. J. Wagner, *J. Am. Chem. Soc.*, **125**, 332 (2003).

8 Y. Zhang and H. Guan, *J. Cryst. Growth*, **256**, 156 (2003); Y. W. Zhang, Z. G. Yan, L. P. You, R. Si, and C. H. Yan, *Eur. J. Inorg. Chem.*, **2003**, 4099.

9 K. Riwotzki, H. Meyssamy, H. Schnablegger, A. Kornowski, and M. Haase, *Angew. Chem., Int. Ed.*, **40**, 573 (2001); K. Riwotzki, H. Meyssamy, A. Kornowski, and M. Haase, *J. Phys. Chem. B*, **104**, 2824 (2000); P. Schuetz and F. Caruso, *Chem. Mater.*, **14**, 4509 (2002); S. Heer, O. Lehmann, M. Haase, and H. U. Güdel, *Angew. Chem., Int. Ed.*, **42**, 3179 (2003); O. Lehmann, H. Meyssamy, K. Kompe, H. Schnablegger, and M. Haase, *J. Phys. Chem. B*, **107**, 7449 (2003).

10 M. Yu, J. Lin, J. Fu, H. J. Zhang, and Y. C. Han, *J. Mater. Chem.*, **13**, 1418 (2003).

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