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ScienceDirect
Chinese Chemical Letters 20 (2009) 857–860
CHINESE CHEMICAL LETTERS
www.elsevier.com/locate/cclet

Synthesis and characterization of $CePO_4$ nanowires *via* microemulsion method at room temperature

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Received 17 October 2008

Abstract

Uniform $CePO_4$ nanowires with diameter of about 25 nm were synthesized by the water-in-oil microemulsion method at room temperature from cerous chloride, sodium orthophosphate, sodium chloride, cyclohexane, Triton X-100 and cetyltrimethyl ammonium bromide (CTAB). The crystal structure and morphology of the nanowires were characterized by XRD and TEM, respectively. The UV–vis absorption was detected by UV–vis spectrophotometer techniques. The results showed that as-prepared nanowires with the hexagonal phase have obvious quantum confinement effect and semiconductor characteristics. Little sodium chloride could play a positive role on the formation of $CePO_4$ nanowires at room temperature. The size of the nanowires can be controlled through the joining of sodium chloride.

Keywords: Nanowires; Cerium phosphate; Microemulsion; Room temperature

Rare earth elements have been applied in advanced technologies such as photocatalyst, fuel cells and luminous materials because of their particular 4f–5d and 4f–4f electronic transition which were different from the other elements [1]. Many rare earth phosphates have been studied because of use in sensors, tribology and heat-resistant materials [2]. Among these phosphates, $CePO_4$ can be applied in luminescent lamp as highly efficient emitter of green light [3]. Even under the temperature of 1200 K, monoclinic $CePO_4$ can keep stable which makes it used in high-temperature materials and ceramic applications [4]. At present, $CePO_4$ nanomaterials were mostly synthesized by means of solid phase method and hydrothermal method. Zhang Youjin synthesized hexagonal and monoclinic $CePO_4$ nanowires through hydrothermal reaction at 373 K and 473 K [5]. Yan Xing fabricated $CePO_4$ nanowires with thickness of 3.7 nm [6], but this process lasted several months and expensive reagents were used. Hu co-workers used microemulsions to hydrothermally fabricate $LaPO_4$ and $CePO_4$ nanorods/nanowires with diameters of 20–60 nm [7]. Up to now, synthesis of $CePO_4$ was mostly at higher temperature or abundant time will be spent. Synthesis of $CePO_4$ nanomaterials at normal temperature has been rarely studied. The microemulsion (W/O) based method is very flexible and convenient to produce nanomaterials [8].

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1001-8417/$ – see front matter
doi:10.1016/j.cclet.2009.02.020

This paper described the formation of hexagonal $CePO_4$ nanowires using a water-in-oil microemulsion method at room temperature. This method can be done well without additional special condition. Results shows that uniform and long hexagonal $CePO_4$ nanowires have been fabricated and the mechanism of formation was discussed.

1. Experimental

The microemulsion was prepared with 59 wt% of cyclohexane as oil phase, 31 wt% (Triton X-100, CTAB, 1-pentanol) as surfactant and cosurfactant, aqueous solution of 0.15 mol L^{-1} $CeCl_3$ and solution of 0.15 mol L^{-1} Na_3PO_4 (10 wt%) as water phase. The surfactant/cosurfactants ratio was 3/2. In a typical synthesis, 3.0 mL of aqueous $CeCl_3$ solution (0.15 mol L^{-1})/Na_3PO_4 solution (0.15 mol L^{-1}) was respectively added with stirring on magnetic stirrer to 25 mL Triton X-100/CTAB in cyclohexane solution to give a clear Ce-containing microemulsion solution with water-to-surfactant molar ratios of $w = [H_2O]/[\text{Triton X-100/CTAB}] \approx 19$. At the same time, appropriate sodium chloride was added and the stirring was kept for 3 h. The transparent reaction mixture became turbid after addition of acetone and white precipitate was slowly formed. White powders were obtained by centrifugation and dried at room temperature for further use. The morphology of sample was observed on the JEM-100CX-α transmission electron microscopy (TEM). The crystalline structure was taken on the D8 Advance X-ray diffractometer using nickel filtered Cu Kα radiation at 1.54 Å.

2. Results and discussion

Phase identification of the as-prepared samples was observed using the XRD pattern (Fig. 1). There were dilated diffraction peaks which were corresponding to Miller indices of (1 0 0), (1 0 1), (1 1 0), (2 0 0), (1 0 2), (2 1 1), (3 0 2). All diffraction peaks can be indexed to the hexagonal phase of $CePO_4$ (JCPDS files No. 034-1380). With the additive of NaCl, the diffraction peaks became sharp. That means $CePO_4$ crystal complete.

The TEM images of the samples were illustrated in Fig. 2. The TEM photographs of the samples (Fig. 2) prepared with different NaCl wt% showed that all the samples exhibited wires. The sample without NaCl had average diameter of 50 nm and length of hundreds of nanometer and the sample synthesized with NaCl had average diameter of 25 nm. With the adding of sodium chloride, the diameter of nanowires lessened gradually. This result was corresponding to broad diffraction peaks shown in Fig. 1. It was possibly because that NaCl was more propitious to cylindrical micelle and tiny microemulsion water core provided ideal reaction space.

The UV–vis spectrum of $CePO_4$ nanowires was shown in Fig. 3. The absorption peaks of a and b were at about 285 nm, c at 235 nm and d at 220 nm, which were all of blue shift. The bands were consistent with reported data [9]. With the decrease of size, the blue shift was more visible which suggests that these nanowires have obvious quantum confinement effect and useful optical properties.

The growth mechanism of $CePO_4$ nanowires was studied. When the microemulsion systems of cerous chloride and Na_3PO_4 aqueous solution were mixed, the milky precipitation can be seen in the first 7–8 min. The above phenomenon

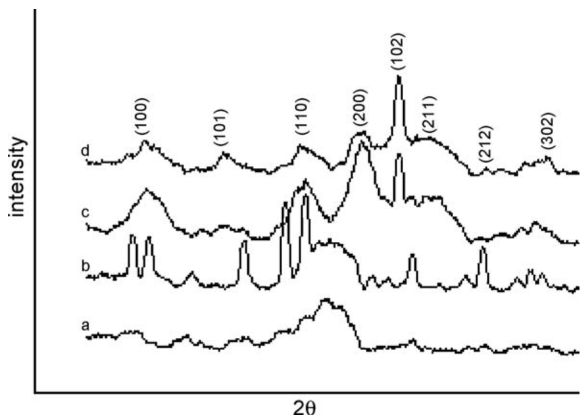


Fig. 1. XRD pattern of $CePO_4$ nanowires. (a) NaCl wt% = 0; (b) NaCl wt% = 0.1; (c) NaCl wt% = 0.2; (d) NaCl wt% = 0.3.

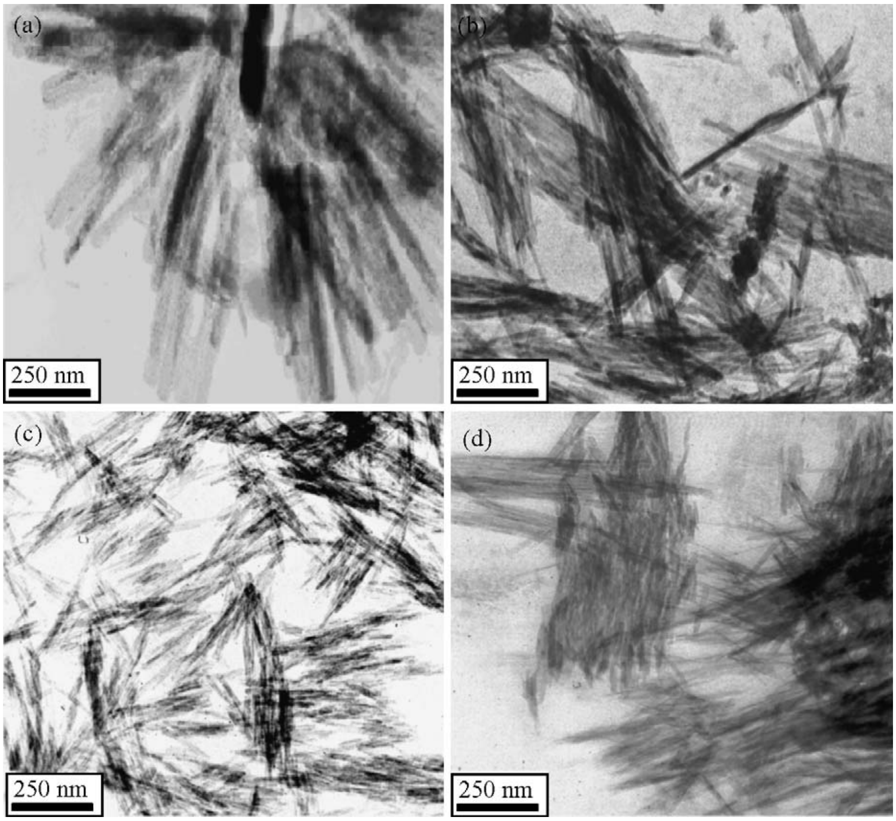


Fig. 2. TEM image of $CePO_4$ nanowires. (a) NaCl wt% = 0; (b) NaCl wt% = 0.1; (c) NaCl wt% = 0.2; (d) NaCl wt% = 0.3.

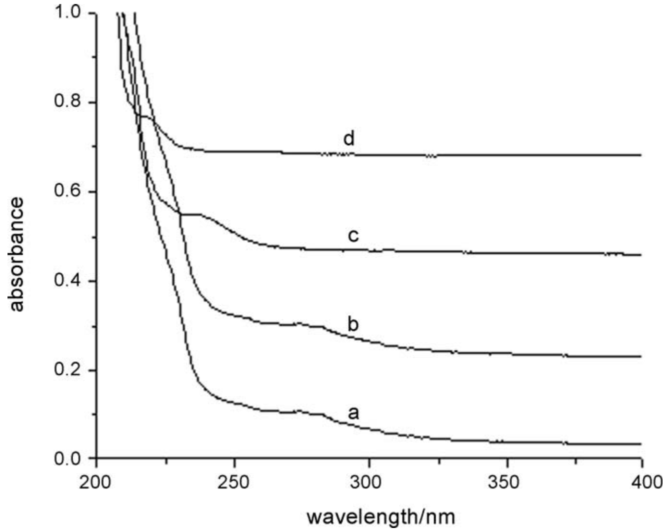
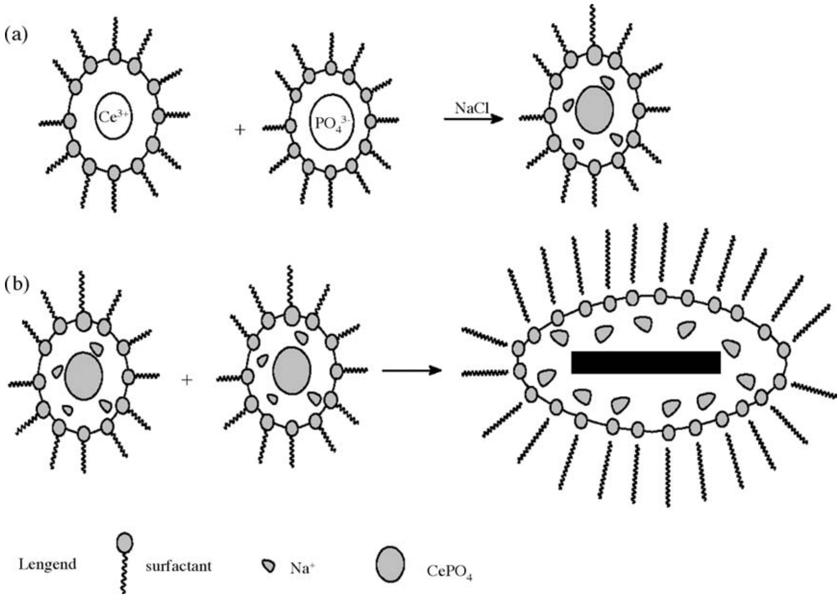


Fig. 3. UV–vis spectrum of $CePO_4$ nanowires. (a) NaCl wt% = 0; (b) NaCl wt% = 0.1; (c) NaCl wt% = 0.2; (d) NaCl wt% = 0.3.

indicates the nucleation and growth of nanoparticles (see Scheme 1). At the beginning of the reaction, the micelles with Ce^{3+} will collide with micelles containing PO_4^{3-} and $CePO_4$ nucleates in the newly forming spherical micelles (see Scheme 1(a)). With prolonged reaction, the diameter of these spherical nanoparticles increases because these micelles collide with each other more resulting in fusion and exchange of the contents. When the appropriate sodium chloride was added, the polarity of inorganic salt ion had an effect on head group of surfactant which could reduce



Scheme 1. The mechanism of reaction. (a) nucleation and growth of spherical particles; (b) further growth of nanowires.

repulsive energy and area of head group [10]. In the process, the $CePO_4$ nucleates captured the fatty aliphatic chain ions and the Na^+ counter-ions continuously from the micelle solution and grow slowly. Then the combination of surfactant grew compact slowly. So diameter of micelle became more less and $CePO_4$ nanowires could be obtained (see Scheme 1(b)).

In summary, at room temperature, uniform and long hexagonal $CePO_4$ nanowires have been fabricated by microemulsion method when the reaction system was in strong acid. Inorganic salt sodium chloride had an important effect on the formation of the $CePO_4$ nanowires, and a small quantity of sodium chloride can make for tinier diameter of $CePO_4$ nanowires. Synthesis of $CePO_4$ nanowires can be obtained within little time and room temperature.

Acknowledgment

We greatly acknowledge financial support by the Awarding Foundation for Middle and Young-Age Scientist of Shandong Province (2005).

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