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Controlled preparation and self-assembly of $NdVO_4$ nanocrystals☆

Li Tian [a, b, *], Yan Li [a], Huifeng Wang [a], Shanmin Chen [a], Jinjing Wang [a], Zhen Guo [a], Qiang Liu [a], Qi Luo [a], Yingjie Li [a], Fafa Wu [a, b]

[a] School of Materials Science and Engineering, Hunan Provincial Key Defense Laboratory of High Temperature Wear-resisting Materials and Preparation Technology, Hunan University of Science and Technology, Xiangtan 411201, China
[b] State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

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ABSTRACT

Phase-pure t-$NdVO_4$ nanocrystals with different shapes have been synthesized by facile and repeatable hydrothermal methods. The as-synthesized t-$NdVO_4$ nanoparticles were characterized by various techniques of X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). The growth process and assembly behavior of t-$NdVO_4$ nanorod arrays were investigated. The results show that the morphology of t-$NdVO_4$ nanocrystals is greatly related to the pH value of precursor solution and that strong basic solution is not in favor of the formation of t-$NdVO_4$ nanoparticles. Due to the strong adhesive action and stabilization of OH^- ions to some crystal faces of $NdVO_4$, neodymium vanadate crystallite grows into oriented short nanorods and then into nanorod arrays. The shape, crystalline and dimension of $NdVO_4$ nanocrystals can be effectively governed in our work.

1. Introduction

Rare earths materials are important functional materials with extensive application in the field of photocatalyst, phosphors, and so on.[1–3] Neodymium orthovanadate is an important inorganic material which has been intensively investigated in recent years because of its attractive properties and potential application.[4–12] It can be widely utilized as polarizer, phosphors, catalysts and laser host materials[13–18] due to the tetragonal zircon structure, in which each Nd^{3+} ion is dodecahedrally surrounded by eight O ions and lies between the neighbored slightly distorted VO_4^{3+} tetrahedron. Nowadays, some literatures report the preparation,[16–19] polarization,[12] structure[13] and properties like optoelectronic,[5] magnetic,[14] photocatalytic,[16,17] EPR,[18] thermal expansivity[19] and photoluminescence[20] properties. Especially, $NdVO_4$ nanoparticles have lots of unique photoelectric performances, which could be suggested to use extensively into the following fields of X-ray imaging, biological labeling, solid state lasers, displays and fluoroimmunoassay products.

Talking about the preparation strategies, $NdVO_4$ nanoparticles have been synthesized by different fabrication techniques,[15–20] such as hydrothermal synthesis, microwave method, sol–gel preparation and sonochemical operation, and so on. For example, Xu et al synthesized $NdVO_4$ nanowires by a simple composite molten salt method.[16] Single crystals of $NdVO_4$ were grown via the Czochralski method using Nd_2O_3 and V_2O_5 as starting materials by Kaczmarek et al.[18] Peng's group fabricated high-ordered $NdVO_4$ nanotubes using porous anodized aluminum oxide template (AAO) combined with sol–gel method.[19] As we all know, the achievement

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* Corresponding author. School of Materials Science and Engineering, Hunan Provincial Key Defense Laboratory of High Temperature Wear-resisting Materials and Preparation Technology, Hunan University of Science and Technology, Xiangtan 411201, China.
E-mail address: 1060072@hnust.edu.cn (L. Tian).

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of inorganic functional materials with particular nanostructures and novel morphology is related to the fabrication methods to a great degree. It is a challenge to form highly ordered arrays of inorganic functional materials by simple synthesis routines, especially without some templates like inorganic AAO or organic polymers.

In our research work, facile and repeatable hydrothermal synthesis method was employed to obtain uniform $NdVO_4$ nanorod arrays with tetragonal zircon structure by adjusting the pH value of precursor solution. In the synthesis process, no organic solvents and polymer templates were added in the precursor solution. This feasible and simple fabrication method is environmental-friendly which could be extended and applied to prepare other rare earth vanadate nanostructures.

2. Experimental

2.1. Synthesis of t-$NdVO_4$ nanoparticles

All chemicals used in this work were of analytic purity and used without further purification. In a typical preparation procedure of t-$NdVO_4$ nanoparticles, 1.15 mmol of EDTA-2Na (0.428 g) and 1.0 mmol $Nd(NO_3)_3\cdot 6H_2O$ (0.443 g) were put into a beaker and dissolved by 5.0 mL of distilled water under vigorous stirring to form a chelate complex. In another beaker, 1.0 mmol NH_4VO_3 (0.117 g) was dissolved by 5.0 mL of NaOH aqueous solution. Then, the above two kinds of solution were put together into a Teflon-lined stainless steel autoclave of 20 mL capacity, and the pH value of the mixture was tuned by NaOH aqueous solution to 8, 10, 12 and 14, respectively. Subsequently, the temperature of hydrothermal reaction was set at 180 °C and the hydrothermal time was set to 3, 6, 12, 24, 36, 48 and 58 h, respectively. After the reaction finished, the autoclaves cooled naturally to room temperature. The precipitation were separated by centrifugation, washed with deionized water and ethanol for several times, and then dried in a vacuum oven at about 80 °C for 24 h.

2.2. Characterization of t-$NdVO_4$ nanoparticles

The phase purity and crystal structures of the samples were characterized by powder X-ray diffraction (XRD) and electron microscopy. Powder XRD patterns were collected on a diffractometer (Bucker D8 Advance) using Cu Kα radiation ($\lambda = 0.1541$ nm) and a graphite monochromator operated at 40 kV and 30 mA at a scanning speed of 10°/min from 10 to 80 °C. Scanning electron microscopy (SEM) images were taken on a JEOL JSM-6330F field emission scanning electron microscope. Samples were gold-coated prior to the SEM analysis. Some of the products were further characterized under a JEM-2010HR transmission electron microscope (TEM) operated at an accelerating voltage of 200 kV. The samples for TEM examination were prepared by suspending solid samples ultrasonicated in alcohol and dripped on a carbon-coated copper grid.

3. Results and discussion

The morphology of the products prepared in the solution with different pH values was examined by SEM. Fig. 1(a–d) shows the SEM images of neodymium vanadate nanoparticles with different shapes synthesized after 21 and 24 h reactions. It is obvious that the pH value of precursor solution has great effect on the morphology of the products. As shown in Fig. 1(a), the samples obtained in weak base solution (pH = 8) are bundle-like nanocrystals which are composed of many nanowires. When the pH value is controlled at 10, numberless nanoparticles formed after 21 h hydrothermal reaction (Fig. 1(b_1)). With the reaction time increasing to 24 h, these nanoparticles self-assemblied to yield uniform nanorod arrays (Fig. 1(b_2)). Adjusting the pH value higher than 12, a large number of rice-like nanograins were produced to 21 h, as shown in Fig. 1(c_1) and (d_1). When the reaction time prolonged to 24 h, the nanograins cavitated themselves and became hollow as the pH value was fixed at 12 (Fig. 1(c_2)), while the nanograins grew much bigger to form microshuttles as the pH value was raised to 14 (Fig. 1(d_2)). It is noticeable that the stronger basic solution will favor the crystal growth and increase the dimension of neodymium vanadate nanoparticles. It is also indicated that $NdVO_4$ nanocrystals prefer to form at relatively weaker alkaline condition. On the base of the above analysis, the precursor solution with the pH value less than 12 is a better media for us to receive neodymium vanadate nanoparticles. What's more, it is worth mentioning that the cavitation of nanoparticles maybe strengthen their photoelectric properties. Further study is under the way.

Fig. 2 shows the XRD patterns of the products synthesized in the solution with the pH value adjusted from 8 to 14. As shown in Fig. 2, all the diffraction peaks presented in the XRD patterns can be indexed to the standard crystallographic data (JCPDS card no.

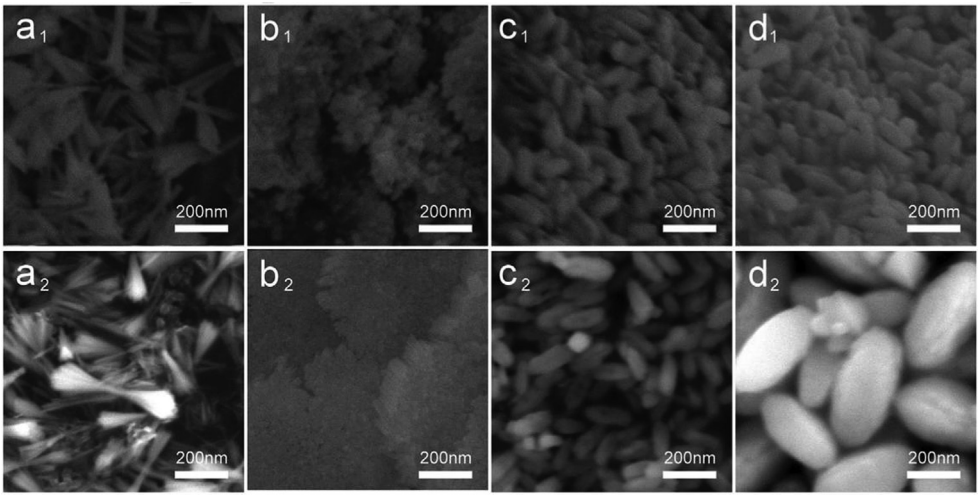

Fig. 1. SEM images of neodymium vanadate nanoparticles prepared in the solution with different pH values at 180 °C for different hydrothermal times: (a) pH = 8; (b) pH = 10; (c) pH = 12; (d) pH = 14; subscript 1: 21 h, subscript 2: 24 h.