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Preparation of Single-Crystalline NdVO₄ Nanorods, and Their Emissions in the Ultraviolet and Blue under Ultraviolet Excitation

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This paper describes a facile sacrificial (NH₄)_{0.5}V₂O₅ nanowires approach to single-crystalline NdVO₄ nanorods. The nanorods have a rectangular cross section of about 30 × 30 nm² to 100 × 200 nm², and length ranging from 400 to 700 nm. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) show that the nanorods grew respectively along the [312] and [101] direction on the (NH₄)_{0.5}V₂O₅ nanowires. Ultraviolet (362 nm) and blue (467 nm) emissions can be observed under excitation of 310 nm at room temperature, suggesting that the nanorods should be good candidates for fabricating UV and blue nanodevices.

1. Introduction

Rare-earth orthovanadates are both important catalysts and good optical materials. For example, ReVO₄ (Re = Pr, Er, Gd, Dy, and Nd) powders were once used in catalyzing the oxidative dehydrogenation of propane;¹ YVO₄ crystals have been applied to optical polarizing components due to their wide transparency range and large birefringence.² Present studies show that Nd-doped YVO₄ is one of the best promising matrixes for diode-pumped solid-state lasers, and the absorption coefficient at 808 nm, which is the standard wavelength of currently available laser diodes, is five times the one in YAG:Nd.³ The Nd-doped GdVO₄ crystal also is a promising matrix for diode-pumped solid-state lasers, and has a higher absorption coefficient, larger emission cross-section, and higher thermal conductivity along the ⟨110⟩ direction than Nd-doped YVO₄. Recently, an end-pumped acoustooptically Q-switched GdVO₄:Nd laser has been demonstrated.⁴ Since a ZnO ultraviolet nanowire nanolaser has been fabricated,⁵ considerable attention has been attracted to fabricate optical one-dimensional (1D) nanostructures, because well-controlled nanostructures could bring in new applications, and greatly enhance the performance of many currently existing devices as a result of their one-dimensionality.⁶ However, 1D nanostructures of rare-earth orthovanadates have not been reported up to date except nanoparticles,⁷ so it is very important to develop an approach to synthesizing 1D nanostructures of rare-earth orthovanadates to meet demands in fabricating new optical nanodevices. NdVO₄ has been studied rarely until now except as a catalyst. On the basis of the present reports that there are up-conversion emissions in UV and s blue wavelength region in many Nd-containing materials, we think that NdVO₄ probably has good optical properties. If NdVO₄ is fabricated into nanorods, it is possible to obtain a novel nanolaser. Finally, we have successfully synthesized NdVO₄ nanorods and observed their UV and blue emissions with 310 nm pumping.

Over the past several years, many methods have been developed to prepare 1D nanostructures such as surfactant-assisted,⁸ microemulsion-mediated,⁹ and polymer-controlled hydrothermal reaction;¹⁰ reverse micelle inducement;¹¹ chemical

vapor deposition;¹² sonochemical synthesis;¹³ laser ablation;¹⁴ and so on. Similarly, the template-directed approach also is an efficient way to prepare 1D nanostructures. In this approach, the template serves as a scaffold against which other materials are assembled with a morphology similar (or complementary) to that of the template. For example, single-crystalline Ag₂Se nanowires were prepared by reacting Se nanowire templates with aqueous AgNO₃ solutions at room temperature,¹⁵ and Ag₂SiO₃/SiO₂ composite nanotubes were fabricated by reaction of Ag₆Mo₁₆O₃₃ nanowires with tetraethyl orthosilicate.¹⁶ Herein, we report the synthesis of single-crystalline NdVO₄ nanorods by the hydrothermal reaction of (NH₄)_{0.5}V₂O₅ nanowire templates with Nd(NO₃)₃ at 180 °C, but the NdVO₄ nanorods only originate from dendrites converted by (NH₄)_{0.5}V₂O₅ nanowires, and do not retain the morphology of the templates. The templates only play a role as a growth matrix and reagent so another growth mechanism has been proposed, and their optical properties have been measured. (NH₄)_{0.5}V₂O₅ nanowires were synthesized by using a previously reported procedure, having a uniform diameter of 20–80 nm and a length up to 0.5 mm.¹⁷

2. Experimental Procedure

A two-step strategy was used for sample 1. Step 1: Nd₂O₃ powders (0.164 mmol) were dissolved in 20% nitride acid, and the solution was adjusted to pH 5–6 with 15% NH₃·H₂O, then mixed with (NH₄)_{0.5}V₂O₅ nanowires (0.164 mmol). The mixture was again adjusted to pH 5–6 with 15% NH₃·H₂O and 20% nitride acid, stirred for 10 min, and then transferred to a 50 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 180 °C for 24 h, then cooled to room temperature. Step 2: The above mixture was adjusted to pH ~7 with 30% NaOH aqueous solution, and hydrothermally reacted again for 24 h at 180 °C. The final gray precipitates were filtered, washed with deionized water to remove remnant ions, and dried at 80 °C in air. Meanwhile, the one-step strategy was also used for other samples, i.e., the same reagents were respectively treated for 24 (sample 2) and 48 h (sample 3) according to step 1.

The structure of the products was examined by an X-ray diffractometer (XRD, Shimadzu XD-3A) with graphite monochromatized Cu Kα radiation. The morphology of the products

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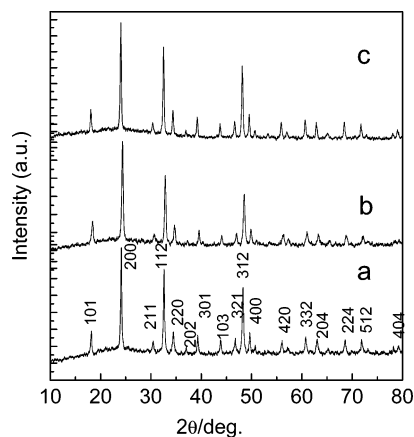


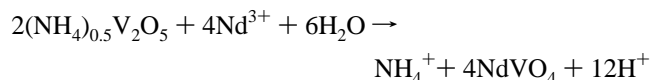
Figure 1. XRD patterns of the products: (a) sample 1; (b) sample 2; and (c) sample 3.

was characterized by a field-emission scanning electron microscope (SEM, LEO-1530VP) and a transmission electron microscope (TEM, JEOL-JEM 200CX at 200 kV). The optical properties were measured by a UV-vis spectrophotometer (UV-24001PC, Shimadzu) and a fluorescence spectrometer, using a Xe lamp with an excitation wavelength of 310 nm (RF-5301 PC, Shimadzu).

3. Results and Discussion

3.1. The Morphology and Structure of NdVO₄ Nanorods.

The formation of NdVO₄ nanorods is strongly dependent on the pH of the solution. Under the condition of present concentration, if solution pH is more than 12, Nd(OH)₃ appears in final products; if solution pH is less than 2, NdVO₄ nanorods are dissolved easily so that it is not helpful to form the nanorods, so an optimal pH is confirmed as about 5–6. The chemical reaction equation formula is included as follows:



Because the reaction can produce a little acid, a two-step strategy must be carried out to maintain the pH of the solution. Figure 1a shows the XRD pattern for sample 1 obtained by the two-step strategy, which can be indexed as tetragonal NdVO₄ (JCPDS No. 15-769, $a = 7.329 \text{ \AA}$ and $c = 6.4356 \text{ \AA}$). SEM images of sample 1 (Figure 2a,b) show that the nanorods have rectangular cross-sections of about $30 \times 30 \text{ nm}^2$ to $100 \times 200 \text{ nm}^2$, and a length ranging from 400 to 700 nm. Figure 2c is the energy-dispersive X-ray spectrum (EDX) of a single nanorod, which indicates that the nanorod consists of Nd, V, and O with an atomic ratio of 1:1:3.7, and the composition approaches the right stoichiometry of NdVO₄, and the rest of the peaks originate from the Au coating. Figure 3 shows TEM images of sample 1. The overview (Figure 3a) further reveals that the nanorods have rectangular cross-section ranging from $\sim 30 \times 30 \text{ nm}^2$ to $\sim 114 \times 114 \text{ nm}^2$. TEM images and SAED patterns (insets) of a single nanorod indicate that the nanorods grew along the [312] (Figure 3b) and [101] (Figure 3c) direction, respectively, and the former has sharp growth tips, whereas the latter only has flat growth tips.

3.2. Possible Formation Mechanism of the NdVO₄ Nanorods. To study the growth condition and mechanism of the nanorods, the one-step strategy is also used for preparing sample 2 and sample 3. Their XRD patterns are respectively shown in parts b and c of Figure 1, which can still be indexed as tetragonal

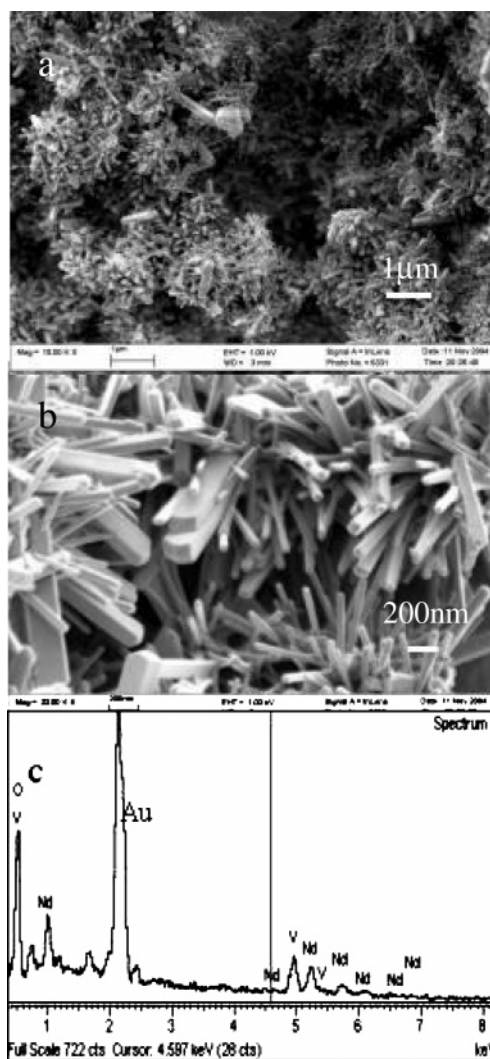


Figure 2. SEM images of sample 1: (a) low-magnification image; (b) high-magnification image; and (c) EDX spectrum of a single NdVO₄ nanorod.

NdVO₄. The TEM image of sample 2 (Figure 4a) indicates that they consist of self-assembled nanoparticles, and keep the morphology of the templates. A few dendrites on the templates can be observed, which show that the single-crystalline nanorods originate from dendrites. Figure 4b is a comblike nanowire composed of dendrites, and the local magnified image in the box in Figure 4c reveals that the NdVO₄ nanorods have both morphologies with sharp and flat growth tips, indicated by white and black arrows, respectively, i.e., the NdVO₄ nanorods growing along the [312] and [101] direction. Figure 4d shows primitive morphology that NdVO₄ nanorods grew on the template, and local magnified images are shown as insets. The NdVO₄ nanorods with sharp and flat tips are respectively indicated as arrows in insets (1) and (2), which shows that the angles between the (NH₄)_{0.5}V₂O₅ nanowire and the nanorods growing along [312] and [101] direction are about 85° and 70°, respectively. Figure 4e is the TEM image of sample 3, indicating the coexistence of particles and rods, and the particles occupy about 90%. The pH of the final suspension after hydrothermal reaction is less than 2, so we do not think that low pH is helpful in forming nanorods. When the pH of the solution is too low, only V₂O₅ nanowires exist. If (NH₄)_{0.5}V₂O₅ nanowires are replaced by NH₄VO₃ powders and similarly treated according to the one-step or two-step strategy, only NdVO₄ nanoparticles can be obtained. Figure 4f shows the nanoparticles produced

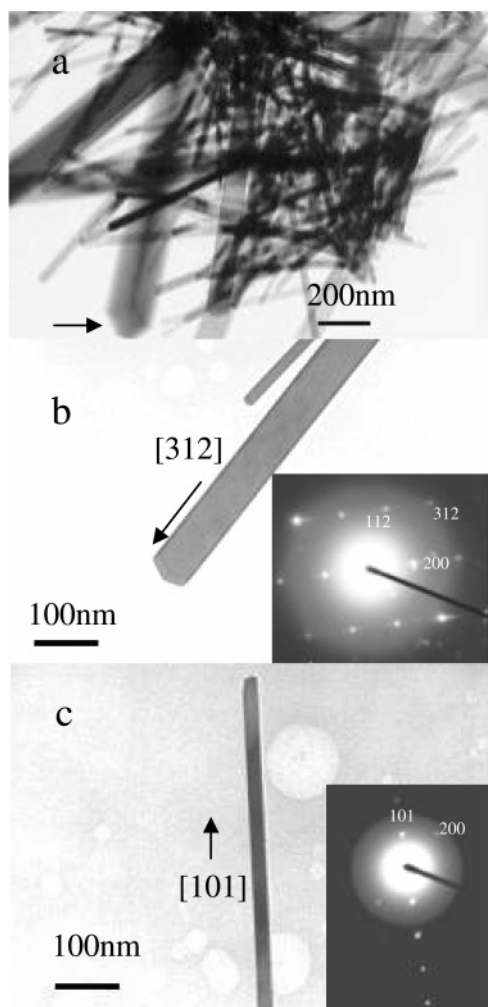


Figure 3. TEM images of sample 1: (a) overview; (b) TEM image and SAED pattern of individual NdVO_4 nanorod along [042]; and (c) TEM image and SAED pattern of individual NdVO_4 nanorod along [020].

by the hydrothermal reaction of NH_4VO_3 with Nd^{3+} for 24 h. Therefore, we think that the nanowire precursors play an important role in synthesizing the nanorods.

On the basis of the above observation, a dendrite-growth mechanism on nanowire templates has been proposed. As shown in Figure 5, when the templates were mixed with Nd^{3+} ions, Nd^{3+} ions were adsorbed on the surface (Figure 5a), and reacted with the templates to form NdVO_4 nanocrystallite nuclei on the surface. As reaction proceeded, the nuclei grew into dendrites while templates were partly consumed (Figure 5b). Because growth tips of the dendrites were observed, we supposed that the dendrites were the top-growth process of solid–liquid–solid (SLS), i.e., the nuclei accepted Nd^{3+} and VO_4^{3-} ions to grow into the nanorod on the top. VO_4^{3-} ions originated from dissolution of $(\text{NH}_4)_{0.5}\text{V}_2\text{O}_5$ nanowires or NdVO_4 nanoparticles. Finally, the templates were completely consumed and converted to NdVO_4 nanorods, as shown in Figure 5c.

3.3. Optical Properties. The produced nanorods show interesting optical properties. The color of the pure $(\text{NH}_4)_{0.5}\text{V}_2\text{O}_5$ nanowires is dark green, but the products became slightly gray. $(\text{NH}_4)_{0.5}\text{V}_2\text{O}_5$ nanowires show neither absorption nor photoluminescence (PL) properties in the UV–vis wavelength region, but NdVO_4 nanorods have strong absorption peaks at 275, 593, 753, 807, and 878 nm, and obvious UV and blue emissions. As shown in Figure 6, the peak at 275 originates from ultraviolet (UV) absorption of VO_4^{3-} of NdVO_4 nanorods,^{7a} while the

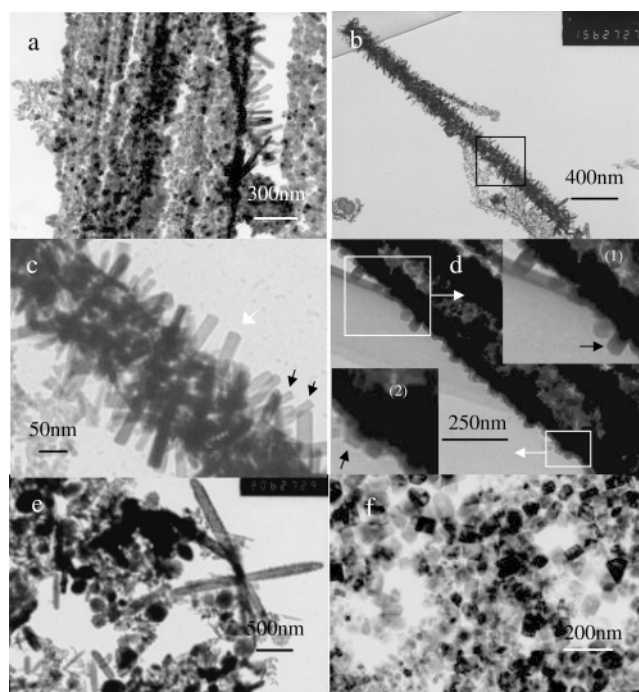


Figure 4. TEM images of various nanoparticles: (a) overview and (b) dendrites of sample 2; (c) the magnified image in the box in panel b; (d) primitive morphology of NdVO_4 growing on the template (one-step strategy, 12 h); (e) TEM image of sample 3; and (f) NdVO_4 nanoparticles prepared by hydrothermal reaction of NH_4VO_3 with Nd^{3+} for 24 h.

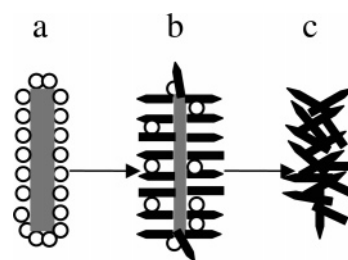


Figure 5. Schematic illustration of the NdVO_4 nanorod growth mechanism: (a) Nd^{3+} ions adsorbed on the surface of $(\text{NH}_4)_{0.5}\text{V}_2\text{O}_5$ nanowires; (b) NdVO_4 nanorods growing on $(\text{NH}_4)_{0.5}\text{V}_2\text{O}_5$ nanowires; and (c) $(\text{NH}_4)_{0.5}\text{V}_2\text{O}_5$ nanowires completely converted to NdVO_4 nanorods. The circles represent Nd^{3+} ions.

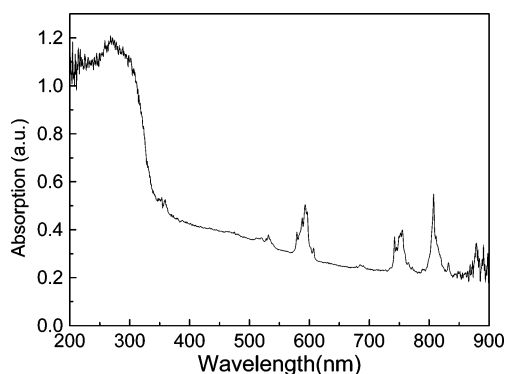


Figure 6. UV–vis spectrum of the NdVO_4 nanorods.

peaks at 593, 753, 807, and 878 nm can be attributed to the Nd^{3+} transition of NdVO_4 nanorods from $^4\text{I}_{9/2}$ to $^4\text{G}_{5/2}$, $^4\text{F}_{7/2}$, $^4\text{F}_{5/2}$, and $^4\text{F}_{3/2}$.¹⁸

Figure 7a,b shows the UV and blue emissions of NdVO_4 nanorods upon excitation of 310 nm at room temperature. Because NdVO_4 nanorods are composed of Nd^{3+} and VO_4^{3-} ,

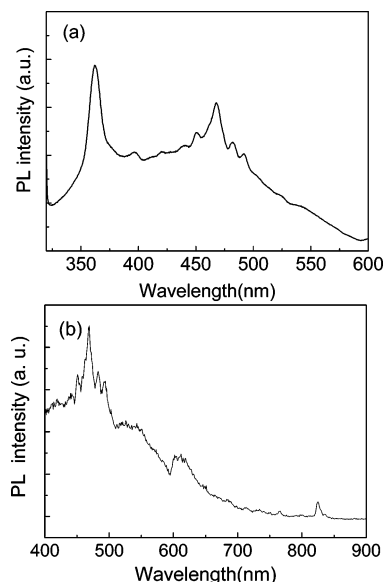


Figure 7. (a, b) Room-temperature photoluminescence (PL) spectrum of NdVO₄ nanorods upon excitation of 310 nm.

their PL properties can be attributed to Nd³⁺ transitions of the nanorods. The emissions at 362 and 467 nm can be assigned to Nd³⁺ transitions from the ⁴D_{3/2} and the ⁴G_{11/2} state to ⁴I_{9/2}, respectively. The rest of the emissions such as at 396, 420, and 450 nm can be attributed to Nd³⁺ transitions from the ⁴D_{3/2} state to the ⁴I_{11/2}, ⁴I_{13/2}, and ⁴I_{15/2} level, and the emissions at 438, 482, 492 and 825 nm correspond to Nd³⁺ transitions from ²P_{1/2}, ²G_{9/2}, ²K_{5/2} + ²G_{9/2}, and ⁴F_{5/2} to ⁴I_{9/2}. These emissions used to appear in some Nd-doped crystals under infrared excitation,¹⁹ but it is the first report on those emissions for NdVO₄ nanorods with 310 nm pumping. Because of these optical properties, the nanorods can be fabricated into UV or blue nanolasers.

4. Conclusions

Large-scale single-crystalline NdVO₄ nanorods have been prepared by hydrothermal reaction of (NH₄)_{0.5}V₂O₅ nanowires with Nd(NO₃)₃ solution at 180 °C. About 95% of the nanorods have a rectangular cross-section of ~60 × 60 nm², and a length ranging from 400 to 700 nm. Owing to their interesting UV and blue emissions, they could be applied in fabricating optical nanodevices; meanwhile due to their optionally exposed facets, the nanorods as catalysts will have stronger selectivity than the nanoparticles.²⁰

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