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# Hydrothermal Synthesis and Characterization of $\text{YVO}_4$ and $\text{YVO}_4\text{:Eu}^{3+}$ Nanobelts and Polyhedral Micron Crystals

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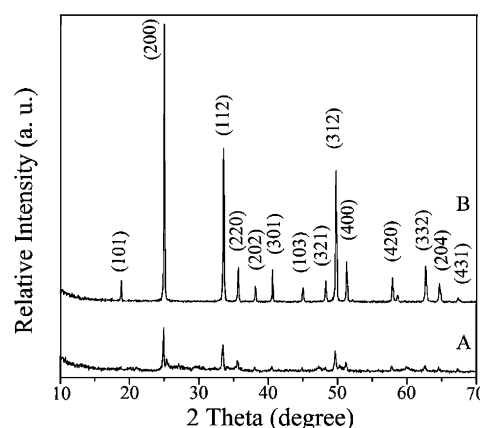
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$\text{YVO}_4$  and  $\text{YVO}_4\text{:Eu}^{3+}$  nanobelts and polyhedral micrometer crystals have been successfully synthesized by hydrothermal treating the mixture of  $\text{NH}_4\text{VO}_3$  and  $\text{Y}(\text{NO}_3)_3$  without the aid of any surfactants and templates. The thickness, widths, and lengths of  $\text{YVO}_4$  nanobelts are about 40–60 nm, 110–180 nm, and several micrometers, respectively. Such nanobelts can grow along the [010] direction.  $\text{YVO}_4$  polyhedral micrometer crystals have flat faces and regular shapes. The influences of pH values on the morphologies of  $\text{YVO}_4$  have been investigated. The photoluminescence properties of  $\text{YVO}_4\text{:Eu}^{3+}$  nanobelts and polyhedron microcrystals have been discussed.

## Introduction

Yttrium orthovanadate ( $\text{YVO}_4$ ), an important optical material, has many wonderful characteristics including good thermal, mechanical, and optical properties, which make it play an important role in almost any device involving the artificial production of light and display fields, such as excellent polarizer<sup>1,2</sup> and laser host material.<sup>3,4</sup>  $\text{Eu}^{3+}$ -doped  $\text{YVO}_4$  has been used as a red phosphor in color television and cathode ray tubes.<sup>5,6</sup> In recent years, one-dimensional (1D) nanostructures of vanadium oxides and their derivatives including nanobelts,<sup>7–11</sup> nanorods,<sup>12,13</sup> nanowires,<sup>14,15</sup> and nanotubes<sup>16,17</sup> have received considerable interest because of their size- and shape-dependent properties and potential applications in electric field-effect transistors,<sup>18,19</sup> lithium batteries,<sup>8,20,21</sup> chemical sensors or actuators,<sup>7,22,23</sup> and nanodevices.<sup>14</sup> Although a variety of methods, such as surfactant-assisted solution and hydrothermal/solvothermal synthesis, have been developed to prepare 1D nanostructures of vanadium oxides and their derivatives; the reports on 1D  $\text{YVO}_4$  nanostructures are sparse, and considerable efforts have been devoted on the synthesis of  $\text{YVO}_4$  nanocrystals. For example, Haase et al.<sup>24</sup> synthesized  $\text{YVO}_4\text{:Eu}^{3+}$  colloidal nanoparticles using  $(\text{Y, Eu})(\text{NO}_3)_3$  and  $\text{Na}_3\text{VO}_4$  as raw materials via a hydrothermal method. Boilot et al.<sup>25</sup> have reported the synthesis of  $\text{YVO}_4\text{:Eu}^{3+}$  nanocrystals by precipitation of citrate complexes of rare-earth salts with sodium orthovanadate. Zhang et al.<sup>26</sup> developed a hydrothermal route to the fabrication of  $\text{YVO}_4\text{:Er}^{3+}$  nanocrystals using a citrate–yttrium–vanadate complex as the precursor. Cao et al.<sup>12</sup> prepared spindlelike  $\text{YVO}_4\text{:Eu}^{3+}$  particles by a sonochemical method. For the synthesis of 1D  $\text{YVO}_4$  nanostructures, 1D nanostructured precursors are usually used as templates. Wu et al.<sup>27</sup> prepared the rodlike, olivelike, and pineapple-like nanocrystals of the  $\text{YVO}_4\text{:Eu}$  under hydrothermal conditions by using porous silicon substrates,  $\text{V}_2\text{O}_5$  nanowires, and CTAB additives at pH 6–7, respectively. Tao et al.<sup>28</sup> demonstrated in situ hydrothermal synthesis of  $\text{YVO}_4$  nanorods and microtubes using  $(\text{NH}_4)_0.5\text{V}_2\text{O}_5$  nanowire templates. However, although nanobelts



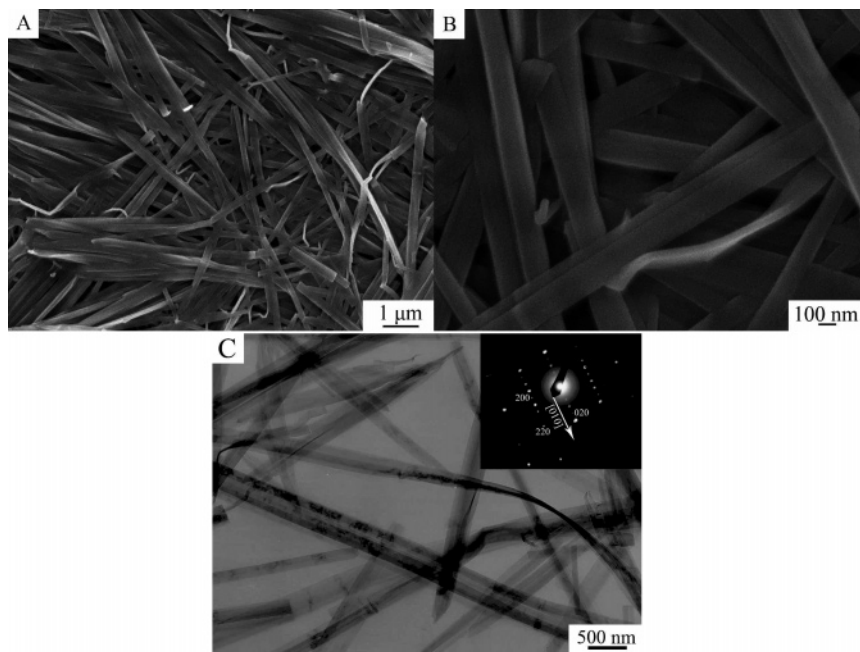
**Figure 1.** XRD patterns of  $\text{YVO}_4$  nanobelts and polyhedral micrometer crystals synthesized at 180 °C for 24 h. (A) pH = 1; (B) pH = 2.

are expected to represent important building blocks for nanodevices, the synthesis of  $\text{YVO}_4$  nanobelts is still challenging to chemists and material scientists. Herein, we report a simple approach for the synthesis of tetragonal  $\text{YVO}_4$  nanobelts and polyhedron microcrystals by hydrothermal treating the mixture of  $\text{NH}_4\text{VO}_3$  and  $\text{Y}(\text{NO}_3)_3$  under acid conditions in absence of any surfactants and templates. The photoluminescence (PL) properties of  $\text{YVO}_4\text{:Eu}$  nanobelts and polyhedron microcrystals are investigated.

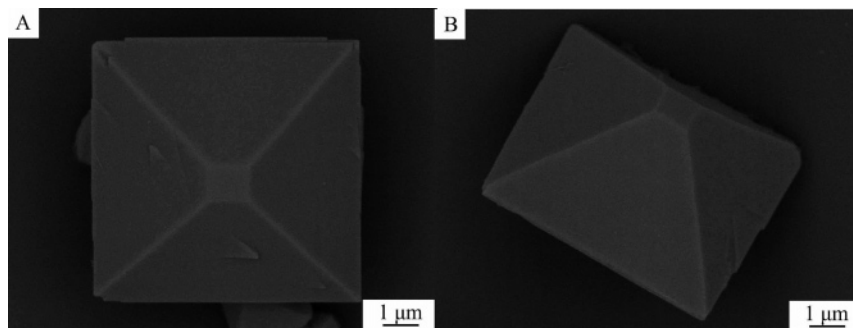
## Experimental Section

**Synthesis of  $\text{YVO}_4$  Nanobelts and Polyhedral Micrometer Crystals.** Ammonium metavanadate (0.117 g,  $\text{NH}_4\text{VO}_3$ ) was dissolved in 40 mL of distilled water to form a clear solution, and then 40 mL of yttrium nitrate (0.025 mol/L) solution was added to the  $\text{NH}_4\text{VO}_3$  solution and stirred for 5 min to form a yellow mixture. Hydrochloric acid was added dropwise under stirring until the pH value of the mixture was adjusted to about 1, 2, 3, and 4, respectively. The well-stirred buff solution was poured into a 100-mL autoclave with a Teflon liner and heated subsequently at 180 °C for 24 h and then air cooled to room temperature. The yellow precipitate was collected and washed

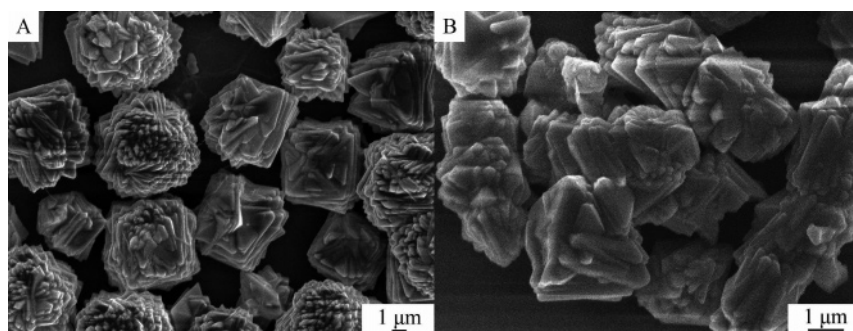
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**Figure 2.** SEM images of YVO<sub>4</sub> nanobelts synthesized at pH = 1. (A) Low magnification; (B) high magnification; (C) TEM image.



**Figure 3.** SEM images of YVO<sub>4</sub> polyhedral micron crystals synthesized at pH = 2. (A) Top view; (B) tilted view.



**Figure 4.** SEM images of YVO<sub>4</sub> polyhedral micron crystals synthesized at 180 °C for 24 h. (A) pH = 3; (B) pH = 4.

with distilled water and anhydrous alcohol several times and then dried in vacuum at 60 °C for 10 h.

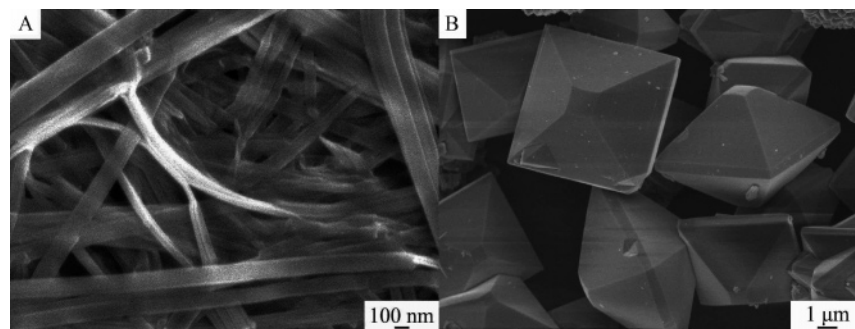
**Synthesis of Europium-Doped YVO<sub>4</sub> Nanobelts and Polyhedral Micrometer Crystals.** Europium-doped samples were prepared by the same procedure, except for adding an additional 5% (total molar ratio) EuCl<sub>3</sub> into yttrium nitrate solution at the initial stage.

**Characterization.** The morphology and composition of the samples were inspected using a field-emission scanning electron microscopy (FE-SEM, JSM 6700F) equipped with an energy-dispersive X-ray spectrum (EDS, INCAx-sight) and transmission electron microscopy (TEM, JEM 2000EX). The crystal structures of the resulting products were characterized by powder X-ray diffraction (XRD, Rigaku D-max-γA XRD with Cu Kα

radiation,  $\lambda = 1.54178$  Å). PL spectra of the resulting products were dispersed in distilled water to form a suspension solution and measured by a fluorescence spectrophotometer (Hitachi F-4500) at room temperature.

## Results and Discussion

Figure 1 shows XRD patterns of YVO<sub>4</sub> nanobelts and polyhedral micrometer crystals synthesized at 180 °C for 24 h. As shown in Figure 1A, most of the diffraction peaks of YVO<sub>4</sub> nanobelts synthesized at pH 1 can be indexed to tetragonal crystalline phase YVO<sub>4</sub> with lattice contents  $a = 7.12$  Å and  $c = 6.29$  Å (JCPDS 170341). As the pH value is adjusted to 2, all the diffraction peaks of YVO<sub>4</sub> polyhedral micrometer crystals



**Figure 5.** SEM images of YVO<sub>4</sub>:Eu<sup>3+</sup> nanobelts and polyhedral micrometer crystals synthesized at 180 °C for 24 h. (A) pH = 1; (B) pH = 2.

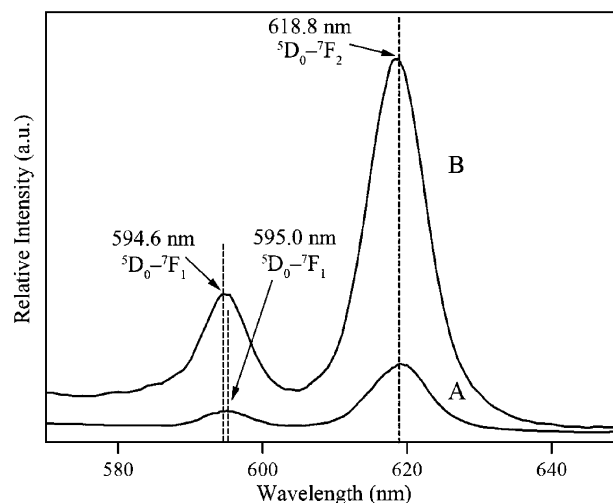
(Figure 1B) can also be ascribed to tetragonal crystalline phase YVO<sub>4</sub> with lattice contents  $a = 7.12 \text{ \AA}$  and  $c = 6.29 \text{ \AA}$  (JCPDS 170341). In comparison with Figure 1A, the diffraction peaks are sharp and strong, indicating that YVO<sub>4</sub> polyhedral micrometer crystals have high crystallinity.

Figure 2 presents typical SEM and TEM images of YVO<sub>4</sub> nanobelts synthesized at pH 1. As shown in Figure 2A, a low-magnification SEM image shows that the products are composed of a large quantity of 1D YVO<sub>4</sub> nanobelts with typical lengths up to several micrometers. In a high-magnification SEM image in Figure 2B, it is clear that the geometrical shape of YVO<sub>4</sub> nanostructures is a belt. The thickness and widths of YVO<sub>4</sub> nanobelts are in the range of 40–60 and 110–180 nm, respectively. The belt-shaped morphology of YVO<sub>4</sub> can be confirmed by the TEM image in Figure 2C. The sizes of the nanobelts are consistent with those in Figure 2A. The electron diffraction (ED) pattern taken from an individual nanobelt (the inset in Figure 2C) indicates that the nanobelts are single crystalline and can grow along the [010] direction.

The pH value of reaction solution plays an important role in controlling the morphologies of the resulting products. As the pH value increases to 2, the morphology of the product is quite different from that in Figure 2. As shown in parts A and B of Figure 3, one can observe that YVO<sub>4</sub> micrometer crystals have flat faces and regular shapes. As the pH value increases to 3–4 (parts A and B of Figure 4), irregular YVO<sub>4</sub> microcrystallines are formed. However, when the pH value decreases to 0, no precipitate is found, and the color of the solution turns to dark green.

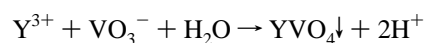
To determine the optical properties, YVO<sub>4</sub>:Eu<sup>3+</sup> nanobelts (Figure 5A) and polyhedron microcrystals (Figure 5B) are fabricated at pH 1 and 2, respectively. The sizes and shapes of the products are similar to that of pure YVO<sub>4</sub> in Figure 2 and 3. The EDS results (not shown here) confirm the presence of oxygen (O), yttrium (Y), vanadium (V), and Europium (Eu) in the YVO<sub>4</sub>:Eu<sup>3+</sup> nanobelts and polyhedron microcrystals.

The hydrothermal synthesis process is free of any surfactants and templates. It is supposed that the formation of YVO<sub>4</sub> nanobelts and micrometer crystals is mainly determined by the internal structure, and pH value plays a key role in their selective formation. Byrappa et al.<sup>29</sup> have reported that there are four YVO<sub>4</sub> molecules in a tetragonal unit cells, the structural unit of YVO<sub>4</sub> is a chain of alternating edge-sharing [VO<sub>4</sub>] tetrahedra and [YO<sub>8</sub>] polyhedra, and the chains are joined laterally by the edge sharing [YO<sub>8</sub>] dodecahedra.<sup>29</sup> As the (010) face is richer in Y than others faces, one can observe that the [010] growth direction can bear more positive charges, and the anisotropic growth is strongly influenced by the pH. Our experimental results confirm that the [010] growth direction is inhibited when the pH value is higher. When the pH is 1, the oxonium cations (H<sub>3</sub>O<sup>+</sup>) cannot perturb the YVO<sub>4</sub> growing along the [010]



**Figure 6.** The PL spectra of the YVO<sub>4</sub>:Eu<sup>3+</sup> nanobelts and polyhedral micrometer crystals synthesized at 180 °C for 24 h (570–650 nm,  $\lambda_{\text{exc}}$  = 265.0 nm). (A) pH = 1; (B) pH = 2.

direction, and the rate is faster than others directions, which limits the anisotropy growth of YVO<sub>4</sub> and leads to the formation of beltlike YVO<sub>4</sub> nanostructures. When the pH values increase, due to preferential ionic interaction, the hydroxide anions (OH<sup>−</sup>) will compete with the vanadate ions during the hydrothermal process and avoid the [010] direction growth, so the anisotropic growth is not perturbed, and the final morphologies of the YVO<sub>4</sub> is the polyhedron microcrystals. It is supposed that the crystallization process of YVO<sub>4</sub> is related to the formation of various polyvanadate ions at different pH values.<sup>10</sup> The overall hydrothermal reaction can be explained as follows



When the pH value decreases to 0, no precipitate appears, and the color of the solution turns dark green because V<sup>5+</sup> is reduced to V<sup>4+</sup> at low pH value.<sup>10</sup>

The PL spectra of YVO<sub>4</sub>:Eu<sup>3+</sup> nanobelts and polyhedron microcrystals at the room temperature are shown in parts A and B of Figure 6, respectively. Two strong PL emission peaks centered at around 595.0 and 618.8 nm (strongest) excited with 265.0 nm ultraviolet can be seen clearly (UV–vis absorption spectrum of YVO<sub>4</sub>:Eu<sup>3+</sup> nanobelts, see Supporting Information Figure S1). As the emission from the europium ions dominate these spectra, the characteristic feature of the emission bands are the expected peaks arising from <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub> and <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub>, respectively.<sup>30</sup> The emission bands around 595.0 nm can be contributed to the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub> magnetic dipole transitions; the emission bands around 618.8 nm can be contributed to the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> forced electric-dipole transitions, and their high intensities



are a consequence of the absence of an inversion symmetry at the Eu<sup>3+</sup> lattice site (D<sub>2d</sub> symmetry). Compared with Figure 6A, the PL emission peaks of YVO<sub>4</sub>:Eu<sup>3+</sup> polyhedral microcrystals (shown in Figure 6B) are sharp and strong; it is possibly due to their different quenching abilities of the adsorbed chemical species of the solution on the surface to the emission from Eu<sup>3+</sup> ions. As the samples were prepared in water and measured in suspension, the surface of the YVO<sub>4</sub> may be covered with hydroxyl species such as yttrium or europium hydroxides, bending vanadates, adsorbed water molecules, and surface OH groups, which act as the efficient quenchers of the excited europium ions.<sup>30</sup> The absorption between quenching species and crystal surfaces is affected by the sizes and shapes of YVO<sub>4</sub>, so the differences of PL intensity of the samples may be attributed to the different quenching abilities of the adsorbed species on the surface to the emission from Eu<sup>3+</sup> ions; that is why the luminescence intensity of the polyhedron microcrystals is obviously stronger than the nanobelts.

## Conclusion

In summary, we have demonstrated a facile route to synthesize tetragonal YVO<sub>4</sub> nanobelts and polyhedron microcrystals nanobelts and micropolyhedrons using commercial NH<sub>4</sub>VO<sub>3</sub> and Y(NO<sub>3</sub>)<sub>3</sub> as the reacting reagents in the acid surrounding without any surfactants and templates. The influences of pH values on the morphologies of the resulting products have been investigated. The PL spectrums show that the body-centered tetragonal YVO<sub>4</sub>:Eu<sup>3+</sup> exhibited two fluorescence emission peaks centered at around 595.0 and 618.8 nm as the excitation wavelength is 265.0 nm. The synthesis of YVO<sub>4</sub> and YVO<sub>4</sub>:Eu<sup>3+</sup> crystals in the acid surrounding will provide a new route to other lanthanon vanadate with controlled shapes and sizes.

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**Supporting Information Available:** UV-vis absorption spectrum of YVO<sub>4</sub>:Eu<sup>3+</sup> nanobelts synthesized at 180 °C for 24 h. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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