Hydrothermal Synthesis of Single-crystal β-$AgVO_3$ Nanowires and Ribbon-like Nanowires

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This paper describes for the first time a routine hydrothermal approach to the large-scale synthesis of one-dimensional (1-D) monoclinic β-$AgVO_3$ nanowires and ribbon-like nanowires. The whole process was actualized without the aid of any templates or surfactants. Some factors that affect the shape of 1-D β-$AgVO_3$ nanomaterials were briefly discussed.

Over the past decade, 1-D nanostructures have attracted intense interest because of their distinctive geometries, novel physical and chemical properties, and potential applications in electronics, optoelectronics, and memory devices.[1,2] As 1-D structures have efficient transport of electrons, nanowires can be applied in detecting the theoretical operating limits of lithium batteries.[3] In recent years, there have been many reports on the synthesis of vanadium oxides. For example, the syntheses of metal vanadium oxides (MVO) were reported by our group[4,5] and Yu et al.[6]

Metal vanadium oxides (MVO) have been used in commercial lithium battery as cathode active material to power cardiac defibrillators due to their high-specific capacity.[7,8] Just like other oxidation states of silver and vanadium, $AgVO_3$ is a typical practical battery material, and its electrochemical property highly depends on its synthetic and processing methods.[9,10] Several methods have been reported in case of the synthesis of $AgVO_3$ such as precipitations, solid-state reactions, and wet chemical reaction at low temperature.

Previously, because of the convenience of controlling the composition, silver vanadium, $AgVO_3$ has been prepared by heating the component metal oxides Ag_2O and V_2O_5 in 1:1 molar ratio. Kittaka et al. have proposed a mechanochemical method by ball milling of an Ag_2O–V_2O_5 mixture to obtain an amorphous $AgVO_3$ phase.[11,12] Up to now, there is no report on the fabrication of 1-D nanostructures via hydrothermal process. The hydrothermal synthetic route has advantages to obtain high-crystallized and high pure powders with narrow grain size-distribution. Therefore, this method has also been used for 1-D nanostructure single-crystal growth. In this paper, we report for the first time a low temperature process without using any templates or surfactants to prepare β-$AgVO_3$ nanowires and nanobelts with high aspect ratio. The influence of pH value and NH_4^+ cation on the morphologies of products has also been discussed.

In a typical procedure, two reagents: (a) silver carbonate (Ag_2CO_3), (b) silver acetate (AgAc), and ammonium metavanadate (NH_4VO_3) (with molar ratio Ag:V = 1:1) were separately put into four beakers with 25-mL distilled water. Under vigorous stirring, the NH_4VO_3 was dissolved into water at 80 °C, two reagents were successively added to the NH_4VO_3 solution to form heterogeneous solutions, and then the mixed solution was separately put into two 60-mL Teflon-lined autoclaves till 80% of its volume was filled. The autoclaves were sealed and maintained at 180 °C for 14 h, and then cooled to room temperature naturally. The brownish-yellow precipitate was collected and washed several times with deionized water and absolute ethanol. The final product was dried in vacuum at 60 °C for 8 h.

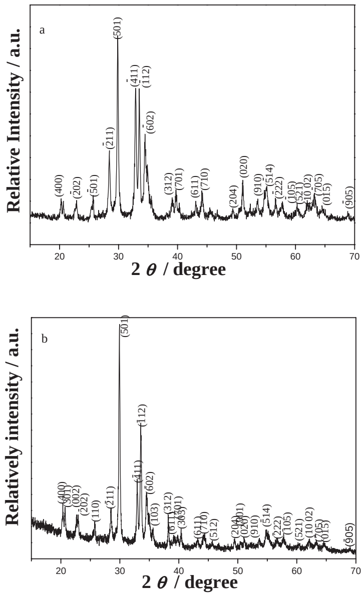

Figure 1. XRD patterns of as-prepared samples, (a) the β-$AgVO_3$ powder from reagent a, (b) the β-$AgVO_3$ powder from reagent b.

X-ray powder diffraction (XRD) was performed using a Rigaku D/max-γA X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation ($\lambda = 0.1541874$ nm). Figure 1 shows the typical XRD pattern of the β-$AgVO_3$ powder. Figure 1a is the XRD pattern of the as-prepared β-$AgVO_3$ from reagent a, and Figure 1b shows the XRD pattern of the β-$AgVO_3$ from reagent b. All the reflection peaks in Figure 1a and Figure 1b can be assigned to the phase of β-$AgVO_3$ monoclinic structure [space group $I2/m$ (12)] with cell parameters of $a = 17.856$, $b = 3.589$, and $c = 8.034$ Å, which are in good agreement with the values reported in the literature (JCPDS card 29-1154, $a = 17.87$, $b = 3.58$, and $c = 8.036$ Å). It is noticeable that the (501) reflection plane is extremely strong compared with the standard reflection intensity, which is probably related to the preferential growth of β-$AgVO_3$ nanowires and nanobelts. The products are proved to be well crystallized and pure by XRD pattern.

The FESEM images were taken with a Field Emission Scanning Electron Microscope (JEOL-6300F, 15 kV). The TEM images were obtained by using a Hitachi H-800 Transmission Electron Microscopy at 200 kV. The HRTEM image and the corresponding SAED pattern were obtained by using a JEOL 2010 HRTEM at 200 kV. Representative FESEM, TEM and HRTEM images of the as-prepared β-$AgVO_3$ products obtained at 180 °C for 14 h are shown in Figure 2. It can be seen in Figures 2a and 2b that the products consist of a large quantity of β-$AgVO_3$ nanowires and belt-like nanowires with the diameters ranging from 18 to 400 nm and lengths up to several tens of micrometer. The FESEM indicates some characteristic features of nanobelts. Figures 2c and 2d show the representative TEM images and ED patterns of the as-prepared single β-$AgVO_3$ nanowire and belt-like nanowire. The lattice fringes in Figure 2e show the integrality of crystallinity of the nanowire. The inter-planar spacing was measured as 5.13 Å. The stripes image represents that monoclinic $AgVO_3$ has preferential growth along $(\bar{3}01)$ plane. Besides, the SAED pattern in Figure 2f also reveals the single crystalline nature of the obtained β-$AgVO_3$ belt-like nanowires.

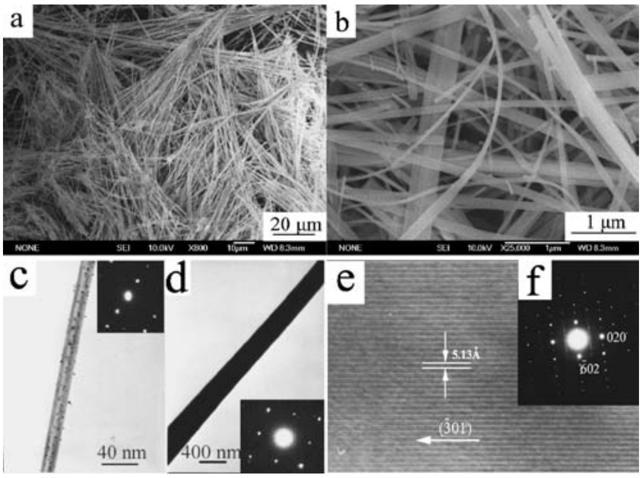

Figure 2. FESEM images of β-$AgVO_3$ nanowires (a) and belt-like nanowires (b), TEM and ED images of single β-$AgVO_3$ nanowire (c) and single β-$AgVO_3$ belt-like nanowire (d), HRTEM image (e) and SAED pattern (f) taken from single β-$AgVO_3$ belt-like nanowire.

The samples were also characterized by X-ray photoelectron spectra (XPS) (the spectra is not shown). The binding energies of Ag3d at 367.8 and 374 eV, V2p at 516.4 and 524.78 eV, and O1s at 529.8 eV were measured. The atomic ratio of Ag, V, and O in β-$AgVO_3$ calculated from the peak areas of Ag3d, V2p, and O1s was 1:1.075:2.7. The result revealed that the obtained nanowire crystals were nearly stoichiometric composition of $AgVO_3$ within the experimental errors.

The influence of reaction temperature and reaction time on the shape transformation of 1-D β-$AgVO_3$ nanomaterials has also been investigated. It is generally believed that temperature can affect the crystal growth, and the low temperature is of benefit to obtain crystal with smaller grain. In our research, there is a tendency that we acquire metastable α-$AgVO_3$ at lower temperature; higher temperature is preferable for the anisotropic growth of β-$AgVO_3$ crystal and result in the product with higher aspect ratio and higher crystallinity. When strong-acidic silver salt (e.g. $AgNO_3$) was used as the starting material, the product was not β-$AgVO_3$. So we chose weakly acidic silver salts as silver sources. The morphologies of Ag_2CO_3 and AgAc are grain. The products obtained by hydrothermal process with different silver reagents and NH_4VO_3 show nanowires (a reagent) and belt-like nanowires (b reagent) 1-D structures. After reaction, pH value of the solution was ascertained between 7.0 and 8.4. When pH value of the solution is less than 7.0, 1-D β-$AgVO_3$ is not obtained. It is worth noting that if we substitute $NaVO_3$ for NH_4VO_3 in the whole process of hydrothermal reaction, 1-D morphology of the resulting product was not found, and the product was not single-phase β-$AgVO_3$. Therefore, we deduce that NH_4^+ also plays a key role in fabricating 1-D structure of β-$AgVO_3$.

In summary, we have firstly fabricated single-crystalline silver metavanadate (β-$AgVO_3$) nanowires and belt-like nanowires with high aspect ratio via a hydrothermal process. Careful control of the reaction factors (such as temperature, reaction reagents, and pH value of the solution, etc.) is indispensable for 1-D nanostructural growth of β-$AgVO_3$.

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