Synthesis and Electrochemical Properties of Single-crystal CdV_2O_6 Nanowire Arrays

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Single-crystal cadmium vanadate (CdV_2O_6) nanowire arrays with the average diameter of 100 nm and length of up to 20 µm were fabricated by a hydrothermal process at 140 °C for 12 h. Electrochemical test shows that these nanowire arrays deliver a relatively large discharge capacity of 90 $mA\,h\,g^{-1}$ vs Li metal at 0.1 $mA\,cm^{-2}$ (voltage window of 3.2–2.0 V) compared with that of bulk CdV_2O_6. The obtained sample might find possible application as an electrode material in lithium ion batteries.

Nanostructured materials, especially one-dimensional (1-D) systems, have attracted increasing interest among scientists for their important role in future technological advances in electronics, optoelectronics, and memory devices.[1,2] As the smallest dimension structures for efficient transport of electrons, nanowires can be applied to detect the theoretical operating limits of lithium batteries.[3] Recently, many efforts have been made to synthesize 1-D nanorods and nanowires together with the test of their electrochemical properties. For example, β-FeOOH nanorods and nanowires with their electrochemical tests were reported by Wang et al.[4] and Xiong et al.,[5] respectively.

Nowadays, vanadates have generated a new interest as an electrode material.[6,7] As a kind of monoclinic Brannerite type vanadate, CdV_2O_6 is proposed as possible anodes for "rocking-chair" or "lithium ion" batteries[8] normally used. In conventional routes, bulk CdV_2O_6 was prepared by heating an equimolar mixture of NH_4VO_3 and CdO,[9] or V_2O_5 and CdO at 600 °C for 20–48 h,[10] which needs harsh reaction conditions. To our knowledge, there is no report on the fabrication of 1-D CdV_2O_6 nanowire arrays as well as the electrochemical properties. The hydrothermal process is one of the more successful ways to grow crystals of many materials such as quartz and malachite. This technique has also been used to grow dislocation-free single crystals; grains formed in this process could have a better crystallinity than those from other processes.

Herein, a low-temperature hydrothermal process was developed to fabricate CdV_2O_6 nanowire arrays with high aspect ratio. The obtained sample delivers a larger discharge capacity than that of bulk CdV_2O_6, which might find possible application as an electrode material in lithium ion batteries.

In a typical procedure, 1 mmol of $CdCl_2{\cdot}2.5H_2O$ and 2 mmol of NH_4VO_3 were put into separate beakers with 25-mL distilled water, and magnetically stirred for 20 min. After that, the solution of $CdCl_2$ was added slowly to the NH_4VO_3 solution to form a heterogeneous solution. The resulting solution was transferred into a Teflon-lined stainless autoclave. The autoclave was sealed and maintained at 140 °C for 12 h, then allowed to cool to room temperature. The products were filtered off, washed several times with distilled water and absolute ethanol, and then dried in vacuum at 60 °C for 5 h.

X-ray powder diffraction (XRD) pattern was determined using a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation ($\lambda = 1.541874$ Å). Transmission electron microscope (TEM) image and selected area electron diffraction (SAED) pattern were characterized by Hitachi H-800 transmission electron microscope (TEM) with a tungsten filament and an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) image was obtained on a Hitachi (X-650) scanning electron microscope.

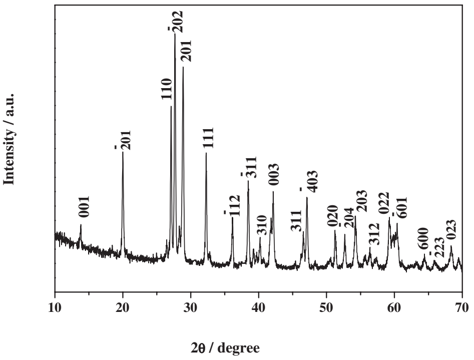

Figure 1. The XRD pattern of CdV_2O_6 sample obtained at 140 °C for 12 h.

The electrochemical performances were examined with metallic lithium as anode at room temperature. The positive electrodes were fabricated by pasting slurries of the as-prepared CdV_2O_6 (85 wt %), carbon black (Super P, 10 wt %) and polyvinylidene (PVDF, 5 wt %) dissolved in *N*-methylpyrrolidinone (NMP) on Al foil strips by doctor blade technique. Then the strips were dried at 160 °C for 24 h in an air oven, pressed under 20 MPa pressure and kept at 120 °C for 12 h in vacuum. The electrolyte was 1 M $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC) /diethyl carbonate (DEC); the separator was Celgard 2500. The cells were assembled in the glove box filled with highly pure argon gas. The cells were galvanostatically cycled in the 3.2–2.0 V range at a current density of 0.1 $mA{\cdot}cm^{-2}$.

Figure 1 shows the typical XRD pattern of the sample prepared by hydrothermal treatment at 140 °C for 12 h with the initial pH of 7.0. All the reflection peaks in Figure 1 can be indexed to the phase of CdV_2O_6 monoclinic structure [space group $c2/m$ (12)] with cell parameters of $a = 9.356$ Å, $b = 3.560$ Å, and $c = 6.985$ Å, which are in good agreement with the values reported in the literature (JCPDS Card 72-0546, $a = 9.359$ Å, $b = 3.568$ Å, and $c = 6.980$ Å). It is noticeable that the ($\bar{2}02$) reflection plane is extremely strong compared with the standard reflections, which is probably related to the preferential growth of CdV_2O_6 nanowire arrays. The products are proved to be well crystallized and pure by XRD pattern.

Representative SEM and TEM images of the as-synthesized CdV_2O_6 products obtained at 140 °C for 12 h are shown in

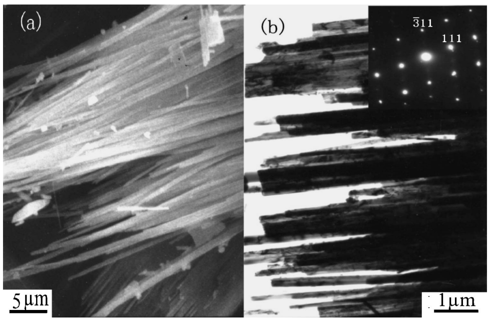

Figure 2. Representative SEM (a) and TEM (b) images of CdV_2O_6 sample obtained at 140 °C for 12 h.

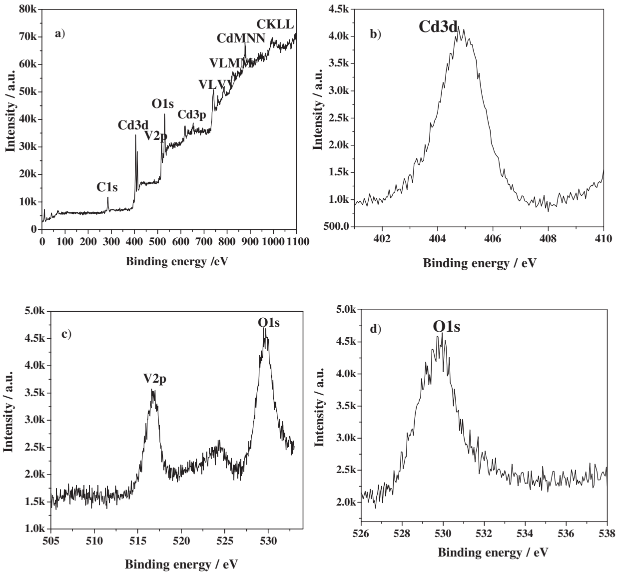

Figure 3. XPS spectra CdV_2O_6 nanowire arrays obtained at 140 °C for 12 h.

Figure 2. It can be seen in Figures 2a and 2b that the products are composed of a large number of dense nanowires with the average diameter of 100 nm and lengths of up to 20 μm, which leads to the high aspect ratio of the CdV_2O_6 nanowire arrays. The selected area electron diffraction (SAED) pattern in Figure 2b reveals the single crystal nature of the obtained CdV_2O_6 nanowire arrays.

The sample prepared is further confirmed by X-ray photoelectron spectroscopy (XPS), as shown in Figure 3. The XPS survey in the range of 0–1100 eV (Figure 3a) reveals that no contaminant within the sensibility limit of the technique is detected. The C1s peak used to calibrate the acquired spectrum is located at bonding energy of 284.95 eV. The Cd3d core-level spectrum (Figure 3b), the V2p core-level spectrum (Figure 3c) and the O1s core-level spectrum (Figure 3d) indicate that the observed values of the binding energy are 404.90, 516.75, and 524.4, as well as 528.80 eV, respectively, which are well consistent with the literature values reported previously for Cd^{2+}, V^{5+}, and O^{2-}.[11] The analysis of the Cd3d, V2p, and O1s peaks gives Cd:V and V:O atomic ratios of 1:1.92 and 1:2.97, which are similar to the stoichiometric composition of CdV_2O_6 and consistent with the XRD analysis of Figure 1.

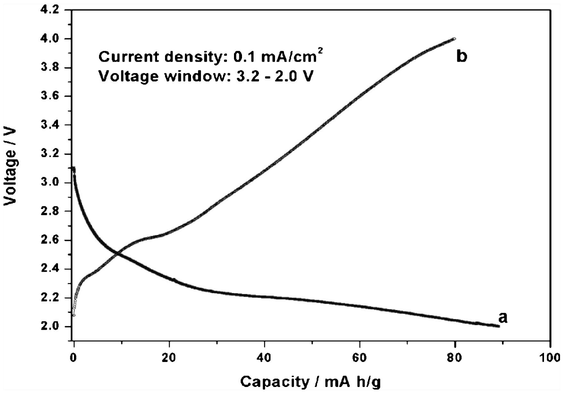

Figure 4. Charge–discharge curves of CdV_2O_6 nanowire arrays on the first cycle: (a) discharge curve and (b) charge curve.

Electrochemical performance of the as-prepared CdV_2O_6 in the cell configuration of Li/CdV_2O_6 was evaluated. Figure 4 shows the discharge curves of CdV_2O_6 on the first cycle with cut-off voltage of 2.0 V at a current density of 0.1 mA/cm^2. The discharge capacity of CdV_2O_6 nanowire arrays can reach about 90 mA h/g, corresponding to the lithium intercalation of about 1.0 Li per CdV_2O_6, which is much higher than that of bulk CdV_2O_6 (79 mA h/g).[7] The increased capacity may be attributed to the increased surface area and the 1-D nanostructures of CdV_2O_6.

In summary, single-crystal cadmium vanadate (CdV_2O_6) nanowire arrays with high aspect ratio were fabricated via a hydrothermal process. Electrochemical test show that these nanowire arrays deliver a larger discharge capacity than that of bulk CdV_2O_6. The obtained sample might find possible application as an electrode material in lithium ion batteries.

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