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V_2O_3 ultrathin nanosheets: Controlled synthesis and electrical properties

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ABSTRACT

Graphene-like structure of V_2O_3 had been synthesized by a top-down precursor-pyrolyzation strategy. The first-order transformation of V_2O_3 disappeared with the increasing of temperature. It represents a positive temperature coefficient semiconductor behavior. It is a noteworthy and promising candidate for ultrathin energy-storage devices. The discharge capacity of V_2O_3 nanosheets is maintained at 300 mAh/g after 75 cycles at the current density of 200 mA/g, which exhibits excellent discharge capacity and superior cycling stability. Flower-like precursors composed of nanosheets were also successfully synthesized by adjusting temperature and time. V_2O_3 has perfectly inherited the morphology of its precursors. The new method demonstrated here provides a new way in the preparation of other ultrathin nanosheets materials.

1. Introduction

Vanadium oxides and their derivative compounds have been at the forefront of applied research because of their promising applications in sensors, catalysts, optical switching, Li-ion batteries and so on [1–3]. As the rhombohedral V_2O_3 possesses a three-dimensional(3D) V–V framework and tunneled structures, V_2O_3 is an appealing candidate for excellent electrode materials [4]. Recently, V_2O_3–OMC composites were prepared, whose reversible capacity was maintained at 536 mAh/g after 180 cycles at 0.1 A/g [5]. As is known, V_2O_3 is the prototype system for the Mott transition as a function of temperature, doping, pressure, or size which can induce the metal-to-insulator transition (MIT) between a paramagnetic metal (PM) and a paramagnetic insulator [6]. Compared to the MIT behaviors of other irregular V_2O_3particles, the transition temperature of V_2O_3 pseudocubes synthesized by Xie at al. was drastically depressed from 133 K to 36 K [7]. Recently, V_2O_3 with different crystalline structures and morphologies have been synthesized by different methods. Belt-like V_2O_3@C composite was synthesized by thermal treatment under an inert atmosphere [8].V_2O_3 nanocrystals were synthesized in the Na_2SO_4 salt matrix through mechano-chemical–thermal reduction between V_2O_5 and Na_2SO_3 [9]. The colloidal route to V_2O_3 nanocrystals with a metastable bixbyite crystal structure was developed and the structure was studied in detail [10]. If the morphology of materials became quasi-two-dimensional, many extraordinary properties were discovered which could provide new opportunities in integrated electronic systems [11]. Herein, based on the past experience [12], without any surfactant, graphene-like structure of V_2O_3 had been synthesized by a top-down precursor-pyrolyzation strategy controllably. Interestingly, the first-order transformation of these ultrathin V_2O_3 nanosheets disappeared with the increasing of temperature, which should produce temperature-induced reversible metal insulator transition. It represents a positive temperature coefficient semiconductor behavior. At 200 mA/g, the discharge capacities of ultrathin V_2O_3 nanaosheets still are maintained at 300 mAh/g after 75 cycles, which exhibited excellent discharge capacity and superior cycling stability. Meanwhile, controllable synthesis of 3D flower-like structure precursor composed of nanosheets was successfully realized by adjusting temperature and time. With the help of Ar, V_2O_3 had perfectly inherited the morphology of its precursors. The new method demonstrated here paves the way for fascinating strategy in the preparation of other ultrathin nanosheets materials as well as a better understanding of their potential applications in the future.

2. Experimental

0.234 g NH_4VO_3 was dissolved in 40 mL ethanol under magnetic stirring for 20 min, then transferred into 50 mL autoclave,

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sealed and maintained at 250 °C for 24 h. Then the precursor powder was calcined at 600 °C in Ar for 3 h (heating rate 5 °C/min). X-ray diffraction (XRD) was measured on a Philips X'pert diffractometer with Cu Kα radiation (λ=1.541874 Å). A Raman SPEX 1403 spectrometer with Ar^+ laser at an excitation wavelength of 514.5 nm is used to examine Raman spectra. SEM was obtained using JEOL-JSM-6700F. The electrical conductivity of the samples was measured on a Keithley 4200 station. Electrochemical measurements were performed using coin-type 2016 cells. Lithium metal was used as the counter electrode, and the separator was a Celgard 2400 microporous membrane. Cell assembly was carried out in a glove box filled with high-purity argon gas. The charge/discharge tests were performed within a range of 0–3 V at 200 mA/g.

3. Results and discussion

All the peaks from Fig. 1a can be assigned to the rhombohedral crystalline phase (space group: R-3c, a=4.932 Å, c=13.99 Å) of V_2O_3 which are in agreement with the literature values (JCPDS No. 84-0317). To get a clear evidence into the composition of the as-obtained sample, the Raman spectrum is also shown in Fig. 1b. The Raman peaks at 277 cm^{-1} and 522 cm^{-1} can be assigned to A1g modes of the products and the Raman peak at 403 cm^{-1} can be assigned to the bending vibration of V–O bond which is in accordance with the reported literature [13–14]. The TEM image of the products is shown in the inset of Fig. 1b. It presents the overlap of lamellar structure, which is consistent with the SEM images. Fig. 1c shows that the products in SEM images are all V_2O_3 nanosheets, and there is no other morphology from view. According to the higher magnification image (Fig. 1d), we infer that the shape of the samples consists of many ultrathin sheets with thickness under 10 nm.

As we all know, V_2O_3 undergoes a first-order transformation from a monoclinic anti-ferromagnetic insulator (AFI) to a rhombohedral PM around −120 °C, accompanied by a jump in the resistivity of about seven orders of magnitude. From around 77 °C to around 277 °C, V_2O_3 shows a broad second-order transformation to a second metal (PM) phase [6]. Recently, researches have shown that the phase transition temperature of V_2O_3 has been greatly influenced by particle size and morphology [7]. In addition, when the materials were prepared to quasi-two-dimension just like the structure of graphene, the properties might have changed unexpectedly. The planar resistivity and conductivity of the sheets are carried out as shown in Fig. 2. Different from previous reports V_2O_3 pseudocubes with thickness of 10 nm still exhibited the transition temperature at 36 K [7], the first-order transformation of V_2O_3 ultrathin nanosheets disappeared and there had no resistivity jump from 0 to 300 K. The result showed that an increasing response of electric conductivity was observed, displaying the typical semiconductor conducting behavior of V_2O_3 nanosheets. A similar situation was also reported in VS_2 which is a noteworthy and promising candidate for ultrathin energy-storage devices [15]. The electrochemical property of V_2O_3 nanosheets composite was also explored. The discharge capacity curve of the V_2O_3 nanosheets is shown in the inset of Fig. 2b. It exhibits an initial discharge capacity of 480 mAh/g. The discharge capacity of the product shows a slight increase with the cycle number. This phenomenon is attributed to the reversible growth of a polymeric gel-like film resulting from kinetically activated electrolyte degradation [16]. The reversible discharge capacity after 75 cycles is still maintained at 300 mAh/g which is much higher than the values of the reported uncoated V_2O_3 [5]. It may be attributed to the low resistance, high effective surface and short diffusion distance that result from the structures of ultrathin V_2O_3 nanosheets, which facilitate the intercalation and de-intercalation of Li-ions.

Further on, to investigate the growth process of these ultrathin V_2O_3 nanosheets, we have studied the precursors taken at various stages of reaction time and temperature. Flower-like structures were obtained when the time is 1 h at 250 °C (Fig. 3a) and the temperature is 200 °C for 24 h (Fig. 3c). As time prolongs or the temperature raises, the flower-like spheres become loose and the thickness of nanosheets decreases gradually (Fig. 3b). When the temperature and time are both up to 250 °C for 24 h, all the products of precursors transform into very thin sheets (Fig. 3d) in accordance with the shape of the sample (Fig. 1d). The SEM images

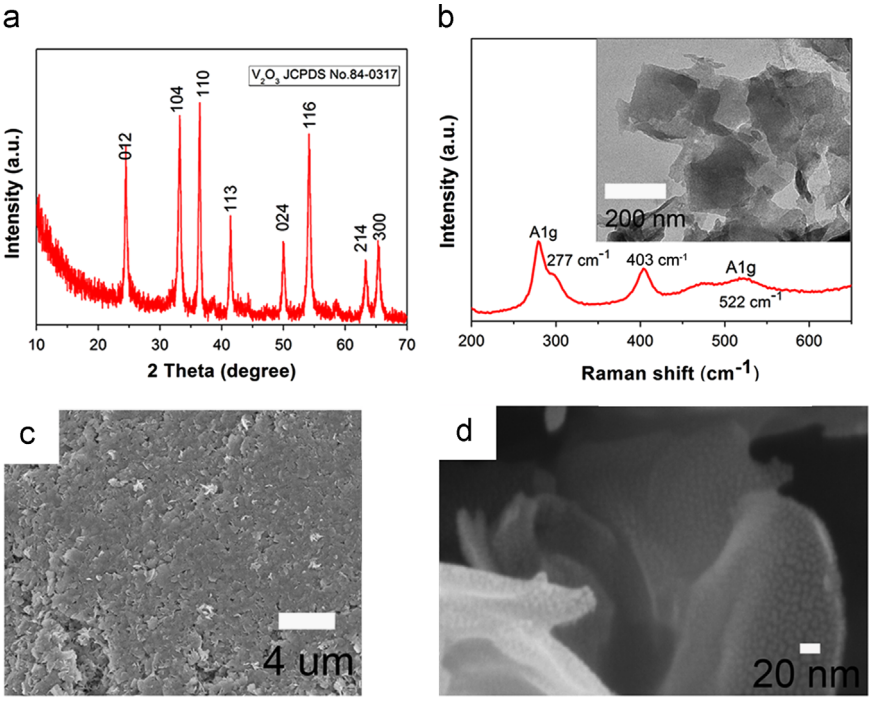

Fig. 1. (a) XRD (b) Raman (inset TEM images) (c) low and (d) high-magnification SEM of the products.