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Synthesis of dandelion-like V_2O_3/C composite with bicontinuous 3D hierarchical structures as an anode for high performance lithium ion batteries

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ABSTRACT

The dandelion-like V_2O_3/C composite was synthesized by a simple and facile template-free solvothermal method followed by a suitable thermal treatment. The dandelion-like V_2O_3/C composite is constructed by bicontinuous 3D hierarchical structures, which are formed by interconnected nanoparticles and interconnected pores, respectively. Moreover, the surface of interconnected nanoparticles is uniformly coated with an ultrathin carbon layer. Upon evaluation as an anode material for LIBs, the as-synthesized product shows superior electrochemical performance. Under the current density of 0.1 A g^{-1}, the specific discharge capacity of V_2O_3/C composite is 737 mA h g^{-1} after 100 cycles. Moreover, after 1000 cycles at a high current density of 2 A g^{-1}, the sample exhibits a discharge capacity of 315 mA h g^{-1} which is 94% of the first-cycle discharge capacity. This excellent electrochemical performance can be ascribed to its unique hierarchical structure with 3D interconnected nanopores and uniform carbon coating.

1. Introduction

Lithium ion batteries (LIBs), as a representative of the modern high-performance rechargeable batteries, have been applied to many fields, such as portable mobile devices, military power supply, hybrid electric vehicles [1–3]. Nevertheless, commercial LIBs cannot meet the gradually increasing demand of storing energy devices, just because the utilized graphite anode has low theoretical capacity [4]. Thus, much emphasis has been placed on seeking a suitable anode material that possesses the benefits of high power density and large energy density [5,6]. Due to their low cost, abundance, special layered or open-framework structure as well as their high specific capacity, vanadium oxides (such as VO_2 (M), VO_2 (B), VO_x, V_2O_3) have been researched as anodes for rechargeable LIBs [7–14]. Among them, V_2O_3 has been regarded as an ideal anode material for LIBs because it possesses the advantages of low toxicity, high specific capacity and volumetric energy densities, etc. [15]. However, there are seldom reports for V_2O_3 anode material applied in LIBs because of its metastability, poor conductivity and cycling stability until now [16,17].

It is well documented that the electrochemical performances of transition metal oxides (TMOs) electrodes are intimately correlated to their morphology [18,19]. The design and synthesis of hierarchically porous structures of three-dimensional (3D) TMOs constructed by nanosized building units have received tremendous interest in the realization of high-performance LIBs [20,21]. Among these, 3D hierarchically porous TMOs materials consisting of interconnected nanopores have attracted special attention due to their stable 3D hierarchical structure, high specific surface area and excellent interconnected pore structure [22]. This is because 3D hierarchically porous TMOs assembled from nanoscaled building units could shorten the diffusion length of Li-ion and electron, which leads to an improvement in rate performance. Meanwhile, the high specific surface area enables sufficient contact between the electrolyte and active material and provides more reaction sites on the surface, resulting in the increase in specific capacity. Moreover, the interconnected pore structure possesses the ability to greatly facilitate Li^+ transfer and effectively alleviate the structural strain caused by volume change during repeated charge-discharge cycles, leading to enhanced cycle performance. However, current strategies for the synthesis of hierarchically porous structures of TMOs mainly involve the use of complicated templates and tedious multi-step processes [21–23]. Hence, the development of a facile strategy to synthesize hierarchically structured TMOs with 3D interconnected pores for LIBs is highly desirable and very challenging work.

Recently, it is reported that vanadium trioxide composited with

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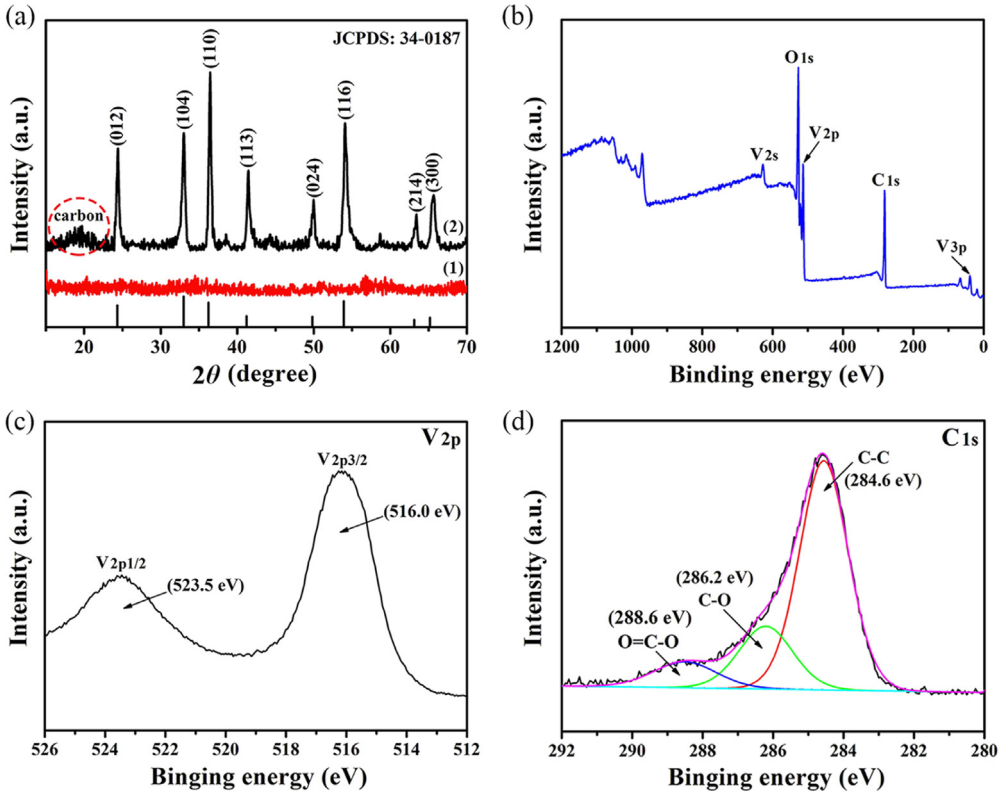

Fig. 1. XRD patterns (a) of the precursor and the calcined product; XPS spectra of V_2O_3/C composite: (b) survey spectrum; (c) V2p spectrum; (d) C1s spectrum.

highly conductive carbon material can preserve the inner active substance and enhance their conductivity and cycle life [24–30]. For example, the composite of V_2O_3-ordered mesoporous carbon exerted a reversible capacity of 536 mA h g^{-1} after 180 cycles at a rate of 0.1 A g^{-1} [31]. Zhang et al. reported that V_2O_3 modified by reduced grapheme oxide exhibited a reversible capacity of 270 mA h g^{-1} after 250 cycles at a rate of 0.5 A g^{-1} [32]. Dong et al. reported that V_2O_3/amorphous carbon nanocomposite delivered a discharge capacity of 780 mA h g^{-1} after 100 cycles at a current density of 0.2 A g^{-1} [33]. Therefore, a combination of TMOs with 3D interconnected porous structure and coating with conductive carbon might lead to significant improvement of electrochemical properties for lithium-ion batteries.

Herein, the conductive carbon uniformly coated dandelion-like V_2O_3 was successfully prepared for the first time by a simple and facile template-free solvothermal method followed by thermal treatment at 600 °C for 4 h under N_2/H_2 (95–5%) atmosphere. The as-prepared V_2O_3/C composite consists of bicontinuous 3D hierarchical structures, one consisting of interconnected V_2O_3/C nanoparticles and the other consisting of interconnected nanopores. When evaluated as an anode material for LIBs, the V_2O_3/C composite shows a discharge capacity specific of 737 mA h g^{-1} at the rate of 0.1 A g^{-1} after 100 cycles. The formation process of the dandelion-like V_2O_3/C composite and the reason for superior lithium storage performance are discussed in detail.

2. Experimental section

2.1. Material synthesis

In a typical procedure, $VO(acac)_2$ (0.1856 g) and urea (0.42 g) were dispersed in 30 mL of ethylene glycol, followed by adding 5 mL of the mixed solution of 30% hydrogen peroxide and deionized water with the volume ratio of 1:4 under vigorous magnetic stirring for 1 h to form a bright yellow solution at ambient temperature. Then this obtained mixture was transferred to a 50 mL Teflon-lined stainless-steel autoclave that was sealed and maintained at 200 °C for 8 h. After naturally cooling down to ambient temperature, the gray precipitates were separated and washed with absolute ethanol and deionized water, and then dried at 70 °C for 12 h. The final products were acquired after calcined at 600 °C for 4 h under N_2/H_2 (95–5%) atmosphere.

2.2. Material characterization

The XRD patterns of the samples were recorded on a Bruker X-ray diffractometer (D8 Advance) using a Cu Kα radiation source. The FE-SEM (Field emission scanning electron microscopy) images and the TEM (Transmission electron microscopy) images of as-obtained products were characterized by using Hitachi S-4800 scanning electron microscope and JEOLJEM-2100 F microscope, respectively. The specific surface area and pore size distribution were estimated from N_2 adsorption–desorption analysis which was measured on a Gas Sorption System (Micro-metrics Instruments, ASAP 2420). TGA (Thermogravimetry analysis) was performed on a thermogravimetric analyzer (Perkin Elmer, TG/DTA 6300) in air atmosphere. The sample was also analyzed by X-ray photoelectron spectroscope (XPS, Kratos, ULTRA AXIS DLD) with monochrome Al Kα ($h\nu$ = 1486.6 eV) radiation. All binding energies were calibrated by referencing to C1s (284.6 eV).

2.3. Electrochemical measurements

The working electrode was fabricated with V_2O_3/C as active material, acetylene black as conductive material and polyvinylidene fluoride (PVDF) as adhesive at a mass ratio of 70:20:10 in N-methylpyrrolidone (NMP) solvent to form a homogeneous slurry. The obtained slurry was pressed on Cu foil and dried at 120 °C for 24 h under a vacuum. Lithium metal foil and Celgard 2400 were used as the negative electrode and separator, respectively. The electrolyte was 1 mol L^{-1} LiPF6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 vol). The as-obtained model test cells were assembled in an argon-filled glove box and galvanostatic charge/discharge tests were