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Synthesis of V_2O_5 micro-architectures via in situ generation of single-crystalline nanoparticles

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Abstract

Rose-like crystalline particles of ammonium vanadium sulfate hydroxide ($NH_4V_3(OH)_6(SO_4)_2$) were synthesized by a solvothermal route using dimethyl sulfoxide (DMSO)–water as the solvent. Following a thermal decomposition process, rose-like V_2O_5 micro-architectures were fabricated via the in situ generated single-crystalline nanoparticles. When used as the cathode material in lithium-ion batteries, the rose-like V_2O_5 micro-architecture exhibited high initial discharge capacity. Sphere-like precursor was also prepared via selecting suitable carboxylic acid. This facile synthesis method would be used to prepare various vanadium oxides with different morphologies as well as other compounds.

Keywords: V_2O_5; Ammonium vanadium sulfate hydroxide; Micro-architecture; Decomposition

1. Introduction

Vanadium oxide (V_2O_5) has attracted much interest [1], owing to its excellent properties for various important applications, such as in lithium batteries [2], actuators [3], sensors [4] and catalysis [5]. Compared to bulk V_2O_5, vanadium oxides with nano- and micro-structures have significantly improved the performances in devices for energy storage and sensing [6]. Until now different one-dimensional V_2O_5 nano-structures have been prepared by various methods [7–12]. Recently, great interest has been paid to prepare V_2O_5 arrays, for instance, V_2O_5 nanofiber arrays and single-crystal V_2O_5 nanorod arrays were fabricated by template-based sol–gel reaction [13] and electrodeposition [14], respectively, which exhibited higher current density and energy storage density than sol–gel-derived V_2O_5. Hollow V_2O_5 microspheres self assembled from nanorods were obtained by a poly (vinylpyrrolidone)-templating process [15]. Spherical-like $V_2O_5(HDA)_{0.83}\cdot 1.8H_2O$ nanotube clusters were synthesized via intercalation of neutral surfactant hexadecylamine [16]. Rose-like nano-structured V_2O_5 film was fabricated via carrying out the drop-casting of a suspension of V_2O_5 particles, which were photoswitchable between superhydrophobicity and superhydrophilicity due to the cooperation between the photosensitivity of V_2O_5 and submicron- to micron-scale apertures [17].

Herein, we developed a simple way to fabricate rose-like V_2O_5 micro-architectures. The synthesis was performed in a DMSO–water mixed solvent using ammonium metavanadate and oxalic acid as reactants. By careful adjustment of the synthesis parameters, rose-like ammonium vanadium sulfate hydroxide $NH_4V_3(OH)_6(SO_4)_2$ crystal particles were obtained, and the corresponding rose-like V_2O_5 micro-architecture was obtained via thermal decomposition of the crystals in situ. When used as cathode material in lithium-ion batteries, the rose-like V_2O_5 micro-architecture exhibited high initial discharge capacity. This facile method to fabricate V_2O_5

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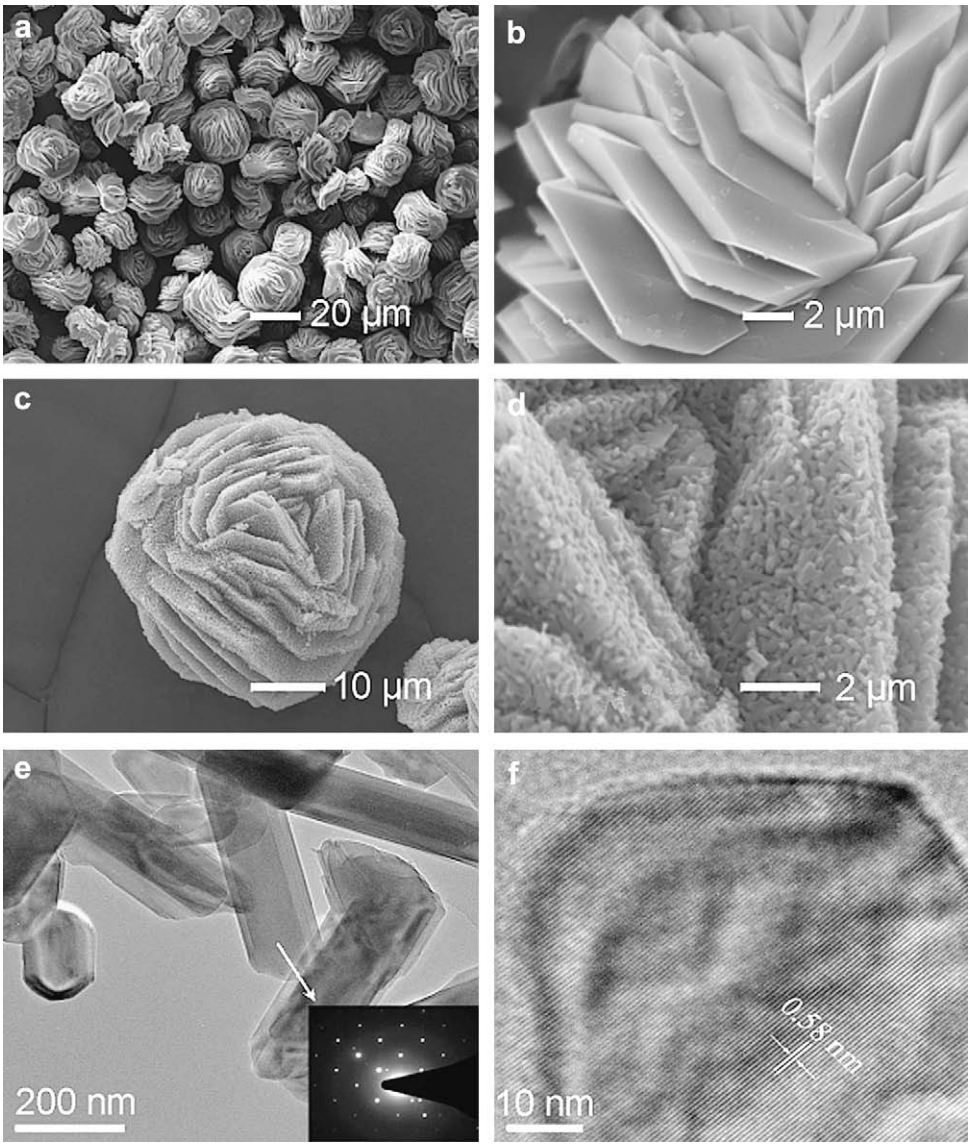

Fig. 1. SEM images of the as-prepared precursors (a, b), the calcined product (c, d) and TEM images (e, f) of the calcined rose-like micro-architectures, the inset in (e) is the selected area electron diffraction (SAED) measured from the particle indicated by the arrow.

micro-architectures with well-defined morphologies would be of great significance to design other complicated micro-architectures with advanced functions.

2. Experimental

2.1. Preparation of materials

All chemicals are commercially available and were used as-received. The synthesis was performed via a hydrothermal method in a dimethyl sulfoxide (DMSO)–water mixed solvent. In a typical procedure, 0.01 mol oxalic acid was dissolved in the DMSO–H_2O (5 ml–25 ml) mixed solvent and then 0.005 mol ammonium metavanadate (NH_4VO_3) was added into the solution under stirring for 2 h at room temperature. After that the solution was transferred to a 50-ml Teflon-lined stainless autoclave, sealed, kept at 180 °C for 24 h and cooled to room temperature. The black product was filtered, washed with deionized water and absolute ethanol, and dried at 60 °C for 12 h. The dried product was calcined at 500 °C for 2 h. By variation of the molar ratio of oxalic acid to NH_4VO_3, the amount of DMSO and the moiety of carboxylic acid including acetic (the molar ratio of acetic acid/$NH_4VO_3 = 4.0$) and lactic acid (the molar ratio of lactic acid/$NH_4VO_3 = 6.0$), a series of precursors were synthesized under the identical condition. All the experimental operations should be operated with good ventilation to avoid the unfavorable odor due to the oxidation products of the DMSO during the hydrothermal reaction.

2.2. Characterizations

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-2500 diffractometer using Cu Kα radiation. Scanning