Materials Letters 132 (2014) 247–250

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Synthesis of diverse structured vanadium pentoxides particles by the simplified hydrothermal method

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ARTICLE INFO

Article history:
Received 15 February 2014
Accepted 14 June 2014
Available online 21 June 2014

Keywords:
Vanadium pentoxide
Shcherbinaite phase
Nano-belt
Micro-flower
Micro-plane-flower
Hydrothermal method

ABSTRACT

In this letter, we utilize a simplified hydrothermal method without any addition of catalyst to synthesize one-and three-dimensional structured pure vanadium pentoxide (V_2O_5) particles, V_2O_5 nano-belt, micro-flower and micro-plane-flower. The synthesis is made possible by the formation of shcherbinaite phase and its cleavaging property along (001) facet by physical force. The V_2O_5 nano-belt has been derived from the V_2O_5 precursor in de-ionized (D.I.) water without catalysts by using stirred autoclave system. And V_2O_5 micro-flower and micro-plane-flower have been synthesized in ethylene glycol solvent under controlled pH condition by HNO_3 or NH_4OH. The synthesized nano-belts are less than 100 nm in width and less than 50 nm in thickness, respectively. The diameters of the synthesized micro-flower and micro-plane-flower are 5–8 μm. It is demonstrated that the prepared specimens are pure V_2O_5 composition with shcherbinaite phase.

1. Introduction

Vanadium pentoxides (V_2O_5) have received much attention due to their wide range of applications such as lithium ion secondary batteries [1,2], gas sensors [3], oxidation catalysts [4], electrochemical capacitors [5] and electrochromic devices [6]. Many researchers have studied to synthesize diverse structures of V_2O_5 for improving performance of their applications since the properties of solid state materials strongly depend on their structure and morphology. Various synthetic methods for different diverse structure of V_2O_5 have been reported including the sol–gel method [7], ion exchange procedure [8], self-assembly with template-assisted synthesis [1,9], precipitation method [10] and hydrothermal method [11–13]. Among many synthetic methods, the hydrothermal method is the most well-known technique which consists of simple processes such as preparation of solution, heat treatment, and collection of synthesized particles [14].

Yi Xie group and Guicun Li group have reported the synthesis of one-dimensional V_2O_5 nano-structure, such as nano-belt and nano-roll, via the hydrothermal method using a NH_4VO_3 precursor and H_2SO_4 additives with D.I. water or using V_2O_5 precursor and H_2O_2 solvent [11–13]. Moreover, Clivia M. Sotomayer Toress group have reported synthesis of three-dimensional vanadium oxides (VO_x or $Cs_2V_6O_{16}$) structures [15,16]. However, simplifying of synthetic conditions and improving synthesizing yield with pure V_2O_5 composition are still remained as challenging in the hydrothermal method.

In this report, we have effectively synthesized V_2O_5 nano-belts, micro-flower and micro-plane-flower via the simple hydrothermal method. It is the first report about synthesis of pure V_2O_5 microsphere structures without catalysts or seed material via the hydrothermal method. We also report the synthesis of V_2O_5 nano-belt structure from V_2O_5 in D.I. water solution without any additives. Using stirred autoclave system and formation of shcherbinaite phase accelerate splitting effect, and facilitate simplified synthesizing condition.

2. Experimental

V_2O_5 nano-belts, micro-flower and micro-plane-flower particles were synthesized by the hydrothermal method in different solvents and additives. The detail of synthetic procedures for the synthesis of V_2O_5 nano-belts are as followings: 1 g of commercial V_2O_5 was dissolved in 200 ml of D.I. water with stirring. After 3 h stirring, the solution was placed in stirred autoclave system with 300 ml Teflon liner [IL-SHIN AUTOCLAVE, 300-SACS]. The stirred autoclave system was maintained at 473 K for 12 h under stirring with 90 rpm.

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http://dx.doi.org/10.1016/j.matlet.2014.06.086
0167-577X/

For the synthesis of V_2O_5 micro-flower, 1 g of V_2O_5 was dissolved in 200 ml of ethylene glycol with stirring and HNO_3 was added droplet by droplet until a pH of 0.155 was reached. After 3 h stirring, the solution was placed in the normal autoclave system with a 300 ml Teflon liner [IL-SHIN AUTOCLAVE, 300-PV]. The autoclave was maintained at 423 K for 24 h.

For the synthesis of V_2O_5 micro-plane-flower, the precursor and solvent were used in the same way as the micro-flower synthesis, and NH_4OH instead of HNO_3 was added until a pH of 10 was reached. The solution was placed in a stirred autoclave system and was maintained at 473 K for 18 h under stirring with 90 rpm.

After heat treatment, the autoclave and stirred autoclave systems were cooled to room temperature by air cooling. Each precipitated particle was collected and washed with acetone three times, and then dried in a dry oven at 373 K for 10 h.

Each synthesized specimen was characterized by an X-ray diffraction (XRD, Rigaku, SmartLab) with Cu K_α radiation to investigate the crystal structure and phase. The morphologies and sizes of the synthesized specimen were observed by field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-7100F).

3. Results and discussion

Fig. 1(a)–(c) shows the image of synthesized V_2O_5 nano-belts and XRD pattern. As shown in Fig. 1(a), the nano-belts have smooth surface and high flexibility. The width and thickness are less than 100 nm and 50 nm, respectively. From the low magnification image of FE-SEM (Fig. 1(b)), it is clear that the synthesizing yield of nano-belt is very high. Most of the peaks of XRD pattern (Fig. 1(c)) can be indexed to a shcherbinaite phase of V_2O_5 and its space group is Pnmm (JCPDS 41-1426). From the confirmation of the shcherbinaite phase, we may accept that the composition of synthesized nano-belts is pure V_2O_5 because the shcherbinaite phase can be formed when it contains over 97.55% of V_2O_5 composition [17]. The formation of shcherbinaite phase comes from the prepared solution composed of V_2O_5 powder as solute and D.I. water as solvent in the synthesis process of nano-belts. In addition, the XRD pattern does not show any valid peaks from possible impurities such as vanadium oxide hydrate.

In XRD pattern of synthesized nano-belts, the peak which is indexed to (001) facet does not appear. The cause of absence of the (001) facet peak can be explained by a synthesizing mechanism of nano-belts. The dissolved V_2O_5 in D.I. water is formed into a layered frame at 473 K under the pressure of 11 atm in a stirred autoclave. Next, the layered bulky frame is separated layer by layer through dehydration of the interstitial water molecule between the V_2O_5 layers [13]. This separation is made possible by the weak bonding between each V_2O_5 layer. It comes from principle of bulky V_2O_5 formation as followings: the layered structure built up from VO_3 square pyramid sharing corner and edges with V_2O_5 layers held together by weak interaction between vanadium atoms and oxygen atoms [17]. After separating the layers, each layer is split into a nano-belt structure by stirring in stirred autoclave system along the (001) facet. The splitting is attributed by one of the characteristics of the shcherbinaite phase that is cleavage along (001) facet by physical force [17]. As a result, the formation of shcherbinaite phase leads to simplify the synthetic condition and stirred autoclave system accelerates to split into nano-belts. The synthesis mechanism of nano-belt structure is presented in Fig. 1(d).

The Figs. 2 and 3(a)–(c) show that synthesized micro-flowers and micro-plane-flowers images and XRD patterns. Both the micro-flower and micro-plane flower particles have three-dimensional micro-sphere shape and rough morphology. The diameters of micro-flowers and micro-plane-flowers are 5–8 μm, respectively. As shown in the low-magnification images of FE-SEM (Figs. 2 and 3(b)), each micro-sphere structured particles was synthesized in the whole sample. The analysis of XRD patterns (Figs. 2 and 3(c)) demonstrates that both synthesized micro-flower and micro-plane-flower are shcherbinaite phase of pure V_2O_5. The micro-sphere structured V_2O_5 particles have been synthesized by the two steps. In the first step, V_2O_5 nano-rods or nano-sheets are formed. The formation of nano-rod and nano-sheets can be explained through the coordination

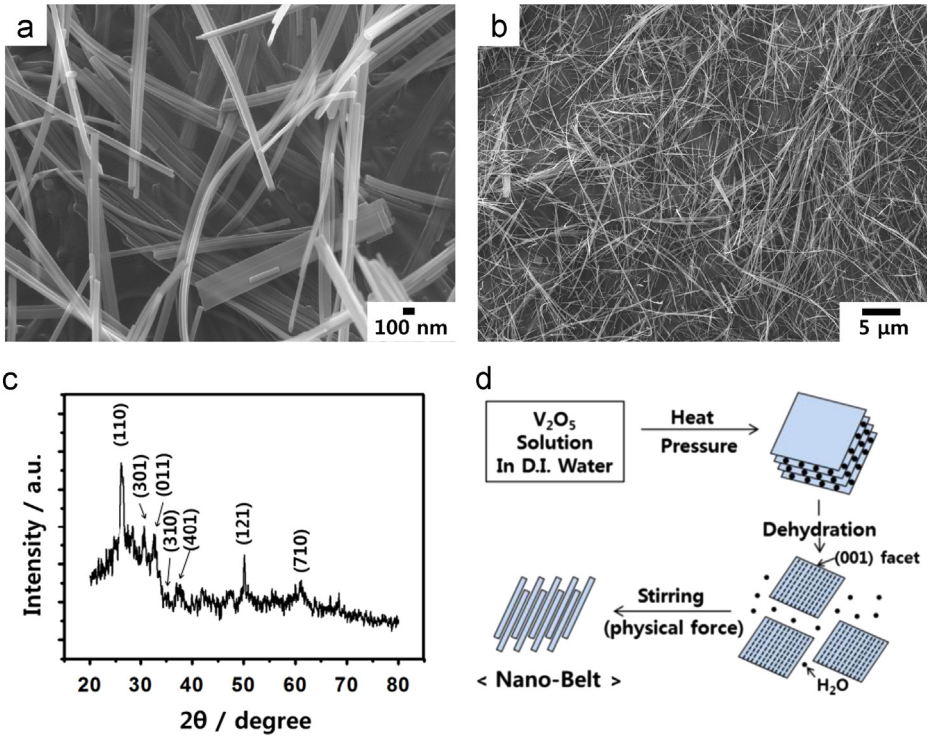

Fig. 1. V_2O_5 nano-belts: (a and b) high and low magnification FE-SEM images, (c) XRD pattern, and (d) schematic illustration of synthesis mechanism.