Materials Chemistry and Physics 148 (2014) 1089–1094

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Yarn ball-like tungsten oxide microspheres synthesized via solvothermal process

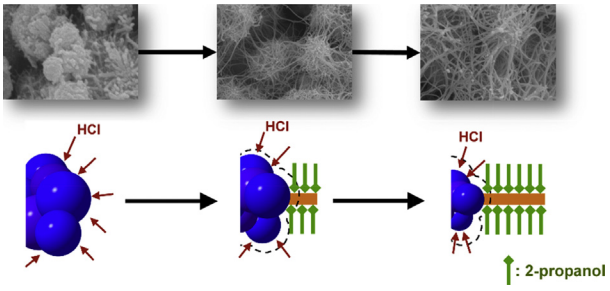
Liang-Yih Chen [a], Ching-Hsiang Chen [d], Wen-Hui Chang [b], Shih-Chieh Hsu [c], Shiow-Huey Chuang [b, *]

[a] Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, Section 4, Keelung Road, Taipei 106, Taiwan
[b] Department of Applied Chemistry, National University of Kaohsiung, Kaohsiung 81148, Taiwan
[c] Department of Chemical and Materials Engineering, Tamkang University, New Taipei 25137, Taiwan
[d] Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 106, Taiwan

HIGHLIGHTS

- A yarn ball-like microspheres of WO_x were synthesized via simple solvothermal method.
- The growth direction of nanowire of yarn ball-like microsphere was along [010].
- The phase change occurred when the postannealing temperature was above 400 °C.
- The morphology of tungsten oxide will be influence by the organic solvent.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 April 2014
Received in revised form
1 August 2014
Accepted 22 September 2014
Available online 27 September 2014

Keywords:
Oxides
Chemical synthesis
Heat treatment
Crystal structure

ABSTRACT

In this study, yarn-ball-like tungsten oxide microspheres were synthesized using a solvothermal method. Highly oriented (020) plane yarn-ball-like tungsten oxide microspheres were assembled using tungsten oxide nanowires approximately 5–15 nm in diameter and tens of microns in length. After the post-annealing treatment, the morphologies of the tungsten nanowires transformed into aggregated nanoparticles approximately 20–80 nm in diameter. The morphologies and structures of the as-synthesized yarn-ball-like tungsten oxide microspheres and aggregated nanoparticles treated postannealing were characterized using field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FT-IR), and Raman spectroscopy. This study proposes the possible growth mechanism of yarn-ball-like tungsten oxide microspheres assisted by solvent molecules.

1. Introduction

Tungsten oxide (WO_x) is a transition metal oxide that has attracted considerable attention because of its compelling electronic and chemical properties that make it applicable in photocatalysis [1,2], gas sensing [3–5], electrochromic [6–8], thermoelectric [9], ferroelectric [10], field emitting [11], and gas-chromic materials [12]. Tungsten oxide can exhibit numerous crystal phases and morphologies, which can extend its use and applicability [13]. With the advent of nanotechnologies, the synthesis and analysis of WO_x nanostructures have become increasingly prominent [14,15]. The nanostructuring of WO_x can enhance the performance of this essential and functional material, providing

* Corresponding author.
E-mail addresses: shiow_huey_chuang@msn.com, shchuang@nuk.edu.tw (S.-H. Chuang).

http://dx.doi.org/10.1016/j.matchemphys.2014.09.023
0254-0584/

it with unique properties that do not exist in its bulk form. To date, nanosized tungsten oxides of various morphologies have been explored, such as nanowires [16], nanotubes [17], nanorods [18], nanowalls [19], urchin-like shapes [20], nanosheets [21], nanoflowers [22], and nanoplates [23]. These WO_x nanomaterials have been synthesized using a hydrothermal or solvothermal method with various tungsten precursors [16–24]. To control the morphologies of nanomaterials further, the growth conditions have been modulated through solvents [25], tungsten precursor concentration [26], or assistant reagents [27–29].

Three-dimensional (3D) nanostructured materials consisting of one-dimensional WO_x nanomaterials, such as nanowires, nanorods, and nanoribbons, have attracted considerable research interest because of their unique physical, chemical, and optical properties [15,20,28,30]. Studies have synthesized 3D WO_x without using an assistant reagent or crystal seeds [22,25,26,30]. Liu et al. dissolved WCl_6 in ethanol to synthesize urchin-like WO_x in a monoclinic $W_{18}O_{49}$ phase through a solvothermal method at 200 °C [25]. Similarly, Zhao et al. obtained flower-like WO_x in an orthorhombic WO_3 phase and using WCl_6 and ethanol at 100 °C for 24–72 h [22]. Sun et al. used WCl_6 and cyclohexanol at 200 °C to obtain bundled WO_x nanowires in a monoclinic $W_{18}O_{49}$ phase [30]. Qin et al. added WCl_6 to 1-propanol to synthesize WO_x nanomaterials at 200 °C and observed that the structures and morphologies of WO_x nanomaterials were modulated by the tungsten precursor concentration [26]. Low WCl_6 concentration for one-dimensional nanowire bundles in a monoclinic $W_{18}O_{49}$ phase and high WCl_6 concentration for nanosheets with monoclinic WO_3. Based on these results, we deduced that the morphologies of the product were highly influenced by the solvents and tungsten precursor concentrations.

In this study, we synthesized 3D WO_x nanomaterials from WCl_6 and 2-propanol by using a solvothermal method. Through the Ostwald ripening process, high-oriented yarn-ball-like WO_x microspheres were formed. The formation process, crystal phases, and morphologies of the products were investigated. In addition, the morphological and phase changes of the as-synthesized ball-like tungsten oxide microspheres after the postannealing process were examined. All of the products were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray powder diffraction (XRD), Raman spectroscopy, and Fourier-transform infrared spectroscopy (FT-IR).

2. Experimental section

WCl_6 (99.9$^+$%, Sigma–Aldrich) and 2-propanol (anhydrous, 99.5%, Sigma–Aldrich) were used as received and stored under nitrogen.

Yarn ball-like tungsten oxide microspheres were synthesized by solvothermal method. WCl_6 (0.794 g, 2.00 mmol) was dissolved in 20 mL of 2-propanol and a pale yellow solution was obtained after stirring. Then the solution was transferred into a Teflon-lined autoclave. The solvothermal reaction was conducted at 180 °C for 24 h (P1), 48 h (P2) and 72 h (P3). Blue precipitates were collected and washed several time with 2-propanol and *n*-hexane. The final product was dried at 80 °C for 1 day.

A JEOL JSM-6330TF field emission scanning electron microscope was used to investigate the morphology. Transmission electron microscope (TEM) images were collected by using a JEOL JEM 3010 microscopy working at 200 KV. X-ray powder diffraction (XRD, Rigaku, Multiflex, 2 KW) measurements were carried out using Cu Kα (λ = 0.154 nm) radiation. 532 nm diode laser excited Raman spectra were acquired from the RAMaker system mounted with one TE cooled CCD of 1024 × 128 pixels as integrated by Protrustech Corporation Limited. Fourier-transform infrared spectroscopy (FT-IR, Perkin Elmer Spectrum RX1) was used to characterize the vibration modes between the atoms in the products. The scan range was 4000–400 cm^{-1} and the resolution is 4 cm^{-1} under eight scans. A.

3. Results and discussion

Fig. 1(a)–(d) shows the SEM images of tungsten oxide nanomaterials synthesized at 180 °C for 24 h (P1), 48 h (P2), and 72 h (P3), respectively. For P1, urchin-like spheres ca. 1 μm in diameter

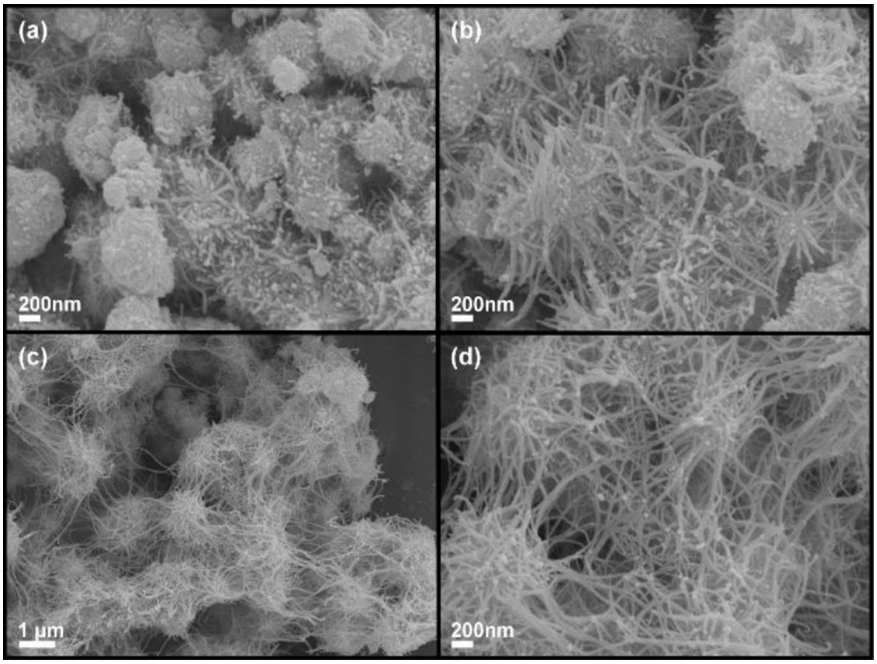


Fig. 1. SEM images of tungsten oxide synthesized by solvothermal method at different reaction times of (a) 24 h (P1); (b) 48 h (P2) and (c)–(d) 72 h (P3).