Journal of Alloys and Compounds 661 (2016) 82–91

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Large-scale synthesis and electrochemical properties of hydrated tungsten trioxide-based hierarchical microstructures

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ARTICLE INFO

Article history:
Received 6 October 2015
Received in revised form
4 November 2015
Accepted 23 November 2015
Available online 30 November 2015

Keywords:
Electrode materials
Hydrothermal synthesis
Electrochemical properties
Scanning electron microscopy
Transmission electron microscopy

ABSTRACT

Hierarchically self-assembled micro-/nanostructures of o-$WO_3.1/3H_2O$ were successfully synthesized by surfactant-assisted hydrothermal reaction at 180 °C for 76 h in acidic medium (pH = 1). The effect of the surfactant n-alkyl chain length $C_nH_{(2n+1)}SO_4Na$ (with n = 10, 12 and 14) on the morphology and the crystallite sizes were investigated. The as-synthesized samples were characterized by different techniques. When sodium decylsulfate is used, agglomerates of irregular particles of orthorhombic $WO_3.1/3H_2O$ (o-$WO_3.1/3H_2O$) are obtained. The sample obtained by the use of sodium dodecylsulfate, consists of o-$WO_3.1/3H_2O$ microdisk-like structure formed by self-assembled nanosheets (with an average thickness of about 20 nm), resembling chrysanthemum flower. O-WO3.1/3H_2O microsheres-like 3D architectures constructed from 2D sheets intervened out-of-order, resembling sand roses, are obtained with sodium tetradecylsulfate as surfactant. The prepared o-WO3.1/3H_2O hierarchical assemblies are used as electrode materials to study the electrochemical properties in propylene carbonate containing 1 M $LiClO_4$ solution, by cyclic voltammerty. It was found that o-WO3.1/3H_2O microdisks and microspheres exhibit reversible redox behavior accompanied by reversible intercalation/deintercalation of Li^+ cations into crystal matrix. It has been revealed also that higher currents were measured for microdisk-like structure and higher diffusion coefficient of Li^+ (2.93×10^{-10} cm^2/s) compared to microsphere-like structure (2.02×10^{-10} cm^2/s).

1. Introduction

Many chemists and material scientists have paid close attention to the study of the organization of complex micro-/nano-architectures, especially three-dimensional (3D) hierarchical architectures which are assembled by nanoscaled building blocks such as zero-dimensional (0D) nanoparticles, one-dimensional (1D) nanofibers, and two-dimensional (2D) nanosheets [1–4]. These hierarchical architectures combining the features of nano-scale building blocks have novel physical and chemical properties different from those of the mono-morphological structures such as mechanical, thermal, catalytic and photocatalytic properties [3,5–7]. To control the morphology of inorganic materials at the micro- and nano-scale level is one of the hot issues for material chemists because the intrinsic properties of nanomaterials are closely related to their morphology, size, and crystallinity [8]. Thus, **developing easy**, economic and environmentally benign synthetic routes which can produce 3D hierarchical micro-/nanostructures is very important to nanoscience and synthetic chemistry. Hydrothermal approach is becoming an increasingly attractive method [8,9]. The Teflon-lined autoclave provides high pressure for the accelerated chemical reaction at relatively low temperature (100–250 °C), which makes it possible to prepare highly crystalline oxide micro-/nanostructures [3,10,11].

As one of the most important oxide nanomaterials, tungsten oxides and other transition metal oxides have been studied widely [12–16]. In particular, orthorhombic $WO_3.1/3H_2O$ oxide possesses a layered structure which is composed of two types of octahedra [17–19]. The **first is WO_6 octahedra which share four oxygen atoms with adjacent octahedra (in the ab plane) and the two others with the octahedra in the upper and lower layer. The second is $WO_5(OH_2)$ octahedra** which contain a coordinated water molecule with W–OH_2 bond and an opposite terminal W=O bond along the [001] direction (Fig. 1). It should be pointed out that within the ab plane, all tungsten atoms in different octahedral

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http://dx.doi.org/10.1016/j.jallcom.2015.11.177
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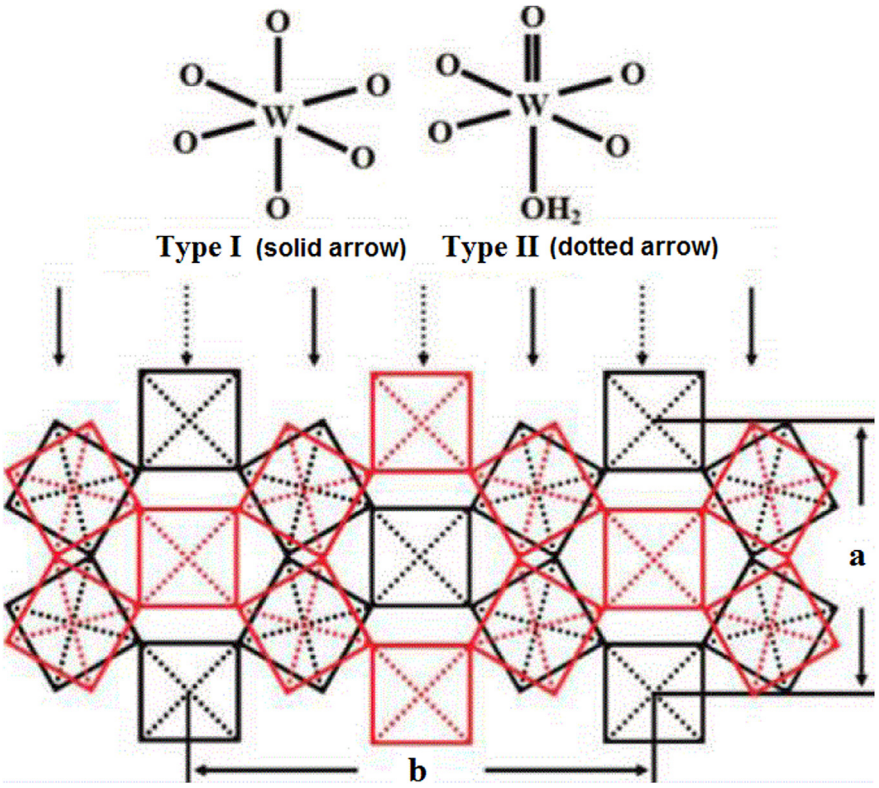

Fig. 1. Schematic illustration of the orthorhombic $WO_3.1/3H_2O$ structure.

blocks are connected by covalent bonding. However, one layer out of two shifted by a/2 along the [001] axis resulting **in** relatively weaker interaction between adjacent layers [20–23].

In this paper, we report a simple surfactant-assisted hydrothermal process for the preparation of hierarchically-assembled, hydrated tungsten oxide nano/microstructures. The resulting products are characterized in detail. The surfactant n-alkyl chain length appears to play a determining role in the morphology and the crystallite sizes. A growth mechanism is proposed to explain nano/microstructures formation. Furthermore, the electrochemical properties of the o-$WO_3.1/3H_2O$ microdisks and microspheres are discussed. We will also tackle the relationships between the electrochemical properties of o-$WO_3.1/3H_2O$ and the structural and morphological ones.

2. Experimental details

2.1. Samples preparation

All of the chemical reagents used in the experiments were of analytical grade. A typical process for the preparation of hierarchical nanostructures of hydrated tungsten trioxide was as follows: an aqueous solution of $Na_2WO_4.2H_2O$ was acidified by adding HCl (3 M) to get a pH of 1. After 30 min of magnetic stirring, aqueous solution of $C_{10}H_{21}SO_4Na$ (DSS), $C_{12}H_{25}SO_4Na$ (SDS) or $C_{14}H_{29}SO_4Na$ (STS) was added to the mixture in the molar ratio $Na_2WO_4.2H_2O$:$C_nH_{(2n+1)}SO_4Na$ of 1:2. **Then**, the obtained solution was transferred into Teflon-lined steel autoclave with a capacity of 23 mL. Hydrothermal treatments were carried out at 180 °C for 72 h. The autoclave was cooled down to room temperature naturally after the heating process. The resultant products were thoroughly washed with distilled water and ethanol several times to remove any organic by-products, and was dried at 80 °C.

2.2. Characterization

The crystalline structure of samples were characterized by X-Ray diffraction (XRD) using an X'Pert Pro Panalytical diffractometer with CuKα radiation (λ = 1.5406 Å). The XRD measurements were carried out by a step scanning method (2θ range from 3 to 70°), the scanning rate is 0.03°/s and the step time is 3 s.

Scanning electron microscopy (SEM) images were taken by a Cambridge Instruments Stereoscan 120 at an accelerating voltage of 10 KV. Transmission electron microscopy (TEM) images were recorded on TECNAI G 20 electron microscope operating at 200 KV. The sample consists in one droplet of the powder being dispersed in ethanol which was deposited onto a carbon copper grid and left to dry in **the** air.

Fourier-transform infrared spectra (FTIR) were recorded from 4000 to 400 cm^{-1} on a Nicolet 380 Spectrometer in pellets samples dispersed in KBr.

X-ray photoelectron spectroscopy (XPS) analyses were performed using a Thermo VG Scientific ESCALAB 250 spectrometer, equipped with a monochromatized microfocused AlKa X-ray source (hν = 1486.6 eV, powered at 20 mA and 10 kV) and a spot size of 650 μm in diameter. Data acquisition and processing were performed with the supplier's Avantage software (version 1.85). **Due to adventitious hydrocarbon contamination, the peak-binding energies were calibrated by setting the C1s component to 285 eV**.

Electrochemical studies were recorded using a BioLogic SP150 potentiostat/galvanostat apparatus, and a three-electrode cell with the stainless steel grid as the counter-electrode and the Ag/AgCl as the reference electrode. The obtained working electrode was as follows [12]; 10 μL of a suspension containing 1 mg of o-$WO_3.1/3H_2O$ microspheres in 1 mL of water, were dropped onto an ITO-coated glass (active surface area = 1 cm^2). After drying at room