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Chemical and structural analysis of solvothermal synthesized tungsten oxide nanotube without template and its hydrogen sensitive property

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ABSTRACT

Tungsten oxide nanotubes were synthesized by solvothermal process without template. The steric effect and the concentration of WCl_6 are the dominant factors for the formation mechanism of the nanotube. The steric effect was experimentally and systematically studied with solvents including ethanol, isopropanol, n-propanol and butylalcohol, which have different molecular configuration and length, while the effect of concentration was investigated by characterizing the nanostructured productions. The samples have been investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). The surface chemistry of the nanotube is characterized by X-ray photoelectron spectroscopy (XPS). The results indicated that the solvents species and WCl_6 concentration obviously diversified the morphologies of the products; the nanotubes synthesized with isopropanol composed of $W_{18}O_{49}$ phase; the crystal defects (O atom vacancy) formed during rapid crystallization could be modified by heat treatment. The DC electrical response of the nanotube thin film to hydrogen was measured the temperature range from 200 °C to 300 °C, which indicated a decline in electrical resistance with good sensitivity, and showed the mechanism that the reaction limited process works at low temperature, whereas the diffusion limited process works at higher temperature.

1. Introduction

Tungsten oxide (WO_3) belongs to a family of the indirect band gap (~2.6 eV) [1] semiconductors, which have attracted most interest in the past several decades. In particular, various WO_3 nanostructures (nanoparticles [2], nanorods, nanowires [3] and nanosheet [4]) are of special interest as promising candidates for photocatalyst, electrochromic devices, and gas sensors due to their small size with high surface-to-volume ratio and novel properties. Yong et al. [5] synthesized $W_{18}O_{49}$ nanorods for photoelectrodes in dye-sensitized solar cell application for the first time by typical solverthermal process, and the cell characteristics were characterized. The properties of the cell of WO_3 nanorods were highly improved by coating thin TiO_2 layer on WO_3 nanorods surface. Yan et al. [6] synthesized WO_3 nanoparticles by thermal decomposition of ammonium tungstate loading on g-C_3N_4, and the samples showed photocatalytic activity in O_2 evolution up to 77 times higher than that of WO_3 samples without loading on g-C_3N_4. Hieu et al. [7] synthesized nanowire-like structure WO_3 by DC sputtering tungsten metal on substrate of porous single-wall carbon nanotubes, followed by thermal oxidation process. The results showed that the nanowire-like WO_3 exhibited rapid response and recovery times of 7 and 8 s at 250 °C.

Recently, numerous approaches to improving the performance of sensitivity of sensors have been considered. Among many possible approaches, introducing a one-dimensional (1-D) nanostructure (nanowires [8], nanorods [9], and nanotubes [10]) as the sensitive layer is one of the most promising candidates. As their high surface area and monodisperse, the sensors can exhibit Ultra sensitivity and fast response time because a few gas molecules are sufficient to change the electrical properties of the sensing elements. Meng et al. [11] synthesized hexagonal WO_3 nanowires by a vapor transport method using WO_3 powder as a raw material. The temperature dependence of the response was discussed in relation to the formation of NO^{2-} and NO^{3-} ions on the surface of WO_3. The response slightly increased with decreasing diameter if the nanowires are regional depleted in NO_2, while it largely increased if the nanowires are in volume depletion. Ma et al. [12] deposited monoclinic WO_3 nanorods with diameters of 50–150 nm and lengths of 5–20 μm directly onto porous silicon without catalyst by thermal evaporation. The porous silicon/WO_3 nanorods showed a good response and recovery characteristics to 250 ppb NO_2 at room temperature.

The solvothermal processes has been developed as an effective method for synthesizing nanostructured metal oxides [13,14]. This process can be described as a reaction of precursors in a close

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system in the presence of a solvent. It is possible to control the shape and size of products by adjusting the processing parameters, such as types of solvents and reactants, surfactants, reaction temperature and time. The organic surfactants or polymers, used as the "shape modifier", are usually employed to tune and control the morphologies and sizes of the final products as they are known to either promote or inhibit the crystal growth through modifying crystal facets dynamically [14,15,4,16]. Zhao [17,18] reported the solvothermal synthesis of various hollow structured WO_3 (including tube) by two steps: firstly the tungsten acid precursors with different structures were prepared; and then the productions were obtained by sintering the tungsten acid precursors at high temperature. They also proposed the possible formation process of the hollow structure: the 6-fold coordinated complex species $[WCl_m(-OC_2H_5)_{6-m}]^{2-}$ formed after WCl_6 dissolved in ethanol and served as a barrier against the hydrolysis of WCl_6 with residual water; and then the solid spheres formed due to homogeneous nucleation and aggregation growth; the urea added as chelating agent specifically was adsorbed onto sphere interfaces and guided the oriented attachment of hollow spheres, eventually resulting in the formation of nanotubes.

Moreover, the morphology formation process is another key issue, and many researchers have discussed it in different standpoints. Zhao and Miyauchi [19] first reviewed the reactions of aluminium compounds (aluminium hydroxide, aluminium alkoxides, and aluminium salts) in various organic solvents (alcohols, glycols, aminoalcohols, and inert organic solvents), and discussed reaction mechanisms and effects of the starting materials on the products. Some important conclusions are: (1) solvent molecules are incorporated between the boehmite layers through the covalent bondings, and the interlayer spacing of the product increased with increasing the carbon number of the alcohol; (2) hydrolysis of the alkoxides takes place via the water molecules formed by dehydration of the solvent alcohols at relatively low temperature; (3) crystal defects may form during the rapid crystal growth and cannot be eliminated because of the low solubility of the oxide crystals in organic solvents. Demazeau [20] summarized the role of the solvent in the solvothermal processes: (1) Orientation to a metastable structural form; (2) formation of metastable compounds by chelating effect acting as template; (3) oxidation–reduction agent. According to these literatures, the chelating effect of the organic solvents that tuned the products morphologies was identified. However, the steric effect of the solvents chelated or adsorbed on the crystalline on the morphology and crystalline structure of production during the solvothermal process has not yet been discussed. Furthermore, the formation mechanism of the surface defects and chemical composition of nonstoichiometric WO_3 are not thoroughly understood. Moreover, the hydrogen sensing potential of WO_3 is not fully exploited.

2. Experimental

2.1. Preparation of samples

Tungsten hexachloride (WCl_6, purity 99.5%, Huajing Powder materials Science & Technological Co., Ltd., Changsha) was dissolved in solvent with continuous magnetic stirring under the N_2 atmosphere and the transparent solution was obtained. The transparent solution was transferred into Teflon-lined autoclave with a capacity of 50 ml, and then the well cleaned alumina substrate (1 mm in thickness, ultrasonicated for 10 min with HCl solution, deionized water and ethanol, respectively.) was vertically placed in the solution. Solvothermal treatments were carried out at 160 °C for 12 h. The obtained films and powders were rinsed with ethanol and acetone for three times and dried at 100 °C for 2 h subsequently.

2.2. Characterization

X-ray diffractometer (XRD, Dmas-2200, Rigaku, Tokyo, Japan with Cu Kα radiation $\lambda = 0.154056$ nm) was used to analyze the crystal structures of the obtained samples. The morphologies of the samples were characterized by scanning electron microscopy (SEM, CamScan Apllo300) and transmission electron microscopy (TEM, JEOL JEM-2100). X-ray photoelectron spectroscopy (XPS, Escalab 250xi) measurements were carried out to study the nature of the chemical components and bonding on the surface of samples. The XPS data processing involved background subtraction and curve fitting. The W4f core spectrum was analyzed using a mixed doublet (Lorentzian–Gaussian) function. The background was taken into account by a Shirley-type background due to elastically scattered electrons. The fitting analysis was performed by setting a range in which the expected values of the fitting parameters (peak position, peak width, intensity, intensity ratio, mixing ratio and splitting) varied freely.

2.3. H_2 sensing characterization

Pt wire contacts were attached with a moderate-temperature silver paste to the two ends of the thin film and annealed at 550 °C for 1 h for electrical measurements. The conductance of the thin films was obtained by measuring the current through the film at a constant voltage of 5 V. The samples under test were placed in the sealed alumina tube inside a Faraday cage in the electrical furnace and exposed to different concentrations of hydrogen vapor which were controlled by mass flow meters after being mixed in the gas-mixer. All gases were injected with the flow rate of 600 ml/min parallel to the films. Gas sensitive properties of the films were studied in temperature range of 200–300 °C, and the currents values were measured using a multimeter (Keithley 2601).

Sensor response, R_s, is defined as $(I_{gas} - I_0)/I_0$, where I_0 was the base resistance of the film measured in dry synthetic air, and I_{gas} was that observed at the end of the H-loading process.

3. Results and discussion

3.1. Morphology and crystal structure

Fig. 1 presents the SEM image of the well aligned nanotube film and the TEM images of individual nanotube that were synthesized with 0.01 M/L WCl_6 in isopropanol. The prepared tungsten oxide nanotube film on alumina substrate had a high yield and a uniform, well oriented morphology over a large area of view as shown in Fig. 1a. The nanotubes were dispersed over a standard holey-carbon grid for TEM investigation. Fig. 1b and c shows the HRTEM images of the nanotubes, the individual nanotube shown in Fig. 1b has a hollow structure. Meanwhile, there are several layers out of the tube as shown in Fig. 1c, suggesting that the nanotube shows a multiwall nanostructure and the unclosed walls (black arrow) reveals the growth process. The spacing of the lattice fringes is measured to be about 0.378 nm.

Fig. 2 presents the typical X-ray diffraction patterns of the prepared nanotubes with the strongest intensity at 2θ of 23.45°. The reflection pattern of the sample coincides with that of nonstoichiometric tungsten oxides $W_{18}O_{49}$, whose cell parameters are $a = 1.8280$ nm, $b = 0.3775$ nm, $c = 1.3980$ nm. (JPCDS Card No: 05-0392). And the high intensity at a 2θ value of around 23.45°, indexed to (010) direction and agreed with the HRTEM result. To our best knowledge, there are a number of tungsten oxide nanostructures (e.g., nanorods [21,22] or nanowires [4,23]), in which (010) is the dominant growth direction.

3.2. Imaged crystallization model and experimental data

We imaged the growth process of the nanotube based on the TEM image shown in Fig. 1c. The surfactants and solvents chelating or adsorption on the crystal surface restrained the facet growth have been identified [18–20,24]. However, the steric effect must be considered due to the organic solvent molecules accumulated on the surface, and the effect would be responsible for the bending of crystal surface. The steric effect is proposed as the dominant driving force for the formation of the nanotube in the present work. The effect usually plays a significant role in the organic reactions due to the intrinsic softness and plasticity of organic molecules. However, the growth behaviors of inorganic nanoparticles are affected by this effect when dimensions reduce to several dozens of atom layers. There are several polymorphic forms of