



Nitridation of one-dimensional tungsten oxide nanostructures: Changes in structure and photoactivity



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ARTICLE INFO

Article history:

Received 31 July 2017

Received in revised form 5 October 2017

Accepted 6 October 2017

Available online 7 October 2017

Keywords:

Tungsten oxide

Oxynitride

Tungsten nitride

Bandgap

Photoelectrochemistry

ABSTRACT

In the search for stable, visible light active photoelectrodes, hydrothermally synthesized tungsten oxide nanowires were modified via nitrogen incorporation into their structure. To this end, nanowires were heat-treated in ammonia/nitrogen atmosphere at different temperatures. This procedure caused transitions in their structure that were investigated along with the photoelectrochemical properties of the samples. Results were subsequently compared to the reference samples treated in inert nitrogen atmosphere. Morphological changes and structural transitions were followed by transmission and scanning electron microscopy and X-ray diffraction. Bandgap energies were determined from the UV–vis spectra of the materials, while photoelectrochemical properties were tested by linear sweep photovoltammetry and electrochemical impedance spectroscopy. Pristine tungsten oxide nanowires were first transformed into tungsten oxynitride and then tungsten nitride during high-temperature calcination in ammonia atmosphere. Electron microscopic investigation revealed that, along with phase transition, the initial fibrous morphology gradually converted into nanosheets. Simultaneously, bandgap energies significantly decreased in the calcination process, too. Photoelectrochemical measurements demonstrated that photoactivity in the treated samples was not improved by the decrease of the bandgap. This behavior might be explained with the deterioration of charge carrier transport properties of the materials due to the increased number of structural defects (acting as trap states), and current ongoing work aims to verify this notion.

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1. Introduction

As a promising material, nanostructured tungsten oxide (WO_3), besides TiO_2 , is one of the most investigated oxide semiconductors. Its high stability in acidic medium, accompanied by inherently attractive transport properties (hole diffusion length and electron Hall mobility is $\sim 12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, compared to TiO_2 that is $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [1], make WO_3 suitable for a wide variety of possible applications in photovoltaics, photocatalysis, and gas

sensing, etc [2–4]. Photoelectrochemical (PEC) properties of tungsten oxide nanostructures have been widely studied in the literature. Etched and reduced WO_3 nanoflakes showed increased photocurrent density (1.10 mA cm^{-2} at 1.0 V vs Ag/AgCl) compared to the pristine WO_3 (0.62 mA cm^{-2}), which was assigned to the formation of oxygen vacancies on a rough surface. [5] Su et al. prepared tungsten oxide films containing nanowire arrays. The highest photocurrent topped 1.43 mA cm^{-2} using an irradiation source emitting at the edge of the visible light (400 nm). [6] Hydrogen treatment of tungsten oxide can also soar the photoactivity by an order of magnitude of the pristine WO_3 , along with the improvement in the photostability of the structure [7].

These materials possess a relatively wide bandgap (2.5–2.8 eV), implying that only the higher-energy region of the solar spectrum (UV and the higher energy visible part, i.e., blue/violet light) can be utilized in the photogeneration of electron–hole pairs. To widen

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the restricted absorption range, the bandgap energy can be modified by, for example doping with various transition metals, nitrogen, sulfur or carbon [8–11]. The latter modifications are accompanied by the variation in the electrochemical properties as well. A review by Janáky dealt with the change of band structure and photocatalytic activity after doping WO_3 with different type of elements [12]. Liu et al. investigated nitrogen-doped graphene and reached a 1.8-fold increase in the photoactivity compared to the pure nanoporous WO_3 photoelectrode [13].

PEC performance of pristine WO_3 can be further enhanced by nitridation (i.e., nitrogen doping or alloying). A recent review by Domen discussed the bandgap narrowing with the substitution of oxygen with nitrogen [14]. As Fig. 1 demonstrates, the N 2p orbital can form a filled energy state above the O 2p state. These types of tungsten oxynitrides and nitrides are generally more stable than other known non-oxide semiconductors [14].

There are several ways to realize nitrogen-doped tungsten oxide or tungsten nitride nanostructures; for instance, depositing nitrogen-doped WO_3 thin films employing reactive magnetron sputtering in nitrogen atmosphere [15], or synthesizing tungsten nitride nanorods via a hydrothermal method using tungstic acid and ammonium sulfate [16]. The simple thermal treatment is a straightforward method to synthesize mesostructured tungsten nitride with the calcination of tungstic acid powder in ammonia atmosphere at 700 °C or nanoporous layers in ammonia atmosphere up to 600 °C [17]. The nitrogen content as well as the PEC properties are influenced by the annealing time. In certain instances, the photocurrent becomes 18-times higher than that of the pure WO_3 , however, high-temperature annealing (~600 °C or above) decreases the photoresponse because of the degradation of the crystalline structure [18]. Nanoporous WO_3 photoelectrodes were heat-treated in NH_3/N_2 atmosphere with different compositions at 450 °C and the highest photocurrent density was attained in 1:2 $\text{NH}_3:\text{N}_2$ mixture [13]. The suggested mechanism of the annealing process is as follows. Ammonia decomposes at high temperature, and the resulting nascent nitrogen helps in creating a specific atmosphere inside the furnace that reacts with the sample to form nitrogen doped/alloyed tungsten oxide or tungsten nitride [17,19].

Here, we report the ammonia treatment of hydrothermally synthesized tungsten oxide nanowires in 1:2 $\text{NH}_3:\text{N}_2$ atmosphere at different annealing temperatures. The morphological, structural, and photoelectrochemical changes were followed along with the incorporation of nitrogen into the structure. Results are discussed in comparison to the samples treated in inert nitrogen atmosphere. Most importantly, the bandgap narrowing was not mirrored by the alteration in the PEC properties, highlighting the importance of other structural factors—beyond light absorption—that dictates photoactivity.

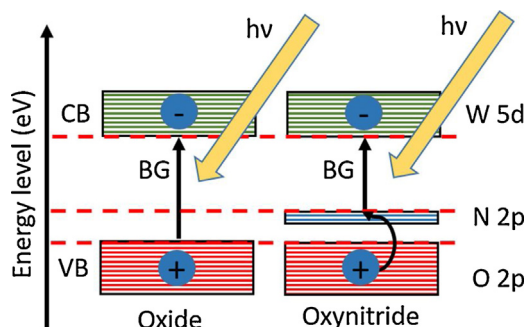


Fig. 1. Narrowing the bandgap (BG) during nitrogen incorporation into the oxide structure.

2. Experimental

2.1. Synthesis of tungsten oxide nanowires

Tungsten oxide nanowires were synthesized via a hydrothermal route. First, 3.56 g sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, Sigma Aldrich) and 4.28 g sodium sulfate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, Sigma Aldrich) were dissolved in 115 cm^3 deionized water. Then, the pH of the solution was adjusted to 1.5 via adding nitric acid (3 $\text{mol} \cdot \text{dm}^{-3}$) dropwise to the clear continuously stirred solution. After 30 min stirring, the solution was transferred into a Teflon-lined stainless steel autoclave and heat treated at 180 °C for 24 hours. Finally, the product was obtained by membrane filtration, washed with deionized water, and then dried at 80 °C overnight.

2.2. Preparation of ammonia-treated tungsten oxide nanowires

Nanowires were heat treated in 1:2 ammonia/nitrogen atmosphere with a flow rate of 120 $\text{cm}^3 \text{s}^{-1}$ at different temperatures. On the contrary, the reference samples were heat treated only in pure nitrogen atmosphere.

2.3. Morphological and Structural Characterization

Morphological changes of the samples were investigated by transmission and scanning electron microscopy techniques (TEM, SEM), using an FEI Tecnai G² 20 X Twin microscope at 200 kV accelerating voltage and a Hitachi S4700 Field Emission SEM, respectively. For SEM studies, the samples were spread on a carbon tape surface, which was attached to an aluminum sample holder, while TEM samples were sonicated in isopropyl alcohol before being dropped on a copper mounted holey carbon film and dried subsequently. The crystal structure of the samples was analyzed by phase identification via X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation ($k = 1.5406 \text{ \AA}$) in a Rigaku Miniflex II instrument. The X-ray photoelectron spectra (XPS) were collected with a SPECS instrument using a PHOIBOS 150 MCD 9 hemispherical electron energy analyzer, using the $\text{K}\alpha$ radiation of the Al anode ($h\nu = 1486.6 \text{ eV}$). The X-ray gun was operated at 210 W (14 kV, 15 mA), and the analyzer in FAT mode, with 20 eV pass energy. Five scans were averaged to obtain a single high-resolution spectrum. The binding energy scale was corrected by the deconvolution of the complex C 1s region as the carbon peak was fixed at 285.1 eV. Raman spectra of the samples were measured at 532 nm laser excitation energy with 5 mW power using a Thermo Scientific DXR Raman Microscope. Typically, ten scans were recorded and averaged with 1 cm^{-1} resolution in the 200–3500 cm^{-1} range. Diffuse reflectance UV–vis spectroscopy was used to investigate the bandgap energy of the catalysts with fiber optic system consisting of a Micropack HPX-2000 light source and an Ocean Optics USB2000 detector. The detector has 2048 pixel resolution in the 200–1100 nm wavelength range.

2.4. Photoelectrochemical measurements

2.4.1. Preparation of photoelectrodes for photoelectrochemical measurements

All samples were dispersed in isopropanol ($c = 5 \text{ mg cm}^{-3}$) by ultrasonic treatment for 30 min before deposition. The samples were spray-coated on a preheated (140 °C) glassy carbon electrode surface, using an Alder AD320 type airbrush and a homemade spray-coater robot, operated with 1 bar compressed air. The

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