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## Electrochromism of hexagonal sodium tungsten bronze nanorods

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## ABSTRACT

Single-crystalline sodium tungsten bronze (Na-WO<sub>3</sub>) nanorods with typical diameters of 10–200 nm and lengths of several microns have been prepared via a simple hydrothermal method. The as-prepared Na-WO<sub>3</sub> nanorods crystallize in a hexagonal structure and elongate along the <001> crystallographic direction. The as-prepared Na-WO<sub>3</sub> nanorods have eight diagnostic Fourier transform infrared (FTIR) absorptions at 3604, 3545, 1622, 1600, 983, 790, 480 and 430 cm<sup>-1</sup>, which represent specific fingerprints of the vibrational features of hexagonally tunnel-structured Na-WO<sub>3</sub> containing tunnel water molecules. The as-prepared Na-WO<sub>3</sub> nanorods exhibit a typical cathodic electrochromism, which is related to a proton-electron double insertion process. X-ray diffraction results indicate a phase transformation of hexagonal Na-WO<sub>3</sub> nanorods during the electrochromic process, of which the involved local structural evolutions such as water decomposition and proton insertion have been discussed by using FTIR spectroscopy. The results suggest that, during the electrochromic coloration process, the inserted protons might occupy the small trigonal tunnel positions instead of the large hexagonal ones.

## 1. Introduction

Smart windows (or dynamic glazings) have attracted great interest in recent years due to their significance in maximizing the energy efficiency of buildings [1–5]. The key to smart windows is a material or system that can change its optical properties (i.e., absorbance, transmittance, or reflectance) under controlled conditions. In this regard, electrochromic (EC) materials [2,4], which exhibit a persistent and reversible color change induced by an external electrical potential, are promising for smart window applications; more importantly, EC smart windows can respond actively to the ambient conditions and/or user preferences to achieve simultaneously energy efficiency and user comfort [5]. EC smart windows have been under extensive investigation since 1980s and commercial products have recently been emerging on the market [3]. However, the benefits of EC smart windows have yet to be realized at scale, due to their drawbacks related to cost, durability, and functionality [6]. Apparently, the success of EC smart windows will depend on not only the potential benefit that will be realized by the end user, but also a sophisticated design of materials to make the devices durable and affordable.

Thanks to the rapid development of nanotechnology, the application of EC nanomaterials for high performance EC devices has attracted great interest [6–10]. EC nanomaterials usually have small featured sizes and large surface areas, thus enabling efficient contact and fast

ionic transfer between the electrolyte and electrodes. Not surprisingly, EC nanomaterials have widely been reported with superior performance over their bulk counterparts, such as higher coloration efficiencies and faster switching [6–10]. More importantly, new or enhanced EC properties have been discovered as the material dimension appears typically at the nanometer scale, e.g., the recent reported plasmonic electrochromism in semiconductor nanocrystals [11] and transparent conductive oxide nanocrystals [12], which are of particular interest for constructing smart windows to modulate the near infrared (NIR) solar radiation [13]. It must be pointed out that, however, the combination of size, composition, and dimensionality at nanometer scale not only opens a myriad of opportunities for high performance EC devices, but also brings about a great complexity in understanding the involved thermodynamics and/or kinetics. For example, the same small sizes and active surfaces that endow novel or improved properties of EC nanomaterials may entail at the same time the danger of their structural instability during the operation/service [10]. In this regard, systematic studies dedicated to a better understanding of the structure-property relationship of EC nanomaterials are still necessary and important for their practical applications [6].

In this work, we discuss the electrochromism of sodium tungsten bronze (Na-WO<sub>3</sub>) nanorods, which crystallize in an interesting hexagonal tunnel structure, with one-dimensional chains of Na<sup>+</sup> ions and water molecules being embedded in the open channels of corner-linked

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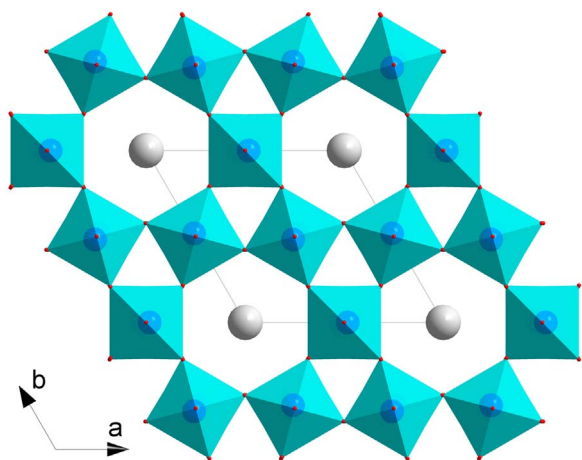


Fig. 1. Polyhedral representation of hexagonal sodium tungsten bronzes Na-WO<sub>3</sub>. The structure is viewed down the *c* axis of a hexagonal unit cell. Tunnel species (Na<sup>+</sup> ions and water molecules) are represented by grey spheres.

WO<sub>6</sub> octahedra (Fig. 1) [14]. Compared to amorphous and monoclinic WO<sub>3</sub> – the most common phases synthesized and studied for EC smart windows, the application of hexagonal WO<sub>3</sub> as active EC materials as well as the involved electrochromism have not been extensively studied [15–17]. Hexagonal Na-WO<sub>3</sub> nanorods have previously been reported with novel photochromic properties, of which the involved photochromism is strongly associated with the tunnel species [14]. It is then reasonable that the electrochromism of hexagonal Na-WO<sub>3</sub> nanorods may involve also distinctive features. The small featured sizes and structural openness of Na-WO<sub>3</sub> nanorods may facilitate the ion insertion/extraction during the electrochemical cycles [14–18], hence representing an interesting material system to understand the structure-property relationship of hexagonal WO<sub>3</sub> nanomaterials for their practical applications.

## 2. Experimental procedures

### 2.1. Chemicals and materials

Reagent-grade sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 96%), sodium tungstate dihydrate (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O), oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), and indium tin oxide (ITO) glass substrates (25 mm × 25 mm × 1 mm, surface resistance 30–60 Ω/square) were purchased from Sigma-Aldrich Co. and used as received. Distilled water was used throughout the experiment.

### 2.2. Synthesis of Na-WO<sub>3</sub> nanorods

Hydrothermal synthesis of Na-WO<sub>3</sub> nanorods in this work followed a published procedure [14]. In a typical synthesis, 11.4 g Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O was dissolved in 150 mL water, and to this solution 15 mL concentrated H<sub>2</sub>SO<sub>4</sub> was added drop-wise under constant stirring. White precipitation was formed immediately upon the mixing and gradually changed color to light-yellow. The precipitation was separated from the reaction solution by centrifugation, washed four times with distilled water (by filtration), and finally dissolved in 300 mL oxalic acid aqueous solution (0.4 M). The obtained solution was used as precursors for the synthesis of Na-WO<sub>3</sub> nanorods.

30 mL of the obtained precursor solution was transferred into a Teflon-lined autoclave (capacity 40 mL). After adding 1 g of Na<sub>2</sub>SO<sub>4</sub> powder, the autoclave was sealed and heated at 180 °C for 24 h. After the reaction, the autoclave was cooled down to room temperature by tap water. The obtained white precipitate was filtered, washed with water to remove the residual ions/chemicals, and then dried at 60 °C for 5 h to give the as-prepared Na-WO<sub>3</sub> nanorods.

### 2.3. Preparation of electrochromic electrodes

Samples for electrochemical measurement were prepared by spin coating of the as-prepared Na-WO<sub>3</sub> nanorod suspension onto ITO glass substrates at 2000 rpm. Before the spin coating process, the ITO glass substrates were cleaned sequentially in ultrasonic baths of ethanol and acetone, each for about 10 min. The Na-WO<sub>3</sub> nanorod suspension was prepared by adding 0.04 g of the as-prepared materials into 20 mL ethanol under ultrasonic dispersion. The spin coating process was repeated several times to form a uniform nanorod coating on the ITO glass substrates. Finally, an annealing treatment at 250 °C for 2 h was performed to increase the adherence between the Na-WO<sub>3</sub> nanorods and the ITO glass substrates.

### 2.4. Characterization

Crystal structure of the as-synthesized materials was determined by X-ray diffraction (XRD, Bruker AXS D8 Advance diffractometer with Cu Kα<sub>1</sub> radiation). The morphology and chemical composition of the as-prepared materials were investigated by field-emission scanning electron microscopy (SEM, Zeiss Supra 55VP) and transmission electron microscopy (TEM, JEOL JEM-2010), both equipped with energy-dispersive X-ray spectrometers (EDS). Attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 8700 FTIR Spectrometer (Thermo Scientific) with a spectral resolution of 2 cm<sup>-1</sup>. Optical properties were measured on a Perkin-Elmer Lambda 1050 UV/Vis/NIR spectrophotometer with a 150 mm integrating sphere accessory. Electrochromic properties were characterized on an Autolab electrochemical workstation (PGSTAT302N). A three-electrode electrochemical cell was prepared, where Pt wire, Na-WO<sub>3</sub> nanorods on ITO glass, Ag/AgCl electrode, and 1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution act as counter electrode, working electrode, reference electrode, and electrolyte, respectively. All measurements were performed at room temperature.

## 3. Results and discussion

### 3.1. Structural features of Na-WO<sub>3</sub> nanorods

Fig. 2 shows a typical XRD pattern of the as-synthesized materials. The XRD reflections are sharp and intensive, indicating that the as-prepared materials are well crystallized. The XRD pattern can be indexed on the basis of a hexagonal phase of sodium tungstate bronze (Na-WO<sub>3</sub>) with lattice dimensions of *a* = 7.331 Å and *c* = 3.891 Å (JCPDS 81–0577). Detailed XRD analyses suggest that the hexagonal

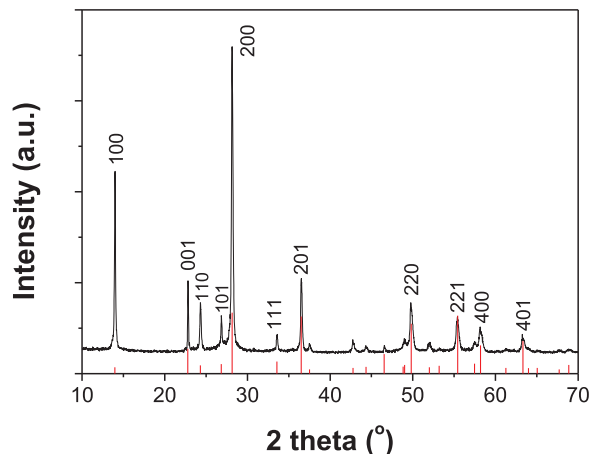


Fig. 2. XRD pattern of the as-synthesized materials. The bars at the bottom represent the calculated diffraction pattern of hexagonal Na-WO<sub>3</sub> (JCPDS 81–0577). Miller indices are given to the main reflections.

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