



Facile microwave-assisted hydrothermal synthesis of hexagonal sodium tungsten bronze and its high response to NO₂

Tiago A. Martins^a, Thales R. Machado^{a,b}, Mateus M. Ferrer^a, Sonia M. Zanetti^{c,*}, Elson Longo^c

^a INCTMN-UFSCar, São Carlos, São Paulo, 13565-905 Brazil

^b DQJO, Universitat Jaume I, Castellón, 12071 Spain

^c INCTMN-UNESP, Araraquara, São Paulo, 14801-907 Brazil

ARTICLE INFO

Article history:

Received 21 June 2016

Received in revised form

25 August 2016

Accepted 27 August 2016

Available online 27 August 2016

Keywords:

Microwave-assisted hydrothermal method

Gas sensor

Sodium tungsten bronze

Nanoplates

ABSTRACT

Single-phase hexagonal sodium tungsten bronze ($\text{h-Na}_x\text{WO}_{3+x/2} \cdot y\text{H}_2\text{O}$) was synthesized via a microwave-assisted hydrothermal method. A reaction time of 4 min was sufficient to obtain well-crystallized nanoplates with a thickness of 5–16 nm and length of 5–500 nm. The structure, morphology, and composition of the obtained material were characterized by X-ray diffraction and scanning electron microscopy. H₂O molecules and Na species were detected in the hexagonal channels of the tungsten bronze structure. The gas sensing properties were also measured, suggesting that $\text{h-Na}_x\text{WO}_{3+x/2} \cdot y\text{H}_2\text{O}$ can be a promising material for NO₂ detection due to the high response observed.

© Published by Elsevier B.V.

1. Introduction

Tungsten bronze structures (M_xWO_3 , where M represents species in the interstitial sites of a modified WO₃ matrix) have attracted increasing attention because of their ferroelectricity, superconductivity, and potential applications including solar filters, smart windows, and humidity sensors [1–4]. However, the gas sensing properties associated to tungsten bronze structures have rarely been reported. Among other metal oxides, such as SnO₂, TiO₂, ZnO, and In₂O₃, hexagonal WO₃ is a well-known gas sensor with high sensitivity, selectivity, enhanced response, and recovery time [5]. Tungsten bronze structures could be potentially used for this application because of the structural similarities with WO₃. Both materials are formed by octahedral WO₆ arrays, which originate hexagonal channels. For M_xWO_3 , the hexagonal channels are filled with M species, including alkali metals (Cs, Li, K, and Na) and some small molecules, such as water or ammonium [2,3].

Moreover, these species play an important role on the final properties of the prepared materials because the presence of Na in $\text{h-Na}_x\text{WO}_{3+x/2} \cdot y\text{H}_2\text{O}$ induces the formation of trap centers, improving the photocatalytic activity. The cation also modifies the number of adsorption sites of $\text{h-Na}_x\text{WO}_{3+x/2} \cdot y\text{H}_2\text{O}$, which can lead to an improved response of the gas sensor.

Different strategies have been reported to prepare tungsten bronze structures, such as hydrothermal processes [3], solid-state reactions [6], and sol-gel methods [7]. High temperatures and/or long periods are generally necessary to synthesize single-phase tungsten bronzes [3,6].

In this study, we report the synthesis of $\text{h-Na}_x\text{WO}_{3+x/2} \cdot y\text{H}_2\text{O}$ using a microwave-assisted hydrothermal method, which is cost-effective due to its fast kinetic process [8]. We also demonstrate that $\text{h-Na}_x\text{WO}_{3+x/2} \cdot y\text{H}_2\text{O}$ can act as a NO₂ sensor, with the advantages of potential selectivity, facile synthesis, and high sensibility at concentrations that affect the human health [9–11].

2. Experimental procedure

The following procedure was used to synthesize the $\text{h-Na}_x\text{WO}_{3+x/2} \cdot y\text{H}_2\text{O}$ powder. Firstly, 2 g of Na₂WO₄ · 2H₂O (99%, Sigma-Aldrich) was dissolved in 45 mL of distilled water under stirring at room temperature for 5 min. Then, 5 mL of a 3 M HCl solution was added under continuous stirring for an additional 5 min. The yellowish product was placed in a closed Teflon reaction cell and heated using a conventional microwave furnace (2.5 GHz, 800 W) at 150 °C for 4 min. The resulting precipitate was washed several times with distilled water, and dried at 80 °C for 12 h under air atmosphere (MH sample). The resulting powder was heat-treated at 300 °C for 2 h with a heating rate of 5 °C min^{−1} to eliminate volatiles (MH300C sample).

* Corresponding author.

E-mail address: zanetti@iq.unesp.br (S.M. Zanetti).

The samples were characterized by X-ray diffraction (XRD, Rigaku D/Max-2500 V/PC, Cu-K α radiation), Raman spectroscopy (iHR550 micro-Raman spectrometer, Horiba Jobin-Yvon, Japan) coupled with a CCD detector operating with an Ar-ion laser (Melles Griot, USA), Fourier transform infrared spectroscopy (FTIR, Bruker, Equinox 55), UV–Vis absorption (Varian Cary 5 G), field emission scanning electron microscopy (FE-SEM, Zeiss Supra 35), and energy dispersive X-ray spectroscopy (EDX, LEO, model 440, Leica).

The sensor devices were fabricated on alumina substrates with interdigitated pre-printed Ag-Pd electrodes on the top and a Ag-Pd heating resistor on the bottom to control the working temperature during the measurements. The sensor elements were prepared by mixing 10 mg of $\text{h-Na}_x\text{WO}_{3+x/2} \cdot y\text{H}_2\text{O}$ powder with 5 μL of α -terpineol in a mortar to obtain a slurry that was coated on the substrate. The thick film was dried at 60 $^\circ\text{C}$, followed by heating at 300 $^\circ\text{C}$ for 2 h to remove organics.

The sensing tests were carried out in a 220 mL-glass chamber under gas flow. Synthetic air was used as both carrier and purging gas at a constant flow rate of 100 $\text{cm}^3 \text{min}^{-1}$, and 100 ppm of NO_2 in air was used as analyte gas. The desired NO_2 concentrations were obtained using calibrated mass-flow controllers.

The sensor resistance was measured continuously using a Keithley 6437 picoammeter (bias voltage of 1 V). Synthetic air flowed through the chamber during heating (working temperature

of 200 $^\circ\text{C}$), and then the specific NO_2 concentration flowed during 10 min. Finally, the NO_2 flow was removed, and the chamber was purged with synthetic air during 20 min for cleaning. This procedure was repeated for each NO_2 concentration (10–80 ppm). The sensor response was calculated using $S = R_g/R_a$, where R_g and R_a are the resistances in NO_2 and in air flow, respectively. The response and recovery times were defined as the time required by the sensor to reach 90% of the total resistance variation in the case of adsorption and desorption, respectively.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the MH and MH300C samples. All peaks were indexed to pure $\text{h-Na}_x\text{WO}_{3+x/2} \cdot y\text{H}_2\text{O}$ with a $P6/mmm$ space group (Inorganic Crystal Structure Data No. 071931). Both MH and MH300C samples show narrow and intense diffraction peaks with a crystallite size of 22 and 15 nm, respectively. The crystallite size decrease after the heat treatment might be related to the loss of structural water at around 300 $^\circ\text{C}$, which is common for hydrated tungsten oxides [12].

The FTIR and Raman bands shown in Fig. 1(b) and Fig. 1(c) are summarized in Table 1. The detected bands are in good agreement with previous studies. Specifically, the bands at 3604 and 3545 cm^{-1} of the FTIR spectra, and the bands at 320 and 948 cm^{-1}

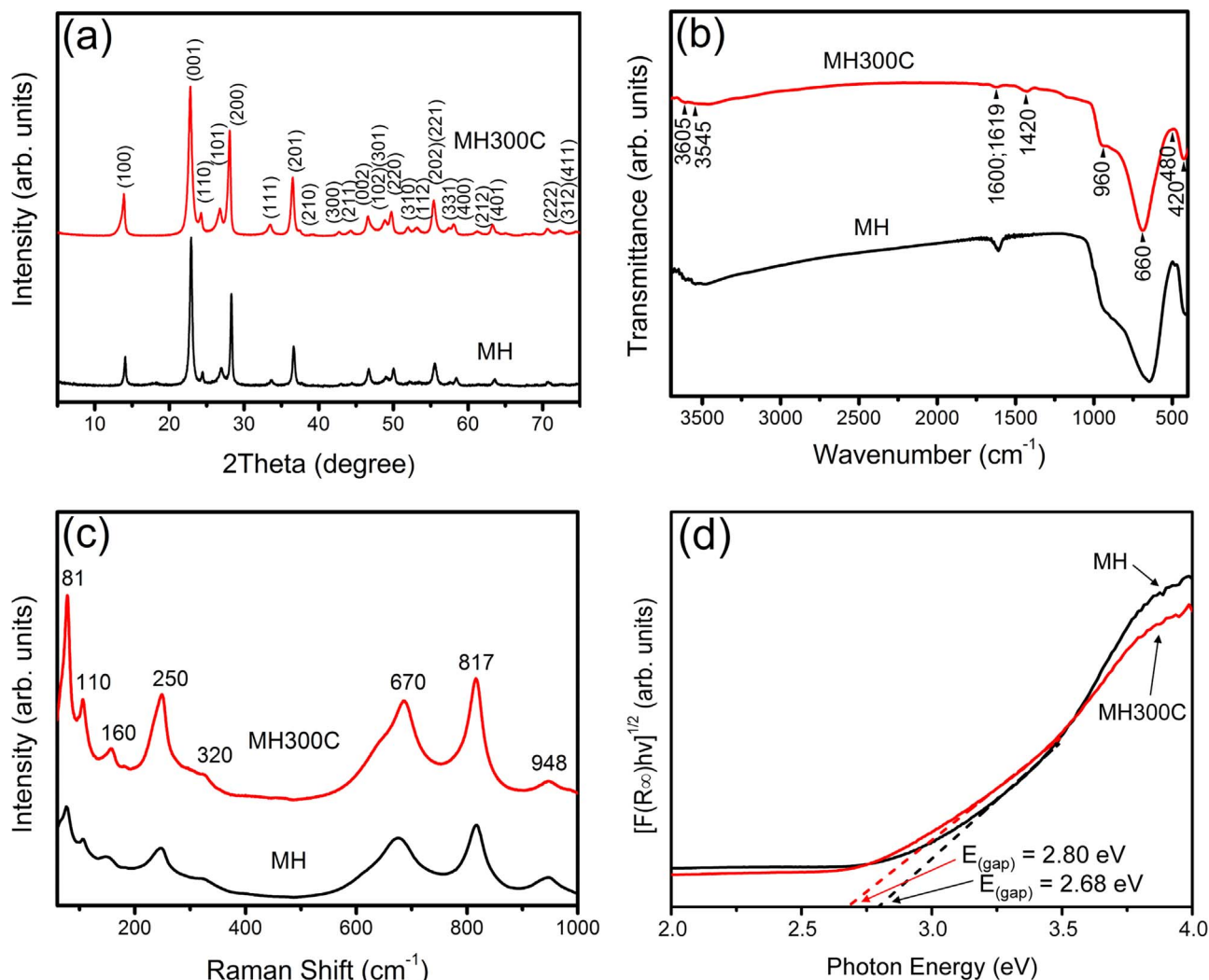


Fig. 1. (a) XRD patterns, (b) FTIR spectra, (c) Raman spectra, and (d) UV–Vis absorption spectra for the MH and MH300C samples.

Download English Version:

<https://daneshyari.com/en/article/1640924>

Download Persian Version:

<https://daneshyari.com/article/1640924>

[Daneshyari.com](https://daneshyari.com)