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Biomorphic synthesis of hollow CuO fibers for low-ppm-level *n*-propanol detection via a facile solution combustion method

Chengjun Dong[a], Xinxin Xing[a], Nan Chen[a], Xu Liu[a], Yude Wang[a,b,*]

[a] School of Physical Science and Technology, Yunnan University, 650091 Kunming, People's Republic of China
[b] Yunnan Province Key Lab of Micro-Nano Materials and Technology, Yunnan University, Kunming 650091, People's Republic of China

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ABSTRACT

Hollow CuO fibers were successfully fabricated using a facile solution combustion method by incorporating cotton fibers as biotemplate. XRD patterns along with Rietveld refinement confirm the formation of CuO with monoclinic phase. The length of the as-synthesized CuO fibers is at micrometer scale, and the average fiber diameter ranges from several nanometers up to order of micrometers. After combustion reaction, a large amount of coalescent particles left on the surface of the cotton fibers to form porous walls of CuO. By totally removing cotton body at 600 °C, hollow CuO fibers were obtained. A possible growth mechanism of hollow CuO fibers using cotton fibers as templates was given based on experimental data. When used as a sensing material in gas sensor, it exhibited a superior sensitivity and good selectivity toward low-ppm-level (1–100 ppm) *n*-propanol. Theses findings not only provide a novel approach to fabricate hollow CuO fibers via a solution combustion route, but also explore a promising gas sensor toward *n*-propanol.

1. Introduction

Various one-dimensional (1D) oxide materials have been extensively studied because of their unique geomaterial and electronic characteristics. The main reasons are not only from fundamental scientific interest, but also from their promising applications in variety of functional devices [1–3]. Among them, copper oxide (CuO) is well known as a p-type oxide semiconductors, which is suitable for a number of applications in sensors (gas sensors and biochemical sensors), catalysts, superconductors, anode material for Lithium-Ion-Battery and supercapacitor, and son forth. Especially, CuO has demonstrated considerable candidates as gas sensors to detect different gases, as exemplified in Table 1 [4–12]. To date, devise methods such as electrospinning, e-beam evaporation, and biosynthesis have been performed to synthesize CuO with nanostructures of nanowires [13], nanofibers [14], nanotube [15], nanorods [16]. Recently, the synthesis method and applications of nanostructured CuO have been comprehensively reviewed [17]. Nevertheless, a novel approach of fabrication 1D CuO is still undergoing.

In recent years, using natural biomaterials as template to fabricate biomorphic functional materials have emerged to be an active research field [18]. For instance, cotton [19–22], pollen [23], butterfly wing [24], yeast cell [25], wood [26], paper [27], sponges [28], and leaves [29], etc., have been adopted as biotemplates. Among those biological systems, cotton fibers have attracted special attention because of their advantages of low cost, excellent absorbing capacity, and more uniform morphology. Based on cotton fibers, many oxidations, such as In_2O_3 [19], CuO [20], TiO_2 [21], TiC [22] have been reported to be fabricated. In general, the precursor coupled with biotemplate was thermally decomposed and then the template body was further removed at higher temperature. Subsequently, the functional materials were fabricated with morphologies and structures resembling those of nature living thins. However, it is still highly of necessity to incorporate biotemplates into other synthesized approach such as solution combustion route to explore its features and extend its applications.

A solution combustion method is a widely employed technique to synthesize nanomaterials, especially for oxides due to its simplicity, low cost, energy- and time-efficiency. The exothermicity of the combustion reaction can provide a localized energy supply for synthesis, which avoids the continuous dependence for high, externally applied processing temperature to keep the reaction going [30,31].

* Corresponding author at: School of Physical Science and Technology, Yunnan University, 650091 Kunming, Peoples' Republic of China. Fax: +86 871 65031410.
E-mail addresses: ydwang@ynu.edu.cn, wangyd99@163.com (Y. Wang).

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Table 1
Examples of the sensing properties based diverse CuO to different gases.

Microstructure	Gas	Concentration (ppm)	T (°C)	Response	$\tau_{res}/\tau_{recov(s)}$	Ref.
Nanobelt	H_2S	10	135	4.7	28/80	[4]
Nanoleave	Ethanol	1500	260	8.22		[5]
Uchin-like	H_2	500	200	9.3		[6]
Nanowire	CO		350	5.5		[7]
Nanowire	NH_3	100	200	3.1	360/1800	[8]
Nanocube	Formaldehyde	0.8	250	1.15	68/151	[9]
Flower	Ethyl-acetate	1000	260	4.6		[10]
Nanoparticle	Ethanol	100	200	2.39	7/5	[11]
Needlelike	Benzaldehyde	100	260	8.89	80.8/38.3	[12]
Nanofiber	*n*-Propanol	100	200	4.66	19.18/63.00	This work

In our recent report, we successfully fabricated diverse morphologies of porous CuO using surfactant as soft templates via a solution combustion method [32]. Here, we made an attempt to fabricate CuO using biotemplate of cotton fibers based on the same strategy. After destruction of combustion precursor containing both oxidizer and fuel, the cotton fibers were dried and ignited. The hollow CuO fibers were obtained by completely removing template via thermal treatment at 600 °C. The phase, microstructure, as well as morphology of as-synthesized CuO fibers are thoroughly characterized accompanying with the supposed growth mechanism. Ultimately, the gas sensor was fabricated based on hollow CuO fibers to detect low-ppm-level *n*-propranl. The gas-sensing properties and corresponding gas-sensing mechanism were discussed in great details.

2. Experimental

2.1. Materials synthesis

All chemical used were of analytical grade and they were used as received without any further purification. The cupric nitrate ($Cu(NO_3)_2{\cdot}3H_2O$) and glycine were used as an oxidizer and a fuel, respectively. Stoichiometric composition of the oxidizer and fuel were calculated based on completely combustion reaction in the following [33]:

$$9Cu(NO_3)_2 \cdot 3H_2O + 10C_2H_5NO_3 \xrightarrow{\Delta} 9CuO + 14N_2 + 20CO_2 + 52H_2O \quad (1)$$

To start with, 9 mmol $Cu(NO_3)_2{\cdot}3H_2O$ and 10 mmol glycine were dissolved into 50 ml deionized water to form a homogeneous solution under stirring. Afterwards, 1 g dried and loose cotton fibers were immersed into the above solution. After 24 h, the cotton was taken out and dried at 80 °C. Subsequently, the dried cotton was put in a crucible and then transferred to a preheated furnace at the temperature of 400 °C for 10 min. The combustion reaction was completed in several seconds and the cotton fibers were burnt off. Finally, the temperature was further increased up to 600 °C at a rate of 1 °C/min and maintained for 2 h. When it was naturally cooled down to room temperature, the carbon was completely removed and crystallized CuO with fluffy appearance in black was left.

2.2. Instrumentation

X-ray diffraction (XRD) patterns of the products were measured by step scanning on a Rigaku TTRIII X-ray diffractometer with Cu Kα radiation (incident X-ray wavelength of 1.540 Å). The morphology and microstructure of CuO fibers were observed by a scanning electron microscope (SEM, FEI QUANTA200) and a transmission electron microscopy (TEM, JEOL JEM-2100). The Raman spectra were recorded on a Raman imaging microscope (Ranishaw Model 2000) under a 514.5 nm Ar^+ laser excitation. The thermal decomposition in air was determined by an American TA SDT-2960 thermal analyzer. The sample was heated at air in the temperature range from room temperature to 800 °C at the heating rate of 20 °C/min. X-ray photoelectron spectroscopy (XPS) was utilized to examine the surface chemistries of the samples in ESCALAB system with Al *Kα* X-ray radiation at 15 kV. All XPS spectra were accurately calibrated by the C 1s peak at 284.6 eV.

2.3. Gas-sensing measurements

The gas-sensing property test was conducted on a commercial measuring system WS-30A (Weisheng Electronics Co., Ltd, China) (Fig. S1(a) in Supplementary information). First, the sensor was fabricated by coating as-synthesized CuO fibers dispersed in water as a sensing layer with a thickness of about 0.5 mm on a prefabricated alumina tube (7 mm in length and 1.5 mm in diameter) with two pairs of gold electrodes and platinum wires. From Fig. S1(c), a real sensor was presented. The sensor was dried and calcinated in air at 400 °C for 3 h to guarantee the good contact between Au electrodes and product. Then a Ni–Cr heating wire (resistance = 25 Ω) was inserted in the alumina tube to form an indirect-heated gas sensor, and the operating temperature of the sensor can be adjusted through varying the heating voltage (V_h), as shown in Fig. S1(b). The circuit voltage (V_c) was set at 5 V, and the output voltage (V_{out}) was set as the terminal voltage of the load resistor. During the test, the desired amounts of target gas were injected into the chamber. An evaporator and two fans are installed to obtain the desired gas concentration immediately in the chamber. The gas response of the sensor (β) in this article was defined as R_g/R_a, where R_a is the resistance in air and R_g is the resistance in gas. The response or recovery time was expressed as the time taken for the sensor output to reach 90% of its corresponding equilibrium value.

3. Results and discussion

Fig. 1 shows the original XRD data along with the Rietveld refinement pattern for as-synthesized hollow CuO fibers. The Rietveld refinement was accomplished over Maud program composed by Ferrari et al. [34] with satisfactory convergence factors of R_{wp} = 6.69% and R_p = 4.85%. Also, the difference curve at the bottom makes sure a reliable fit of the experimental data. For clarity, all Rietveld refinement parameters were refined as listed in Table S1. As depicted by the black curve in Fig. 1, the diffraction peaks are perfectly indexed as monoclinic CuO structure (JCPDS: 48–1548) with the C2/c space group. The purple bars in Fig. 1 represent the Bragg positions. The lattice parameters obtained from the refinement are a = 4.6836 Å, b = 3.4424 Å, and c = 5.1298 Å, respectively, which matches well with the reported values [35]. The peaks appear high intensities without any secondary phases, indicating the higher crystallinity and purity in nature.