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Inducing analytical orthogonality in tungsten oxide-based microsensors using materials structure and dynamic temperature control

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ABSTRACT

The influence of material structure and dimension on the chemical sensing performance was investigated as a function of sensor operating temperature. Polycrystalline tungsten oxides (WO_3) were prepared both as nanowires of different diameters ($d \approx 100$ nm, 175 nm; $l = 4$–5 μm) using a template-directed electrodeposition process, and as a continuous film through thermal decomposition of peroxytungstate solution. The WO_3 materials were integrated with microscale conductometric platforms featuring millisecond dynamic temperature control up to 500 °C. The nanowires and film were assessed for efficacy as transducers in gas-phase chemical sensors using these platforms, both in a fixed-temperature operating mode and in a dynamic pulsed-temperature operating mode. Statistical analysis of the tungsten oxide chemiresistor responses to analytes at varied operating temperatures revealed that orthogonal information can be obtained from stoichiometrically similar materials; the differences were exaggerated by probing the sensor responses with different dynamic temperature programs. We conclude that nanowire sensors yield non-redundant analytical information with respect to their complementary film-based sensor. These results demonstrate that as sensors move to nanoscale structures, unique interactions will differentiate the materials and the devices' performance from their microscale counterparts.

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1. Introduction

How do the size, dimension and morphology of a sensing material impact its performance? Metal- and metal-oxide-based nanostructures have been attracting significant interest in chemical sensing applications [1–9] owing to the small size and related characteristics (e.g., surface area, surface-to-volume ratios, quantum confinement). Of particular interest to us is the emerging role of nanomaterials as the active chemiresistor in chemical sensing applications [8–17]. Preliminary results do suggest that there are benefits to be gained by employing these nanostructured sensing materials in terms of response speed and sensitivity, which may be attributed to an increased diffusion rate of analytes through the sensing materials and their large surface-to-bulk ratio, respectively [5–9]. However, whether the differences in scale and structure of sensing materials create only similar sensors with improvements in their response speed and sensitivity, or result in quasi-unique sensors capable of generating orthogonal analytical information about a chemical species is not clear [7,8]. One-dimensional nanomaterials have been recently applied as the active sensing material in chemical sensors as reported by several groups for various sensor configurations [4–6,17–19]. For sensing applications, the nanoparticulate structure is also attractive, as it increases the number of grain boundaries in the active material where sensing interactions are believed to occur [20].

Here we describe a method to determine whether sensing material morphology imparts the potential for analytical orthogonality by probing the responses of three tungsten oxide chemiresistors differing in directed structure and dimensions. As a sensor material, tungsten oxide (WO_3) nanomaterials are receiving a significant amount of attention [21–26]. We have prepared two chemical sensors with active materials based upon polycrystalline nanowires of different diameters, and one sensor with a polycrystalline film. We determine that the three structures, while possessing similar surface chemistry and nanoparticulate building blocks, can provide analytically different transient responses based upon their thermal operating history and the selected target analyte.

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2. Experimental

2.1. Tungsten(VI) oxide materials preparation

Polycrystalline tungsten oxide nanowires were made via template-directed electrodeposition followed by calcination. Briefly, one side of a track-etched polycarbonate filtration membrane (d_{pore} = 50 nm or 100 nm, l_{mem} = 6 μm) was coated by thermal evaporation with a silver film to serve as a working electrode. The WO_3 nanowires were deposited at constant potential (−0.5 V vs. Ag/AgCl) in the template from a peroxytungstate solution (Supplemental Fig. 1) [27]. Nanowires were isolated by first dissolving the Ag working electrode in 25% nitric acid, followed by dissolution of the template in chloroform. The nanowires were collected by centrifugation, and washed with chloroform and 2-propanol several times. After each wash, the nanowires were collected by centrifugation and then redispersed by sonication. The nanowires were finally dispersed in 2-propanol. Thin films of WO_3 were prepared via thermal decomposition of the peroxytungstate solution [28] to make comparisons between nanowire-based active sensing materials and film-based materials. To determine the effect of sintering on nanowire morphology, an aliquot of nanowire dispersion was allowed to dry in a small glass tube that was subsequently heated in a furnace to 480 °C in air for 1 h. The sintered nanowires were then dispersed in 2-propanol and deposited onto a TEM (transmission electron microscopy) grid for analysis. The WO_3 materials were characterized by optical, scanning electron and transmission electron microscopies. X-ray photoelectron spectra (XPS) were measured using monochromatic Al K (alpha) radiation. A Shirley background was applied to the W 4f spectra, which were then fit using Voigt profiles. All spectra were referenced to the surface oxide of the aluminum substrate at 74.4 eV.

2.2. Sensor preparation and evaluation

The WO_3 materials were deposited onto three individual microhotplate sensor platforms in a multi-element array that facilitates conductometric measurements with control of sensor operating temperatures [11,29,30]. The microhotplate platforms are 100 μm platforms suspended over a pit etched into the substrate silicon. A poly-silicon heater, embedded in the microhotplate platform, provides temperature control for materials processing or conductometric (chemiresistive) sensor operation. Electrical contact for simple resistive measurements is made to the sensing material (film or nanowires) via interdigitated platinum electrodes, which cover the surface of the microhotplate. The digits are nominally 2 μm wide with 2 μm gaps. All materials were deposited from freshly sonicated dispersions in 2-propanol (nanowires) or water:2-propanol solution (peroxytungstate solution) using a microcapillary pipette (id_{cap} = 75 μm). After the solvent dried, the sensing materials were calcined to 480 °C in flowing zero-grade dry air for 1 h. Sensor testing was carried out using a computer-controlled, automated gas-flow and data-collection system. Analytes were delivered in zero-grade dry air from gas cylinders.

The sensor response levels were calculated as $(G_{gas} - G_{air})/G_{air}$, where G_{gas} is the conductance of the sensor in the presence of an analyte, and G_{air} is the conductance of the analyte in the background condition of dry air. The response times were calculated as the time for the conductance to change from 10% to 90% of the total conductance change ($G_{gas} - G_{air}$). All analyses of TPS data were done using custom programs in a commercial software package. Conductance measurements of different materials at fifteen ramp and fifteen base temperatures were concatenated to form a multi-dimensional sensor response that was used for all analysis.

To analyze the similarity/orthogonality of responses of any two WO_3 morphologies (M_1, M_2) at two operating temperatures (T_1, T_2), we used Pearson's correlation coefficients. If $g(M_1, T_1)$ is a one-dimensional vector of conductance response of M_1 at temperature T_1 to any of the test analytes (CH_3OH or CO) during different trials, and $g(M_2, T_2)$ a one-dimensional vector of conductance measurements made using M_2 at temperature T_2, then the correlation between responses of M_1 at T_1 and M_2 at T_2 is calculated as

$$\frac{n\sum g(M_1,T_1)g(M_2,T_2) - \sum g(M_1,T_1)\sum g(M_2,T_2)}{\left(\left(n\sum g(M_1,T_1)^2 - \left(\sum g(M_1,T_1)\right)^2\right)\left(n\sum g(M_2,T_2)^2 - \left(\sum g(M_2,T_2)\right)^2\right)\right)^{1/2}}$$

where n in the number of trials. Only the absolute values of the correlation coefficients with significance $p < 0.05$ (t-test) are shown.

For visualizing the sensor response, we used principal component analysis (PCA), which is a linear dimensionality reduction technique [31]. In PCA, the six-dimensional sensor array responses (1 ramp and 1 base temperature per sensing element; three elements) were projected onto the first two or three dimensions, defined by the first few eigenvectors (with largest eigenvalues) of the response covariance matrix that captures most of the variance in the dataset.

3. Results and discussion

For our studies, polycrystalline nanowires composed of WO_3 were prepared by the adaptation of a literature electrochemical deposition method [27] to template-directed synthetic methodology [32,33]. As deposited, the nanowires are largely amorphous as demonstrated by TEM studies (Fig. 1a). However, nanocrystals of WO_3 with diameters of 10–15 nm were also observed in the as-deposited nanowires, and were surrounded by amorphous material. After calcining the WO_3 nanowires at 480 °C in air for 1 h and examining again by TEM, it was apparent that the wires had completely converted to crystalline material, while retaining the nanocrystalline size of 10–15 nm (Fig. 1b–e). The nanowires themselves, then, are built of nanocrystals with many grain boundaries along and within the length of the wire. To provide a dramatically different assembly of nanoparticles for comparison with the nanowire materials, WO_3 films were prepared by the thermal decomposition of a microdrop of the peroxytungstate solution [28]. The chemical states of the tungsten oxide materials were probed by XPS (Fig. 2). Tungsten is identified from a survey scan from the 4s, 4p 1/2, 4p 3/2, 4d 5/2 and 4f 7/2 peaks at 596.4 eV, 493.9 eV, 425.4 eV, 244.5 eV and 35.4 eV, respectively. High-energy-resolution region scans (Fig. 2, inset) for both the nanowires and the film were well fit by Voigt profiles, indicating that a single chemical species is present at the surface for both the film and the nanowires, each having an energy of 35.5 eV for the W 4f 7/2 peak, in good agreement with previous reports for tungsten(VI) oxide [34].

Further characterization of the materials was conducted after the WO_3 nanowires were isolated from their template and then integrated with temperature-controlled microsensor platforms ("microhotplates," see Section 2 for more information about the National Institute of Standards and Technology (NIST) microsensor technology) via microcapillary pipette [35]. The microhotplate platform also provides a convenient method for calcining the materials. Fig. 3 shows SEM (scanning electron microscopy) micrographs of (a) a microhotplate and various tungsten oxide sensor materials (b and c; see also Supplemental Fig. 2) nanowires prepared in a 100 nm pore-diameter template deposited on a microhotplate, and subsequently calcined at 480 °C in dry air and (d) a nanostructured film prepared by thermal decomposition of a peroxytungstate precursor. As deposited from the dispersion, the nanowires sparsely cover

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