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Ferric oxide nanoparticle-functionalized tungsten oxide nanoneedles and their gas sensing properties

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Abstract

The aerosol assisted chemical vapor deposition of Fe_2O_3 nanoparticle-functionalized tungsten oxide nanoneedles and their gas sensing properties are presented here. Material analysis demonstrates the incorporation of 4 to 15 nm Fe_2O_3 nanoparticles at the surface of the tungsten oxide nanoneedles. Gas sensing tests show improved tungsten oxide sensitivity, to toluene, ethanol and hydrogen, with the highest sensitivity (six-fold) to toluene, due to its functionalization with Fe_2O_3. This enhancement is nearly similar to the enhancement obtained when functionalizing tungsten oxide with platinum, suggesting that the sensing performance of tungsten oxide could be improved to a same extent using second-phase nanoparticles of metal oxides, which are less expensive and more abundant than precious metals such as Pt.

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Keywords: Tungsten oxide; functionalization, ferric oxide, platinum, AACVD; gas sensor

1. Introduction

Nanostructured semiconducting metal oxides such as nanoneedles have demonstrated exceptional chemical and physical properties, due to their large number of surface sites, which facilitate surface reactions. These characteristics have favored the use of these materials in different solid-state devices, including gas sensors. Due to the increasing demand of more sensitive, selective and stable gas sensors, the optimization of metal oxides is still

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being largely studied. Thus, several studies have demonstrated that metal oxides functionalized with second-phase constituents, either nanosized metals or other metal oxides, have a drastic effect on sensing performance, often improving the sensing properties of both the host metal oxide and the second-phase constituent [1].

In the literature, there are various conceptual routes to functionalize metal oxides with second-phase nanoparticles, based either on liquid-phase or vapor-phase synthesis. However, synthesizing nanostructured materials in the vapor-phase has potential advantages, including the growth of materials with greater purity, higher throughput, and the possibility of integrate materials directly into devices. Aerosol-assisted chemical vapor deposition (AACVD) is a vapor-phase method, which was used previously to grow in a single-step highly sensitive tungsten oxide nanoneedles functionalized with metal (e.g. Pt) nanoparticles [2].

Here we extend this method to synthesize tungsten oxide nanoneedles functionalized with Fe_2O_3 nanoparticles and study the gas sensing properties of these modified nanostructures to various reducing gases, including hydrogen, ethanol and toluene.

2. Materials and methods

Tungsten oxide nanoneedles functionalized with ferric oxide nanoparticles were co-deposited at 390 °C via AACVD of a solution containing tungsten hexacarbonyl (20 mg, $W(CO)_6$), Sigma-Aldrich, ⩾97%) and ferric chloride hexahydrate (3 mg, $FeCl_3{\cdot}6H_2O$, Sigma-Aldrich, ⩾ 99.6%) dissolved in methanol (5 ml, Sigma-Aldrich, ⩾ 99.9%). The aerosol droplets were transported to the heated substrate using a nitrogen gas flow (200 sccm). The time taken to transport the entire volume of solution was typically about 45 minutes. Plain polymeric foils (Upilex-S, 125 µm, UBE) were used for film analysis, whereas flexible-transducing platforms based on the same polymeric foils were used for gas sensor fabrication. The fabrication of the flexible-transducing platforms and the integration of non-functionalized and Pt-functionalized tungsten oxide nanoneedles into these platforms via AACVD was described previously [2-3]. All samples were annealed at 390 °C for 1h with a constant flow of air (50 sscm) after AACVD.

The morphology of the films was examined using Scanning Electron Microcopy (SEM – Carl Zeiss, Auriga Series, 3 KV), the film structure using X-ray Diffraction (XRD – Bruker, AXS D8- Advance, Cu Kα radiation operated at 40 KV and 40 mA). High Resolution Transmission Electron Microscopy (HRTEM – FEI Tecnai F20, 200 kV) was performed after removing the film from the polymeric platform by sonication.

Gas sensors were tested in a continuous flow test chamber [3]. Briefly, the system was provided of three mass flow controllers and mixtures of pure synthetic air (3X, Praxair) and either calibrated toluene (C_7H_8, Praxair), hydrogen (H_2, Praxair) or ethanol (EtOH, Praxair) in synthetic air were adjusted in order to obtain the desired concentrations. The electrical resistance of the sensors was measured using a multimeter (Keithley 2700) configured with 20-channels relay multiplexer. The sensor response (R) was defined as $R= R_a/R_g$, where R_a is the sensor resistance in air at stationary state and R_g represents the sensor resistance after 10 minutes of analyte exposure. Four replicates were performed for each analyte and concentration.

3. Results and discussion

Generally, the AACVD of $W(CO)_6$ co-reacted with $FeCl_3{\cdot}6H_2O$ resulted in the formation of adherent uniform films with a blue color as-deposited, which after annealing became yellow. Overall, SEM of the films grown on the plain polymeric foils and the flexible-transducing platforms showed uniform non-aligned nanoneedles, with diameters ranging between 50 and 100 nm and lengths of ~10 µm. An example of the SEM images of the functionalized nanoneedles integrated into the flexible device is shown in Fig. 1.

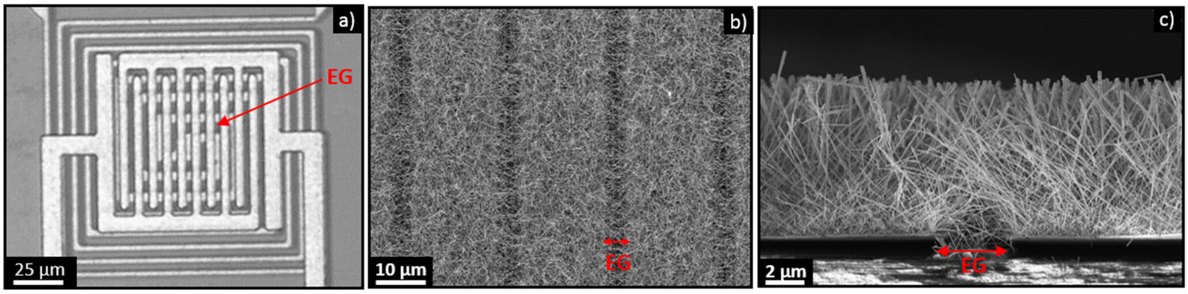

Fig. 1. (a) Photograph of the flexible-transducing platform prior to growing the sensing nanostructures; SEM images of the (b) top and the (c) cross-section of the flexible gas sensor device after growing the tungsten oxide nanoneedles functionalized with Fe_2O_3 nanoparticles. EG represent the electrode gap

XRD of the films (Fig. 2a) indicated the presence of monoclinic phase tungsten oxide (P21/n space group, a=7.306 Å, b=7.540 Å, c=7.692 Å, and β=90.88º; ICCD card no. 72-0677), consistent with our previous results for non-functionalized or Pt-functionalized tungsten oxide nanoneedles [2]. Diffractions associated to iron compounds (Fig. 2) were not observed in the films, likely due to the low iron contents used for the AACVD. In contrast, HRTEM displayed nanoparticles at the surface of the nanoneedles and EDX confirmed the presence of tungsten and iron (Fig. 2b). HRTEM revealed crystalline structures, with the nanoparticles displaying planar spacing of 2.81±0.15 Å, consistent with the internal lattice spacing of the cubic Fe_2O_3, and the nanoneedles displaying planar spacing of 3.55±0.16 Å, consistent with the monoclinic phase identified for tungsten oxide nanoneedles using XRD [3].

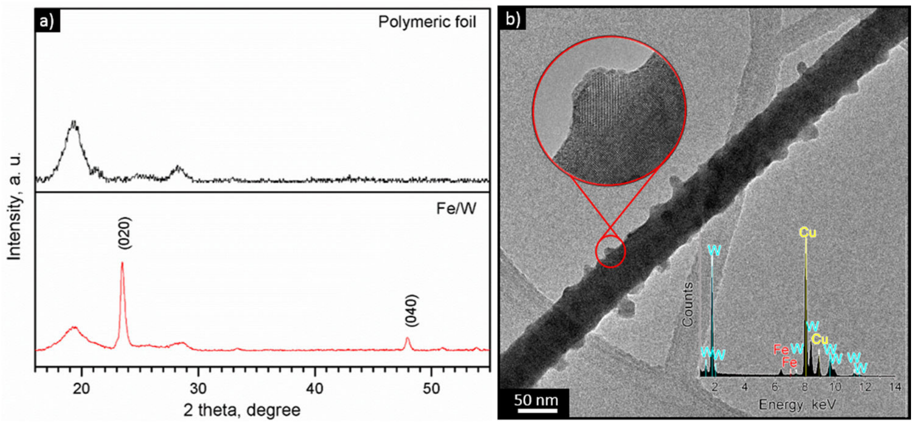

Fig. 2. (a) XRD patterns of the Fe_2O_3-functionalized tungsten oxide nanoneedles grown onto the polymeric foils; HRTEM of a single nanoneedle functionalized with Fe_2O_3 nanoparticles (inset show the EDX spectra of the structure)

Test to toluene, ethanol and hydrogen showed typical direct dependences of the response to analyte concentration, with closely similar tendencies for Pt- and Fe_2O_3-functionalized nanoneedles and noticeable higher and faster responses of the functionalized nanoneedles compared to those non-functionalized (Fig. 3a). The sensitivity to each analyte, defined as the ratio between the change in sensor response (ΔR) for a fixed change in analyte concentration (ΔC) is shown in Fig. 3b.

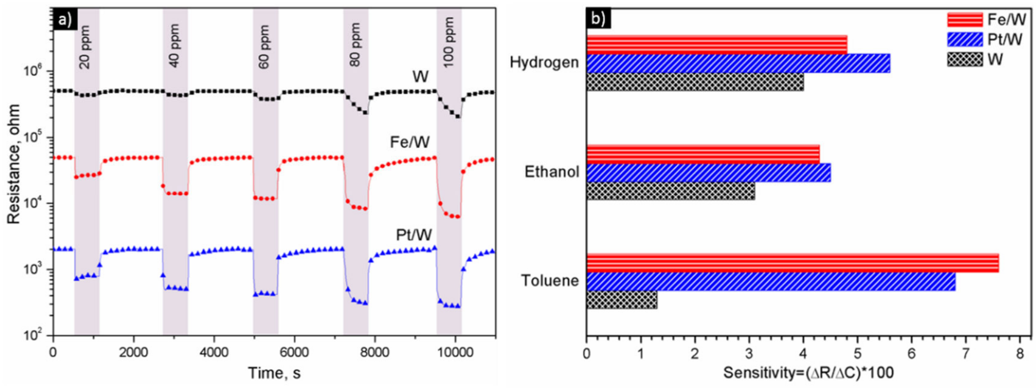

Fig. 3. (a) Sensor resistance changes to various concentrations of toluene; (b) sensitivity to hydrogen, ethanol and toluene. W represents the response for non-functionalized structures and Fe/W and Pt/W represent the response for Fe_2O_3 and Pt functionalized structures

4. Conclusion

Tungsten oxide nanoneedles functionalized with Fe_2O_3 nanoparticles were synthetized using a co-deposition method via AACVD at 390 °C. The gas sensing properties of these modified nanostructures demonstrated improved responses to toluene, hydrogen and ethanol, with up to six-fold increase in sensitivity to toluene, compared to non-functionalized tungsten oxide nanoneedles. These output characteristics were similar to those recorded for tungsten oxide nanoneedles functionalized with Pt nanoparticles, demonstrating that the use of Fe_2O_3 provides almost the same enhancement as the precious metal Pt.

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