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Nickel doped WO_3 nanoneedles deposited by a single step AACVD for gas sensing applications

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Abstract

One-step Aerosol Assisted Chemical Vapour Deposition (AACVD) method was used for the first time to grow WO_3 nanoneedles (NNs) decorated with NiO metal nanoparticles (NPs) at lower (380°C) deposition temperature. This co-deposition method is demonstrated to be an effective route to incorporate metal NPs into nanostructured materials. A layer of needle-like tungsten oxide film was deposited directly onto transducer alumina substrates from $W(CO)_6$ and $Ni(acac)_2$ precursors. Moreover, the systematic growth study of WO_3 NNs + metal NPs allowed the identification of the parameters required for the formation of nanostructured sensing materials having different metal precursor concentration in a range of 2.5 to 15 mg The results show variations in the sensing properties according to the metal precursor concentration. Improved sensing, to some reducing gases, such as EtOH, H_2S and NH_3 are observed at 200ºC with lower doped tungsten oxide films, whereas higher doped tungsten oxide has shown no response.

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Keywords: AACVD, gas sensor, nanoneedles, nickel doped;

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1. Introduction

The functional properties of materials may be improved by the introduction of intentional impurities (dopants). Moreover, for materials functionalised with metal NPs is of the importance using reduced metal-NP sizes and lower concentrations of metal NPs, which are thought to have a greater influence on the electronic structure of the support and in creating new adsorption sites [1]. For instance, WO_3 NNs decorated with different metal NPs are of interest for gas sensor applications. It is known that by adding noble metal NPs to the surface may improve not only sensitivity and stability, but also selectivity of the gas sensor [2]. We have already demonstrated in our previous works [3-5], that AACVD is a flexible technique for easy implementation and functionalisation of WO_3 NNs with different metal NPs (Au, Pt, Cu). Due to its simplicity, relatively low setup and running costs AACVD is an industrially attractive technique. In AACVD, synthesis, functionalisation and incorporation into a device structure take place in a single processing step and it is a greener method for the production of nanodevices. Therefore, it is an easy route to fabricate doped gas sensors with next generation nanostructured materials, providing potential for tuning functionality of the sensing films.

2. Experimental details

2.1. Experimental set-up and characterization

Ni-doped WO_3 nanoneedles were directly deposited on onto alumina gas sensor substrates using the AACVD method at a lower temperature of 380 °C. The synthesis of Ni-doped WO_3 nanoneedles was carried out by mixing tungsten hexacarbonyl ($W(CO)_6$), with nickel(II) acetylacetonate (2,5-15 mg, $Ni(acac)_2$) precursors in a solvents. The solutions were kept in a glass flask and placed in an ultrasonic humidifier. The aerosol of solvents and the mixture of precursors were transported to the heated zone inside the reactor by using 500 mL/min of nitrogen as a carrier gas. The deposition time was between 30 and 45 min, until all of the precursors had passed through the reactor. After that, all of the samples were annealed at 500 °C for 3 h. The morphology and the structure of the synthesized material have been characterized by ESEM, TEM and XRD, respectively.

2.2. Gas sensing tests

The gas sensors were placed in a continuous flow test chamber and the total gas flow was adjusted to 100 sccm. The resistance change to various contaminant gases and operating temperatures were examined. In order to obtain the desired target gas concentration, mixtures of pure air and pollutant gases were performed using a mass flow controller (Bronkhorst hi-tech 7.03.241). The sensors were exposed to the test gas for 15 min, and subsequently the chamber was purged with air for 30 min, which enabled recording recovery of their baseline resistance. After this process, the sensors were ready for a new measurement. The sensor response (R) was defined as $R = R_a/R_g$ for reducing gases and $R = R_g/R_a$ for oxidizing gases, where R_a and R_g are the sensor resistances at the stationary state in air and after 15 min of exposure to analytes, respectively.

3. Results and discussion

3.1. Material characterization of Ni-doped WO_3 nanoneedles

The as-deposited films strongly adhered to the substrate, with dark blue colour and became white-yellow after the annealing. ESEM and TEM analysis were used to identify the morphology and distribution of the deposited nickel NPs functionalised WO_3 NNs. Fig. 1a-b shows the ESEM images obtained from the as-deposited layers. The results show the formation of a 5 μm thick layer of very compact nanoneedle-like structures, with high density and homogeneous distribution over the substrate. Moreover, presence of well-dispersed metal NPs along the surface of the NNs is observed (Fig. 1c).

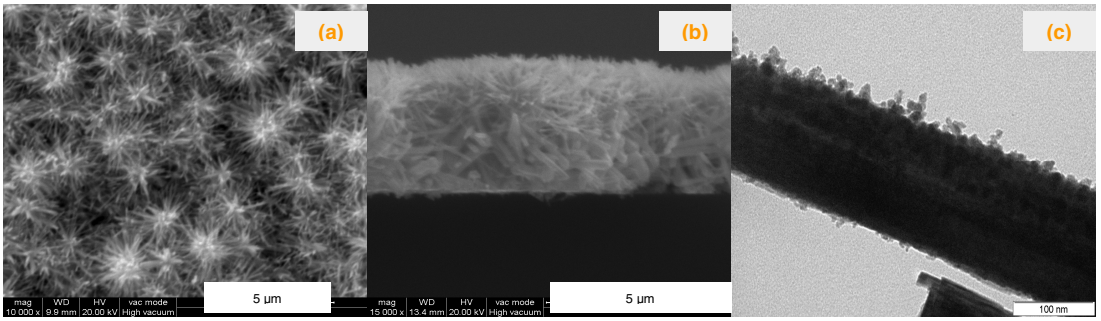

Fig 1: Front view (a) and a cross-section (b) ESEM images of the as-deposited Ni-functionalized WO3 nanoneedles; (c) TEM image of the obtained Ni-functionalized WO3 nanoneedle

The composition analysis was discussed in our previous works [4, 5]. XRD analysis of the samples indicated the presence of the monoclinic phase WO_3 (P21/n space group). Similarly, no peaks for Ni or NiO were observed in the pattern, likely because of their small size (nanoscale) and/or the relatively low amount present. However, the composition of the resultant nanostructures were verified with energy dispersive spectra (EDS) analysis in ESEM and revealed that the samples included W and Ni.

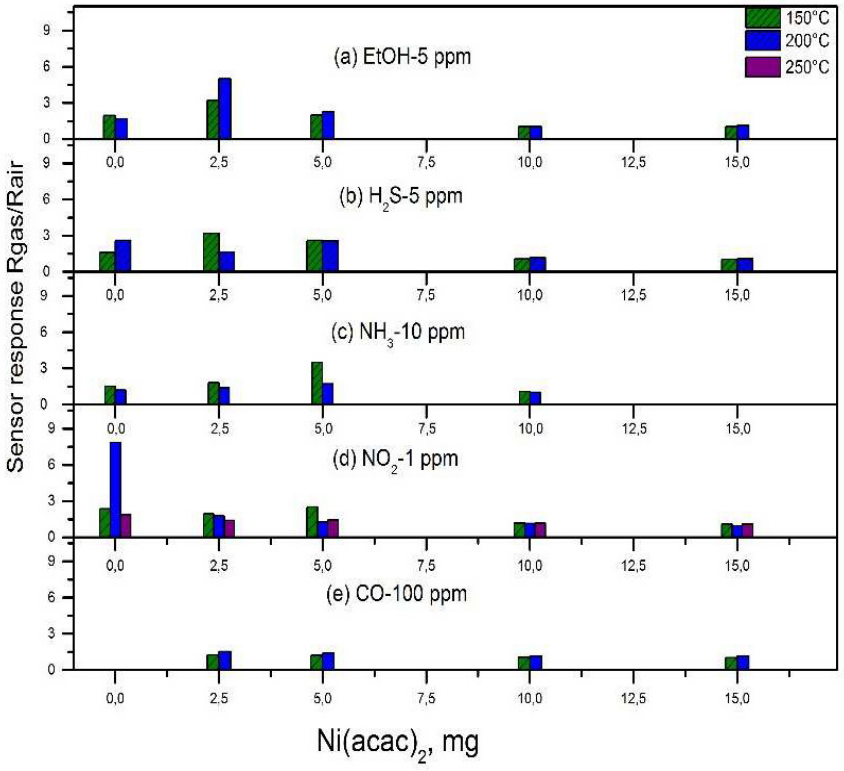

Fig 2: Response comparison of intrinsic and Ni-doped WO_3 sensors to different analytes and temperatures.

3.2. Gas-sensing properties

The response of the Ni-doped WO_3 gas sensor based on NNs to various gases was analyzed at several operating temperatures. The lower (2.5 and 5 mg) Ni-doped WO_3 nanostructures showed higher responses to EtOH and NH_3, respectively, while the response of the higher Ni-doped (10 and 15 mg) sensors was observed to be lower (see Fig. 2). The 2.5 mg Ni-doped sensors showed improved maximum response toward EtOH at 200ºC optimum operating temperature. Alternatively, 5 mg Ni-doped sensors showed improvement in a sensor response towards NH_3 at relatively lower 150ºC operating temperature (Fig. 3).

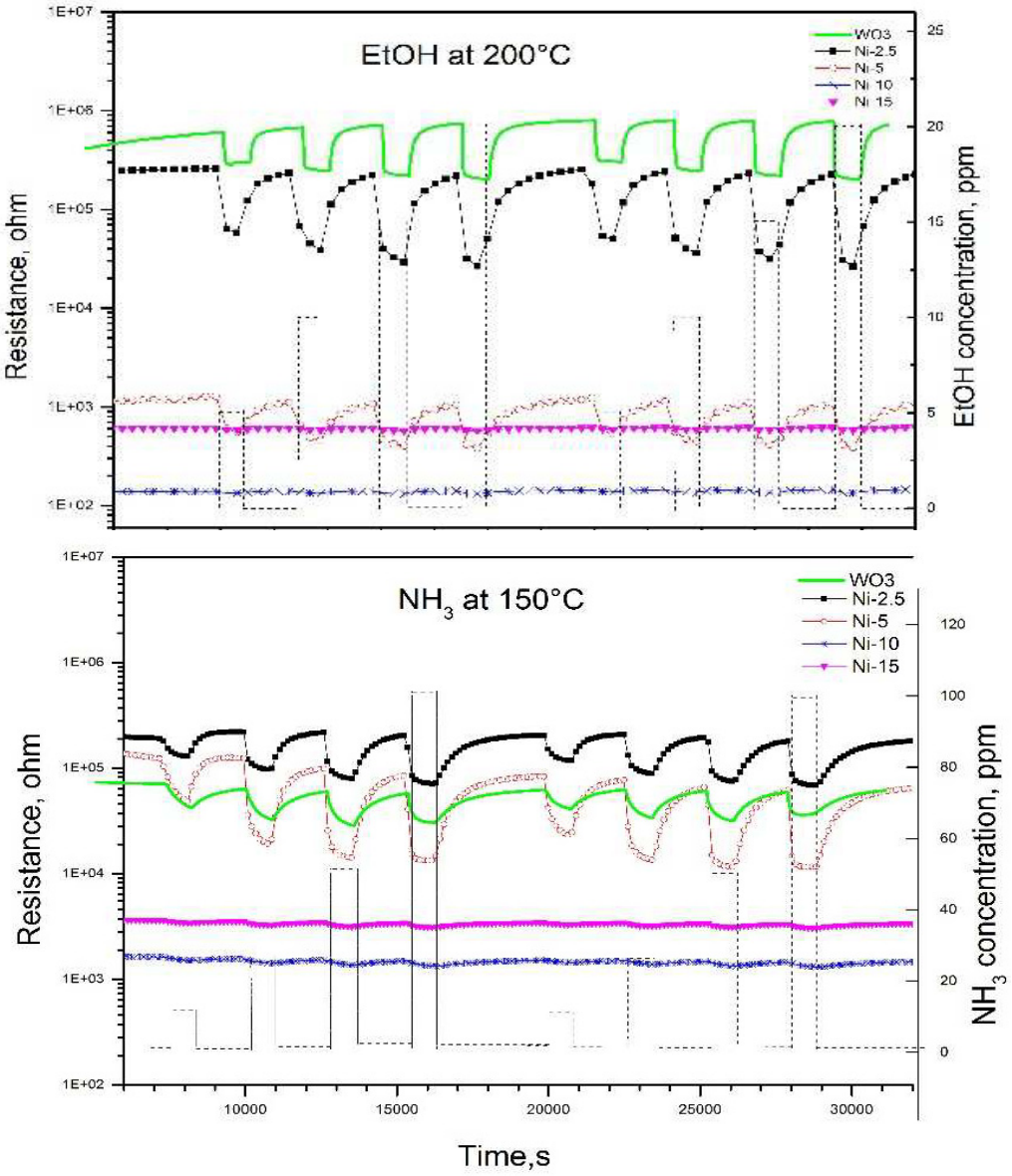

Fig 3: Resistance changes of intrinsic and Ni-doped WO3 gas sensors upon exposure to EtOH at 200 ºC and to NH_3 at 150 ºC.

4. Conclusions

In summary, Ni-doped WO_3 nanoneedles were deposited in a single step by AACVD method. Gas sensing investigation reveals that very low (2.5 mg) Ni-doping can enhance the EtOH sensing properties of the NNs. Alternatively, medium (5 mg) Ni-doping can enhance the NH_3 sensing properties at lower (150°C) optimum operating temperature. The results for higher 10 and 15 mg Ni-doped WO_3 NNs have shown no sensing detection.

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