Ag-decorated SnO_2 nanorods: microwave-assisted green synthesis and enhanced ethanol gas sensing properties

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The green synthesis of gas-sensing materials, which monitor volatile organic compounds, avoid synthesis-induced pollution, and thus is a major challenge faced by scientific researchers. Herein, we report a microwave-assisted green synthesis of Ag-decorated SnO_2 nanorods with water being used as solvent and comparatively non-toxic chemicals being used as reactant. The as-prepared product was characterised by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The results showed one-dimensional Ag-decorated SnO_2 nanorods constituted of tetragonal rutile phase of SnO_2 and cubic phase of Ag were successfully prepared. Ethanol was used as a model system for measuring gas-sensing properties and an enhanced gas-sensing property was found due to Ag decoration. Moreover, a linear dependence of the sensitivity on the ethanol concentration was observed.

1. Introduction: Metal oxides are extensively used in the production of gas-sensing devices, as they offer a variety of advantages ranging from low-cost production to chemical resistance and are suitable for a large number of volatile organic compounds such as methanol, ethanol and formaldehyde etc. The large surface-to-volume ratio of one-dimensional (1D) metal oxide nanostructures and the congruence of the carrier screening length with their lateral dimensions make them become highly sensitive and efficient transducers for transferring surface chemical processes into electrical signals [1, 2]. Among various candidates, 1D SnO_2 materials have been drawn much attention due to their low production cost and excellent chemical and thermal stability [3, 4]. Various synthesis approaches such as thermal evaporation [5], hydrothermal [6–8], templating [9, 10] and electrospinning [11, 12] were made to fabricate 1D SnO_2 materials. Moreover, it was found that the incorporation of 1D SnO_2 with noble metal nanoparticles (NPs), such as Ag or Pt, can enhance the gas-sensing property [13–15]. However, with organic solvent [16], comparatively toxic chemicals [9, 10] and/or intensive energy being used, most of the methods suggested for the synthesis of SnO_2 or decoration of noble metal NPs are still not quite environment friendly. There is therefore a potential conflict between the development of methods of solving the environment problems and the new problems created by the methods themselves.

It was reported recently that there was an environment-friendly and energy-saving microwave method, which could offer uniform nucleation and growth conditions for nanomaterials [17, 18] due to its highly focused local heating for solvents and reactants in remarkable short time.

Up to now, the nano semiconductor/metal prepared through microwave-assisted methods has been seldom reported. In this Letter, we made a microwave-assisted approach to synthesise Ag-decorated SnO_2 nanorods (NRs) in aqueous solution with comparatively non-toxic reactants, such as lysine and citric acid. Experiment results indicated that the Ag-decorated SnO_2 NRs exhibited an improved sensing property. To the best of our knowledge, the use of microwave method to not only synthesise SnO_2 but also decorate Ag has barely been reported.

2. Experiments

2.1. Synthesis of SnO_2 NRs: About 1.35 g of $SnCl_2{\cdot}2H_2O$ and 2.1 g of citric acid were subsequently added into 50 ml of double distilled water (DDW) and mixed slowly. The mixture was heated at 80°C for 30 min to evaporate part of the water. The obtained suspension was transferred into a microwave tube and then reacted at 90°C for 30 min in a microwave reactor (CEM, Discover; power setting of 200 W). The precipitate was collected by centrifugation, rinsed by DDW and dried at 60°C. The as-prepared SnO_2 NRs was then annealed at 500°C in air for 1 h.

2.2. Decoration of Ag on SnO_2 NRs: About 110 mg of SnO_2 NRs was added into 5 ml of DDW to form a suspension solution. Then, $AgNO_3$ (6.2, 12.5, 18.7 and 24.9 mg) and lysine (double molar ratios to $AgNO_3$) were added into the suspension solution, respectively. The mixtures were treated by microwave at 120°C for 15 s with a power of 200 W, then centrifuged and washed by DDW for three times. The corresponding samples are denoted as 5, 10, 15 and 20% Ag-decorated NRs, respectively, according to the molar ratio of Ag to Sn.

2.3. Characterisation and measurement: X-ray diffraction (XRD) patterns of the samples were obtained by using a Rigaku D/max 2550 X-ray diffractometer with a monochromated Cu target radiation source ($\lambda = 1.5045$ Å). The surface morphology and energy-dispersive X-ray spectra (EDS) of the as-prepared samples were investigated by using a Sirion 200 scanning electron microscope (SEM) at an accelerating voltage of 15 kV with gold sputtered on the samples. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded on a JEM-2010 transmission electron microscope under a working voltage of 200 kV. The structure of the sensor is shown in Fig.S1a and b. The gas-sensing properties were measured on a homemade system as shown in Fig.S1c.

3. Results and discussion: As shown in Fig. 1, the diffraction peaks of pure SnO_2 are indexed to tetragonal rutile phase SnO_2 (JCPDS Card No. 41-1445, $a0 = 4.738$ Å and $c0 = 3.188$ Å are marked with inverted filled triangle). No trace of other phases is detected, thus indicating the high purity of the prepared SnO_2. The diffraction peaks of Ag-decorated SnO_2 were indexed to the mixture of tetragonal rutile phase SnO_2 and cubic phase Ag (JCPDS Card No. 87-0717, marked with '+'), which indicated the presence of metallic Ag in the SnO_2 products.

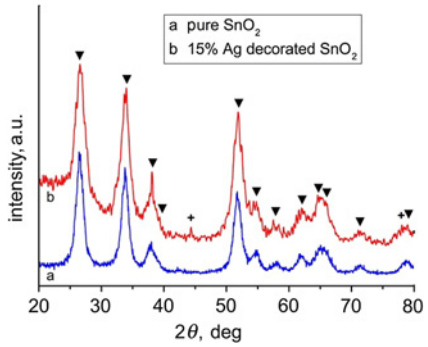

Fig. 1 *XRD patterns of pure SnO_2 and 15% Ag-decorated SnO_2 sample*

As shown in Fig. 2, SnO_2 NRs were clearly obtained with a diameter of 250 nm and a length of 3 μm (Fig. 2*a*). After the Ag decoration, there were small particles (with an average diameter of 40 nm, marked by arrows) on the surface of SnO_2 NRs (Fig. 2*b*). The EDS patterns confirmed the successful decoration of Ag on the surface of SnO_2 NRs (Fig.S2) and the detected content of Ag (17%) was in good agreement with the theoretical value of 15%.

TEM and HRTEM observations were carried out to obtain detailed information about the microstructure and morphology of 15% Ag-decorated SnO_2 NRs. As shown in Fig. 3, the interplanar distance of 0.159 nm agreed well with the crystallographic plane of tetragonal rutile SnO_2 (002). The lattice fringes of 0.144 and 0.123 nm match well with planes of Ag (220) and (311), respectively. It is therefore concluded that Ag NPs were successfully adhered on the surfaces of SnO_2 NRs through the microwave-assisted process in 15 s, which is significantly shorter than those reported by others, at least by several hours [19, 20].

To evaluate the influence of Ag NPs decoration on the gas-sensing properties of SnO_2 NRs sensors, their gas-sensing performance was measured with ethanol as the model gas. As shown in Fig. 4*a*, among all the sensors, 15% Ag-decorated SnO_2 NRs exhibit the highest response to various concentrations of ethanol gas. The enhancement is more obvious in high concentrations, ~1.5 folds for 200 ppm and 2.5 folds for 1000 ppm higher than that of the pure SnO_2. Fig. 4*b* shows the response transients of different gas sensors exposed to 600 ppm ethanol gas at 300°C. The response time and recovery time of the pure SnO_2 and 15% Ag-decorated SnO_2 NRs gas sensors were calculated to be 39 and 45 s, 21 and 28 s, respectively. The response time and recovery time of 15% Ag-decorated SnO_2 NRs gas sensors were 1.8 and 1.6 times shorter than those of the pure SnO_2 gas sensor. Fig. 4*c* shows the response transients of 15% Ag-decorated SnO_2 NRs gas sensor exposed to different concentrations of ethanol gas at 300°C. It is apparent that the responses of the sensor changed rapidly on being exposed to air and to ethanol, indicating the

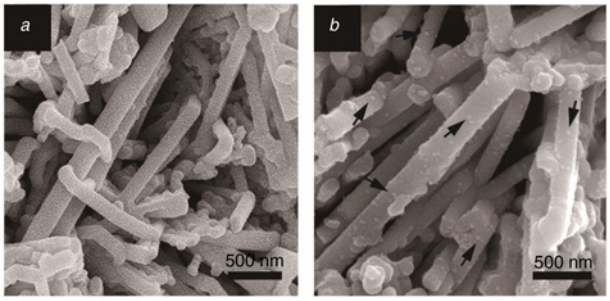

Fig. 2 *SEM images of*
a Pure SnO_2 NRs
b 15% Ag-decorated SnO_2 NRs (Ag NPs as indicated by arrows)

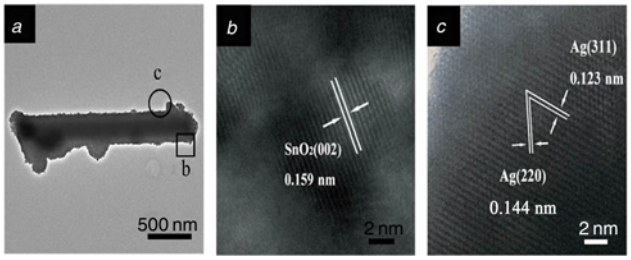

Fig. 3 *TEM image and HRTEM image*
a TEM image of single 15% Ag-decorated SnO_2 NR
b, *c* HRTEM image taken from the squared and circled areas

excellent reproducibility of the sensor. Additionally, to various concentrations of ethanol, the enhanced response of 15% Ag-decorated SnO_2 NRs gas sensor was obvious. The enhancement of gas-sensing response due to Ag NPs decoration can be explained by the chemical sensitisation mechanism: Ag NPs have a high catalytic activity on the dissociation of molecular oxygen, which would accelerate the reactions between ethanol molecules and adsorbed oxygen [21]. Additionally, Ag NPs have large Helmholtz double layer capacitance, which would provide a negative charge layer around the Ag and SnO_2 interface. This negative charge layer could facilitate the dissociative adsorption of oxygen, leading to an enhanced electron charge transfer between ethanol molecule and SnO_2 nanostructures [22]. Fig. 4*d* shows the sensor response versus ethanol concentration in the range of 1–1000 ppm at 300° C. A linear dependence of the responses on ethanol concentrations was observed in the range of 10–1000 ppm, which has rarely been reported by others' works regarding ethanol gas sensing [23, 24]. The inset in Fig. 4*d* shows the linear relationship between the response and the ethanol concentration in the range of 1–50 ppm, which suggest that the as-fabricated gas sensor can be used as a promising candidate for detecting low concentrations of ethanol.

4. Conclusion: In conclusion, by using an environment-friendly and energy-saving microwave method together with comparatively non-toxic reactants, 1D Ag-decorated SnO_2 NRs of 2 μm in length

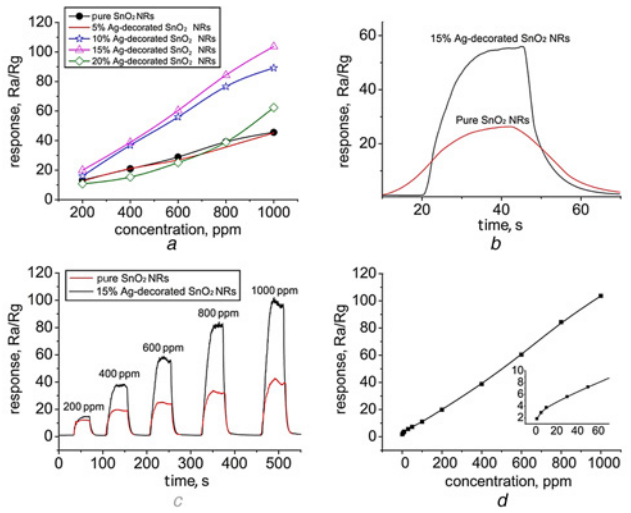

Fig. 4 *Sensor response versus ethanol concentration in the range of 1–1000 ppm at 300°C*
a Responses of different gas sensors as function of ethanol concentration
b Response transients of two gas sensors to 600 ppm ethanol
c Dynamic response of two gas sensors to different ethanol concentrations
d Dependencies of response on ethanol concentration of 15% Ag-decorated NRs sensor, (inset) the linear relationship between the response and the ethanol concentration (1–50 ppm)

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and 250 nm in diameter were greenly synthesised. The decoration of Ag NPs exhibited higher and faster responses to ethanol gas and 15% Ag-decorated gas sensor showed the best performance of approximately two times increased response, 1.8 and 1.6 times of reduced response time and recovery time, respectively. It also showed excellent linearity and a very low detection limit (1 ppm) for ethanol. The results are promising for developing green synthesis of gas-sensing materials with advanced performance and less synthesis-induced pollutions.

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6 References

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