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Solution-processed SnO_2 nanowires for sensitive and fast-response H_2S detection

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ABSTRACT

Solution-processed nanocrystalline semiconductors possess ease of processing, physical flexibility and large area coverage, which are beneficial for developing high performance gas sensors with low cost. Here we reported low-temperature chemiresistive gas sensors based on SnO_2 nanowires that were synthesized and dispersed in solution. The gas sensors were fabricated via a room-temperature spin-coating route and their sensing properties toward H_2S at low temperatures were investigated. The sensors exhibited sensitive response upon H_2S gas exposure at 70 °C with fast response (2 s at 50 ppm) and the response was fully recoverable upon H_2S gas release. The highly sensitive response, combined with the benefit of room-temperature fabrication, make the solution-processed SnO_2 nanowires attractive candidates for the construction of gas sensors.

1. Introduction

As one of the most widely-used materials for gas sensors, tin oxide (SnO_2) is being intensely investigated for developing high-performance gas sensors with low cost [1–5]. It is a wide band gap ($E_g = 3.6$ eV at 300 K) [6,7] semiconductor and the best-understood prototype of oxide-based gas sensors for the detection of various noxious gases especially H_2S [8–13]. Recently, great attention has been focused on the synthesis and applications of one dimensional nanostructured materials such as nanowires, nanobelts, nanorods, and nanotubes [14–17]. One dimensional nanostructures of metal oxides, because of their unique structures and different properties from bulk materials, such as enhanced surface-to-volume ratio and efficient charge transport, have been regarded as the ideal building blocks for gas sensor.

Accordingly, SnO_2 nanowires have been synthesized and studied for H_2S sensing. E. Brunet and co-workers reported H_2S-sensing performance based on SnO_2 nanowires synthesized by spray pyrolysis with subsequent annealing (>500 °C); the sensor could detect H_2S in air at 200 °C with a 1.4 ppm limit of detection [14]. Ramgir et al. investigated the SnO_2 nanowire-based gas sensors fabricated using a thermal evaporation method (900 °C); the sensor showed a fast response kinetics toward 1 ppm H_2S at 150 °C [18]. However, the high temperature required for both SnO_2 nanowires synthesis and H_2S sensor operation remains as a limitation hindering their further development. Compared with high-temperature physical methods [14,18–21], the chemical methods appear to be of particular interest in preparing one dimensional nanostructures because of their facile and controllable synthesis that could be achieved at moderate temperatures. Wang and co-workers demonstrated the synthesis of twisted and branched SnO_2 nanowires with diameters of 1.5–4.5 nm by a solvothermal process at 180 °C [22]. Li and co-workers synthesized SnO_2 nanorods with a diameter of about 5 nm based on the oleylamine-assisted hydrolysis of tin alkoxide in the presence of high content of oleic acid at 180 °C [23]. These colloidal synthesis methods offer low-temperature processing with a powerful degree of freedom to gas sensor.

Here, we are motivated to construct SnO_2 nanowire gas sensors using the solvothermal synthesis method with oleylamine and oleic acid as surfactant. The as-synthesized SnO_2 nanowires were well deposited onto alumina ceramic substrates via a room temperature spin-coating process without further sintering. The SnO_2 nanowires gas sensors exhibited high response sensitivity, fast response and recovery and good repeatability toward H_2S. Their enhanced gas sensing performance at relatively low temperature is encouraging for development of low power consumption gas sensor.

2. Experimental details

2.1. Materials synthesis and sensor fabrication

All chemical reagents were of analytic purity and used directly without any further purification. The SnO_2 nanowires were synthesized by a one-step colloidal method. Firstly, the Sn precursor was prepared by dissolving $SnCl_4 \cdot 5H_2O$ (0.6 g) into oleic acid (OA) (20 mL) and oleylamine (OLA) (2.5 mL) to form a transparent solution mixture. Next, 1.0 mL H_2O and 10 mL ethanol were added with mild stirring at room temperature. The solution was transferred into a 50 mL Teflon-

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lined stainless steel autoclave to react at 180 °C for 3.0 h and then transferred to a cold water bath for cooling down to room temperature. The products were separated by adding 80 mL of ethanol and centrifuging at 6000 rpm for 5 min. Then the precipitate was washed twice by redispersing in toluene, addition of ethanol, and centrifugation. The final product was well dispersed in toluene at a concentration of 20 mg mL^{-1}. The SnO_2 nanowires were observed using a high-resolution transmission electron microscopy (HR-TEM) on a TEM system (JEOL, Model JEOL-2100), using an accelerating voltage of 200 kV.

Based on the as-prepared solution-processed SnO_2 nanowires, thin film sensors were prepared by the layer-by-layer spin-coating deposition technique with a ligand exchange treatment [24,25]. Typically, 60 μL SnO_2 nanowire solution (20 mg mL^{-1}) was deposited dropwise onto the Al_2O_3 substrates pre-patterned with interdigital Ag electrodes and then spun at 1250 rpm for 20 s; this step was repeated twice. Next, three drops of 10 mg mL^{-1} $Cu(NO_3)_2$ in methanol was added dropwise to the substrates, and spun at 1250 rpm for 20 s after a 45 s wait; the $Cu(NO_3)_2$ treatment was repeated twice. Finally, methanol was used to wash the film and then spun dry three times. The film mophology was characterized using scanning electron microscopy (SEM) images (FEI Model Sirion 200 microscope). Fourier transform infrared (FTIR) spectroscopy analysis was conducted with VERTEX 70 (Bruker, Germany) on quartz glass. X-ray photoelectron spectroscopy (XPS) measurements were performed with a VG Multilab 2000 system with Al source; all of the binding energies were referenced to the C 1s peak at 284.6 eV of the surface adventitious carbon.

2.2. Gas-sensing measurements

The gas sensors were tested by a commercial computer-connected source meter system (Model Keithley 2450, Keithley Instruments, USA) under static conditions. When the resistances of the sensors were stable, target gas was injected into the test chamber (3.0 L in volume) by the static gas distributing system. As the sensor resistances reached new equilibrium, the gas was released to recover the sensors in air. The sensor response was defined as the ratio of R_a to R_g, where R_a is the sensor resistance in air (base resistance) and R_g is sensor resistance in target gas. Response time (T_{90}) and recovery time (T_{10}) are defined as the time needed for the sensor to reach 90% of the final resistance value upon target gas exposure and decrease to 10% of the stabilized response in the target gas when placed in clean air, respectively.

3. Results and discussion

3.1. Structure and morphology

The structure and morphology of the SnO_2 nanowires were investigated by TEM and HRTEM. The TEM morphology (Fig. 1a) indicated that the obtained product consisted of large quantities of worm-like wire structures. The HRTEM image shown in Fig. 1b suggested that the average diameter of the SnO_2 nanowires were 3.5 nm which exhibited a high degree crystallinity; the lattice of 0.334 nm and 0.267 nm correspond to the (110) and (101) planes of rutile SnO_2, respectively. Fig. 1c illustrated the evolution of the morphology from SnO_2 dots to ultrathin nanowires over time. The formation of SnO_2 nanowires can be described as an oriented attachment, in which OA and OLA served as surface-selective ligands capping the Sn ions. At the early stage, small-sized SnO_2 dots were formed; with the help of OA and OLA, the dots intend to attach to each other, forming dots attachments or strings. As the reaction continued, annealing and welding of the attached nanocrystals take place, forming long, twisted and branched ultrathin SnO_2 nanowires [22].

3.2. Gas-sensing properties

The as-synthesized SnO_2 nanowires were capped with abundent oleic acid and oleylamine, which enable the solution disperibility and processability [25,26]. The SnO_2 nanowires can be easily deposited into thin films from solution using spin-coating method. However, the long carbon chains of OA and OLA capping on SnO_2 nanowires might hinder both the gas adsorption and carrier transport in the sensor device [25,26,27,28]. Therefore, we conducted a surface ligand exchange treatment to remove most oleic acid and oleylamine. Varieties of inorganic salts ($AgNO_3$, $Cu(NO_3)_2$, $CuCl_2$, $ZnCl_2$, WCl_6, NH_4Cl, typically 10 mg mL^{-1} in absolute methanol) were employed for comparison. As shown in Fig. 2, the response of the as-deposited SnO_2 films (black curve) without ligand exchange treatment was negligible as expected. Among the inorganic salts we employed in this study, $ZnCl_2$, WCl_6, and NH_4Cl-treated sensors had weak response toward H_2S. Although

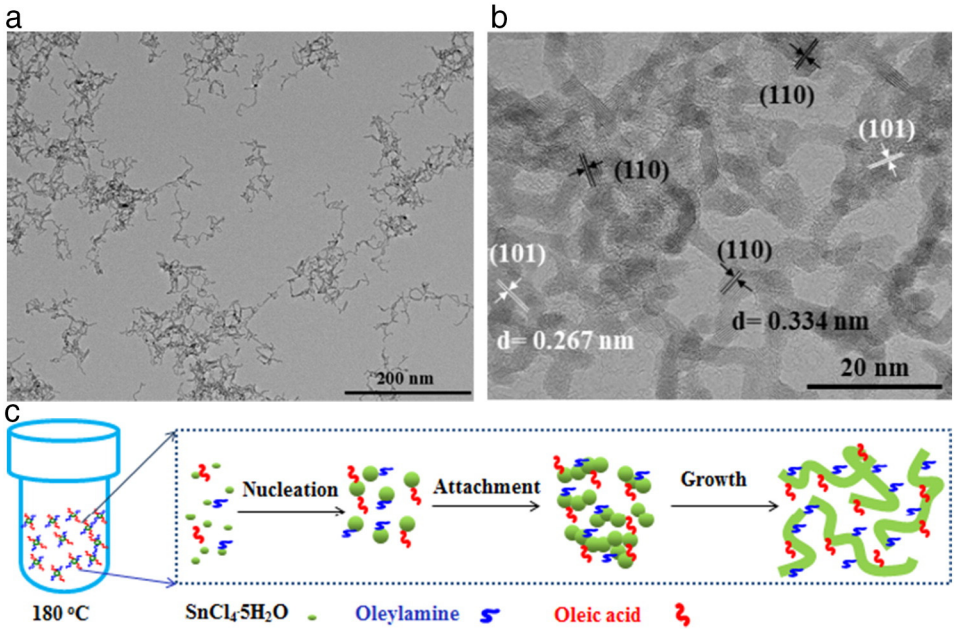

Fig. 1. a) TEM and b) HRTEM image of SnO_2 nanowires and c) schematic illustration of the evolution of the SnO_2 morphology from dots to nanowires.

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