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In_2O_3 and NiO/In_2O_3 Hybrid Nanoicicles for Enhanced NO_2 Gas Sensing at Room Temperature and High Humidity

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Abstract

Single-crystalline In_2O_3 nanoicicles have been synthesized via a thermal vapor-transport route. Growth of the In_2O_3 nanoicicles depends critically on temperature at which oxygen was introduced as well as the indium vapor pressure involved in the synthesis. An aggregated assembly of In_2O_3 nanorods with pyramids at one end first forms, which then evolves into a tapered needle-like geometry as the isothermal time lengthens. Gas-sensing properties of the nanoicicles have been examined against oxidizing NO_2 and reducing H_2S gases, respectively, over a range of aspect ratios of the nanoicicles, working temperatures and humidity levels. The In_2O_3 nanoicicles are then functionalized with NiO nanoparticles. A pronouncedly enhanced sensing response toward NO_2 gas has been found for the NiO/In_2O_3 hybrid nanoicicles at a relatively low working temperature (100 ^oC) and even at room temperature of high relative humidity (80% RH). For the first time, the NiO/In_2O_3 hybrid nanoicicles present a virtually identical room-temperature sensing response of 1.8 against 3 ppm NO_2 over a wide humidity range (4-80% RH); more importantly, the hybrids also show a sensing response of 25 times higher for the oxidizing NO_2 gas than for the reducing H_2S gas. This is attributable to a) the energy-band bending at the p-n heterojunction and b) the augmented effect on electron-depletion width at bridging junctions of neighboring nanoicicles across the sensor electrodes, due exclusively to the narrowing In_2O_3 diameter toward the tip.

Key words: In_2O_3, NiO, nanowire, gas sensor, humidity

Introduction

Chemiresistor-type metal-oxide-semiconductor (MOS) one-dimensional (1D) nanosensors are attractive in practice since sensitive detection of hazardous gases in harsh environments can be implemented by a simple measure of electrical resistance in response to the change of nearby chemical atmospheres. In view of the literature, indium oxide (In_2O_3) 1D nanostructures have demonstrated promising room-temperature (RT) sensing characteristics toward a wide range of toxic or flammable gases among many MOS counterparts being investigated [1,2]. Nonetheless, presence of atmospheric moisture tends to interact favorably with the In_2O_3 surface and interfere facilely with target gases so that deteriorated sensitivity and stability often result [3]. To resolve this, we have prepared 1D n-type semiconducting In_2O_3 nanostructures with well-defined, un-bundled nanoicicle geometry for room-temperature gas sensors. Decoration of p-type semiconducting NiO nanoparticles on the nanoicicles has been implemented to form hierarchical hybrid architecture with distinguished RT sensing properties when wet air was used as the carrier gas.

Results and Conclusions

Fig. 1 shows In_2O_3 nanoicicles with a well-defined tapered geometry when oxygen was introduced at 900 ^oC. The nanoicicles with a good crystallinity of cubic (bixbyite) structure (JCPDS no. 6-416) were uniformly grown on the initially gold-covered substrate and were unbundled without any noticeable aggregation.

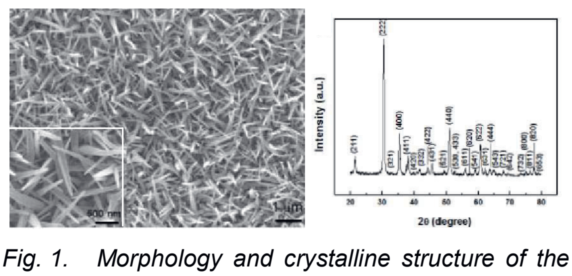

Fig. 1. Morphology and crystalline structure of the pristine In_2O_3 nanoicicles.

Gas-sensing sensitivity of the In_2O_3 nanoicicles against 10 ppm NO_2 in dry air (relative humidity (RH) of 4%) appears to show a maximum at an aspect ratio of about 11 in Fig. 2. An optimal junction density between the neighboring nanoicicles appears critically important to the sensing response of the nanosensor; at which, the electron flow across the electrodes would be much hampered by the augmented electron-depletion width at the contacting junctions when the nanoicicles were exposed to the electron-withdrawing NO_2 gas.

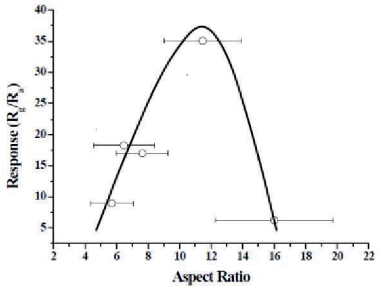

Fig. 2. Sensing response of the pristine In_2O_3 nanoicicles against 10 ppm NO_2 gas at 100 °C and 4% RH when the aspect ratio of nanoicicles was varied.

Fig. 3a shows microstructure of the NiO/In_2O_3 hybrid nanoicicles; of which, pearl-like NiO nanoparticles with a diameter about 5 to 10 nm have been decorated on surface of the In_2O_3 nanoicicles uniformly. The NiO particles appear to adhere adhesively on the In_2O_3 at the interface, as shown in the inset of Fig. 3b.

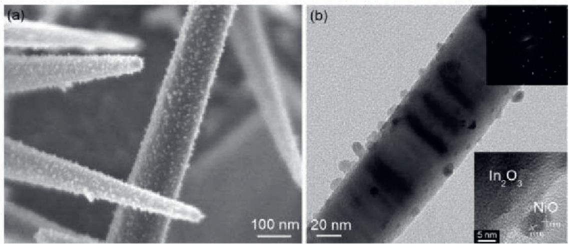

Fig. 3. (a) FE-SEM and (b) HR-TEM images of the NiO/In_2O_3 hybrid nanoicicles. The insets of (b) show a selected area diffraction and an enlarged view at the NiO- In_2O_3 interface, respectively.

Fig. 4a shows that the NiO/In_2O_3 hybrid nanoicicles present an enhanced sensitivity against 30 ppm NO_2 in dry air (4% RH) when compared to the pristine In_2O_3 counterpart. The maximum sensing response occurs at about 100 °C. The hybrid nanoicicles also show a high sensitivity when wet air (80% RH) was used as the carrier gas for NO_2. As shown in Fig. 4b, the hybrids present RT sensing responses of 4.5, 2.3, and 1.8 against 30, 15, and 3 ppm NO_2 at 80% RH, respectively, which are virtually identical to that of 4% RH counterpart. A substantially longer desorption time is yet required than that for the gas adsorption at RT. In addition, the hybrids show a selective sensing of 25 times higher for the oxidizing NO_2 gas than for the reducing H_2S gas (Fig. 4c). This is attributable to the energy-band bending at the p-n heterojunction and the augmented electron-depletion width at the bridging junction of neighboring nanoicicles across the sensor electrodes, due exclusively to the narrowing In_2O_3 diameter toward the tip.

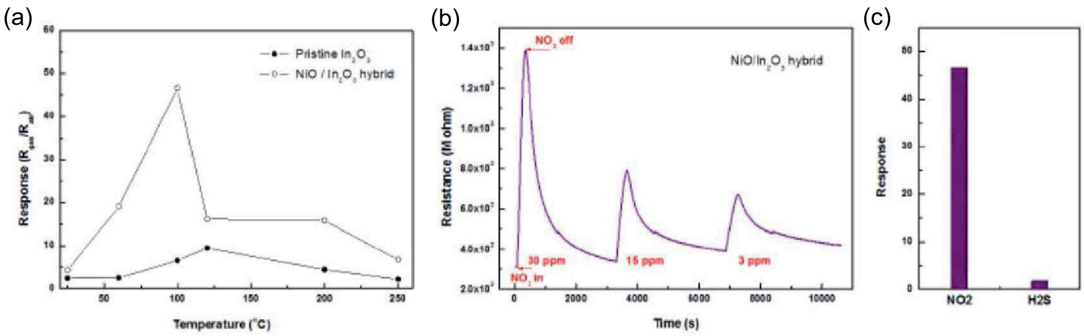

Fig.4. (a) A summary of gas-sensing response of the pristine In_2O_3 and the NiO/In_2O_3 hybrid nanoicicles toward 30 ppm NO_2 at a low relative humidity (4% RH) over a temperature range from RT to 250 °C. (b) Dynamic NO_2 sensing properties of the NiO/In_2O_3 hybrid nanoicicles at RT with a high relative humidity (80% RH). (c) Selective sensitivity of the NiO/In_2O_3 hybrid nanoicicles against 30 ppm NO_2 and 28 ppm H_2S at 100 °C, respectively.

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