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Research Article

CuO-In_2O_3 Core-Shell Nanowire Based Chemical Gas Sensors

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The CuO-In_2O_3 core-shell nanowire was fabricated by a two-step method. The CuO nanowire core (NWs) was firstly grown by the conventional thermal oxidation of Cu meshes at 500°C for 5 hours. Then, the CuO nanowires were immersed into the suspension of amorphous indium hydroxide deposited from the $In(AC)_3$ solution by ammonia. The CuO nanowires coated with $In(OH)_3$ were subsequently heated at 600°C to form the crystalline CuO-In_2O_3 core-shell structure, with In_2O_3 nanocrystals uniformly anchored on the CuO nanowires. The gas sensing properties of the formed CuO-In_2O_3 core-shell nanowires were investigated by various reducing gases such as hydrogen, carbon monoxide, and propane at elevated temperature. The sensors using the CuO-In_2O_3 nanowires show improved sensing performance to hydrogen and propane but a suppressed response to carbon monoxide, which could be attributed to the enhanced catalytic properties of CuO with the coated porous In_2O_3 shell and the p-n junction formed at the core-shell interface.

1. Introduction

There is an increasing demand for highly sensitive gas detecting devices in abundant applications ranging from daily life devices to industrial process control. Metal oxide based gas sensors, which rely on change of electrical conductance due to the interaction with the surrounding gas, have been extensively investigated in the past decades [1, 2]. An efficient strategy to improve sensor performance is to adopt the nanostructured sensing materials that have a high surface area to volume ratio and thus a strong interaction happens between the surrounding gas and the material [3–6]. Semiconductor gas sensors show a resistance change upon exposure to toxic and dangerous gases [7, 8]. Among various types of the nanostructured sensing materials, one-dimensional (1D) nanowires (NWs) with high surface area/volume ratio and less agglomerated configuration are advantageous to accomplish high gas sensitivity and rapid response speed [9–11].

Cupric oxide (CuO), with a bandgap of 1.0–1.9 eV, is intrinsically a p-type semiconductor mainly due to the Cu vacancies [12]. Copper oxide nanowires have been extensively studied for gas sensing in recent years. CuO nanowires exhibited good response to reducing gases, making it promising to be developed for an efficient gas sensor [13]. CuO nanowires had been synthesized by various methods such as wet chemical methods [14, 15], templating methods [16, 17], electrospinning [18], or thermal oxidation of copper [19–22]. Chen et al. demonstrated a H_2S sensor using the vertically aligned CuO nanowire. The sensor showed a good selectivity to H_2S compared with the responses to H_2, CO, and NH_3 [23]. Li et al. also reported that CuO NWs based sensor showed high sensitivities to H_2S and the nanowires were synthesized by a template-assisted electrodeposition method [24]. Wang et al. prepared high quality single-crystal CuO nanowire arrays by the thermal oxidation of copper slices. Then the surfaces of CuO nanowires were modified by magnetron-sputtered ZnO nanoparticles. This composite structure effectively enhanced the selectivity of CuO nanowire gas sensor for detection of CO [25].

In this work, we report the sensing properties of the In_2O_3 nanoisland decorated CuO NWs to different reducing gases.

The In_2O_3 nanoisland decorated CuO NWs were prepared by a two-step method: thermal-oxidation followed with dip-coating and calcination. The gas sensing properties of CuO-In_2O_3 composite nanowire based sensor have not yet been studied to our best knowledge. An enhancement in the gas sensing properties was observed in accordance with the p-n junction created between these two nanomaterials.

2. Experimental

2.1. Preparation of CuO-In_2O_3 Core-Shell Nanowire. Firstly, the pure CuO nanowires were prepared by the conventional thermal oxidation of copper following the procedures described in literature [19]. The pure copper meshes (thickness: 0.5 mm, diameter: 3 mm and pore diameter: 100 μm, and purity of 99.998%) were polished with sandpaper to remove the oxide layer of the surface and then the copper was washed in ethanol for 5 min by ultrasonic treatment to remove the possible contaminated grease. Finally, they were rinsed using deionized water and dried naturally in oven at room temperature.

The cleaned copper meshes were placed in a quartz boat and heated in a tube furnace in air. The heating-up step was ramped at a speed of 4°C/min until the temperature reached 500°C and then the temperature was constant at 500°C for 5 hours that was found to be optimum for achieving the high quality nanowires. Then the temperature was cooled down also at a ramping speed of 4°C/min.

The CuO-In_2O_3 composite nanowire sensor was prepared by dip-coating method followed by a thermal decomposition as described in Figure 1. 1 mol/L indium acetate aqueous solution and 3 mol/L of ammonia solution were mixed together according to a ratio of 1 : 1 by volume to obtain the milky indium hydroxide suspension. One drop (about 0.5 mL) of as-prepared indium hydroxide milky suspension was then injected by syringe onto the surface of the CuO nanowire fabricated earlier. Then, these coated CuO nanowires were placed in oven to make them fully dry and subsequently were heated at 600°C for 5 hours to obtain the CuO-In_2O_3 core-shell nanowires.

The surface morphology of the two samples was analyzed using scanning electron microscope equipped with an energy dispersed X-ray spectroscopy (SEM-EDX, FEI, USA). EDX spectrum was used to examine the elemental composition of the core-shell nanowires.

2.2. Sensor Fabrication and Measurements. The whole mesh with the obtained CuO-In_2O_3 core-shell nanostructure on top surface was placed onto a commercial interdigitated gold electrode with the alumina as the substrate. Then a clean alumina brick was put on the top of the mesh to ensure a good contact between the nanowires and the gold electrodes as shown in Figure 2.

The sensing measurements were conducted in a conventional gas flow apparatus. The electrical resistance of the sensors was measured by a computer controlled Agilent multimeter (100 M, Agilent 34405A). During the electrical measurement, commercially supplied certified gases containing 1500 ppm of CO, C_3H_8 and 4 vol% H_2 in nitrogen, and pure oxygen were diluted by nitrogen, respectively, to obtain different concentrations of the test gases in various oxygen backgrounds. The total gas flow rate was maintained at 250 sccm/min and the flow rate of different gases was controlled independently using computer controlled, precalibrated, electronic mass flow controllers (D07-19B, Beijing Senvenstar Electronics, China). The sensitivity (S) of a gas sensor is calculated as follows:

$$S = \frac{R_a - R_g}{R_g} * 100\%, \quad (1)$$

where R_a and R_g are resistance of a sensor in air and in detected gas, respectively.

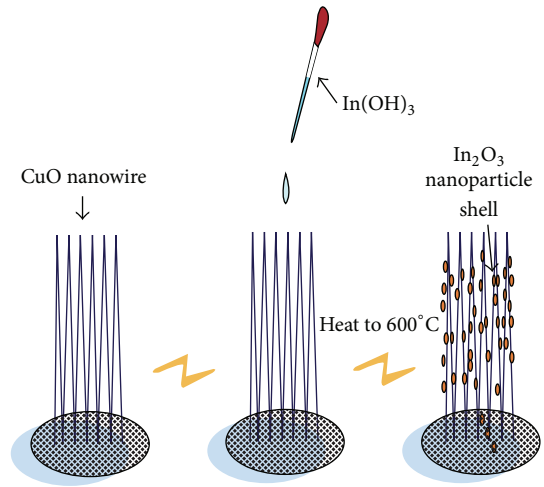

Figure 1: The procedures for making the CuO-In_2O_3 core shell nanowires.

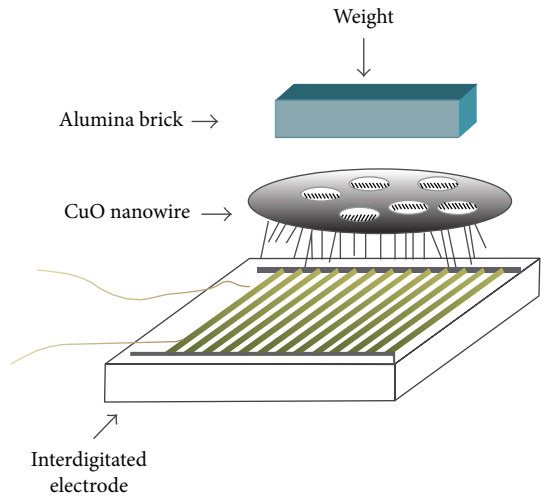

Figure 2: Schematic view of the sensor using the CuO-based nanowires. The alumina tile was used to make a good contact between the nanowire arrays with the gold electrodes.

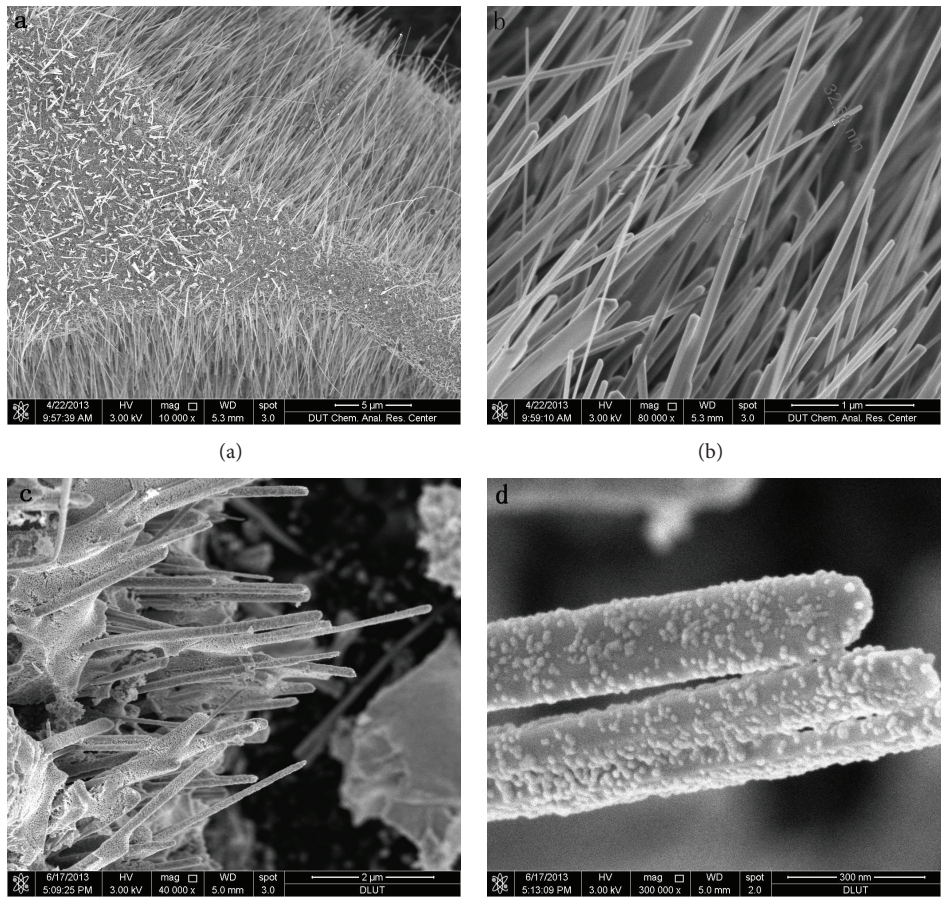

Figure 3: SEM images of ((a)-(b)) pure CuO nanowires and ((c)-(d)) CuO-In_2O_3 core-shell nanowires with different magnifications.

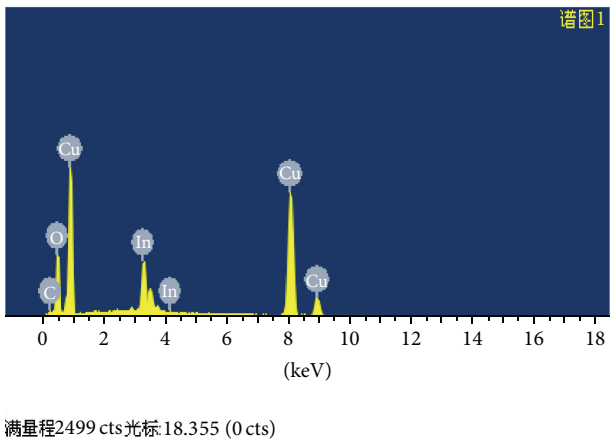

Figure 4: Elemental analysis of the CuO-In_2O_3 core-shell nanowire by EDX.

Table 1: Summary of elemental composition of CuO-In_2O_3 analyzed in Figure 5. (C^* residuals might be from the background or in the sample.)

Chemical elements	Weight percentage	Atom percentage
C^*	2.85	9.33
O	18.67	45.90
Cu	64.67	40.04
In	13.81	4.73
Sum	100.00	100

3. Results and Discussion

3.1. Nanowires Synthesis and Microstructure Characterizations. Figures 3(a) and 3(b) show the overall view of the microstructure of the CuO grown on the top of the copper meshes. The copper oxide nanowires protruded almost vertically from the copper substrate. The direct vapor-solid (VS) mechanism had been proposed to explain the growth mechanism in which the cupric oxide was formed initially and served as the precursor for further being oxidized to CuO by maintaining enough oxide vapor pressure at a temperature above 400°C [19]. As observed in Figure 3(b), the as-prepared CuO nanowires have a length ranging from a few microns to 40 μm and a diameter of about 100 nm.

Figures 3(c) and 3(d) show the SEM images of the CuO-In_2O_3 composite nanowires. X-ray energy spectrum of the CuO-In_2O_3 core-shell nanowires (see Figure 4 and Table 1) confirmed the existence of indium oxide. Therefore, during

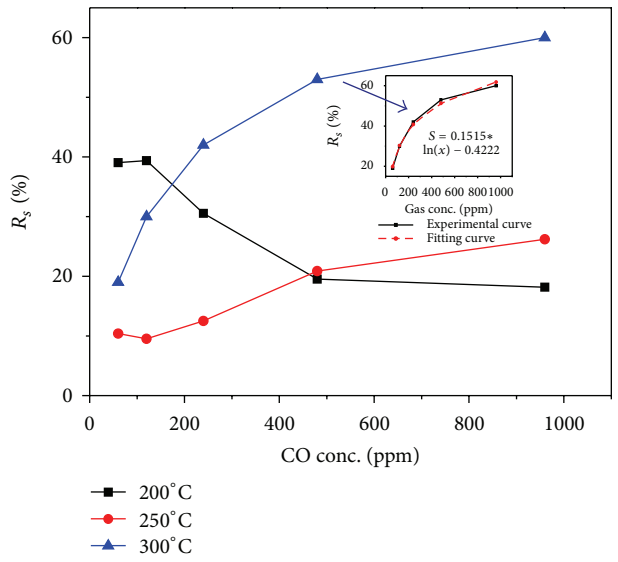

Figure 5: Sensitivity of pure CuO nanowires based gas sensor to carbon monoxide at different temperatures. Inset is the fitting results for the curve at 300°C.

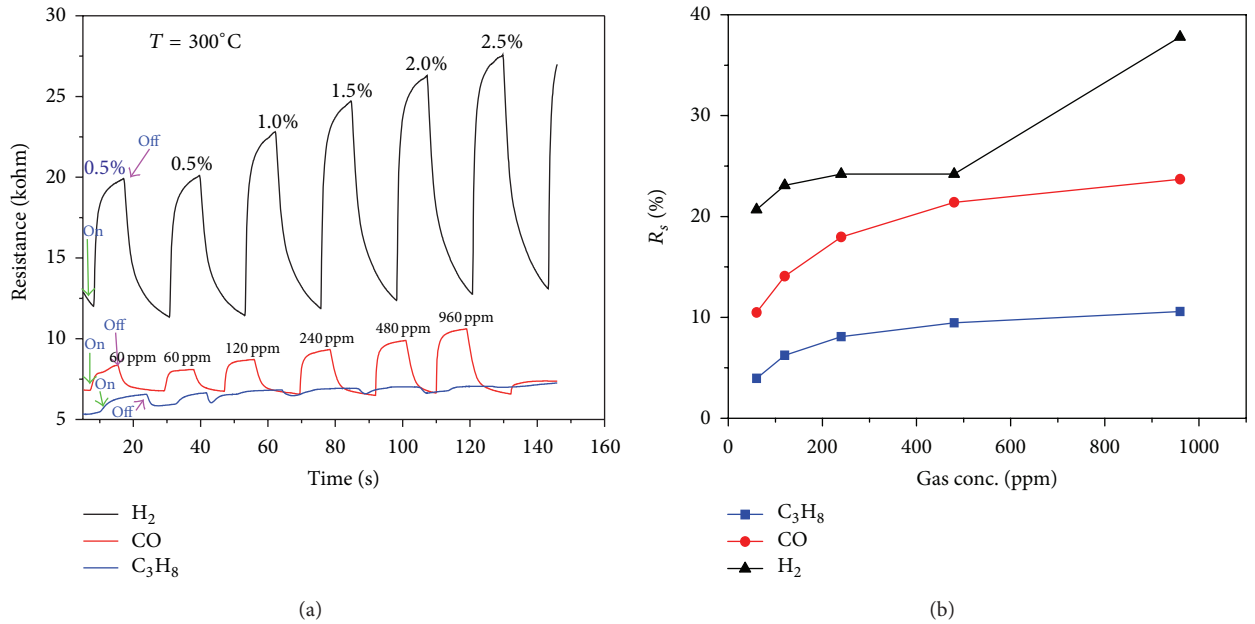

Figure 6: (a) Response curve and (b) sensitivity plot of CuO nanowires based sensor to H_2, C_3H_8, and CO at 300°C.

the synthesis, the $In(OAc)_3$ which has a higher decomposition point (800°C) could be converted to the milky, amorphous indium hydroxide with lower decomposition point (600°C) according to

$$In(OAc)_3 + 3NH_3 + 3H_2O \longrightarrow In(OH)_3 + 3NH_4OAc \quad (2)$$

This amorphous indium oxide would be expected to uniformly adhere to the surface of CuO nanowire during the dip-coating and subsequently was heat-treated at 600°C to be transformed into the oxide according to the reaction:

$$2\,In(OH)_3 \longrightarrow In_2O_3 + 3H_2O \quad (3)$$

As shown in Figures 3(c) and 3(d), after the thermal treatment, the CuO nanowire core remained leading to a successful formation of the CuO-In_2O_3 micro-p-n heterojunction.

3.2. Sensing Properties. For a metal oxide semiconductor-type gas sensor, the sensing mechanism is involved with the catalytical combustion of the reducing gases with the preadsorbed oxygen on the oxide surface. The form of the adsorbed oxygen on oxide is dependent upon the operating temperature. At elevated temperatures above 200°C, the preadsorbed oxygen at the surface of the oxide would extract electrons from the surface layer (known as Debye layer)

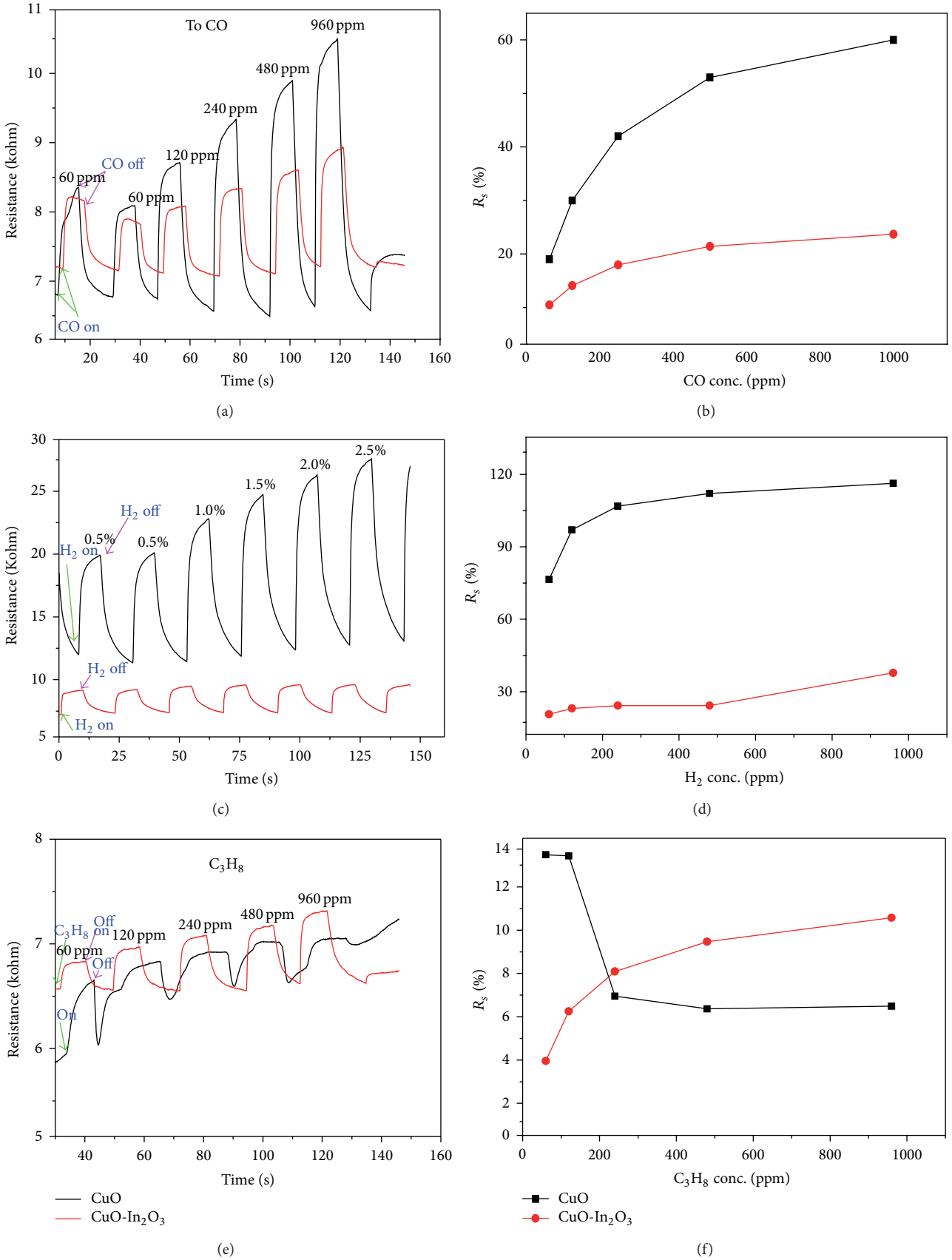

FIGURE 7: Comparison of response and sensitivity of CuO and CuO-In_2O_3 composite nanowire gas sensor to different gases at 300°C. ((a)-(b)) CO; ((c)-(d)) H_2; ((e)-(f)); C_3H_8.

usually forming O^{2-}. Therefore, the reaction below could occur during the sensing process:

$$CO + O^{2-} = CO_2 + e^- \quad (4)$$

$$2H_2 + O^{2-} = 2H_2O + 2e^- \quad (5)$$

$$C_3H_8 + 5O^{2-} = 3CO_2 + 4H_2O + 10e^- \quad (6)$$

The released electrons would then go back to the surface conduction band of the oxide leading to the change of the resistance. This forms the basics of such type of gas sensors. For a p-type sensing oxide, the hole would be neutralized with the released electrons from the desorbed oxygen ions leading to an increase in the resistance while for an n-type oxide the resistance would decrease due to the increased electron concentrations.

Figure 5 indicates the sensitivity of CuO nanowires gas sensor to carbon monoxide within a concentration range from 60 ppm to 1100 ppm at three temperatures: 200°C, 250°C, and 300°C. The sensitivity of the sensor to CO was largest at 300°C. The sensitivity at 300°C has a relationship with the CO concentrations according to the following equation (also see inset of figure):

$$S = 0.1515 * \ln(x) - 0.4222 \quad (\text{the unit of } x \text{ is ppm}). \quad (7)$$

Figure 6 shows a comparison of the response curve and sensitivity plot of the CuO nanowire based sensor to CO and propane at 300°C. The response time and recovery time of the sensor to CO are approximately 25 s and 65 s, respectively. The sensor showed a higher sensitivity relative to that to propane as shown in Figure 6(b).

Figures 7(a)–7(f) show the response of the CuO-In_2O_3 core-shell p-n junction nanowire based sensor to different reducing gases such as CO, hydrogen, and propane at 300°C. The response of the pure CuO based sensor was shown for the comparisons. Figures 7(a) and 7(b) show that, with the decoration of the n-type In_2O_3 nanoparticles, the resistance of the core-shell nanowire increased in presence of the reducing gases still showing a p-type conduction. This indicated that the gas sensing properties were still dominated by the CuO nanowire.

As shown in Figures 7(a) and 7(b), the sensitivity of the CuO-In_2O_3 based sensor to CO and H_2 at 300°C decreased relative to that shown by the pure CuO based sensor. However, as shown in Figures 7(c)–7(f), the sensitivity of the CuO-In_2O_3 composite based sensor to propane was significantly enhanced. More obviously, the response time of the CuO-In_2O_3 composite nanowire gas sensor to propane is significantly shortened: only about 12 s.

The copper oxide has been reported to be doped with different metal nanomaterials (oxide) to form a donor-type or acceptor-type level to improve its gas sensing performance, increasing its sensitivity or selectivity [26–28]. p-n junction has also been adopted in literature to particularly enhance the sensitivity of the gas sensors by using the difference in the opposite response of the p and n sensing materials to reducing gases [26–28]. Therefore, the enhanced sensitivity of the CuO-In_2O_3 based sensor to propane could be attributed to p-n microheterojunction in which the oxygen adsorption was enhanced, thus enhancing reactions (5)-(6) and releasing more electrons during sensing process as suggested in the literature. However, the decrease in the sensitivity to CO and hydrogen also indicated that the catalytic role played by the In_2O_3 nanoparticles could be responsible [26–28]. The coated In_2O_3 seems to be suppressing the catalytic oxidation of CO and hydrogen with oxygen (reactions (4)-(5)) at the surface of CuO. However, the reasons are still not certain and need more investigations.

4. Conclusion

The CuO-In_2O_3 core-shell nanowire was prepared using a two-step assembly method: thermal oxidation of Cu meshes to form the CuO nanowire core followed with a dip-coating method forming the In_2O_3 nanoparticle shell on the surface of CuO. The semiconductor-type sensor using the CuO-In_2O_3 core-shell nanowires showed an enhanced response to hydrogen and propane which could be attributed to the enhanced adsorption of oxygen induced by the p-n microheterojunction while a suppressed response to CO was also observed which could be due to the fact that the catalytic properties of CuO core to CO were reduced by the decorated In_2O_3 nanoparticle shell.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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