CuO/ZnO Heterostructured Nanorods: Photochemical Synthesis and the Mechanism of H2S Gas Sensing

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ABSTRACT: This study reports on the structural properties of CuO/ZnO nanorods and the mechanism by which bundles of these nanorods are able to sense H2S gas. The CuO/ZnO nanorods were prepared by deposition of CuO nanostructures on the hydrothermally grown ZnO nanorods using a photochemical method. Scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to confirm that the heterogeneous nanostructure of the CuO/ZnO nanorods was highly crystalline. The H2S gas sensing properties of CuO/ZnO nanorod bundles was evaluated in air containing dilute H2S gas at sensing temperatures (Ts) ≤ 500 °C. The response of CuO/ZnO nanorod sensors to H2S gas was enhanced compared to that of bare ZnO nanorods. The heterostructured nanorods showed an exponential increase in sensing tendency with Ts. X-ray photoelectron spectroscopy analysis results indicated that the enhanced response of CuO/ZnO nanorod sensors is due to the chemical conversion of CuO into CuS upon H2S exposure, which acts as an electrical gate in the CuO/ZnO sensor.

1. INTRODUCTION
One-dimensional (1D) nanostructured materials with chemoresistance, such as SnO2, WO3, ZnO, and V2O5, have shown good sensing properties including speedy response and recovery.1−5 Among these 1D semiconducting materials, ZnO, a wide band gap material (3.37 eV) with a wurzite crystal structure, has been studied for gas sensing applications. Various gases have been tested for ZnO nanowire/nanorod sensor studies including ethanol, acetone, nitric oxide, ammonia, and hydrogen.6−11 Primarily known for its presence in air pollution as a toxic gas, H2S is an important target molecule for ZnO gas sensors and for most of other metal oxide sensors.

Recently, to improve the gas sensing properties of ZnO, various materials have been employed to modify its surface properties. For example, the application of noble metal elements (Pt, Pd, Ag, Au, etc.) onto the surface of a metal oxide is a widely accepted technique for enhancing the interaction of reducing gases with the adsorbed oxygen on the metal oxide surface.11−16 The deposited noble metal provides preferred adsorption and activation sites for the target analyte, from which activated fragments are spilled over onto the semiconductor and react with the ionosorbed oxygen. Aside from noble metals, metal oxides also have been used to make heterostructures with sensing nanomaterials. Metal oxide composites can provide electric junction properties at the interface of heterostructures. Among the many surface doping materials, CuO, a p-type semiconducting material with an energy band gap of 1.2 eV, can be used in a range of applications including solar energy devices, electronics, sensors, magnetic storage media, batteries, and catalysis.17−25 In the application of CuO for gas sensors, two types of sensing behaviors of CuO have been reported: adsorption-induced surface depletion and chemical conversion with a change in the electrical potential. Although data on gas sensing of several gases using CuO/metal-oxide heterostructured materials have been reported,26 little data are available pertaining to H2S sensing using CuO/ZnO heterostructured nanorods. Additionally, the basic surface reaction underlying the sensing mechanism of CuO/ZnO is not fully understood.

For the first time, we report the H2S sensing properties of CuO/ZnO heterostructured nanorods and the mechanism of these materials. Our heterostructured CuO/ZnO NRs showed much enhanced gas response compared to bare ZnO NRs. Current study elucidates the role of CuO on ZnO for H2S gas sensing and investigates the effects of CuO coverage of CuO/ZnO NRs on H2S gas responses. We believe this new finding and mechanism study of CuO/ZnO heterstructured NRs present important results in the points of novel sensing material and mechanism study applicable to other heterostructure nanomaterials. The CuO/ZnO heterostructured nanorods were synthesized by photochemical deposition of CuO onto hydrothermally grown ZnO nanorods. The morphology of CuO/ZnO heterostructured nanorods was controlled by modulation of various growth conditions and evaluated by SEM, XRD, TEM, EELS (electron energy loss spectroscopy),
and XPS. The H$_2$S gas sensing mechanism of CuO/ZnO nanorods was investigated using XPS analysis at various $T_S$. The exponential increase of gas response with $T_S$ was observed for the CuO/ZnO sensor, similar to bare ZnO. When CuO/ZnO nanorods are exposed to H$_2$S exposure, chemical conversion of CuO into metallic Cu$_2$S was observed. From these results, we propose an electrical gating model as the sensing mechanism, in which the chemical conversion of CuO into CuS destroys the p/n junction of CuO/ZnO. In addition, we have found the optimum coverage of CuO nanoparticles onto ZnO nanorods to gain the maximum gas response.

2. EXPERIMENTAL SECTION

Synthesis of CuO/ZnO Heterostructured Nanorods Bundle Powder. ZnO nanorods (powder) were synthesized using a hydrothermal reaction. A precursor solution was prepared using zinc chloride (ZnCl$_2$, 98+%, Acros organics), ammonium hydroxide (NH$_4$OH, 28 wt % NH$_3$ in H$_2$O, SIGMA-Aldrich) and deionized water (D.I. water). The dispersion was heated to 150 °C with constant stirring (at approximately 300 rpm) in a 120-mL Teflon autoclave for 4 h. The details of the experimental synthesis method for preparing ZnO nanorod bundles were described in a previous report.27 For the photochemical coating process of CuO, 50 mg of ZnO nanorods (powder) was dispersed in 100 mL of D.I. water by sonication for several minutes. Two milliliters of the dispersion were mixed into an aqueous solution of Cu-(NO$_3$)$_2$·3H$_2$O (98%, Aldrich) at various concentrations (0.025–1 mM). The total volume of Cu salt precursor with ZnO nanorods was 10 mL. After mixing the precursor, it was UV-irradiated (ca. 312 nm, UVITEC, LF-215LM) for 5 min ~2 h. The starting temperature of the photochemical process was room temperature and the working temperature rose to 35 °C during 2 h of UV irradiation. The color of the ZnO mixed precursor was converted from white to brown after UV irradiation and the precipitate was separated from the products by centrifugation. The CuO/ZnO heterostructured nanorods bundle powder was washed in D.I. water. Between washings, the product was centrifuged to increase yield.

Fabrication of ZnO and CuO/ZnO Nanorod Gas Sensors. ZnO nanorods and CuO/ZnO heterostructured nanorods were fabricated on quartz using a simple fabrication procedure [Scheme S1, Supporting Information]. Two Ti/Au electrodes (0.7 × 0.4 cm) were deposited 1 mm apart on a 2 × 1 cm quartz substrate. First, to strengthen adhesion between the Au electrode and quartz, a Ti buffer film of 75-nm thickness was deposited onto the quartz substrate (JNC, China) by thermal evaporation. Then, Au electrodes (∼300 nm thick) were deposited by the same method on the Ti thin film. After electrode deposition, to maintain the concentrations of ZnO nanorods and CuO/ZnO nanorods during deposition, 5 mg of dried ZnO and CuO/ZnO powders were sonicated in 10 mL of D.I. water for 20 min. A droplet of well-dispersed nanorod bundles in D.I. water was placed between the electrodes and dried at 95 °C for 20 min. The droplet coating was repeated 10 times; then, annealing was performed at 500 °C to ensure that the electrodes had established good contacts. The electrodes were electrically connected with 0.3 mm diameter Au wires using Ag paste (CANS P-100). The Ag paste on the sensor was dried at 95 °C for 1 day to maintain good adhesion between the electrodes and the tips of Au wires. The other tips of the Au wires were linked with Pt wires, which were connected to an electrical measuring instrument.

Analysis Techniques. The sample morphology and crystal structure of the CuO/ZnO heterostructured nanorod bundles were observed using field-emission scanning electron micros-
copy (FE-SEM, JEOL JSM-7401F, JEOL), High resolution-transmission electron microscopy (HR-TEM, JEM-2100F, JEOL) and X-ray diffraction (XRD). Through the EELS (JEOL JSM-7401F, JEOL) analysis, atomic mapping of CuO/ZnO nanostructures was observed. The H$_2$S gas sensing properties of the fabricated sensors were tested in a furnace-type sensing system [Scheme S2, Supporting Information]. The horizontal tubular furnace system was used to measure the gas sensing properties. The quartz tube possessed an outer diameter and a thickness of 45 and 2.5 mm, respectively. The thermocouple (TC) was positioned at the center of the quartz tube. Diluted H$_2$S (50 ppm) was passed over the sensor at 400 sccm using a mass flow controller (MFC, MKS Inc.). To measure the electrical properties, Keithley 2400 source meter (Keithley Inc.), which was connected to a computer by general purpose interface bus (GPIB), was applied. During the sensing test, the change of current was measured at constant applied voltage (1 V). The data of current were collected at each second during sensing test. The chemical composition of the samples was analyzed using XPS with Al Kα radiation. Argon ion sputtering (3 keV, 36 μA cm$^{-2}$, ~1 nm/min) was used to remove impurities on the surface of samples and to acquire XPS composition depth profiles.

3. RESULTS AND DISCUSSION

3.1. Characteristics of CuO/ZnO Heterostructured Nanorods. Figure 1 shows the SEM images of the hydrothermally grown ZnO nanorod bundles (Figure 1a) and the CuO/ZnO heterostructures prepared with various photochemical reaction times in 0.05 mM of Cu salt aqueous solution (Figure 1b-d). The average length of ZnO nanorods was approximately 1 μm, with an aspect ratio of ~10. Through the observation of hexagonally faceted ZnO products in the SEM image, the grown ZnO nanorods can be expected to be highly crystalline. The SEM image in Figure 1b clearly indicates that after the 20 min UV-derived photochemical reaction, the growth of spike-shaped CuO nanospikes began to occur on the tips of ZnO nanorods. Figure 1b through 1d show that with increasing photochemical reaction time, CuO nanospikes gathered to form spike-like CuO nanostructures. Spike-like CuO nanostructures consist of numerous CuO nanospikes, which are formed from oriented aggregates of CuO nanoparticles on the surface of ZnO nanorods. With increasing reaction time, these aggregates had not only grown on the tip of ZnO but also on the body surface of ZnO. [Figure S1, Supporting Information.]

In their report, Pacholski et al., 28 who studied the site-specific deposition of Ag nanoparticles at one end of the ZnO nanorod, suggested a hypothesis for the site-specific deposition phenomena: priority of the particular crystallographic planes, for example, ZnO (0001), on the adsorption of Ag$^+$ and the nucleation of Ag nanoparticles and localization of the electrons at the ends of the ZnO nanorods. However, we could not find any conclusive proof that these hypotheses can be applied to our results. From our study, we suggest that the deposition of CuO primarily depends on the geometric arrangement of the ZnO nanorods, similar to the sputtering deposition, which is controlled by the mass transport of reactants. 29

Figure 2 shows XRD patterns of ZnO nanorods and CuO/ZnO heterostructures. The inset figure is a higher magnification XRD spectrum of the CuO/ZnO heterostructure. The ZnO nanorod bundles had a typical wurtzite hexagonal ZnO crystal structure with lattice constants $a = 3.253$ Å and $c = 5.209$ Å (JCPDS card 80–0075). No diffraction peaks from impurities were detected. After CuO deposition, the XRD spectra showed a small peak of CuO(111). (JCPDS card No.80–1916). The breadth and weakness of the CuO peak can be explained by the small grain sizes and low crystallinity of the synthesized CuO nanostructures.

The structure and crystallinity of the CuO/ZnO nanorods were further characterized using TEM analysis. The TEM experiment was performed by dispersing nanorods in an ethanol solution by sonication. These nanostructures were then redeposited onto a carbon-coated Ni grid for a high-resolution TEM experiment. Figure 3 shows typical TEM images of the CuO/ZnO nanostructures and the images of EELS analysis. In Figure 3a, a low-magnification image of the CuO/ZnO nanostructure clearly shows that the spike-shaped CuO nanostructures were deposited onto ZnO nanorods in the 0.05 mM of Cu ion concentration. The average size of CuO nanospikes which were fabricated under UV-irradiation during 30 min in 50 micromol Cu ion solutions was about $137 ± 21$ nm in length and $40 ± 4$ nm in width.

Figure 3b shows a high resolution TEM image of the CuO/ZnO nanorods, revealing that the CuO nanospikes has a polycrystalline structure with atomic spacings of 2.32 and 2.5 Å. The corresponding FFT image (not shown) shows the bright diffraction points corresponding to the diffraction pattern of CuO(111) and Cu(111). The EELS mapping images from 3a are shown in Figure 3c, d, e, and f corresponding to Zn, O, Cu and Zn + Cu, respectively. This elemental mapping confirms that the deposited materials are composed of Cu and O.

We studied the effects of Cu ion concentration on the CuO/ZnO morphologies under fixed irradiation time of 30 min. Figure 4 shows the increment of deposited amount of CuO nanostructure with increasing Cu ion concentrations. The size of CuO loads formed at 1 mM Cu ion solution was over 200 nm, and the particles aggregated with each other. These results indicate that the growth of nanospike type of CuO is depended on UV irradiation time and aggregation rate of CuO nanostructures. The CuO/ZnO heterostructures synthesized in this study has a highly crystalline structure with a wavelength of CuO(111) and Cu(111).
According to a previous study, the concentration of OH$^-$ in the solution can significantly affect CuO synthesis. In the presence of a high concentration of OH$^-$, Cu$^{2+}$ ions form [Cu(OH)$_4$]$^{2-}$ ions. Then, [Cu(OH)$_4$]$^{2-}$ loses two OH$^-$ and one H$_2$O to become CuO via the following reaction:

\[
\text{Cu}^{2+}(\text{aq}) + 4\text{OH}^{-} \rightarrow [\text{Cu(OH)}_4]^{2-}(\text{aq})
\]
\[
\rightarrow \text{CuO}(s) + 2\text{OH}^{-}(\text{aq}) + \text{H}_2\text{O}
\]

Thus, the [Cu(OH)$_4$]$^{2-}$ clusters can be considered a precursor for the formation of CuO. The initially generated CuO nanoparticles are adsorbed on the tip of ZnO nanorods and provide nuclei for further growth. The CuO nuclei develop their own preferred growth pattern during the reaction process and form spike-like assemblies. Finally, the spike-like CuO nanostructures composed of numerous nanospikes are formed. In our work, all of synthesis experiments were performed at room temperature and thus the solid solutions such as ZnO-CuO compound alloy only exists very rarely.

3.2. H$_2$S Sensing Properties of CuO/ZnO Heterostructured Nanorods. The H$_2$S sensing properties of the CuO/ZnO heterostructured nanorod sensors were measured at various sensing temperatures of $T_s$. The sensing data shown in Figure 5 were taken from CuO/ZnO heterostructured nanorods synthesized in 0.05 mM aqueous Cu salt precursor. Diluted H$_2$S gas (50 ppm) was injected to check the gas response and the sample was purged with air after successive injections. At 300 °C $\leq T_s \leq 500$ °C, the sensing results (Figure 5a) showed stable responses and fast recovery after H$_2$S gas exposure and the air purge, respectively. For a reducing gas such as H$_2$S, response ($R$) can be expressed as $R = (I_s - I) / I_s$, where $I_s$ is the signal intensity in the presence of gas and $I$ is the signal intensity in the absence of gas.
in which $I_g$ and $I_a$ indicate current generated during gas and air flow, respectively. With increasing $T_s$, $R$ increased and reached $\sim 890$ at 500 °C. The results of the same pulse length (20 min) of H$_2$S gas injection vs gas response at various sensing temperatures is described in the Supporting Information [Figure S2]. An Arrhenius plot of the gas response vs $T_s$ is shown in Figure 5b. Each gas response of CuO/ZnO sensors is higher than that of bare-ZnO sensors at each experimented temperature (Figure 5b). In Figure 5b, the exponential dependence of this response on the sensing temperature of ZnO nanorod sensors indicates that the H$_2$S sensing mechanism includes an activating process, such as H$_2$S chemisorption or the chemical reaction of ZnO with H$_2$S. Similarly the CuO/ZnO heterostructured nanorods also showed an exponential dependence with a similar slope as ZnO but the response was higher. Such similarity in the response dependence on $T_s$ indicates that both nanorod sensors are based on similar chemical activated processes. H$_2$S gas sensing at temperatures lower than 300 °C was also studied. The results showed that the response was stable upon H$_2$S gas exposure. After air purging, the response did not return to within 10% of the difference between the sensed value and the original value without UV or heat treatment in our sensing system. Figure 5c shows the response and recovery times of CuO/ZnO heterostructured sensor. The response time is defined as a time to reach 90% of maximum sensing response and the recovery time is defined as a time to fall to 10% of maximum sensing response upon air purging. As $T_s$ increased, the recovery time of CuO/ZnO sensors decreased and this tendency is similar to bare-ZnO sensor. However, the tendency of response time is different from that of bare-ZnO; the response time increased with increasing $T_s$. The reason for this trend in response time is not fully understood yet but we think that this is closely related with surface chemistry on CuO/ZnO samples. Figure 6 shows the results of multicycle sensing test results of CuO/ZnO sensor with 20 min of fixed gas exposure interval at different temperatures. The gas H$_2$S injection times of each graph are as follows: (a) 10 min, (b) 10 min, and (c) 2.5 min for each temperature. During multiple cycling test of H$_2$S sensing and recovery, CuO/ZnO sensors showed highly consistent results in gas response and recovery. The maximum error range of gas response of the CuO/ZnO sensors was $-11.2\%$ to $+8.8\%$. In Figure 7, two typical types of gas responses as a function of H$_2$S concentrations at 500 °C are

Scheme 1. Illustrations of the Proposed Growth Model of CuO on ZnO Nanorods: (Top) Nucleation of CuO on the ZnO Nanorod Surface by Photochemical Reaction; (Bottom) CuO Growth on the ZnO Surface under UV Illumination in an Aqueous Precursor Solution of Cu Salt
Figure 5. H₂S gas sensing properties of a CuO/ZnO heterostructured nanorod sensor at various temperatures. (a) Response and recovery of the sensor. (b) Arrhenius-style plot of the gas response of ZnO (red dot) and CuO/ZnO (blue dot). The error ranges of gas response values were displayed in log scale. (c) Response and recovery times of the CuO/ZnO sensor at various temperatures. R is the value of the gas response.

Figure 6. Results of multicycle sensing test of CuO/ZnO sensor with 20 min of gas interval at different temperatures: (a) 500 °C, (b) 400 °C, and (c) 300 °C. The gas H₂S injection times of each graph are (a) 10 min, (b) 10 min, and (c) 2.5 min for sensing temperature of 500, 400, and 300 °C, respectively.

Figure 7. Gas responses as a function of H₂S concentration of CuO/ZnO sensor at 500 °C. (a) Direct recovery after each sensing test, (b) continuous gas response at each step of H₂S gas concentration. The gas injection time of part b is 3 min at each step. The unit of concentration is ppm and highest concentration is 50 ppm. The total flow rate of air diluted H₂S gas is 400 sccm.
shown. The unit of concentration is ppm and highest concentration is 50 ppm and the total flow rate of air diluted H2S gas is 400 sccm. With increasing H2S gas concentration, the gas response was also increased. It was confirmed that the chemical state of CuO/ZnO sensing material was restored after recovery, as shown in Figures 8 and 9.

3.3. H2S Sensing Mechanism of CuO/ZnO Heterostructured Nanorods. XPS was used to study the H2S sensing mechanism of the CuO/ZnO heterostructured nanorods. Figure 8a shows the XPS spectra of Cu 2p of the CuO/ZnO nanorod bundles taken before sensing (red line), after H2S sensing at 500 °C (blue line) and after air purging to recovery (green line). To remove surface contaminants, samples were sputtered with Ar ions for 1 min before XPS measurements were collected. The binding energy of C 1s peak collected from bare-ZnO and bare-CuO/ZnO samples before sputtering was 284.6 eV, and other binding energies of XPS results were corrected by referring C 1s peak position. Before H2S sensing, the Cu 2p binding energies of the CuO/ZnO heterostructured nanorods were 933.8 (Cu 2p3/2) and 953.2 eV (Cu 2p1/2), which correspond to the binding energies of the Cu 2p of CuO.32 Meanwhile, two shakeup lines positioned at ∼943 and ∼963 eV were observed, indicating the paramagnetic chemical state of Cu2+.33 After H2S sensing, the binding energies of Cu 2p3/2 and Cu 2p1/2 obviously shifted to 932.8 and 952.7 eV, respectively, indicating changes in the chemical state of Cu ions. Moreover, two shakeup lines almost disappeared. These results indicate a change in the chemical state of Cu ions and presence of either Cu0 or Cu+. However, the Auger Cu LMM spectrum in Figure 8b, positioned at approximately 917.5 eV, suggests that Cu0 does not seem to be present because its characteristic feature (Cu LMM at 918.7 eV) is not detected.34 These results suggest that the oxidation state of Cu2+ (CuO) changed to Cu1+ (Cu2S) upon H2S gas exposure to CuO/ZnO nanorods. After recovery with air exposure, Cu 2p peak positions shifted back to those of CuO/ZnO nanorods, which were observed before sensing, and the shakeup peaks that had disappeared now reappeared.

In addition to Cu 2p, other XPS peaks were also analyzed. Figure 9 shows XPS spectra of (a) S 2p and (b) O 1s of CuO/ZnO taken before H2S sensing (red line), after sensing at 500 °C (blue line) and after air purging to recovery (green line). After H2S exposure, the asymmetric S 2p peak at 161.8 eV appeared to originate from the combination of S 2p3/2 (161.7 eV) and S2p1/2 (163.0 eV), which correspond to the metal-sulfide bond;34 however, there are no S 2p peaks found in the spectrum before sensing or after air purging in Figure 9a. These results support that the binding energy shifts of Cu 2p and the disappearance of shakeup peaks in Figure 8a were due to the formation of Cu–S bonds upon H2S exposure. In Figure 9b, a
broad feature of the O 1s XPS peak from fresh CuO/ZnO may originate from the sum of three typical peaks corresponding to the lattice oxide in bulk metal oxides, including ZnO and CuO, and adsorbed hydroxide. After H$_2$S exposure, the low binding energy feature at ~529.5 eV of the peak disappeared and was recovered after air purging. These results indicate that the low binding energy peak of O 1s is related to Cu−O bonds, supporting the chemical conversion of CuO into Cu$_2$S upon H$_2$S sensing and the oxidation of Cu$_2$S upon air purging. The detailed descriptions of deconvoluted, normalized O 1s XPS spectra of CuO/ZnO sensor before sensing, after sensing, and after recovery are included in Figure 10. During sensing and recovery, the intensity difference of deconvoluted peak positioned at 529.5 eV of binding energy is found clearly due to the chemical conversion of CuO to Cu$_2$S.

Chemoresistant metal oxide gas sensors work by a similar mechanism based on the reaction of adsorbed oxygen species with the target gas. The H$_2$S gas sensing properties of p-type CuO nanoparticles that are deposited onto the surface of ZnO nanorods form a p/n junction with n-ZnO and confer resistance at the interface with ZnO before sensing. Metal oxide sensing materials showed high resistance due to the adsorption of oxygen species, resulting in a depleted region on the surface. Before sensing, our fresh CuO/ZnO stacked nanorods showed much lower base conductivity (~10$^{-8}$ A at 500 °C) compared to that of the pure stacked ZnO nanorods (approximately 10$^{-6}$ A at 500 °C). This reduced conductivity in the CuO/ZnO sensor is caused by a disturbance from CuO. During H$_2$S gas sensing, the H$_2$S gas removes the adsorbed oxygen species on ZnO and reacts with CuO on the surface of ZnO to convert into metallic Cu$_2$S (eq 2).

$$6\text{CuO}(s) + 4\text{H}_2\text{S}^{(ad)} \rightarrow 3\text{Cu}_2\text{S}(s) + 4\text{H}_2\text{O}(g) + \text{SO}_2(g)$$

In our sensing temperature range of 300 °C ≤ T$_s$ ≤ 500 °C, the Gibbs free energy of the suggested reaction shown in eq 2 is negative, indicating that the reaction is thermodynamically favored. The chemical conversion of CuO into metallic Cu$_2$S causes the change of energy band structure toward that observed in Scheme 2b and increases the conductivity of the nanorods. Upon air purge recovery, the sensing material returns to the same chemical state as the fresh CuO/ZnO through the chemical conversion of Cu$_2$S back to CuO by the reaction with oxygen in air (eq 3), and ionized oxygen species adsorb onto the ZnO again.

$$\text{Cu}_2\text{S}(s) + 2\text{O}_2 \rightarrow 2\text{CuO}(s) + \text{SO}_2(g)$$

The proposed sensing mechanism explains the H$_2$S sensing behaviors of our CuO/ZnO nanorods well. Regardless, a further investigation is required to verify the proposed mechanism in future work.

The tendency of response time in Figure 5c can be explained by proposed sensing mechanism. The sensing temperature affects the formation rate of Cu$_2$S from CuO, which was
confirmed by XPS and XRD analysis [Figure S4 and S5, Supporting Information]. The extent of chemical conversion reaction of CuO at higher temperature is lower than one at lower temperature. These results explain the increasing tendency of gas response time with increasing Ts. However, to explain the exact reason for such tendency further study is required because it can be affected by experimental conditions of sensor fabrication and sensing system. For example, Yamazoe group have reported that the CuO formations from various precursor of Cu ion solution can vary response time of H2S sensing by CuO/SnO2 film sensor.39

3.4. Surface Coverage Effect of CuO in H2S Gas Sensing. In our experiments we found that the CuO coverage on ZnO nanorods strongly affected the H2S gas responses as shown in Figure 11a. The coverage of CuO nanoparticles onto the ZnO nanorods was controlled by changing the Cu salt concentrations from 0 to 100 μM during photochemical growth. The loading amount increased with increasing Cu salt concentrations; The loading amounts of CuO in CuO/ZnO heterostructures were analyzed by EDS (atomic ratio of Cu to Zn) and the values were 2.33% (0.025 mM), 5% (0.05 mM), 6.3% (0.075 mM), and 8.46% (0.1 mM) at different Cu ion concentration of each precursor [Figure S6, Supporting Information]. The error range was about 1%. The results showed that the H2S gas response increased with increasing CuO coverage up to 0.05 μM of Cu salt concentration, reaching a maximum gas response of 890. However, at higher coverage, the response was decreased. Figure 11b shows SEM images of CuO/ZnO heterostructured nanorods that were synthesized at various Cu ion concentrations before (left) and after (right) H2S sensing. After H2S exposure, spike-shaped CuO changes to broad and flat shaped Cu2S. These morphological changes are more clearly observed in regions of higher CuO coverage. The optimal surface coverage of CuO on ZnO in our study is about 7% (Cu2S/Zn = 93.63:1242.64) analyzed by XPS at 0.05 mM of Cu ion concentration. The formation of the high coverage of broad, flat Cu2S can reduce the active sensing area of ZnO nanorods and disturb the target gas sensing on the surface. Moreover, too much CuO coverage on ZnO nanorods leads to only a partial conversion of CuO to metallic Cu2S, and a significant amount of p-type CuO remains. These effects may induce the decline in response upon high CuO coverage.

4. CONCLUSIONS

The CuO/ZnO heterostructured nanorods were synthesized using the photochemical deposition of CuO on hydrothermally grown ZnO nanorods. The presence of high crystalline CuO/ZnO was confirmed by FE-SEM, XRD, TEM, and EELS. Through the modulation of growth conditions such as Cu salt concentration and UV irradiation time, we could control the morphology of the heterostructured nanorods. The nanorod sensors exhibited stable gas response, reversibility and enhanced H2S gas responses compared to pure ZnO nanorods. The H2S gas response of CuO/ZnO nanorod sensors increased exponentially as temperature increased. The chemical conversion of CuO to Cu2S was observed from the XPS analysis of the CuO/ZnO nanorods during H2S sensing, which largely explains the mechanism of enhanced gas sensing by this material. The H2S gas response of CuO/ZnO nanorods was strongly affected by the coverage of CuO on the ZnO nanorods. Through the analysis of morphological changes during sensing at various CuO coverage levels, it was determined that an optimal surface coverage exists that leaves a sufficient amount of the ZnO surface exposed for active sensing to occur but offers a large enough CuO surface coverage for the formation of Cu2S as a conducting channel.

ASSOCIATED CONTENT

Supporting Information

SEM images of CuO formed on ZnO, the schematics of ZnO nanorod sensor structure, gas sensing system, sensing test with same pulse lengths, the Zn LMM Auger signal of CuO/ZnO heterostructured nanorods, O 1s XPS of CuO/ZnO before and after sensing at different temperatures, and EDS analysis data of CuO/ZnO heterostructured nanorods formed at different Cu ion concentration of precursors. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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REFERENCES


