

Laser irradiation-induced Au-ZnO nanospheres with enhanced sensitivity and stability in ethanol sensing

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Abstract

Incorporating noble metal nanoparticles on the surface or inner side of semiconductors to form a hybrid nanostructure is an effective route to improve the gas sensing performance of these semiconductors. In this study, we present novel Au-decorated ZnO nanospheres (Au-ZnO NSs) obtained by laser irradiation of liquids. Structural characterization indicated that the Au-ZnO NSs consisted of single crystalline ZnO NSs with few Au nanoparticles decorated on their surfaces and abundant encapsulated Au nanoparticles with relatively small sizes. Laser irradiation-induced heating-melting-evaporating processes are responsible for the formation of unique Au-ZnO NSs. Gas sensing properties of the Au-ZnO NSs, as gas sensing materials, were investigated and compared with those of pure ZnO NSs. The former showed lower working temperature, higher sensitivity, better selectivity, and good reproducibility. The response values of Au-ZnO NSs and pure ZnO NSs sensors to ethanol of 100 ppm were 252 and 75 at working temperature of 320 °C and 360 °C, respectively. The significant enhancements in gas sensing performance should be attributed to the electronic sensitization induced by the depleted layers between encapsulated Au nanoparticles and ZnO and chemical sensitization originating from the catalytic effects of Au nanoparticles decorated on the surfaces that dissociated molecular oxygen.

Full Text

Preamble

Laser irradiation-induced Au-ZnO nanospheres with enhanced sensitivity and stability in ethanol sensing

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Incorporating noble metal nanoparticles on the surface or interior of semiconductors to form hybrid nanostructures represents an effective strategy for improving the gas sensing performance of these materials. In this study, we present novel Au-decorated ZnO nanospheres (Au-ZnO NSs) synthesized via laser irradiation of liquids. Structural characterization revealed that the Au-ZnO NSs consisted of single-crystalline ZnO nanospheres with a few Au nanoparticles decorated on their surfaces and numerous encapsulated Au nanoparticles of relatively small size. Laser irradiation-induced heating-melting-evaporating processes are responsible for the formation of these unique Au-ZnO NSs. The gas sensing properties of the Au-ZnO NSs were investigated and compared with those of pure ZnO NSs. The Au-ZnO NSs exhibited lower working temperature, higher sensitivity, better selectivity, and good reproducibility. The response values of Au-ZnO NSs and pure ZnO NSs sensors to 100 ppm ethanol were 252 and 75 at working temperatures of 320 °C and 360 °C, respectively. The significant enhancement in gas sensing performance should be attributed to electronic sensitization induced by the depletion layers between encapsulated Au nanoparticles and ZnO, as well as chemical sensitization originating from the catalytic effects of Au nanoparticles decorated on the surfaces that dissociate molecular oxygen.

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Introduction

Gas sensors have attracted considerable attention for detecting and monitoring flammable, explosive, or toxic gases due to growing concerns over the health and safety impacts of worsening gas pollution. Among these devices, metal oxide semiconductor (MOS) sensors are widely investigated because of their high sensitivity, low cost, and easy maintenance. Seiyama et al. initially proposed the principle of gas sensing in 1962, and consequently, various kinds of MOS materials have been explored as gas sensors.

Examples of n-type metal oxides include ZnO, FeO, InO, TiO, and WO, while p-type metal oxides include CuO, NiO, CoO, and CrO. Among candidate gas sensor nanomaterials, ZnO has been extensively investigated given its high conductivity, good stability, and biocompatibility. However, several drawbacks, such as high operating temperature, low sensitivity, and poor selectivity, still limit the application of bulk ZnO as a gas sensor. Numerous

studies have sought to improve the gas sensing performance of ZnO by designing different nanostructures with large surface areas to increase active sites, such as nanocactus, porous nanoflakes, and flower-like structures. Combining noble metal nanoparticles (NPs) (i.e., Au, Ag, or Pt) with ZnO to form hybrid nanostructures represents another efficient strategy for achieving desirable sensing performance.

Two types of noble metal NP-ZnO hybrid nanostructures are currently employed: surface-modified and encapsulated. The gas sensing performance can be enhanced by surface modification due to the catalytic effects of noble metal NPs in dissociating molecular oxygen (chemical sensitization) and electronic interactions that form Schottky junctions between noble metal NPs and ZnO (electronic sensitization). However, this approach faces several limitations. Coagulation and chemical poisoning of noble metal NPs occur at high working temperatures, resulting in loss of catalytic activity. By contrast, encapsulated noble metal NPs are more stable than surface-decorated ones because of the protective ZnO shell. Moreover, the Schottky junction areas in encapsulated NPs are larger than those in surface-modified NPs due to complete surface contact between Au and the ZnO shell. However, the catalytic effects of noble metal NPs inevitably decline and may even disappear in some cases. Therefore, specific noble metal NP-ZnO hybrid nanostructures should be designed to possess the advantages of both chemical and electronic sensitization while preserving the stability of noble metal NPs under severe working conditions.

In this paper, we introduce the preparation of novel Au-decorated ZnO nanospheres (Au-ZnO NSs) containing many small Au NPs encapsulated within ZnO NSs and relatively larger Au NPs decorated on the surface, synthesized using laser irradiation of liquids. As a sensing material, Au-ZnO NS-based sensors possess combined chemical and electronic sensitization and exhibited higher sensitivity and lower working temperature toward ethanol molecules compared with pure ZnO NS-based sensors.

Experimental Section

Chemicals and Materials

Sodium hydroxide (NaOH) was purchased from Sinopharm Chemical Reagent Co. Ltd., while Au (99.99%) and Zn (99.99%) metal plates were obtained from Beijing Goodwill Metal Technology Co. Ltd. (Beijing, China). Ultrapure water was prepared using a Milli-Q-Plus system.

Preparation of Au-ZnO NSs

First, Au colloidal solution was obtained by ablating a piece of Au plate for 3 min in an aqueous solution of 1 mM NaOH using a focused laser of 1064 nm wavelength with an energy density of 80 mJ/pulse (Fig. 1 [Figure 1: see original paper]). Then, the precursor colloidal solution containing Au and ZnO NPs was

synthesized by immersing a Zn plate in 18 mL of the as-prepared Au colloidal solution. The plate was ablated for 10 min using a focused laser of 1064 nm wavelength with an energy density of 100 mJ/pulse. Subsequently, the mixed Au and ZnO colloidal solution was further irradiated by an unfocused laser with 355 nm wavelength and energy density of 40 mJ/pulse under continuous stirring for 40 min. The color of the colloidal solution changed from brown to deep purple after irradiation.

Pure ZnO NSs were prepared by similar processes. Zn colloidal solution was prepared by ablating a Zn plate for 10 min in an aqueous solution of 1 mM NaOH using a focused laser of 1064 nm wavelength. Then, the as-prepared Zn colloidal solution was irradiated with an unfocused laser of 355 nm wavelength under the same conditions. The samples were washed several times with deionized water by centrifugation. The products were then collected and annealed in a muffle furnace at 400 °C for 2 h for characterization and gas sensing measurements.

Characterization

The morphology and structure of the products were investigated using field-emission scanning electron microscopy (SU8020) and transmission electron microscopy (TEM, JEOL JEM-2010, Japan). The X-ray diffraction (XRD) patterns of all samples were recorded using a Rigaku X-ray diffractometer (G2234) with Cu-K radiation ($\lambda = 0.15419$ nm). Photoluminescence (PL) measurements were performed with a fluorescence spectrophotometer (F-4600, Hitachi). A Keithley 6487 Source/Measure Unit (SMU) was used to record current changes and provide power during sensor performance testing.

Gas Sensing Test

Gas sensors were fabricated by dispersing Au-ZnO NSs (or pure ZnO NSs) powders in ethanol or directly coating the powders on the surface of ceramic tubes. Gas sensing measurements were conducted by injecting a certain volume of target gas (e.g., ethanol) into the chamber using a microsyringe. After completion of the measurements, target gases in the chamber were released by flowing fresh dried air into the chamber. A constant voltage (3 V) was applied to the sensor, and the current was measured and acquired via SMU. The sensor response was calculated as follows: $\text{Response} = I_g/I_a$, where I_a and I_g are the electric currents of the sensor in air and target gas, respectively.

Results and Discussion

Scanning electron micrographs of pure ZnO NSs (Fig. 2a) and the corresponding size distribution histogram (inset of Fig. 2a) show a spherical morphology with an average size of 69 nm. Decoration with Au NPs resulted in spherical Au-ZnO NSs (Fig. 2b) with an average size of 73 nm (inset of Fig. 2b), which is close to that of pure ZnO NSs. Transmission electron micrographs (Figs. 2c and d) clearly indicated that Au-ZnO NSs were decorated with a few large Au

NPs at the edges of surfaces and encapsulated with many small Au NPs. The corresponding high-resolution transmission electron micrograph (Fig. 2e) of the area marked with a white dotted square in Fig. 2d reveals the highly crystalline nature of the ZnO NSs. Clear lattice fringes with interplanar spacings of 0.26 and 0.24 nm correspond to the (002) crystalline plane of hexagonal wurtzite ZnO and the (111) crystalline plane of face-centered cubic Au, respectively. The related selected-area electron diffraction pattern (Fig. S1) also indicated the single-crystalline characteristic of ZnO NSs. Furthermore, compared with products without annealing treatment (Fig. S2), the Au-ZnO NSs remained spherical with no coagulation of small Au NPs, suggesting excellent thermal stability.

The phase structures of as-prepared Zn colloidal NPs, pure ZnO NSs, and Au-ZnO NSs were further identified by XRD characterization. The diffraction patterns in Fig. 3a indicate that all three samples contained ZnO in a hexagonal structure (JCPDS card No. 01-076-0704). The XRD pattern of Zn colloids shows broadened peaks of ZnO, indicating small ZnO NP size, and three additional peaks with weak diffraction intensity belonging to metallic Zn. Additionally, peaks at 38.2°, 44.4°, and 64.6° in the diffraction pattern of Au-ZnO NSs were indexed to the (111), (200), and (220) planes of cubic metallic Au (JCPDS card No. 00-004-0784), respectively. The room temperature PL spectrum of pure ZnO NSs (Fig. 3b) displays an emission peak at 380 nm (3.26 eV), which can be ascribed to the band edge emission of the ZnO semiconductor. However, the emission intensity declined dramatically when Au NPs were decorated onto ZnO. This significant decrease in PL emission intensity of Au-ZnO NSs should be attributed to efficient transfer of photogenerated electrons from ZnO to Au, suggesting strong electronic interactions between Au and ZnO.

To investigate the growth mechanism involved in the synthesis of Au-ZnO NSs, products obtained at different irradiation times (0, 5, 20, and 40 min) were analyzed by TEM (Fig. 4 [Figure 4: see original paper]). Prior to laser irradiation, the product consisted of short ZnO nanorods with an average diameter of 11 nm and length of 30 nm (Fig. 4a). The high-resolution transmission electron micrograph in Fig. 4e displays clear lattice fringes with interplanar spacings of 0.25 and 0.24 nm, corresponding to the (101) plane of hexagonal wurtzite ZnO and the (111) plane of cubic Au, respectively. After irradiation for 5 min, a few irregular spherical NPs with an average size of 40 nm were observed (Fig. 4b). High-resolution transmission micrographs in Figs. 4f and S3 reveal the polycrystalline structure of these irregular spherical aggregates, which comprised many small rod-like ZnO crystals and a few Au NPs (indicated by white arrows). Increasing the irradiation time to 20 min resulted in transformation of the irregular aggregates into NSs with an average size of 65 nm (Fig. 4c), which already exhibited Au-ZnO hybrid nanostructures (Fig. 4g). Further increasing the irradiation time to 40 min led to complete consumption of rod-like ZnO nanocrystallites (Fig. 4d) and formation of ZnO NSs (Fig. 4h). However, no obvious increase in ZnO NS size was observed compared with the product obtained at 20 min, suggesting that the ZnO NS size reached a maxi-

imum value under the specific input laser fluence of 40 mJ/pulse. This finding can be reasonably explained by Equation (1), which quantitatively defines the maximum particle size at a given fluence:

$$J^* = \frac{\rho_p \Delta H_m + \rho_l \Delta H_b}{\alpha_p d_p}$$

where J is the laser fluence and α_p is the absorption cross-section. Thus, the required laser fluence J^* that will heat a particle with diameter d_p from room temperature (T_0) to melting temperature (T_m) and boiling temperature (T_b) can be determined. The physical and thermodynamic constants for solids (ρ_p, C_p) and liquids (ρ_l, C_l), as well as melting heat ΔH_m and boiling heat ΔH_b , were adopted from Perry.

A physical heating-melting-evaporating mechanism is considered responsible for the formation of Au-ZnO NSs, similar to the report of Wang et al. ZnO NPs dispersed in liquid were melted under appropriate input laser fluence. Neighboring melted NPs fused together and then remelted into larger NPs due to Brownian motion. A rapid cooling process caused by the surrounding liquid occurred after pulsed laser heating (within 7 ns), leading to formation of ZnO NSs. Some Au NPs were also melted and encapsulated inside ZnO NSs during the melting and remelting processes, while others were decorated on the ZnO NS surfaces.

The synergetic effects of Au NPs on the gas sensing performance of ZnO were explored through gas sensor experiments using pure ZnO NSs and Au-ZnO NSs. Response properties of MOS are highly dependent on operating temperature. The response of pure ZnO NSs under increasing operating temperature reached a maximum value of 75 at 360 °C, whereas the optimum operating temperature for Au-ZnO NSs was 320 °C, lower than that of pure ZnO NSs (Fig. 5a). The corresponding response value was 3.4 times higher than that of pure ZnO NSs. Figure 5b shows the real-time responses of Au-ZnO NS-based and pure ZnO NS-based sensors toward different ethanol concentrations (10–200 ppm) at 320 °C and 360 °C, respectively. Both sensors exhibited similar response values at low ethanol concentrations (< 20 ppm). However, the response of the Au-ZnO NS-based sensor increased rapidly and was 2–4 times greater than that of the pure ZnO NS-based sensor when ethanol concentration exceeded 20 ppm. Plots of response value versus ethanol concentration (Fig. 5c) revealed that both sensors showed approximately linear correlation with ethanol concentration. Stability is also an important parameter for gas sensors. Figure 5d demonstrates that the response of the Au-ZnO NS-based sensor did not decline and remained constant after six cyclic measurements, indicating excellent stability.

Selectivity of gas sensor materials is highly significant for practical applications. The selectivity of pure ZnO NS-based and Au-ZnO NS-based sensors toward ethanol was evaluated by testing against various toxic gases: methanol, formaldehyde, acetone, diethyl ether, benzene, toluene, and chlorobenzene. The responses of both sensors to 100 ppm of different gases at 360 °C and 320 °C are shown in Fig. 6 [Figure 6: see original paper]. The Au-ZnO NS-based sensor exhibited enhanced responses compared with the pure ZnO NS-based

sensor for all gases. Both sensors showed good selectivity to ethanol. The Au-ZnO NS-based sensor displayed diverse responses to different gases: methanol (19.5), formaldehyde (4), acetone (52.5), diethyl ether (5.3), benzene (10.4), toluene (19.6), and chlorobenzene (10.9). Remarkably, the highest response value of 252 was obtained for ethanol, indicating excellent selectivity of Au-ZnO NSs for ethanol detection. Different morphologies with various exposed crystal planes are believed to influence the gas sensing and photocatalytic behavior of metal oxides due to diverse chemisorption abilities of different exposed faces. The morphology of ZnO could affect the selectivity of pure ZnO-based sensors. Hamedani et al. investigated responses of ZnO with three different morphologies (NP, nanorod, and flower-like) to CO, ethanol, and methane, finding that the NP sensor exhibited good selectivity to ethanol. Therefore, the improved ethanol selectivity of the Au-ZnO NS-based sensor could be attributed to the spherical morphology of ZnO and the decorated Au NPs.

We propose a possible gas sensing mechanism for our Au-ZnO NS-based sensor based on electronic sensitization and chemical catalytic effects (Fig. 7 [Figure 7: see original paper]). For pure ZnO, oxygen in air can adsorb on its surface and form oxygen anions by capturing electrons from the conduction band. This process leads to high air resistance of the ZnO sensor due to formation of a depletion layer on the ZnO surface. However, the presence of Au NPs in Au-ZnO NSs changes the energy band structure of ZnO through formation of Schottky barriers. The work function of Au metal (5.1 eV) is larger than that of ZnO (4.65 eV). Thus, conduction band electrons of ZnO transfer into Au NPs, forming depletion layers between the ZnO shell and Au NPs. In our Au-ZnO NSs, Au NPs were both decorated on the ZnO surface and encapsulated inside. Surface-decorated Au NPs could increase the width of the depletion layer in ZnO caused by oxygen absorption, whereas numerous smaller Au NPs would create numerous depletion layers around them when encapsulated. As illustrated in Fig. 7a, these depletion layers might connect with each other and evidently increase the air resistance of the Au-ZnO NS-based sensor. This result agrees well with experimental observations, where the air resistance of the Au-ZnO NS-based sensor (2.1 M Ω) was larger than that of the pure ZnO NS-based sensor (1.7 M Ω). This characteristic implies that Au-ZnO NSs could display better sensitivity than pure ZnO NSs, consistent with the aforementioned sensing performance results.

In addition to electronic sensitization, Au NPs are considered effective catalysts for dissociating molecular oxygen due to their spillover effect. Therefore, more molecular oxygen could be adsorbed on the ZnO surface after decoration with Au NPs. When ZnO is exposed to reducing gases such as ethanol, the chemisorbed oxygen anions react with ethanol molecules, releasing electrons back to the ZnO conduction band (Fig. 7b). This process leads to decreased resistance of the ZnO sensor. The greater the amount of chemisorbed oxygen anions, the larger the decrease in resistance. Thus, the improved sensitivity of the Au-ZnO NS-based sensor toward ethanol compared with the pure ZnO NS-based sensor can be attributed to both electronic and chemical sensitization.

Conclusion

We demonstrated the preparation of novel Au-ZnO NSs containing many small Au NPs encapsulated within ZnO NSs and relatively larger Au NPs decorated on the ZnO NS surfaces using a laser irradiation of liquids approach. The Au-ZnO NSs exhibited perfect structural stability after annealing at 400 °C for 2 h. A heating-melting-evaporating mechanism was responsible for the disappearance of ZnO nanorods and formation of Au-ZnO NSs. Benefiting from this structural stability as a gas sensing material, the Au-ZnO NS-based sensor displayed good reproducibility, with unchanged response values during six cyclic measurements. While the pure ZnO NSs sensor showed a maximum response value of 75 at a working temperature of 360 °C, the Au-ZnO NSs sensor exhibited a reduced working temperature of 320 °C and enhanced sensitivity with a response value of 252 toward 100 ppm ethanol after Au NP decoration. Additionally, the Au-ZnO NSs sensor displayed high selectivity toward ethanol.

This improved sensing performance can be attributed to the catalytic effects of surface-decorated Au NPs and the formation of depletion layers induced by encapsulated Au NPs. Such stable hybrid nanostructured Au-ZnO NSs could be promising candidates for gas sensing materials.

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