

# Sensing Properties of Au Nanoparticle-Functionalized ZnO Nanowires by $\gamma$ -Ray Radiolysis

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## Abstract

$\gamma$ -ray radiolysis was used to functionalize networked ZnO nanowires with Au nanoparticles. The networked ZnO nanowires were prepared through a vapor phase selective growth method. The sensing performances of the Au-functionalized ZnO nanowires were investigated in terms of NO<sub>2</sub>, CO and benzene gases. The Au-functionalized ZnO nanowire sensors showed an applicable, reliable capability to detect the gases, indicating their potential in chemical gas sensors.

**Keywords :** Gas Sensor, Nanowire, Functionalization, Au-ZnO

## 1. INTRODUCTION

One-dimensional oxide nanomaterials, including nanowires, nanofibers, and nanotubes have been considered as ideal building blocks for development of nanoscale sensors, not only because of their chemical and thermal stability, but also due to their higher surface area. In the family of metal-oxide materials, zinc oxide (ZnO) is an *n*-type semiconductor with a wide-band-gap of 3.6 eV and a large exciton binding energy of 60 meV, which make it a promising candidate for use in various electronic devices. Furthermore, ZnO has also been used to detect toxic and combustible gases [1, 2]. Therefore, ZnO nanowires with a higher surface-to-volume ratio will significantly enhance the sensing properties of ZnO in comparison to its other forms such as bulk or thin films.

In general, sensors based on single nanowires have shown higher sensitivity and selectivity. However, their fabrication process involves expensive and tedious lithography processes. In addition, an expensive measurement unit is usually required to measure the infinitesimal current variation during absorption or desorption of gaseous species on the surface of nanowires. Due to the higher fabrication cost and poor reproducibility, the practical applications of single nanowires to chemical gas sensors remain challenging [3]. Networked nanowire-based sensors are an alternative to sensors based on single

nanowires, even though they possess sensitivity that is a little lower, and longer response and recovery times in comparison to single nanowire sensors.

In recent years, many efforts have been devoted to improving the sensing properties of oxide nanowires by catalyst functionalization, metal doping and creation of heterostructures [4-6]. Metallic nanoparticles such as Au, Pt and Pd have been used as catalysts to enhance the sensing properties [7-9]. The metallic nanoparticles functionalized on the surface of oxide materials readily dissociate the gas molecules into ions or neutral chemical species, resulting in higher gas sensitivity [10]. Various methods such as photochemistry [11], arc discharge [12] and sonochemistry [13] have been used to synthesize metallic nanoparticles.  $\gamma$ -ray radiolysis is another effective route to synthesize metallic nanoparticles [14] and can be employed to functionalize oxide nanowires.

In this work, we prepared networked ZnO nanowires by a selective growth method and subsequently functionalized their surfaces with Au nanoparticles via  $\gamma$ -ray radiolysis. The sensing properties of the Au-functionalized ZnO nanowires were investigated at different temperatures in the presence and absence of NO<sub>2</sub>, CO and benzene gases.

## 2. EXPERIMENTAL DETAILS

The preparation of Au-functionalized ZnO networked nanowire sensors includes the following two steps. In the first step, the selective growth of networked ZnO nanowires were carried out, particularly on patterned

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interdigital electrodes (PIEs), by using the well-known vapor-liquid-solid (VLS) growth method. The PIEs were prepared beforehand on  $\text{SiO}_2/\text{Si}(100)$  substrates using a conventional lithography process, followed by the subsequent deposition by sputtering of tri-layers comprising Au(3 nm)/Pt (100 nm)/Ni (50 nm). The Au layer played a role as a catalyst for the selective growth of ZnO nanowires. ZnO nanowires with network junctions were selectively grown on 10- $\mu\text{m}$ -spacing PIEs. The conditions used for fabrication of ZnO nanowires are described in detail in our previous report[15].

In the second step, Au nanoparticles were decorated on the surface of ZnO nanowires using  $\gamma$ -ray radiolysis. The precursor solution for synthesis of Au nanoparticles was prepared by dissolving 0.248 mM of hydrogen tetrachloroaurate (III) hydrate ( $\text{HAuCl}_4 \cdot n\text{H}_2\text{O}$ ,  $n = 3.5$ , Kojima Chemicals Co.) in a mixed solvent of 2-propanol. The prepared solution was stirred for 24 h. Then the prepared networked ZnO nanowires were immersed into the precursor solution. Then they were illuminated with  $10 \text{ kGy h}^{-1}$   $^{60}\text{Co}$   $\gamma$ -rays for 2 h in ambient air at room temperature, in order to achieve optimum size and higher density of Au nanoparticles on the surface of ZnO nanowires[16]. The prepared samples were heat treated at  $500^\circ\text{C}$  for 1 h in air to remove any remaining solvent.

The microstructure of the Au-functionalized ZnO nanowires was investigated using field-emission scanning electron microscopy (FE-SEM, Hitachi-4200) and transmission electron microscopy (TEM, Philips CM-200). Their responses to  $\text{NO}_2$ , CO and benzene were measured using a custom-made sensing system consisting of a horizontal-type tube furnace and mass flow controllers. The sensor was kept inside the tube furnace, and the temperature was varied in the range of  $50^\circ\text{C} - 300^\circ\text{C}$ . The change in resistance in the sensor devices was measured by connecting them to an electrical measuring unit (Keithley 2400) interfaced with a computer. The measurements were performed at various temperatures. The response ( $R$ ) was estimated as  $R = R_g/R_a$ , where  $R_g$  is the resistance measured in the presence of  $\text{NO}_2$ , and  $R_a$  is the resistance in the absence of  $\text{NO}_2$ . The converse was applied for the cases of CO and benzene. Here, the response time and recovery time are defined as the time taken by the sensor to change to 90 % of the initial resistance.

### 3. RESULTS AND DISCUSSIONS

Networked ZnO nanowires were selectively grown on PIE with an Au catalytic layer of  $\sim 3$  nm thickness. Fig. 1a shows a plan-view of selectively-grown networked ZnO nanowires on the 10- $\mu\text{m}$ -spacing PIE. It is evident that the ZnO nanowires grown on the PIE were entangled with each other and eventually formed junctions. Fig. 1b reveals the cross-sectional view of the networked ZnO nanowires, which also definitely confirms the formation of highly dense junctions in the middle space region between the PIEs. The  $\gamma$ -ray radiolysis was used to functionalize the ZnO nanowires with Au nanoparticles. Fig. 2 shows low- and high-magnification images of Au-functionalized networked ZnO nanowires. Fig. 2b clearly reveals that  $\sim 15$  nm diameter Au nanoparticles are uniformly distributed on the surface of the ZnO nanowires.

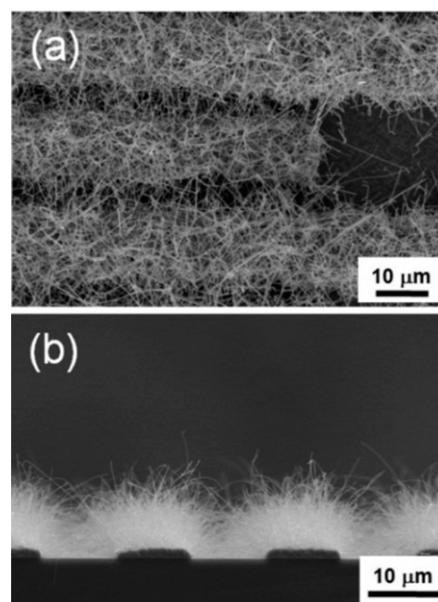


Fig. 1. (a) Plan-view of networked ZnO nanowires grown on patterned electrodes via the selective growth method. (b) Cross-sectional view of the networked ZnO nanowires.

The microstructure of Au nanoparticles functionalized on the surface of ZnO nanowires was further analyzed by TEM. Fig. 3a shows the uniformly-decorated Au nanoparticles on the surface of ZnO nanowires. The lattice fringes of both the ZnO nanowire and Au nanoparticles, observed in the high resolution TEM image, are shown in Fig. 3b. The arrows show Au nanoparticles decorated on the ZnO nanowires. Both the ZnO nanowire and the Au nanoparticles appear free from considerable structural defects such as dislocations or stacking faults. The lattice spacings were in good agreement with those of ZnO and Au.

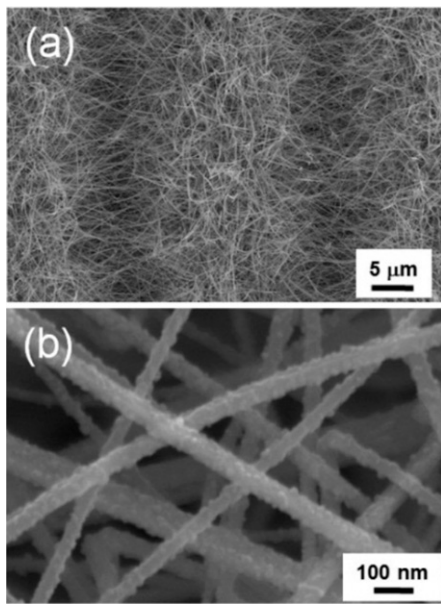


Fig. 2. (a) Plan-view of networked ZnO nanowires functionalized with Au nanoparticles through  $\gamma$ -ray radiolysis. (b) Microstructure of Au nanoparticles decorated on the surface ZnO nanowires grown under  $10 \text{ kG h}^{-1} \text{ }^{60}\text{Co}$   $\gamma$ -rays for 2 h.

The sensing performances of the Au-functionalized networked ZnO nanowires have been tested in terms of their capability to sense  $\text{NO}_2$  gas in a temperature range of 50 to  $300^\circ\text{C}$ . The results are shown in Fig. 4. In general, the ZnO nanowire sensors are most sensitive at  $200^\circ\text{C}$  -  $300^\circ\text{C}$ [17]. In this temperature zone, the interaction of  $\text{NO}_2$  gas molecules with the surface of ZnO materials is likely to be most active. In the Au-functionalized networked ZnO nanowires, the resistance follows the supply/cut off of  $\text{NO}_2$  gas. The response and recovery times shortened rapidly from 240 s to 100 s and 74 s to 33 s as temperature increased from  $50^\circ\text{C}$  to  $300^\circ\text{C}$ . The response time for the Au-functionalized networked ZnO nanowires was similar to the bare ZnO network nanowires[18], whereas the Au-functionalized networked ZnO nanowires showed a much shorter recovery time of 33 s in comparison to 572 s for the bare networked ZnO nanowires. The corresponding response is summarized in Fig. 4e. The sensor response obtained was as low as 0.1 ppm  $\text{NO}_2$ . The best sensing properties of the Au-functionalized networked ZnO nanowires to  $\text{NO}_2$  were obtained at  $250^\circ\text{C}$ , which is shown in Fig. 4c. This is likely to be due to the faster adsorption and desorption of  $\text{NO}_2$  at that temperature. However, the Au-functionalized networked ZnO nanowire sensor shows no significant difference in response value[18]. In order to estimate the

$\text{NO}_2$  gas sensing capability of gas sensors prepared in this work, the response is compared with other ZnO-based one-dimensional nanostructures in Fig. 4f[19- 21].

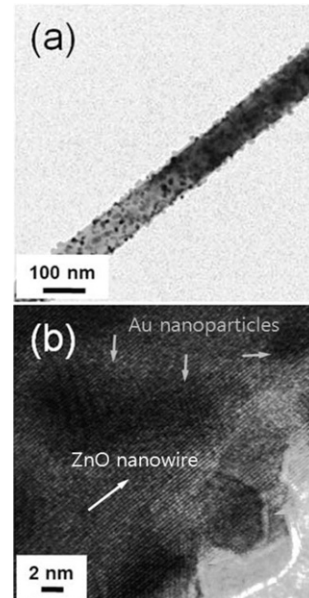


Fig. 3. TEM images of Au nanoparticles on the surface ZnO nanowires with (a) low and (b) high magnifications.

The gas sensing properties of the Au-functionalized networked ZnO nanowires sensors can be explained on the basis of  $n$ -type semiconductors. During exposure of bare ZnO nanowires to  $\text{NO}_2$  gas, the resistance of the sensor increases, but it decreases upon removal of  $\text{NO}_2$ . The adsorbed  $\text{NO}_2$  molecules on the surface of ZnO nanowires are likely to enhance the surface depletion of each ZnO nanowire by extracting electrons from them, creating more surface depletion regions on individual ZnO nanowires. These extracted electrons are released back to the conduction band of ZnO nanowires during desorption of  $\text{NO}_2$ . This adsorption and desorption process naturally leads to a change in resistance of the sensor.

Meanwhile, Au nanoparticles play a role as catalysts by inducing either more adsorption or easy dissociation of  $\text{NO}_2$  molecules. The Au nanoparticles attached to the surface of ZnO nanowires enhance the adsorption of  $\text{NO}_2$  molecules through the spillover effect[10]. The  $\text{NO}_2$  molecules adsorb easily on Au nanoparticles and migrate into ZnO nanowires, which enhance the depletion region further, thereby suppressing the underlying conducting channel more. The overall effect enhances the size of depletion layer and increases resistance.

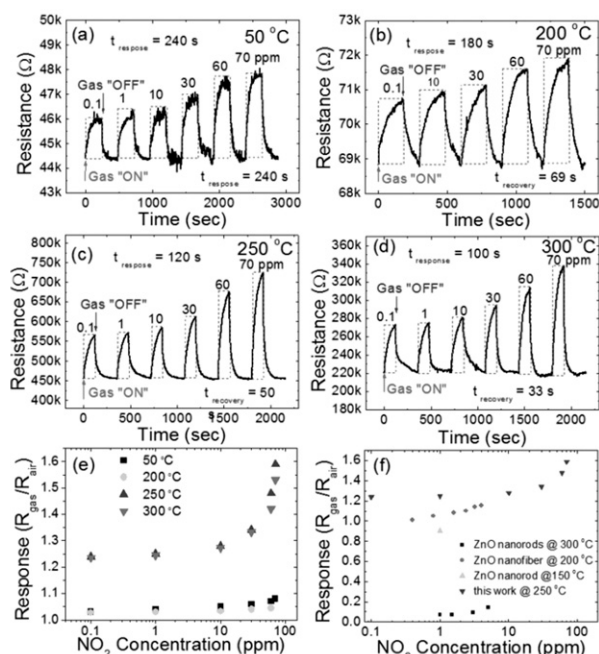


Fig. 4. Response curves of the Au-functionalized ZnO nanowire sensor to NO<sub>2</sub> at (a) 50 °C, (b) 200 °C, (c) 250 °C, and (d) 300 °C. (e) Summary of the responses obtained from the Au-functionalized ZnO nanowires. (f) Responses of Au-functionalized ZnO nanowires compared with other related ZnO gas sensors.

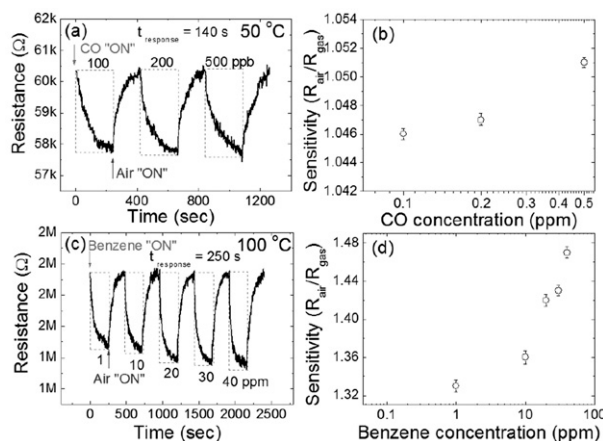


Fig. 5. Response curves and summary of the responses of the Au-functionalized ZnO nanowire sensor to (a) and (b) CO at 50 °C and (c) and (d) to benzene at 100 °C.

The sensing behavior of the Au-functionalized ZnO nanowires was also investigated in the presence of CO at 50 °C and benzene at 100 °C. The typical response curves and the summary of the responses are shown in Fig. 5. The sensor shows a relatively faster response time of 140 s for CO in comparison to 250 s for benzene.

## 4. CONCLUSIONS

Networked ZnO nanowires were successfully functionalized with Au nanoparticles via  $\gamma$ -ray radiolysis. The Au-functionalized ZnO nanowires showed decrements in response and recovery times from 240 s to 100 s and 74 s to 33 s as temperature increased from 50 °C to 300 °C. The Au-functionalized ZnO nanowires showed reasonable response for NO<sub>2</sub> at 250 °C, CO at 50 °C and benzene at 100 °C. The improvement in response is likely due to the spillover effect of Au nanoparticles on the surface of ZnO nanowires.

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