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Functional Nanostructures for Sensitive, Selective, and Reliable Gas Sensors

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Abstract

Oxide semiconductor gas sensors with high response, rapid responding/recovering speed, selectivity, and low humidity dependence are designed by controlling the sizes, dimensions, morphologies, assembled configurations, nano-porosities, p-n junctions and surface modification of oxide nanostructures. The contribution consists of hierarchical and hollow nanostructures for highly sensitive and rapid responding sensors, the enhancement of gas response and selectivity by surface modification of oxide nanostructures, gas sensors using nano-scale oxide p-n junctions, and the strategy to decrease humidity dependence of gas sensing characteristics.

Key words: hierarchical nanostructures, hollow nanostructures, surface modification, p-n junctions, humidity dependence

Hierarchical and hollow nanostructures

The gas response, responding speed, and stability of chemoresistive oxide semiconductor gas sensors are closely dependent upon the sizes, dimensions, morphologies, and porosities of nanostructures. Hierarchical and hollow nanostructures are the higher dimensional structures that are assembled from low dimensional, nano-building blocks such as 0-D nanoparticles, 1-D nanowires/nanorods, and 2-D nanosheets (Fig. 1). Hierarchical nanostructures are advantageous to design the high-performance gas sensors on account of their well-aligned nano-porous structures without sacrificing the high surface area to volume ratio [1]. Hollow structures with thin and permeable shell layers are also very attractive nanoarchitectures for gas sensors [1].

Gas sensing reaction of n-type oxide semiconductors consists of the in-diffusion of analyte gas to the sensor surface and the oxidation of analyte gas with the reaction of negatively charged surface oxygen. The full electron depletion can be achieved when the particle sizes are smaller than 2 times of electron depletion layer, which is very advantageous to accomplish high gas responses. However, as the particle size decreases, the nanoparticles tend to form large and dense secondary aggregates due to strong van der Waals attraction. When the in-diffusion of analyte gases into the inner parts of secondary aggregates becomes difficult, the gas response can be significantly decreased (Fig. 2a). In addition, the sluggish in-diffusion can affect the gas responding speed if the rate of sensing reaction is determined by the gas diffusion.

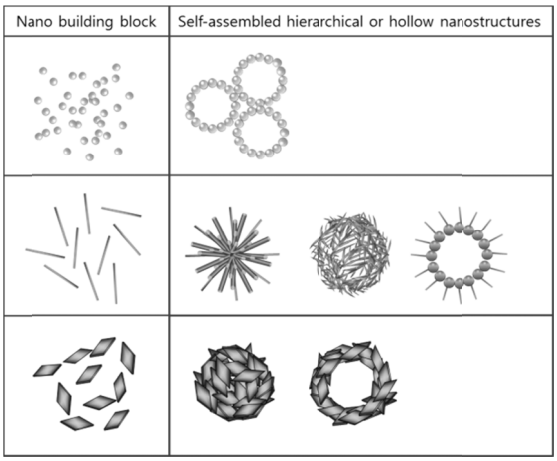

Fig. 1 Various hierarchical and hollow nanostructures that assembled from nano-building blocks such as 0-D nanoparticles, 1-D nanowires, and 2-D nanosheets.

In contrast, high gas response and rapid responding speed can be accomplished simultaneously using hierarchical and hollow nanostructures, which are attributed to the fast and effective diffusion of analyte gas onto the entire sensing surfaces through well-defined porous structures. (Fig. 2b)

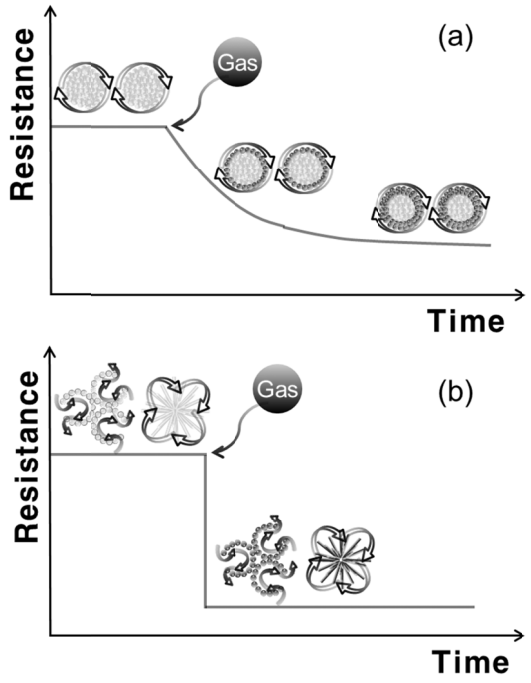

Fig. 2 Schematic sensing transients of (a) agglomerated oxide nanostructures (n-type semiconductor) and (b) hierarchical nanostructures (n-type semiconductor) to reducing gas.

Surface modification of oxide nanostructures

Gas response and selectivity of hierarchical and hollow nanostructures can be enhanced or tuned using the noble metal catalysts or metal oxide additives. The roles of noble metal or metal oxide catalysts on the gas sensing characteristics are the catalytic promotion of surface reaction, the electronic interaction between additive and sensing materials, and the control of acid-base properties. To date, various noble metal catalysts such as Pd, Pt, Au, and Ag have been explored to enhance the gas sensing characteristics of oxide semicondutor gas sensors.

The effect of Rh loading on the gas sensing characteristics of In_2O_3 hollow structures was investigated. Pure and Rh-loaded In_2O_3 (In_2O_3 and Rh-In_2O_3) hollow spheres with the diameters of ~ 2 μm were prepared by hydrothermal reaction of aqueous solution containing indium nitrate, rhodium chloride, and glucose and subsequent heat treatment [2]. The Rh concentration in Rh-In_2O_3 hollow spheres was determined to be 1.67 at% by inductively coupled plasma mass spectroscopy.

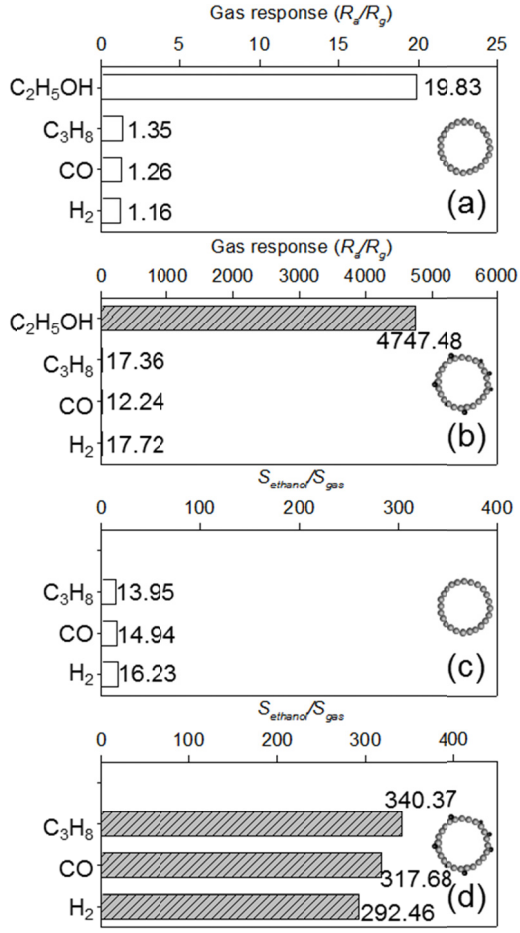

Fig. 3 Gas responses (R_a/R_g, R_a: resistance in air, R_g: resistance in gas) to 100 ppm C_2H_5OH, C_3H_8, CO, and H_2 and selectivity to ethanol ($S_{ethanol}/S_{gas}$, $S_{ethanol}$: gas response to 100 ppm C_2H_5OH, S_{gas}: gas response to 100 ppm interference gas) at 371 °C: (a) gas response of In_2O_3 hollow spheres; (b) gas response of Rh-In_2O_3 hollow spheres; (c) selectivity to ethanol of In_2O_3 hollow spheres; (d) selectivity to ethanol of Rh-In_2O_3 hollow spheres

The gas response (R_a/R_g, R_a: resistance in air, R_g: resistance in gas) of In_2O_3 hollow spheres to 100 ppm C_2H_5OH was 19.83 at the sensor temperature of 371 °C, which was substantially higher than those to 100 ppm C_3H_8, CO, and H_2 (Fig. 3a). The loading of 1.67 at% of Rh markedly increased the response to 100 ppm C_2H_5OH up to 4747.48, while the enhancement in the responses to C_3H_8, CO, and H_2 were not very high (Fig. 3b). The selectivity to ethanol ($S_{ethanol}/S_{gas}$, $S_{ethanol}$: response to 100 ppm C_2H_5OH, S_{gas}: response to 100 ppm interference gas) was calucluated. The $S_{ethanol}/S_{gas}$ values of Rh-In_2O_3 hollow spheres ranged from 292.46 to 340.37, while those of In_2O_3 hollow spheres were in the range between 13.95 and 16.23 (Fig. 3c,d). This clearly indicates that the selectivity to ethanol as well as ethanol response can be enhanced to a significant degree by loading Rh.

Nano scale oxide p-n junctions

The p-n junctions in Si and compound semiconductors have been widely used to fabricate various applications such as transistors, solar cells and light emitting diodes. The regions near the p-n junctions are quite different to those far from the junction in the viewpoint of charge carrier concentration and the potential barrier. This can be used to design oxide semiconductor gas sensors.

There have been many researches on the n-type oxide semiconductor gas sensors such as SnO_2, In_2O_3, ZnO, TiO_2, and WO_3. The representative p-type oxide semiconductors for gas sensor applications are CuO, NiO, Cr_2O_3, and Co_3O_4. The electron depletion layer and hole depletion layer will be formed near the junction of the n- and p-type semiconductors, respectivley. The donor density is one of key parameters to determine the gas response in oxide semiconductor sensors. The charge carrier depletion near the junction can also change the gas responses of n-type and p-type oxide semiconductor sensors. In addition, most of p-type semiconductors can play the roles of catalysts to promote gas sensing reactions. Thus, the formation of oxide p-n junction can be used to enhance the gas selectivity and gas response.

The n-type ZnO nanowires (thickness: 30 - 70 nm) decorated with the discrete configuratoins of p-type Co_3O_4 nano-islands have been prepared by the vapor phase route and their gas sensing characteristics were investigated [3]. Pristine ZnO nanowires were also prepared for comparison. Both of ZnO and Co_3O_4-decorated ZnO nanowires showd the n-type gas sensing behaviors, that is, the resistance increase by oxidizing gas and resistance decrease by reducing gases. This means that the conduction across the Co_3O_4-decorated ZnO nanowires is governed not by p-type Co_3O_4 nanoclusters with discrete configuration but by n-type ZnO NWs with connecting configuration. Thus, the R_g/R_a and R_a/R_g values were used for gas responses to NO_2 and C_2H_5OH, respectively. At the sensor temperature of 200 °C, the response (R_g/R_a) to 5 ppm NO_2 was as high as 46.48 while cross responses (R_a/R_g) to 100 ppm C_2H_5OH, CO, H_2, and C_3H_8 were negligible (Table 1a). This indicates that NO_2 can be measured in a selective manner using pristine ZnO nanowires. However, at 400 °C, the responses to 5 ppm NO_2 and 100 ppm C_2H_5OH become similar, which make the discrimination between NO_2 and C_2H_5OH difficult. In contrast, Co_3O_4-decorated ZnO nanowires showed the selective detection of NO_2 at 200 °C and selective detection of C_2H_5OH at 400 °C. The deposition of discrete p-type Co_3O_4 nanoislands on n-type ZnO nanowires will enlarge the electron depletion layer in a radial direction of ZnO nanowires, which will increase sensor resistance. This is supported by the fact that the resistances in air (R_a) of Co_3O_4-decorated ZnO nanowires sensors were 8 – 60.1 times higher than those of ZnO nanowires sensors at 200 – 400 °C. The increase of R_a will decrease the response to NO_2 (R_g/R_a) and increase the response to C_2H_5OH (R_a/R_g). This says that the formation of oxide p-n junciton can be used to tune the responses to reducing and oxidizing gases. In addition, the catalytic effect of Co_3O_4 nano-island to promote the gas sensing reaction toward C_2H_5OH should be also taken into account.

Table 1: Gas responses of (a) prisinte ZnO nanowires and (b) Co_3O_4-decorated ZnO nanowires to 100 ppm C_2H_5OH and 5 ppm NO_2; (c) the resistances in air of two sensors

(a) ZnO nanowires

T(°C)	response to 5 ppm NO_2 (R_g/R_a)	response to 100 ppm C_2H_5OH (R_a/R_g)
200	46.48	1.0
400	3.45	4.28

(b) Co_3O_4-decorated ZnO nanowires

T(°C)	response to 5 ppm NO_2 (R_g/R_a)	response to 100 ppm C_2H_5OH (R_a/R_g)
200	14.32	1.0
400	1.36	21.94

(c) the resistance in air (R_a) of two sensors

T(°C)	R_a(ZnO)(MΩ)	R_a(Co_3O_4-ZnO) (MΩ)
200	*0.75*	*6.00*
400	*0.31*	*18.8*

Humidity dependence of gas sensors

The resistances, gas responses, responding and recovering speeds of oxide semiconductor gas sensors are known to depend significantly on the humidity because not only the analyte gas but also water vapor interact with oxide semiconductor surfaces. The loading of NiO on hierarchical SnO_2 nanostructures is promising approach to reduce the humidity dependence of gas sensing characteristics to a negligible level [4].

SnO_2 hierarchical structures assembled from nanosheets were prepared hydrothermal reaction and then 1.27 wt% of NiO was loaded. In dry atmospheres, the undoped SnO_2 hierarchical structures showed high and rapid response to 50 ppm CO (dotted line, Fig. 4a). Under the atmosphere of RH 25%, most of gas sensing characteristics such as gas response, responding speed and resistance in air were significantly deteriorated or changed (solid line, Fig. 4a). The loading of 1.27 wt% NiO enhanced the recovery speed in dry atmosphere (dotted line in Fig. 4b). And the NiO-loaded SnO_2 sensor showed the negligible dependence of gas senisng characteristics on humidity (solid line in Fig. 4b). According to diffuse reflectance infrared transform measurement, it is found that the electrochemical interaction between humidity and SnO_2 sensor surface is very small because most of water-related species are abosorbed not on SnO_2 but on discrete configuration of NiO.

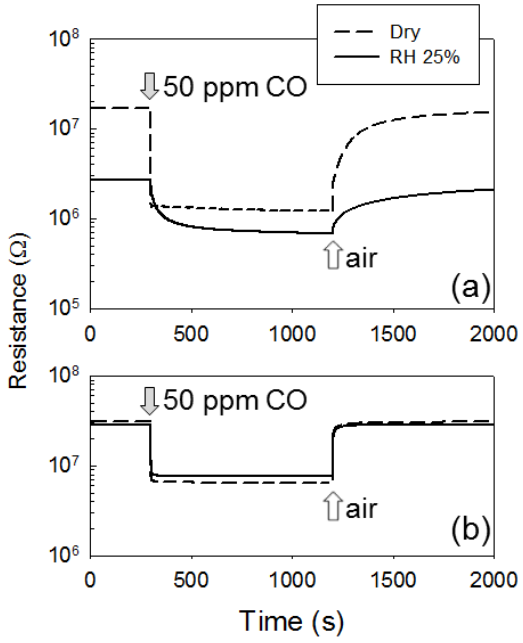

Fig. 4 Sensing transients of (a) SnO_2 hierarchical nanostructures and (b) 1.27 wt% NiO-loaded SnO_2 hierarchical nanostructures to 50 ppm CO at 400 ℃ under dry and humid (RH 25%) atmospheres.

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