Realizing the Control of Fermi Level and Gas-Sensing Selectivity over Gallium-Doped In$_2$O$_3$ Inverse Opal Microspheres †

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Herein, formaldehyde sensors based on gallium-doped In$_2$O$_3$ inverse opal (IO-(Ga$_x$In$_{1-x}$)$_2$O$_3$) microspheres were purposefully prepared by simple ultrasonic spray pyrolysis method combined with self-assembly sulfonated polystyrene spheres template. The well-aligned inverse opal structure, with three different-sized pores, plays dual roles of accelerating the diffusion of gas molecules and providing more active sites. The Ga substitutional doing can alter the electronic energy level structure of (Ga$_x$In$_{1-x}$)$_2$O$_3$, leading to the elevation of Fermi level and the modulation of band gap closed to a suitable value (3.90 eV), hence, effectively optimizing the oxidative catalytic activity for preferential CH$_2$O oxidation and increasing the amount of absorbed oxygen. More importantly, the gas selectivity could be controlled by varying the energy level of adsorbed oxygen. Accordingly, the IO-(Ga$_{0.2}$In$_{0.8}$)$_2$O$_3$ microspheres sensor showed high response toward formaldehyde with fast response and recovery speeds, and ultralow detection limit (50 ppb). Our findings finally offer implications for designing Fermi level-tailorable semiconductor nanomaterials for the control of selectivity and monitoring indoor air pollutant.

Figure 1. (A) Schemes illustrating the preparation of (a-1) inverse opal-In$_2$O$_3$ (IO-In$_2$O$_3$) microspheres, (a-2) Ga-doped IO-In$_2$O$_3$ microspheres (IO-(Ga$_{0.2}$In$_{0.8}$)$_2$O$_3$); (B and C) SEM and (D and E) TEM images of IO-(Ga$_{0.2}$In$_{0.8}$)$_2$O$_3$ microspheres.
Figure 1A illustrated the process of fabrication of inverse opal microspheres. As shown in Figure 1(B,C), the interconnected and well-aligned 3D inverse opal skeletons were observed in IO-(Ga0.2In0.8)2O3, and the sample yielded a long-range ordered hexagonal arrangement of the inverse opal microsphere structure. And, it also could be found that the individual inverse opal microsphere was assembled by packed small nanoparticles. Accordingly, due to the closer distance between the adjacent S-PS spheres (increase in contact area), the IO-(Ga0.2In0.8)2O3 microsphere displayed additional viaholes among the oxide side walls (as indicated by the red arrow in Figure 1C). As shown in Figure 1D,E, a highly aligned inverse opal structure was found in every IO-(Ga0.2In0.8)2O3 microsphere, and it could be found that the IO morphology remained after Ga doping. Besides, all spherical pores (mean pore size, ~160 nm) reflecting the shape of S-PS spheres were well developed and uniform inside the microspheres, and the oxide side walls formed stably between these pore walls, indicating that the inverse opal structure accumulated by many S-PS spheres could be retained even after decomposition of the S-PS sphere templates.

As shown in Figure 2a,b, the IO-(Ga0.2In0.8)2O3 sensor showed the highest formaldehyde response, and reached the maximum (R_a/R_g = 48.8) at 100 ppm formaldehyde at the optimal operating temperature of 200 °C. The orange dotted boxes in Figure 2 highlighted the optimal sensing temperature ranges of the IO-(Ga0.2In0.8)2O3 sensor for selective detection of formaldehyde. The selectivity to formaldehyde over ethanol interference (S_F/S_E) of the IO-(Ga0.2In0.8)2O3 sensor at 150 °C was calculated (Figure 2c). Note that the S_F/S_E value of the IO-(Ga0.2In0.8)2O3 sensor was significantly higher than that of the IO-(Ga0.1In0.9)2O3 and IO-(Ga0.3In0.7)2O3 sensors. The gas-sensing transients of the IO-(Ga0.2In0.8)2O3 sensor toward 0.05-100 ppm formaldehyde at 200 °C are shown in Figure 2d,e. Obviously, the IO-(Ga0.2In0.8)2O3 sensor possessed excellent response-recovery kinetic characteristics in a broad formaldehyde concentration range. And it can be observed that the IO-(Ga0.2In0.8)2O3 sensor still had a response of 1.53 when the formaldehyde concentration was as low as 50 ppb. As shown in Figure 2f, for the IO-(Ga0.2In0.8)2O3 sensor, the response time tended to decrease with increasing formaldehyde concentration, and the sensor showed a long response time at low formaldehyde concentration. However, the recovery time tended to increase when the gas concentration and gas response increased, which emanated mainly from the sluggish surface kinetics of adsorption, dissociation, and ionization of oxygen during the recovery.
As shown in Figure 3, the work function area maps recorded for pure In$_2$O$_3$ and Ga-doped In$_2$O$_3$ are evaluated by employing the Kelvin probe measurements. According to the measured results of the work function values of different IO-(Ga$_x$In$_{1-x}$)$_2$O$_3$ (x = 0 and 0.2) samples, it can be concluded that the Ga doping will cause the elevation of the Fermi level in Ga-doped In$_2$O$_3$ samples.

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