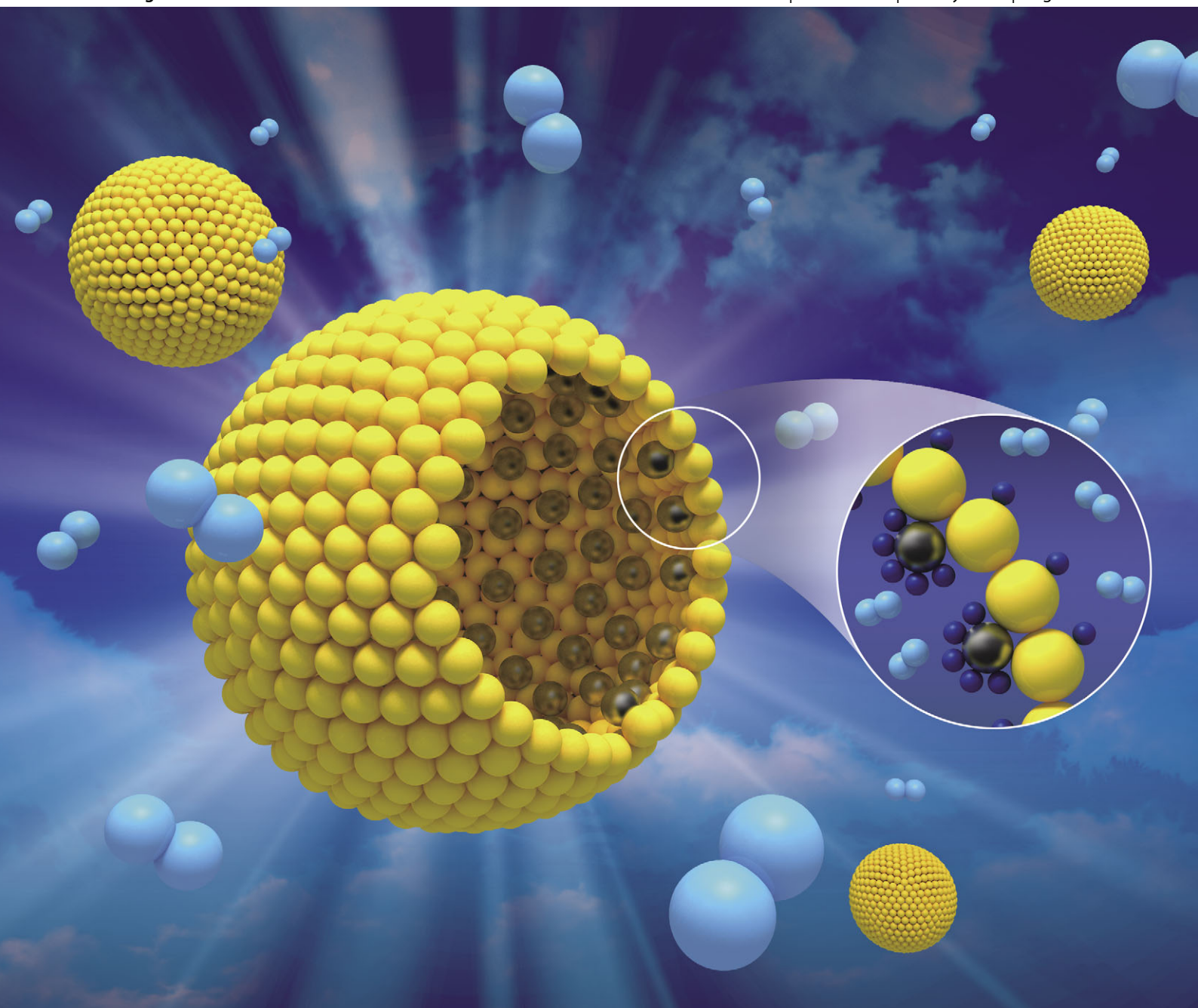


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FEATURE ARTICLE

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Ultra-fast responding and recovering C₂H₅OH sensors using SnO₂ hollow spheres prepared and activated by Ni templates†

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Ultra-fast responding and recovering C₂H₅OH sensors were prepared using nanoscale SnO₂ hollow spheres with NiO-functionalized inner walls. The exceptional ultra-fast recovery characteristics were attributed to the catalytic surface reaction assisted by NiO at the inner shell.

High sensitivity, rapid response and recovery, and selective detection are the three most important parameters in designing oxide semiconductor gas sensors.¹ Rapid response and recovery characteristics, in particular, are required for real-time monitoring of harmful gases and preventing possible disasters due to toxic gases. The gas response and recovery kinetics are closely related to the diffusion of gases onto the sensing surface and the charge transfer interactions on the surface including the adsorption of negatively charged oxygen and the oxidative/reductive interaction between analyte gases and adsorbed oxygen. Gas diffusion in a sensing layer can be facilitated by employing less agglomerated and/or porous nanostructures.² In contrast, the surface reaction is strongly influenced by the operating sensor temperature and/or catalyst employed for promoting gas-sensing reaction.

Oxide hollow spheres are a promising nanostructure for gas sensor applications because the rapid and effective diffusion of analyte gases onto the entire sensing surface *via* nanoscale shells affords high gas sensitivity and rapid response speed.³ Thus far, hollow spheres of SnO₂, In₂O₃, Fe₂O₃, Cu₂O/CuO, WO₃ and CaCu₃Ti₄O₁₂ have been investigated to enhance the gas sensing performances.⁴ As the most representative gas sensing material among these options, SnO₂ has been prepared in the form of hollow structures *via* a soft micelle template route,^{5a} hydrothermal reaction,^{5b} inside-out Ostwald ripening,^{5c} and the coating of Sn-precursors on polymeric templates such as polystyrene,^{5d} polymethyl methacrylate,^{4a} and carbon spheres.^{5e}

Indeed, the responding speeds of the oxide semiconductor gas sensors were greatly enhanced by utilizing hollow nanostructures.^{4b,d} However, even the rapid-responding n-type semiconductor gas sensors with hollow or other nanostructures

still require a prolonged or relatively longer time for recovery from the exposure to reducing gases.⁶ This indicates that rapid recovery remains a major challenge that must be satisfied to achieve real-time monitoring of gas concentration.

In this work, we report on the facile synthesis of NiO-functionalized SnO₂ hollow spheres by the uniform coating of Sn-precursor on Ni spheres, high temperature calcination and subsequent removal of the Ni core. The C₂H₅OH sensing characteristics of this SnO₂ sensor were investigated. To the best knowledge of the authors, this is the first report to study the gas sensing characteristics of SnO₂ hollow spheres prepared using Ni templates. The sensor demonstrated both ultra-fast response (2–5 s) and ultra-fast recovery (4–5 s), the latter of which was explained in relation to the promotion of surface reaction assisted by the NiO particles decorated onto the inner walls of the hollow spheres.

A thin overlayer (~30 nm) of tin hydroxide was uniformly coated *via* controlled hydrolysis on the spherical Ni particles (average diameter: ~300 nm) by stirring Ni-powder-dispersed stock solution containing SnCl₂·2H₂O, (COOH)₂·2H₂O, and N₂H₄·4H₂O for 24 h (Fig. 1a, Figs. S1a and S1b in ESI†). Sn precursor coated Ni spheres were dried and subsequently calcined at 400 °C for 1 h in air to attain crystalline SnO₂ coating layers (Fig. 1b, Fig. S1c in ESI†). During the calcination step, the surface of Ni particles was partially oxidized, resulting in the formation of thin NiO overlayers on Ni spheres (see the ESI† for detailed synthesis procedures). After that, the Ni cores were chemically dissolved using dilute HCl (pH ~2) solution. The resulting SnO₂ hollow spheres exhibited extremely high porosity with large pores separating hollow spheres, inner open spaces and tiny burst holes on the walls as shown in Fig. 1c–e. The ballooning of the shell layer accompanying volume increase during the oxidation of the outermost Ni layer could accelerate the dissolution of Ni cores⁷ and promote the formation of holes on the walls (for example, see arrowed regions in Fig. 1e). This unique morphology facilitates effective penetration of the surrounding gas into the sensing layer, which plays one of the key roles for the high gas sensitivity in this work.

The shell thickness was slightly decreased to ~23 nm due to the densification and crystallization of SnO₂ layers during the heat treatment (Fig. 1f). An interesting aspect is that the SnO₂ hollow spheres were composed of nanoscale primary particles with the average size of 5 nm (Fig. 1g–h). Two lattice planes with the interplanar distances of 2.70 and 3.33 Å and an angle of 66.2° were observed in the lattice fringe (Fig. 1i), which

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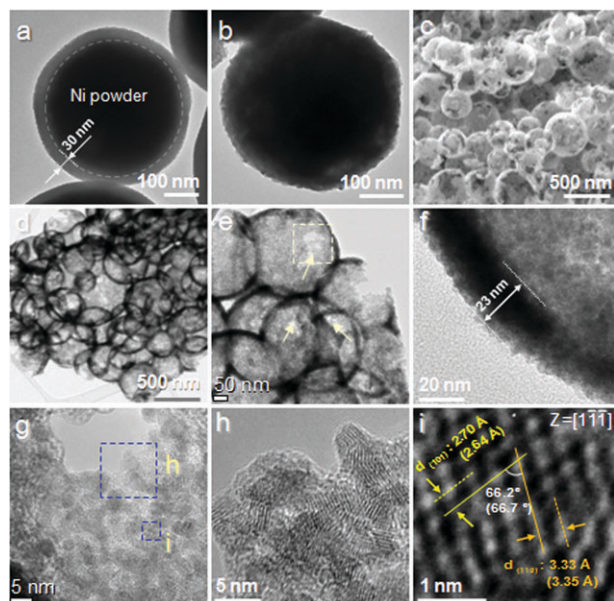


Fig. 1 Morphologies of Sn-precursor- or SnO₂-coated Ni spheres and NiO-functionalized SnO₂ hollow particles: (a) TEM images of Sn-precursor-coated Ni spheres; (b) SnO₂-coated Ni spheres after heat treatment at 400 °C for 1 h; (c–f) SEM and TEM images of SnO₂ hollow spheres prepared by dissolving the Ni core using dilute HCl solution after heat treatment at 400 °C for 1 h; (g) high magnification TEM image of dotted area in Fig. 1e; (h) lattice images of SnO₂ shell (large dotted region in Fig. 1g); (i) lattice fringes from (101) and (110) planes (small dotted region in Fig. 1g), the values in parentheses are theoretical ones.

correspond to (101) and (110) planes of the SnO₂ cassiterite (rutile) crystal structures, respectively.

To examine the gas sensing properties of our SnO₂ hollow spheres and the effect of NiO catalysts on their sensitivity and response/recovery speeds to target gases, we fabricated gas sensor prototypes by screen printing the spheres and heat treatment at 550 °C in air. The hollow and surface morphology was not changed although the crystallite sizes were increased to 15–20 nm during heat treatment (Fig. S2 in ESI†).

The sensors using SnO₂ hollow spheres showed stable response and recovery behaviors (Fig. 2). The gas responses (R_a/R_g , R_a : resistance in air, R_g : resistance in gas) to 20, 50, and 100 ppm C₂H₅OH were 1.75, 2.58 and 3.54, respectively. The times to reach 90% variation in resistance upon exposure to C₂H₅OH and air were defined as the 90% response time (τ_{res}) and the 90% recovery time (τ_{recov}), respectively. The τ_{res} values upon exposure to 20, 50, and 100 ppm C₂H₅OH were 5, 2, and 2 s, respectively. In n-type oxide semiconductors, the response reaction to reducing gas consists of in-diffusion of analyte gas onto the sensing surface and its subsequent oxidation by adsorbed oxygens, *i.e.*, O⁻ or O²⁻, with negative charge. The ultra-fast response speed indicates that the diffusion of analyte gas and its oxidation with O⁻ or O²⁻ occur very rapidly in hollow structures (Fig. 3a).

The most remarkable aspect of the sensing characteristics was the ultra-fast recovery. The τ_{recov} values during recovery after exposure to 20, 50, and 100 ppm C₂H₅OH were 4, 4, and 5 s, respectively, some of the shortest values in the literature. Considering that extended times (20–400 s) are still necessary

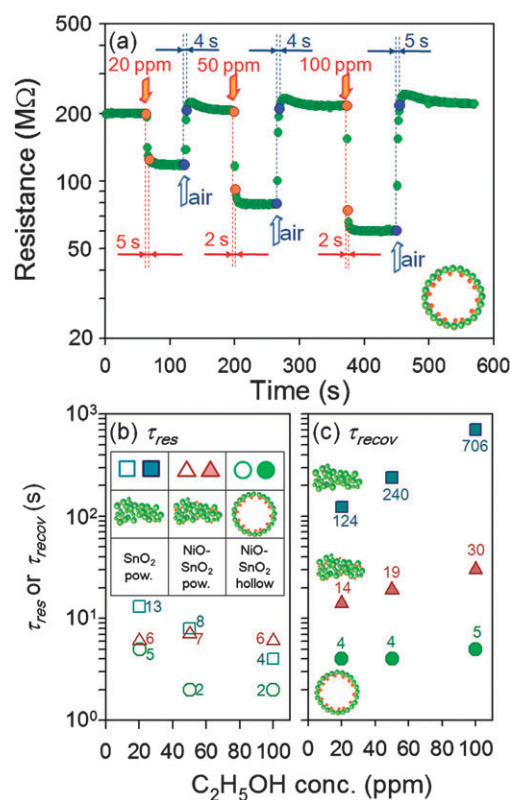


Fig. 2 (a) Dynamic C₂H₅OH sensing transient of NiO-functionalized SnO₂ hollow spheres at 450 °C; (b–c) 90% response and recovery times (τ_{res} and τ_{recov}) of the sensors.

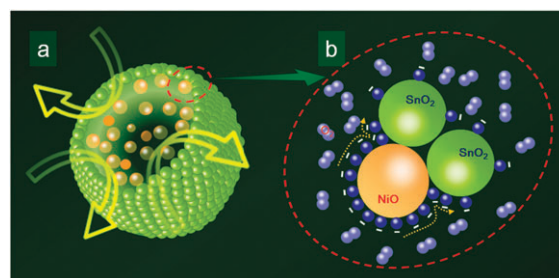


Fig. 3 Schematic diagram illustrating the plausible reason of (a) rapid response and (b) rapid recovery.

for recovery even in the oxide semiconductor gas sensors with fast response,⁶ the ultra-fast recovery of hollow SnO₂ spheres is quite unusual. Catalysts such as Pt, Pd, Fe, and Ni *etc.* are known for their ability to enhance gas response speeds. Jain *et al.*⁸ have reported that the recovery times of a SnO₂ sensor from exposure to LPG were significantly shortened from ~600 s to <10 s by the addition of NiO. Based on earlier reports, NiO phases formed onto the inner shells can serve as a catalyst. Any residual Ni or NiO remaining after dissolution of the Ni core templates will be oxidized into NiO during heat treatment at 550 °C in air. Indeed, a small NiO peak was clearly observed in the XRD pattern of SnO₂ hollow spheres (Fig. S3 in ESI†). Considering the core–shell configuration, this result indicates that the inner wall of the SnO₂ hollow spheres was functionalized with NiO layers. TEM-EDS analysis also confirms the existence of NiO (Fig. S4 in ESI†).

To investigate the role of NiO in the recovery kinetics, the reference sensors using undoped and 1.27 wt% of NiO-doped nanocrystalline SnO₂ powders were measured for the C₂H₅OH sensing characteristics as shown in Fig. S5 and Table S1 in ESI†. The R_a value of the SnO₂ powder sensor was increased ~20 times from 4.05 × 10⁵ kΩ to 9.88 × 10⁶ kΩ by the NiO doping (Table S1 in ESI†). This could be attributed to either the incorporation of acceptor Ni²⁺ at the site of Sn⁴⁺ or the formation of a p–n junction between SnO₂ and NiO. It has been acknowledged that the decrease in donor density arising from the incorporation of an acceptor enhances the gas sensitivity.⁹ However, the addition of NiO into nanocrystalline SnO₂ powders significantly deteriorated the gas response, *i.e.*, R_a/R_g, to 50 ppm C₂H₅OH from 6.37 to 1.54 (Table S1 in ESI†). This can be explained by the counteraction of the n- and p-type sensors upon exposure to reducing gas. Moreover, NiO additives, up to 30 mol%, are known to segregate on the surface of SnO₂ rather than become incorporated into the SnO₂ lattice.¹⁰ Accordingly, the high resistance of the NiO-functionalized hollow SnO₂ sensor (2.00 × 10⁸ kΩ) in the present study was partially attributed to the formation of a p–n junction between the hollow SnO₂ and residual NiO formed from the templates as well as high porosity of hollow sphere structures.

The τ_{res} values of the undoped and 1.27 wt% NiO-doped SnO₂ powders were relatively short (6–13 s) (Fig. 2b), which revealed the fast gas diffusion in both sensors. By contrast, the τ_{recov} value of the undoped SnO₂ powders was very long (124–706 s) while that of the 1.27 wt% NiO-doped SnO₂ powders ranged from 14 to 30 s (Fig. 2c). The recovery reaction includes the following serial reactions: (1) the in-diffusion of oxygen onto the sensing surface, (2) the adsorption of oxygen, and (3) the dissociation and ionization of oxygen. Considering the relatively fast gas diffusion, the 8.9–23.5 times increase in the recovery speed of NiO-doped SnO₂ sensors was attributed to the promotion of surface reactions involving adsorption, dissociation, and the ionization of oxygen by the presence of NiO.

As illustrated in Fig. 3, the full monolayer of oxygen ions is adsorbed easily on the surface of NiO because the Ni²⁺ ions can easily be oxidized into a higher oxidation state (Ni³⁺).¹¹ NiO, thereby, acts as a catalyst to facilitate the oxidation reaction. In contrast, in a pure n-type semiconductor like SnO₂, the concentration of surface oxygen is several orders of magnitude lower than the full monolayer concentration because the chemisorption of oxygen occurs in order to compensate the oxygen deficiency,¹¹ which may retard the recovery reaction involving the chemisorption of oxygen. Thus, the abundant, negatively charged surface oxygens at the surface of NiO can facilitate the transfer of electrons or of negatively charged adsorbed oxygen (O[−]) to the surface of SnO₂ during the recovery reaction (Fig. 3b). This can explain the ultra-fast recovery of NiO-functionalized SnO₂ hollow sensors. To screen an intoxicated automobile driver, a sensor

should be able to detect >0.5 g of C₂H₅OH, which corresponds to [C₂H₅OH] > 200 ppm.¹²

In summary, the SnO₂ hollow spheres, prepared and activated by Ni templates, provide promising gas sensing characteristics, such as ultra-fast response and recovery (≤5 s), as well as sufficient gas response (R_a/R_g = 2.58 to 50 ppm C₂H₅OH). These ultra-fast response and recovery characteristics were attributed to the rapid gas diffusion through the less agglomerated porous shells and the promotion of surface reaction by the NiO inner layers. The simplicity of the techniques outlined in this report offers new means of preparing novel metal-oxide hollow spheres with catalytic inner layers for applications in real-time monitoring gas sensors with ultra-fast responding and recovering speed.

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