

Electronic Supplementary Information (ESI)

Synthesis of rattle-type SnO₂ structures with porous shell

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Experimental section

Chemicals. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, glutamic acid, ethanol, polyvinylpyrrolidone (PVP), tetraethyl orthosilicate (TEOS), potassium stannate trihydrate and concentrated ammonia solution (28 wt%), were of analytical grade and purchased from Shanghai Chemical Corp. Deionized water was used for all experiments.

Synthesis of solid SnO_2 nanospheres. Briefly, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.23 g), and glutamic acid (3.0 g) were dissolved in ethanol (150 mL) with magnetic stirring. The obtained solution was then transferred and sealed into a Teflon-lined stainless-steel autoclave (40 mL in capacity). The autoclave was heated at 180 °C for 48 h, and then allowed to cool down to room temperature. The white products were washed with deionized water and ethanol for 3 times, respectively.

Synthesis of core-shell $\text{SnO}_2 @ \text{SiO}_2$ nanospheres. A solution of polyvinylpyrrolidone (0.325 mL, 12.8 mg mL⁻¹), was added to a SnO_2 solution (0.3 g, 30 mL). The resultant mixture was stirred for 24 h to allow complete adsorption of the polymer on the SnO_2 surface. After this time, the solution was centrifuged (10000 rpm; 5 min) and the supernatant was removed. The volume of the concentrated SnO_2 was then adjusted to 6 mL by dilution with water. The core-shell $\text{SnO}_2 @ \text{SiO}_2$ nanospheres were prepared through a versatile Stöber sol-gel method as follows.¹ Followed by addition of ethanol (18.90 mL) premixed with concentrated ammonia solution (0.84 mL, 28% NH_3 in water) under ultrasound for 15 min. Afterward, a solution of TEOS (1.19 mL) in ethanol (12.80 mL) was added dropwise in 10 min, and the reaction was allowed to proceed for 10 h at room temperature under continuous mechanical stirring. The resultant core-shell $\text{SnO}_2 @ \text{SiO}_2$ nanospheres products were separated and collected, followed by washing with deionized water and ethanol for 3 times, respectively.

Synthesis of core-shell-shell $\text{SnO}_2 @ \text{SiO}_2 @ \text{SnO}_2$ nanospheres. For hydrothermal SnO_2 deposition, $\text{SnO}_2 @ \text{SiO}_2$ particles (0.118 g) were dispersed in 25 mL of

ethanol/water (37.5 vol% ethanol) mixed solvent. To this suspension, potassium stannate trihydrate (113 mg; $K_2SnO_3 \cdot 3H_2O$, Aldrich, 99.9%) were added. After shaking by hand for about 5 min until the salts dissolved, the suspension was transferred to a 40 mL Teflon-lined stainless-steel autoclave, which was then heated in an air flow electric oven at 170 °C for 36 h. The resultant product was separated and collected, followed by washing with deionized water and ethanol for 3 times, respectively.

Synthesis of rattle-type SnO_2 nanospheres. Removal of the organics and crystallization of stannic oxide were achieved by calcination in air by heating the system from room temperature to 600 °C at a rate of 5° min⁻¹. The silica was dissolved in HF for about 30 min. Finally, the rattle-type nanospheres were washed five times with water.

Synthesis of SiO_2 nanospheres. A solution of tetraethylorthosilicate (1.19 mL) in ethanol (12.80 mL) was added dropwise in deionized water (6 mL) with magnetic stirring. The reaction mixture was then stirred for an additional 12 h at room temperature. The resultant colloid was centrifuged (10000 rpm; 30 min) and washed twice with water and twice with absolute ethanol.

Synthesis of hollow SnO_2 nanospheres. For hydrothermal SnO_2 deposition, SiO_2 templates (0.118 g) were dispersed in 25 mL of ethanol/water (37.5 vol% ethanol) mixed solvent. To this suspension, potassium stannate trihydrate (113 mg; $K_2SnO_3 \cdot 3H_2O$, Aldrich, 99.9%) were added. After shaking by hand for about 5 min until the salts dissolved, the suspension was transferred to a 40 mL Teflon-lined stainless-steel autoclave, which was then heated in an air flow electric oven at 170 °C for 36 h. The resultant product was separated and collected, followed by washing with deionized water and ethanol for 3 times, respectively. After annealing the particles at 600 °C for 6 h, the silica was dissolved in HF for about 30 min. Finally, the hollow SnO_2 nanospheres were washed five times with water.

Characterizations. The product was characterized by X-ray diffraction (XRD) using a Rigaku D/Max-2550 diffractometer with Cu K α radiation ($\lambda=1.54 \text{ \AA}$) (40 kV, 350 mA) in the range of 20-80° (2θ) at a scanning rate of 6° min⁻¹. The morphologies of the energy dispersive X-ray (EDX) analysis were obtained on a XL 30 ESEM FEG field emission scanning electron microscope (FESEM). TEM and HRTEM images were recorded with a Tecnai G² 20S-Twin transmission electron microscope operating at an accelerating voltage of 120 and 200 kV, respectively.

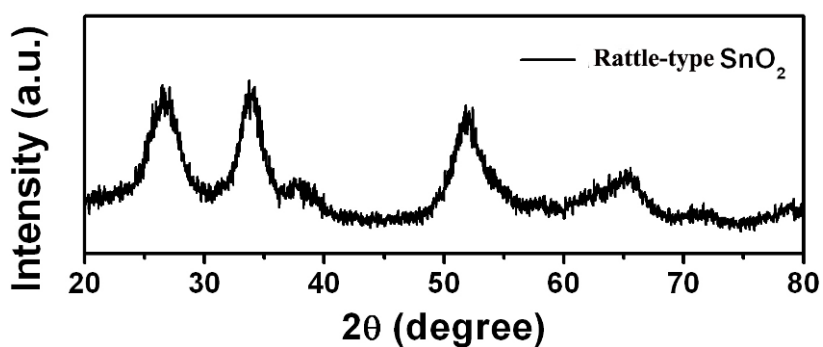


Figure S1 XRD patterns of rattle-type SnO₂ nanospheres.

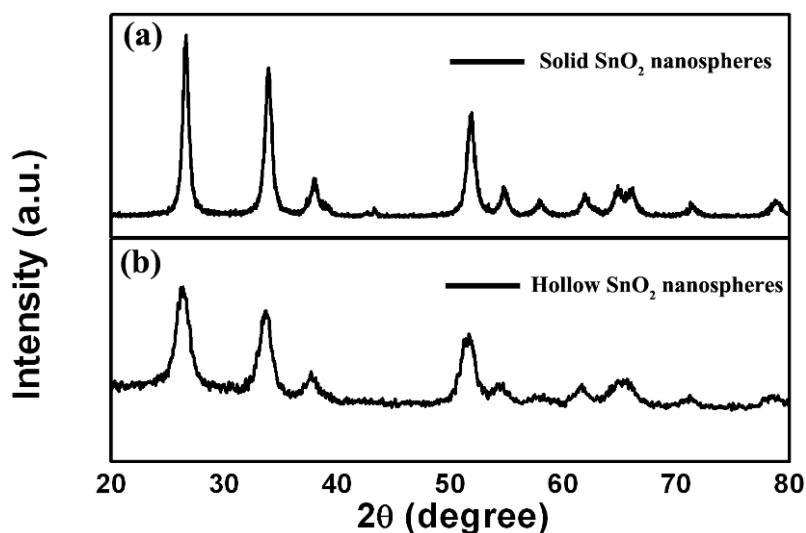


Figure S2 XRD patterns of (a) solid and (b) hollow SnO₂ nanospheres.

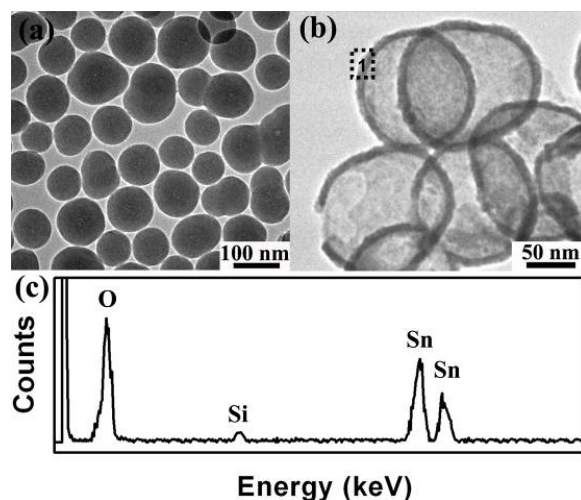


Figure S3 (a-b) TEM images of SiO₂ nanospheres and hollow SnO₂ nanospheres. (c) The EDX spectrum of the hollow SnO₂ nanospheres.

Fabrication and measurement of gas sensor

The product was mixed with deionized water at a weight ratio of 4:1 to form a paste. The sensor was made by a coating ceramic tube with the paste to form a thin 10 μm sensing film. A pair of gold electrodes was installed at each end of the ceramic tube before it was coated with the paste; each electrode was connected with two Pt wires. A Ni-Cr heating wire was inserted into the tube to form an indirect-heated gas sensor. The structure of the sensor is shown in Fig. S4. The details of the sensor fabrication are similar to those reported in the literature.²

The electrical properties of the sensor were measured by a RQ-2 series Intelligent Test Meter (China). The response ($S=R_a/R_g$) of the sensor is defined as the ratio of sensor resistance in dry air (R_a) to that in a target gas (R_g) between 160 and 390 $^{\circ}\text{C}$. The time taken by the resistor to range from R_a to $R_a-90\%$ (R_a-R_g) is defined as the response time, when the sensor is exposed to the target gas. The time taken by the resistor to change from R_g to $R_g+90\%$ (R_a-R_g) is defined as the recovery time, when the sensor is retrieved from the target gas.

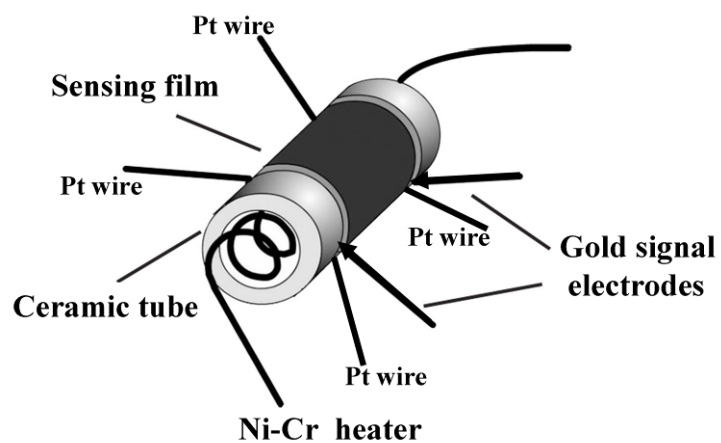


Figure S4 Schematic structure of the gas sensor.

References:

- 1 P. M. Arnal, M. Comotti and F. Schuth, *Angew. Chem. Int. Ed.*, 2006, **45**, 8224.
- 2 L. L. Wang, Z. Lou, T. Fei and T. Zhang, *J. Mater. Chem.*, 2011, **21**, 19331.