Supplementary Material (ESI) for Chemical Communications

Supporting information for

"Ultra-Fast Responding and Recovering C_2H_5OH sensors using SnO_2 Hollow Spheres Prepared and Activated by Ni templates"

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Experimental Section

Preparation of NiO-functionalized SnO_2 hollow spheres:

In 100 mL of distilled water was dissolved 0.005 mol of $SnCl_2 \cdot 2H_2O$ (GR grade, Junsei Chemical, Japan) and HCl solution (35%, Samchun Chemical, Korea) was added dropwise until the solution became completely transparent. The solution became turbid by the addition of 8 g of $(COOH)_2 \cdot 2H_2O$ (GR grade, Kanto Chemical, Japan). Then 80% $N_2H_4 \cdot H_2O$ (Samchun Chemical, Korea) was dripped until the solution pH became 7.1. The solution became transparent again by the addition of $N_2H_4 \cdot H_2O$. While stirring the stock solution vigorously, 2 g of spherical Ni particles (NF32, Toho Titanium Co., Ltd., Japan, mean diameter: 300 nm) was added. The Sn-precursor-coated Ni particles attained by stirring the solution for 24 h were washed with distilled water and acetone and then dried at 60°C for 24 h. The Sn-precursor-coated Ni particles were transformed into SnO_2-coated Ni particles by heat treatment at 400°C for 1 h. Most of the core Ni parts were removed by dissolution in dilute HCl (pH=2) solution for 3 days.

Preparation of NiO-doped SnO_2 powders:

In order to investigate the role of Ni components in gas sensing, the undoped SnO_2 powders (99.9%, 325 mesh, Aldrich, USA) and 1.27 wt% NiO-doped SnO_2 powders were also used as the sensing materials. The Ni components were added by stirring SnO_2 powders in $Ni(CH_3COO)_2{\cdot}4H_2O$ (99.998%, Sigma-Aldrich, USA) aqueous solution, drying, and pulverization.

Gas sensing characteristics:

The NiO-functionalized SnO_2 hollow spheres, SnO_2 powders, and NiO-doped SnO_2 powders were made in a paste form and applied to an alumina substrate with two Au electrodes. The sensor element was heat-treated at 550°C for 1 h to decompose the organic content of the paste. The sensor was placed in a quartz tube and the temperature of the furnace was stabilized at 450°C. The C_2H_5OH concentration was controlled by changing the mixing ratio of 100ppm C_2H_5OH (in air balance) and dry synthetic air. A flow-through technique with a constant flow rate of 500cm^3/min was used. The gas response ($S = R_a/R_g$, R_a: resistance in air, R_g: resistance in gas) was measured at 450 °C. The dc 2 probe resistance of the sensor was measured using an electrometer interfaced with a computer.

Characterization:

The phase and crystallinity of the powders were analyzed by X-ray diffraction (XRD, Rigaku D/MAX-2500V/PC, Cu Kα). The morphology of the precursors and powders were observed by field-emission scanning electron microscopy (FE-SEM, S-4300, Hitachi Co. Ltd., Japan) and high-resolution transmission electron microscopy (HRTEM, Tecnai 20).

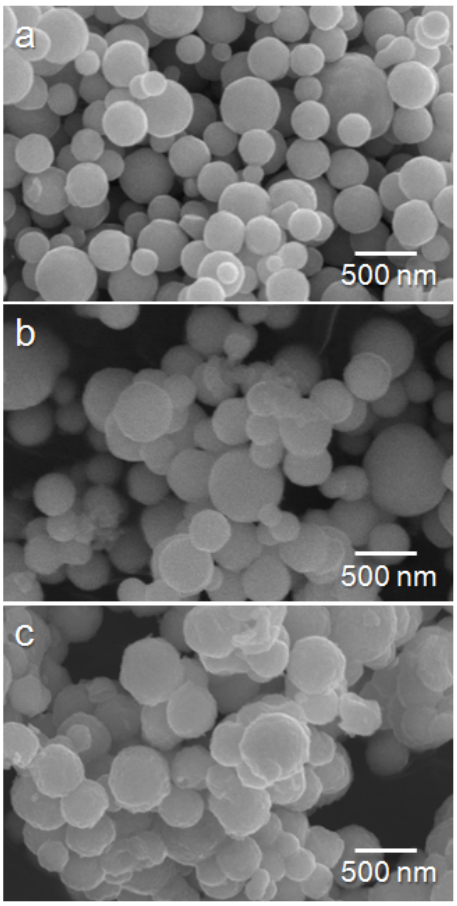


Fig. S1 SEM images of (a) uncoated Ni spheres, (b) Sn-precursor-coated Ni spheres and (c) SnO_2-coated Ni spheres after heat treatment at 400°C for 1 h.

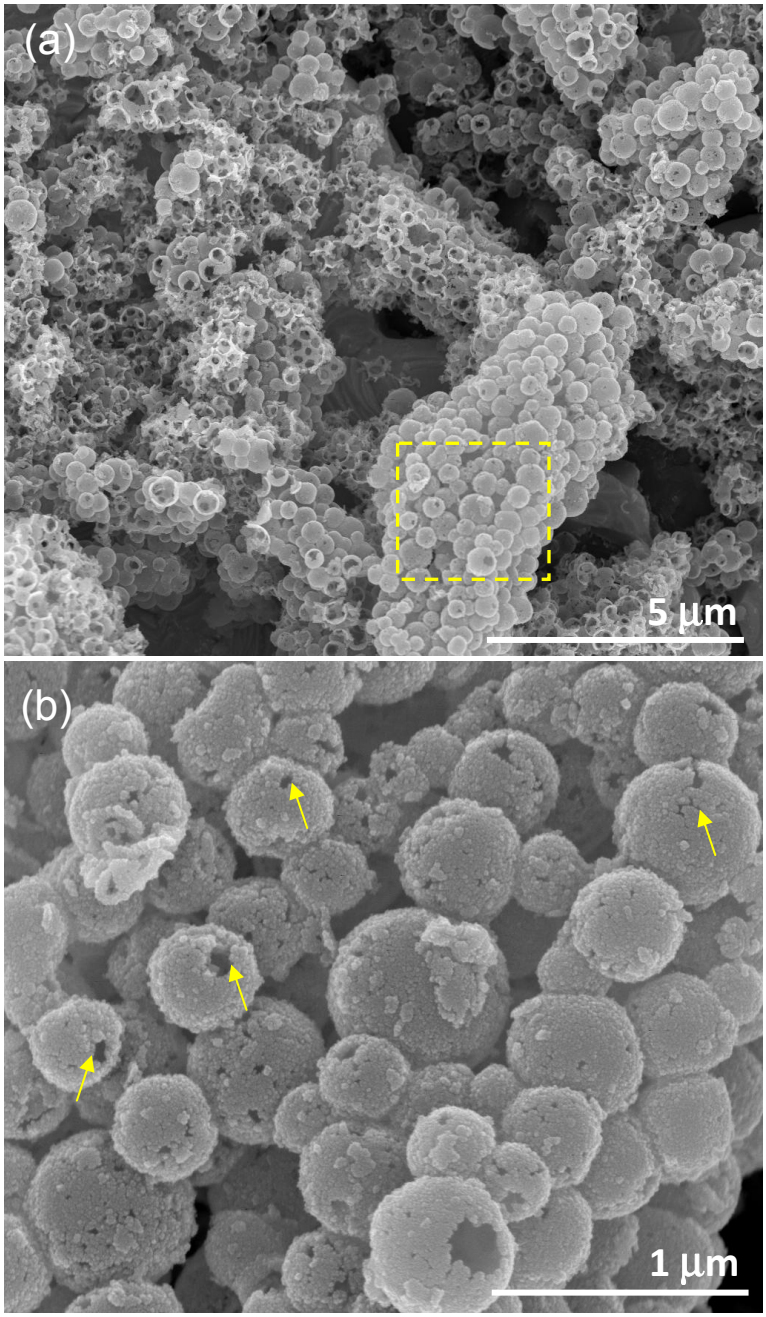


Fig. S2 (a) SEM image of NiO-functionalized SnO_2 sensor after heat treatment at 550°C for 1 h; (b) high resolution image of dotted area in (a). The arrows emphasize small holes on the sphere walls.

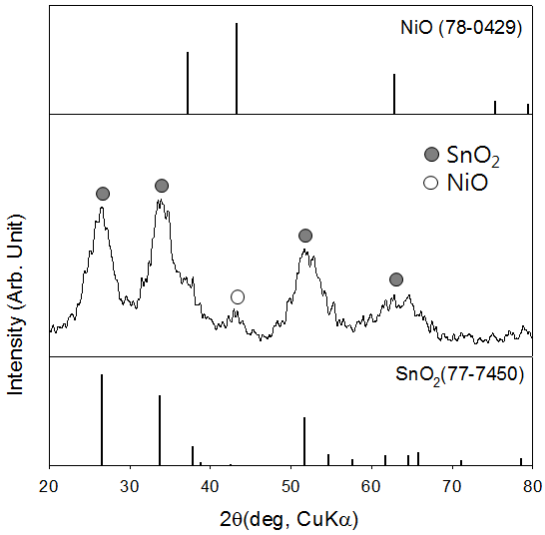
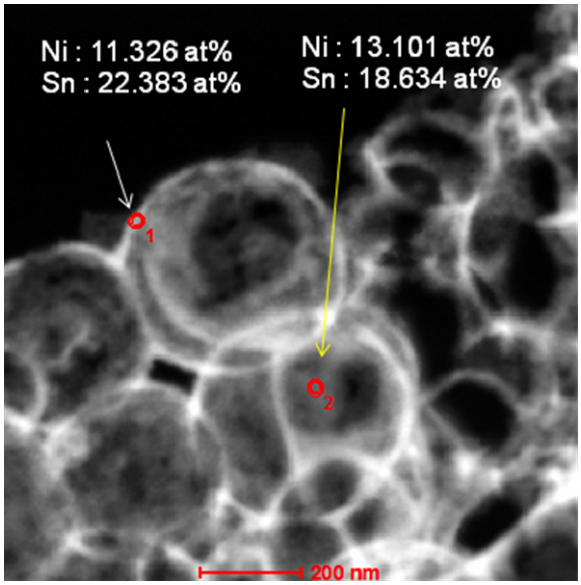


Fig. S3 X-ray diffraction patterns of NiO-functionalized SnO_2 hollow spheres prepared by dissolving the Ni core using dilute HCl solution after heat treatment at 400°C for 1 h.



<Point O_1>

Element	Weight%	Atomic%	Uncertainty%
Sn(L)	60.625	22.383	0.668
Ni(K)	15.172	11.326	0.292
O(K)	24.202	66.289	0.475

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Element	Weight%	Atomic%	Uncertainty%
Sn(L)	54.302	18.634	0.770
Ni(K)	18.881	13.101	0.416
O(K)	26.815	68.264	0.608

Fig. S4 TEM-EDS analysis results of NiO-functionalized SnO_2 hollow spheres prepared by dissolving the Ni core using dilute HCl solution after heat treatment at 400°C for 1 h.

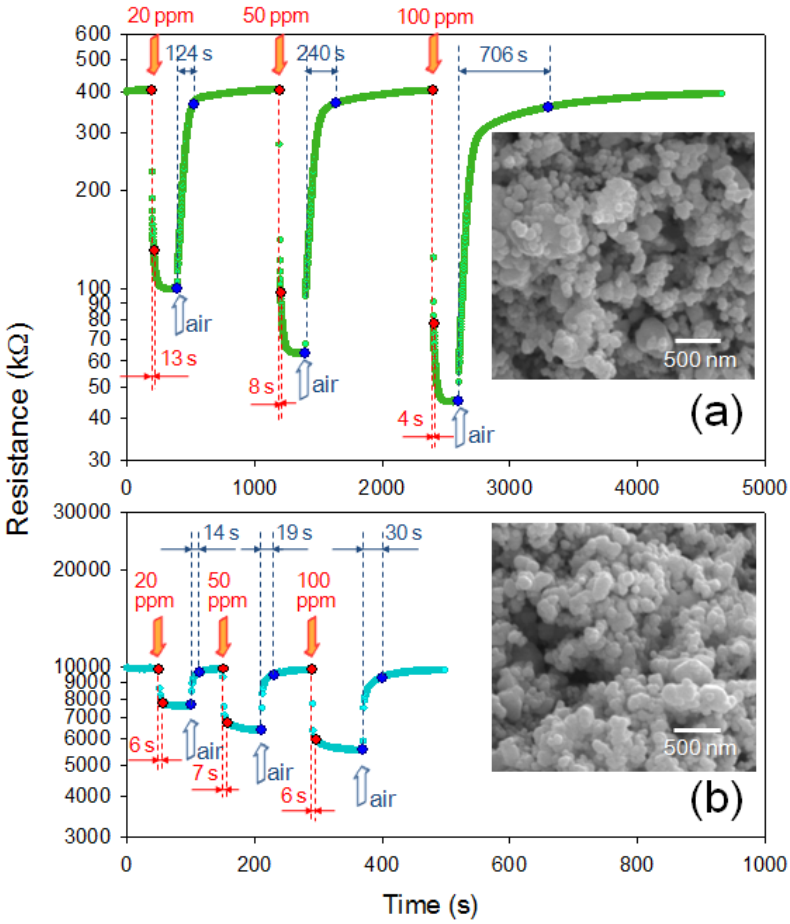

Fig. S5 Dynamic C_2H_5OH sensing transients and SEM images of (a) undoped and (b) 1.27 wt% NiO-doped SnO_2 powders at 450°C.

Table S1. Resistances in air (R_a), gas responses (R_a/R_g), 90% response times (τ_{res}), and 90% recovery times (τ_{recov}) upon exposure to 20-100 ppm C_2H_5OH at 450°C.

		NiO-functionalized Hollow SnO_2	SnO_2 powders[a]	1.27 wt% NiO-doped SnO_2 powders
R_a		2.00×10^5 kΩ	4.05×10^2 kΩ	9.88×10^3 kΩ
R_a/R_g	20 ppm	1.75	4.06	1.30
	50 ppm	2.58	6.37	1.54
	100 ppm	3.54	8.88	1.77
τ_{res}	20 ppm	5 s	13 s	6 s
	50 ppm	2 s	8 s	7 s
	100 ppm	2 s	4 s	6 s
τ_{recov}	20 ppm	4 s	124 s	14 s
	50 ppm	4 s	240 s	19 s
	100 ppm	5 s	706 s	30 s

[a]Commnercial SnO_2 powders