Electronic Supplementary Information

Synthesis of SnO_2 Hollow Nanostructures with Controlled Interior Structures through a Template-assisted Hydrothermal Route

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Experimental Details

Synthesis of SnO_2 Hollow Nanostructures. SnO_2 hollow nanostructures were prepared hydrothermally with the assistance of templates formed through in-situ polymerization of resorcinol and formaldehyde. 2.15 g of stannous sulfate ($SnSO_4$) (or 2.25 g of stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$)) with 3.2 g of resorcinol was dissolved in 30 mL of distilled water to form a mixture. A certain amount of 25 wt% $NH_3 \cdot H_2O$ (0-1.0 mL), 98 wt% H_2SO_4 (0.0-4.0 mL) or 37 wt% HCl (0.0-5.0 mL) solution was then added to the above mixture. Afterward, 7.0 mL of 35 wt% formaldehyde was added under vigorous stirring. The resulting solution was transferred to a 45 mL Teflon-lined stainless steel autoclave and heated in an oven at 85 ^oC for about 48 h. After the autoclave was cooled to room temperature, the intermediate products formed in the autoclave were collected through filtration, washed with distilled water, and dried at 85 ^oC. Subsequently, the intermediate products were calcined at 550 ^oC for 4 h in air to obtain the final product. The core-shell nanostructures prepared with $SnSO_4/NH_3 \cdot H_2O$, $SnSO_4/H_2SO_4$ and $SnCl_2 \cdot 2H_2O/HCl$ are denoted as CSN/$SnSO_4/NH_3$-n, CSN/$SnSO_4/H_2SO_4$-n and

CSN/$SnCl_2$/HCl-n, respectively, where n represents the amount of the $NH_3 \cdot H_2O$, H_2SO_4 and HCl solution added to the reaction system.

Characterization. The transmission electron microscopic (TEM) imaging was performed on a JEOL JEM 3010 electron microscope operating at 300 kV, whereas the scanning electron microscopic (SEM) images were taken on a JEOL JSM-6700F electron microscope operating at 5 kV. The X-ray diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer with Cu Kα radiation (λ=1.5418 Å).

Electrochemical Analysis. The working electrode for the electrochemical test was prepared by mixing the calcined SnO_2 sample (80 wt%), acetylene black (10 wt%), and polyvinylidene fluoride (10 wt% PVDF) in N-methylpyrrolidone (NMP) into a homogenous slurry, which was then spread onto a copper foil and dried at 100 ^{o}C for 24 h under vacuum. 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) (1:1:1 by weight) was used as the electrolyte. The assembly of the cells was conducted in an argon-filled glove box. The batteries were charged and discharged at a rate of 0.5 A g^{-1} between 0.005 and 2.0 V on a LAND CT2001A cell testing apparatus.

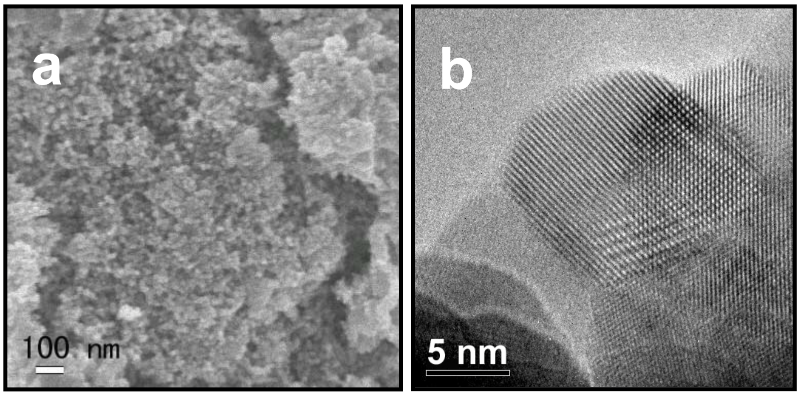

Fig. S1 The magnified SEM and HRTEM images of CSN/$SnCl_2$/HCl-0.0.

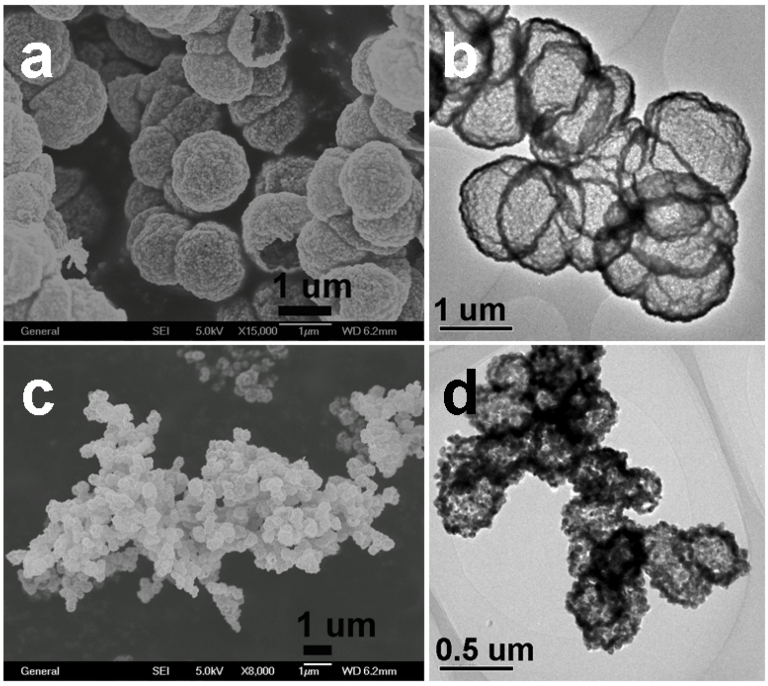

Fig. S2 SEM and TEM images of (a, b) CSN/$SnCl_2$/HCl-1.5 and (c, d) CSN/$SnCl_2$/HCl-5.0.

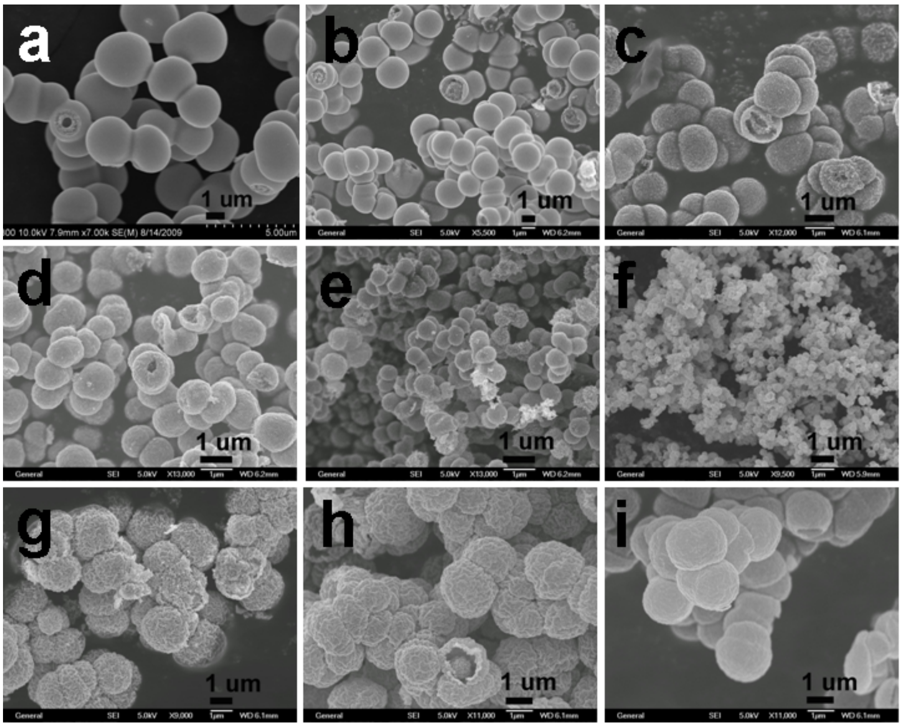

Fig. S3 SEM images of the SnO_2 core-shell nanostructures (a) CSN/$SnSO_4$/NH_3-0.5, (b) CSN/$SnSO_4$/H_2SO_4-0.0, (c) CSN/$SnSO_4$/H_2SO_4-0.3, (d) CSN/$SnSO_4$/H_2SO_4-0.5, (e) CSN/$SnSO_4$/H_2SO_4-1.3, (f) CSN/$SnSO_4$/H_2SO_4-4, (g) CSN/$SnCl_2$/HCl-0.0, (h) CSN/$SnCl_2$/HCl-0.5 and (i) CSN/$SnCl_2$/HCl-1.0

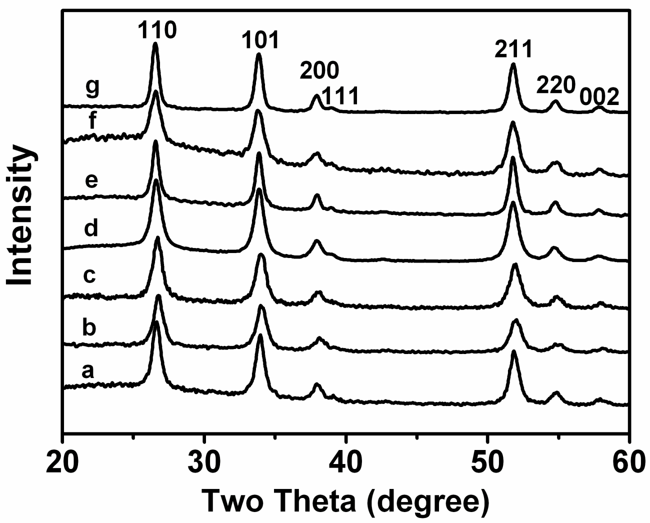

Fig. S4 XRD patterns of the obtained SnO_2 core-shell nanostructures. (a) CSN/$SnCl_2$/HCl-0.0, (b) CSN/$SnCl_2$/HCl-0.5, (c) CSN/$SnCl_2$/HCl-1.0, (d) CSN/$SnSO_4$/NH_3-0.5, (e) CSN/$SnSO_4$/H_2SO_4-0.0, (f) CSN/$SnSO_4$/H_2SO_4-0.5 and (g) CSN/$SnSO_4$/H_2SO_4-1.3.

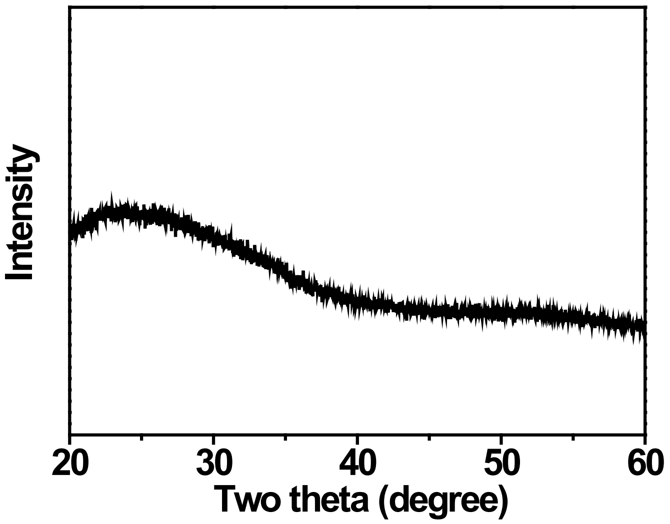

Figure S5. XRD pattern of the intermediate product prepared by using $SnSO_4$ as Sn source with 0.0 mL H_2SO_4 before calcination.

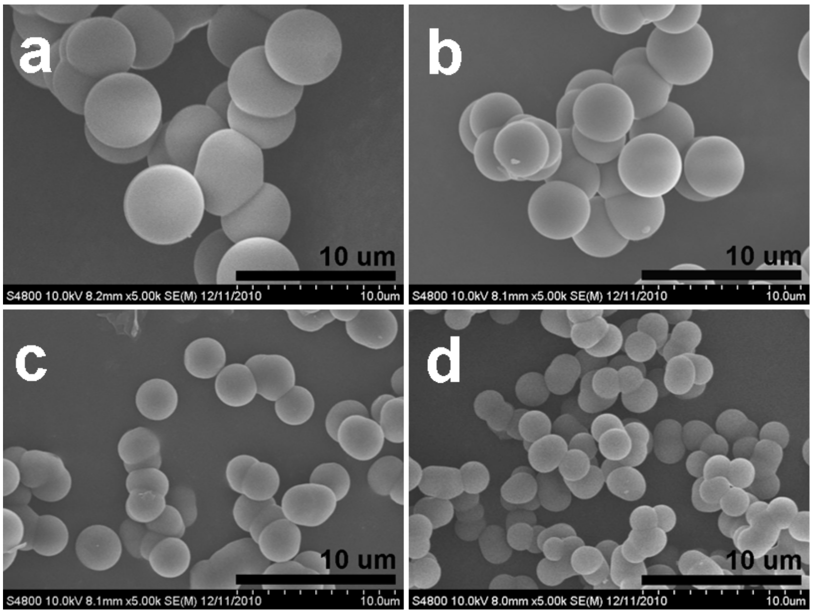

Figure S6. SEM images of the Sn(II)/polymer spheric composites prepared with (a) 0.5 mL $NH_3 \cdot H_2O$, (b) 0.0 mL, (c) 0.5 mL, and (d) 1.3 mL H_2SO_4 acid solutions.

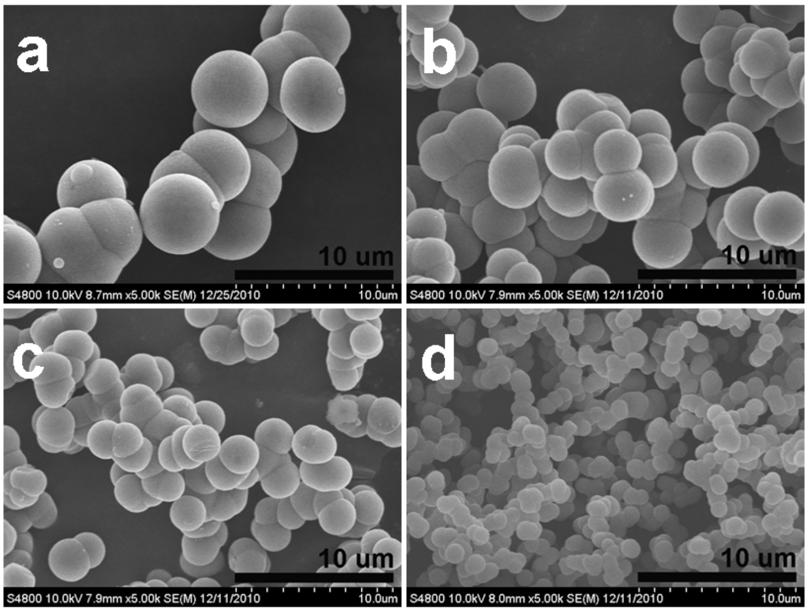

Figure S7. SEM images of the intermediate products prepared with (a) 0.0 mL, (b) 0.5 mL, (c) 1.0 mL, and (d) 5.0 mL added HCl acid solution.

Sample	Core (μm)	Shell-1 (μm)	Shell-2 (μm)	Shell-3 (μm)
CSN/$SnSO_4$/NH_3-0.5	0.4	3.0	1.7	1.0
CSN/$SnSO_4$/H_2SO_4-0.0	0.8	2.2	1.5	—
CSN/$SnSO_4$/H_2SO_4-0.3	0.3	1.6	1.1	—
CSN/$SnSO_4$/H_2SO_4-0.5	0.5	1.2	—	—
CSN/$SnSO_4$/H_2SO_4-1.3	—	0.6	—	—
CSN/$SnSO_4$/H_2SO_4-4.0	—	0.25	—	—
CSN/$SnCl_2$/HCl-0.0	1.5	2.5	—	—
CSN/$SnCl_2$/HCl-0.5	0.8	1.8	—	—
CSN/$SnCl_2$/HCl-1.0	—	2	—	—

Table S1. The shell number and diameter, the core size of the samples obtained at different conditions.

$SnSO_4$ (g)	$SnCl_2 \cdot 2H_2O$ (g)	Resorcinol (g)	Formaldehyde (mL)	H_2SO_4, HCl or $NH_3 \cdot H_2O$ (mL)	Sn wt%	Diameter (μm)
2.15		3.2	7.0	0.5 ($NH_3 \cdot H_2O$)	16.3	5.0
2.15		3.2	7.0	0.0 (H_2SO_4)	17.3	4.0
2.15		3.2	7.0	0.5 (H_2SO_4)	11.1	2.5
2.15		3.2	7.0	1.3 (H_2SO_4)	5.1	1.8
	2.25	3.2	7.0	0.0 (HCl)	13.4	5.0
	2.25	3.2	7.0	0.5 (HCl)	12.0	3.5
	2.25	3.2	7.0	1.0 (HCl)	11.0	2.5
	2.25	3.2	7.0	5.0 (HCl)	4.3	1.0

Table S2. The size and tin content of the Sn(II)/polymer composites prepared at different conditions.