Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Controlled thermal sintering of metal/metal oxide/carbon ternary composite with a multi-scale hollow nanostructure for anode material of Li-ion batteries

Hwan Jin Kim[a], Kan Zhang[a], Jae-Man Choi[b], Min Sang Song[b]*, Jong Hyeok Park[a]*

[a] *School of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea; E-mail: lutts@skku.edu*

[b] *Battery group, Samsung Advanced Institute of Technology, Yongin 446-712, Republic of Korea; E-mail: songms7705@gmail.com*

Experimental Section

Materials

All chemical reagents were purchased from Sigma-Aldrich and were used without further purification.

Synthesis

Colloidal films of 250-nm polystyrene (PS) were prepared on a quartz substrate using the emulsifier-free emulsion polymerization method, followed by evaporation-deposition processes according to our previous report.[1] The tin precursor solution was prepared by dissolving 0.226 g of $SnCl_2$ in 2 mL of ethyl alcohol. The Sn^{2+} precursor solution was dropped onto the PS template and was then transferred onto a hot plate at 50 °C. After drying, the samples were sintered at 700 °C for 2 hours under a pure argon atmosphere to obtain Sn/C and under air to obtain SnO_2. The $Sn/SnO_2/C$ was obtained by sintering under 4-vol% oxygen/argon for approximately 15–45 min, followed by a second annealing step under a pure argon atmosphere. The total sintering time for $Sn/SnO_2/C$ was also 2 hours.

Characterization

Scanning electron microscopy (SEM) of the product was performed using a field emission scanning electron microscope (FESEM, JSM-7000F, Japan). The XRD patterns were obtained with a D500/5000 diffractometer in a Bragg-Brentano geometry under Cu Kα radiation. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (TEM) were performed on a JEOL JEM-2100F (Japan) electron microscope. Thermo-gravimetric analysis (TGA) was conducted using a Seiko Exstar 6000 in an air atmosphere with a heating rate of 10 °C/min.

Characterization of the Electrode Performance

Composite electrode slurry was prepared by mixing the powder sample, carbon black (Super P), and polyvinylidene fluoride (PVDF) and dissolving them in N-methyl-2-pyrrolidone (NMP) at a weight ratio of 80:10:10. Carbon black was used as a conductive additive, and the PVDF was added as a binder. The slurry was deposited on copper foil as a current collector and then vacuum dried at 120 °C for 12 hours. The electrolyte was $LiPF_6$ (1 M) in ethylene carbonate (EC)/diethylene carbonate (DEC)/ethyl-methyl carbonate (EMC) (1:1:1 (v/v/v), Techno SEMICHEM Co., Ltd., Korea). All 2032 coin-type cells were constructed and handled in an Ar-filled glove box. The galvanostatic charge and discharge of the cells were carried out at room temperature using a multichannel battery test system (WonATech) between 0.02 and 3 V. For the evaluation of the rate-capabilities, the various current densities were applied during charge and discharge processes.

Table 1. Component molar ratios of p-IO $Sn/SnO_2/C$ with different sintering times under 4 vol% O_2 in Ar condition.

Samples/component	*Sn (mol)*	*SnO_2 (mol)*	*SnO (mol)*
15 mins	97.48	1.44	1.08
20 mins	95.37	3.57	1.06
30 mins	43.22	55.76	1.02
45 mins	26.78	72.19	1.05
2 hours	0	100	0

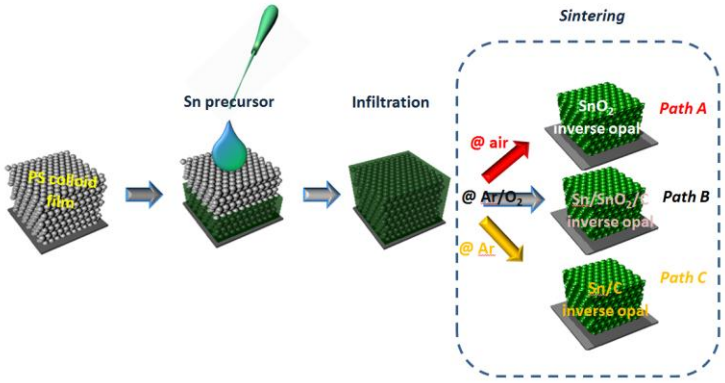

Figure S1. A schematic diagram of the p-IO Sn/C, p-IO Sn/SnO_2/C, and IO SnO_2 syntheses.

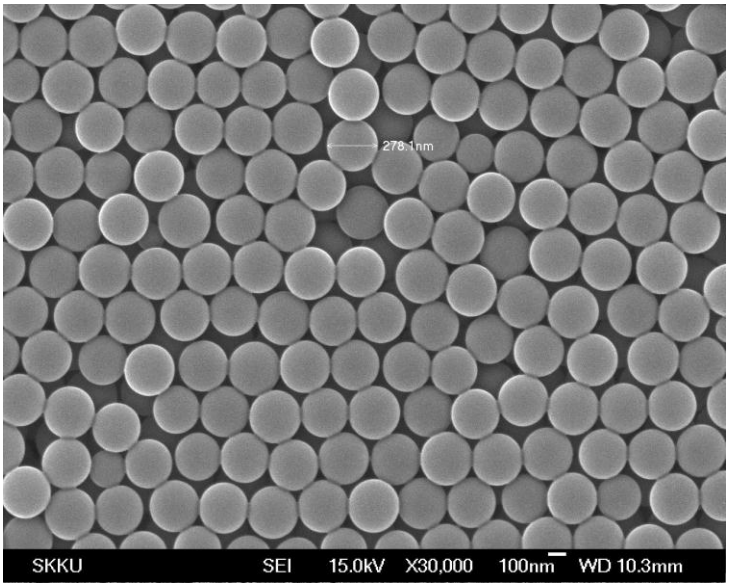

Figure S2. SEM image of PS nanobeads.

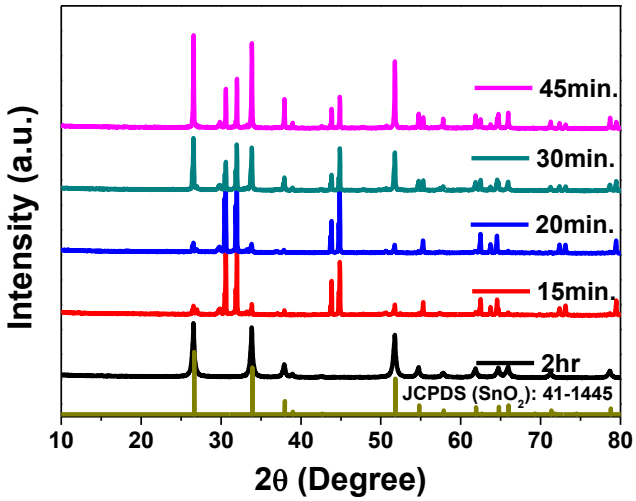

Figure S3. XRD patterns of p-IO Sn/SnO_2/C as a function of sintering time under 4 vol% oxygen in Ar.

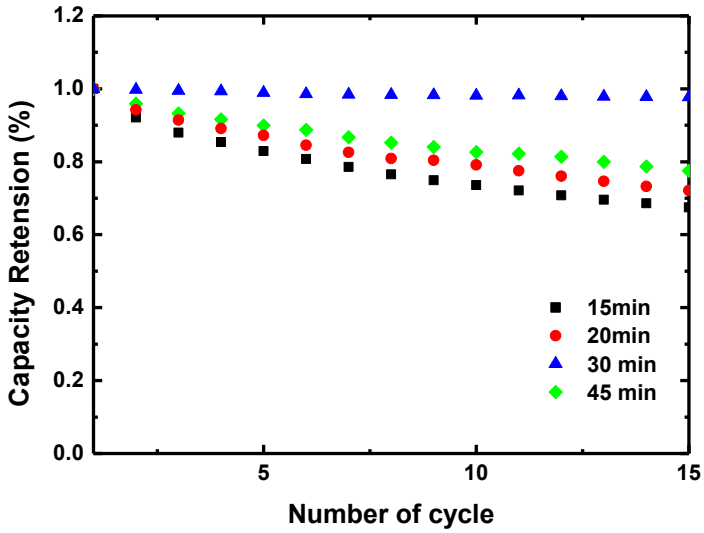

Figure S4. The 0.5C discharge cycle performance of p-IO Sn/SnO_2/C with different sintering time under 4 vol% oxygen in Ar.

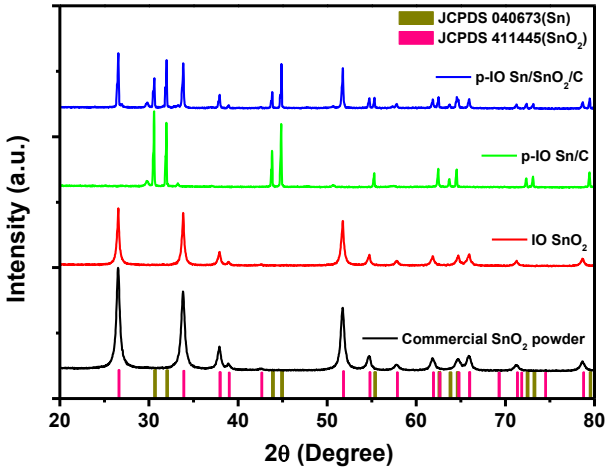

Figure S5. XRD patterns of the commercial SnO_2 nanoparticles, IO SnO_2, p-IO Sn/C, and p-IO Sn/SnO_2/C.

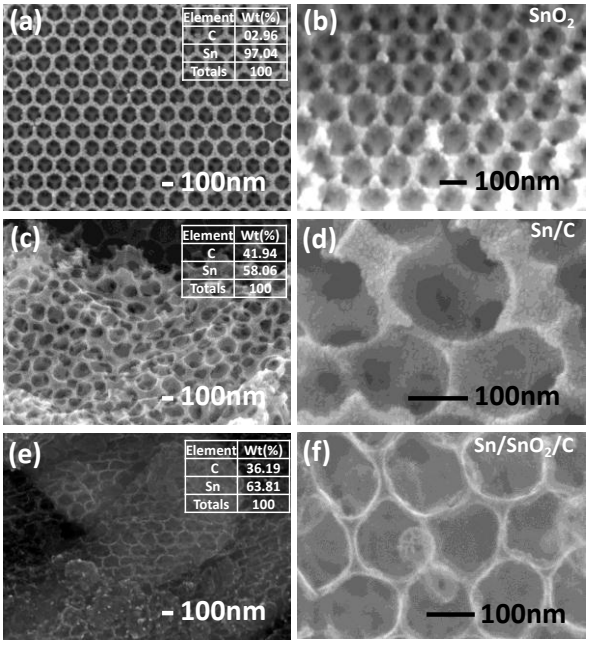

Figure S6. SEM images and the elemental ratios of IO SnO_2 (a–b), p-IO Sn/C (c–d), and p-IO Sn/SnO_2/C (e–f).

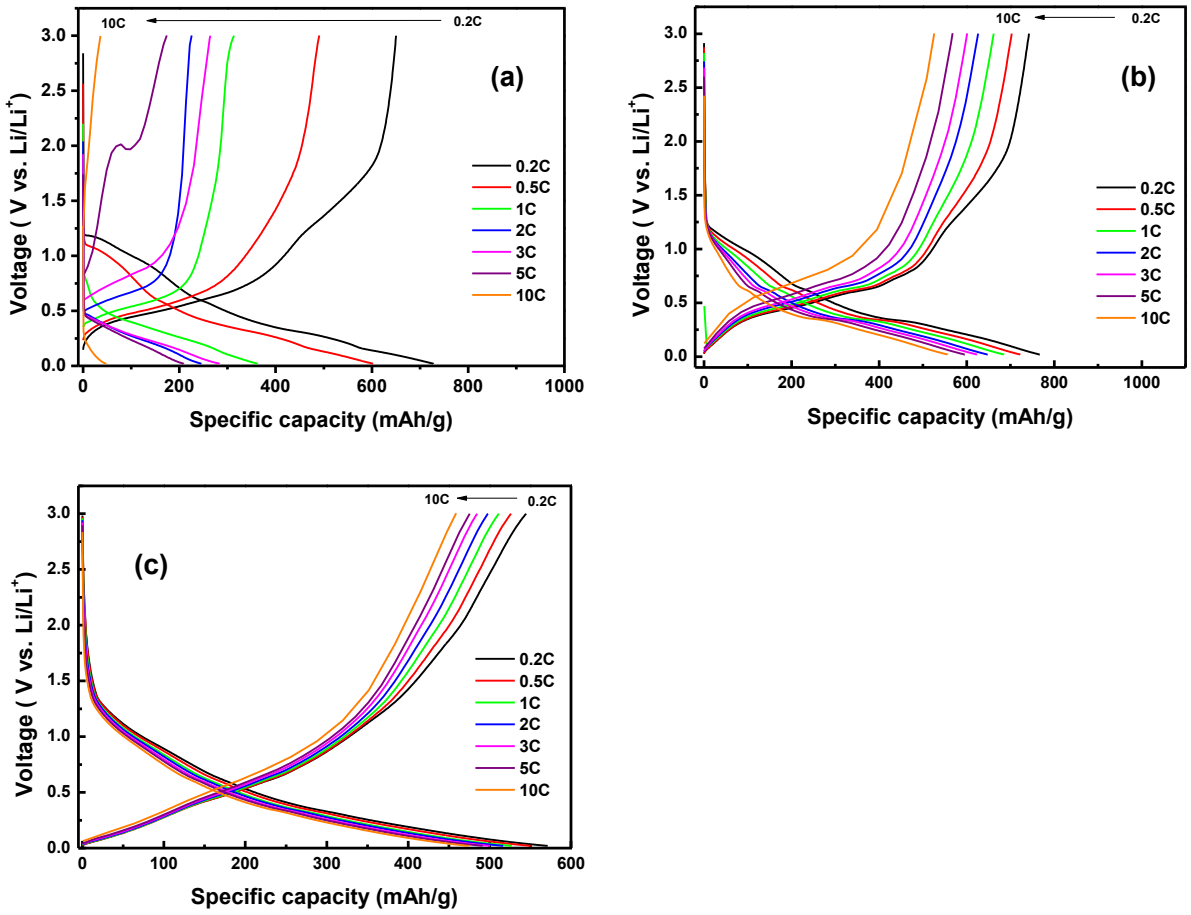

Figure S7. Rated curves of the commercial SnO_2 (a), IO SnO_2 (b) and p-IO Sn/SnO_2/C (c) from 0.2 C to 10 C. All data were obtained after 2cycles with 0.1C charging/discharging rate.