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Experimental details

Preparation of mesoporous TiO₂-Sn@C core-shell microspheres

All chemicals were analytical grade and used without further purification. Amorphous TiO₂ microspheres were prepared according to our previous method.¹ Typically, 2.2 mL of titanium tetraisopropoxide (TTIP) was slowly dropped into 100 mL ethanol containing 0.4 mL of 0.1M KCl aqueous solution. After stirred for 10 min, this suspension was aged in a static condition for 24 h in a closed container at room temperature. Then, the white precipitate was collected, washed with ethanol and deionized water to get monodispersed amorphous TiO₂ microspheres as the precursor. 0.6 g as-prepared TiO₂ precursor was added to 20 mL ethanol-water (1:1) mixed solution, followed by the addition of 0.108 g K₂SnO₃·3H₂O and 0.675 g urea. After stirred for 1h, this suspension was transferred into a 30 mL teflon-lined stainless steel autoclave, and then placed in an oven at 180°C for 12 h. After that, TiO₂-SnO₂ composite was obtained by centrifugation, washed with deionized water and ethanol thoroughly, and dried in an oven at 80°C overnight. This composite was then dispersed in 20 mL ethanol-water (1:1) mixed solution containing 0.4 g glucose, transformed into a 30 mL autoclave, and then kept at 180°C for 18 h. The precipitate was collected by centrifugation and washed with water and ethanol thoroughly. After dried at 80°C, the powders were finally calcined at 700°C under Ar atmosphere for 4 h. TiO₂-Sn@C composite with the black color was thus obtained.

Materials characterization

The morphology and microstructure of the products were obtained using field emitting scanning electron microscopy (FE-SEM, JEOL JSM-7401F) and transmission electron microscopy (TEM, JEOL JEM-2010). The composition and

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crystal structure were characterized by X-ray diffraction measurement (XRD, Rigaku, D/max-Rbusing Cu K α radiation). ICP analysis was conducted by an iCAP6300-type inductively-coupled plasma spectrometer. Raman spectra were recorded from Bruker Optics Senterra R200-L Raman micro-spectrometer ($\lambda=532$ nm, 2 mW). The N₂ adsorption/desorption tests were carried out by Micromeritics ASAP 2010 instrument.

Electrochemical characterization

Electrochemical measurements were performed using 2016-type coin cells assembled in an argon-filled glove box (German, M. Braun Co., [O₂] < 1 ppm, [H₂O] < 1 ppm). For preparing working electrodes, a mixture of the active material, acetylene black, and polyvinylidene fluoride (PVDF) binder at a weight ratio of 80:10:10 was pasted on pure copper foil. Pure lithium foil was used as the counter electrode. A glass fiber (GF/A) from Whatman was used as the separator. The electrolyte consisted of a solution of 1M LiPF₆ in ethylene carbonate and dimethyl carbonate (EC +DMC) (1:1 in volume). The cells were cycled under 500 mA g⁻¹ between cutoff voltages of 2.5 and 0.01 V on a CT2001A cell test instrument (LAND Electronic Co.) at room temperature. Cyclic voltammetry (CV) was implemented on a CHI660D electrochemical workstation.

Figures

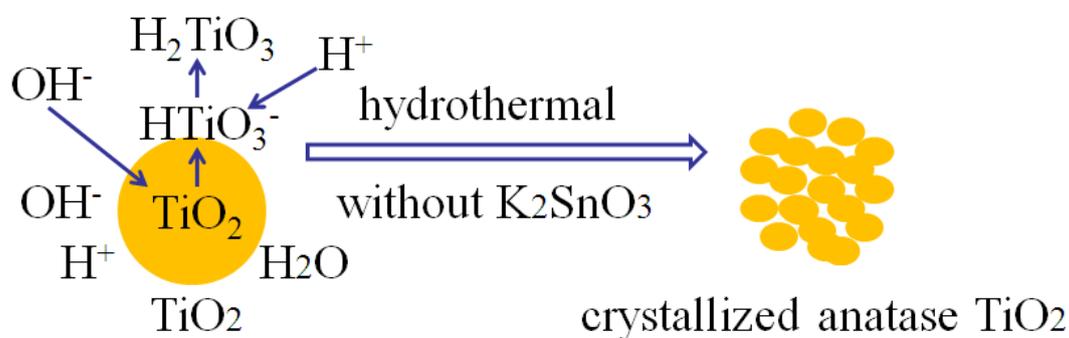


Fig. S1 Schematic illustration of step I hydrothermal reaction if tin source (K₂SnO₃) was not added.

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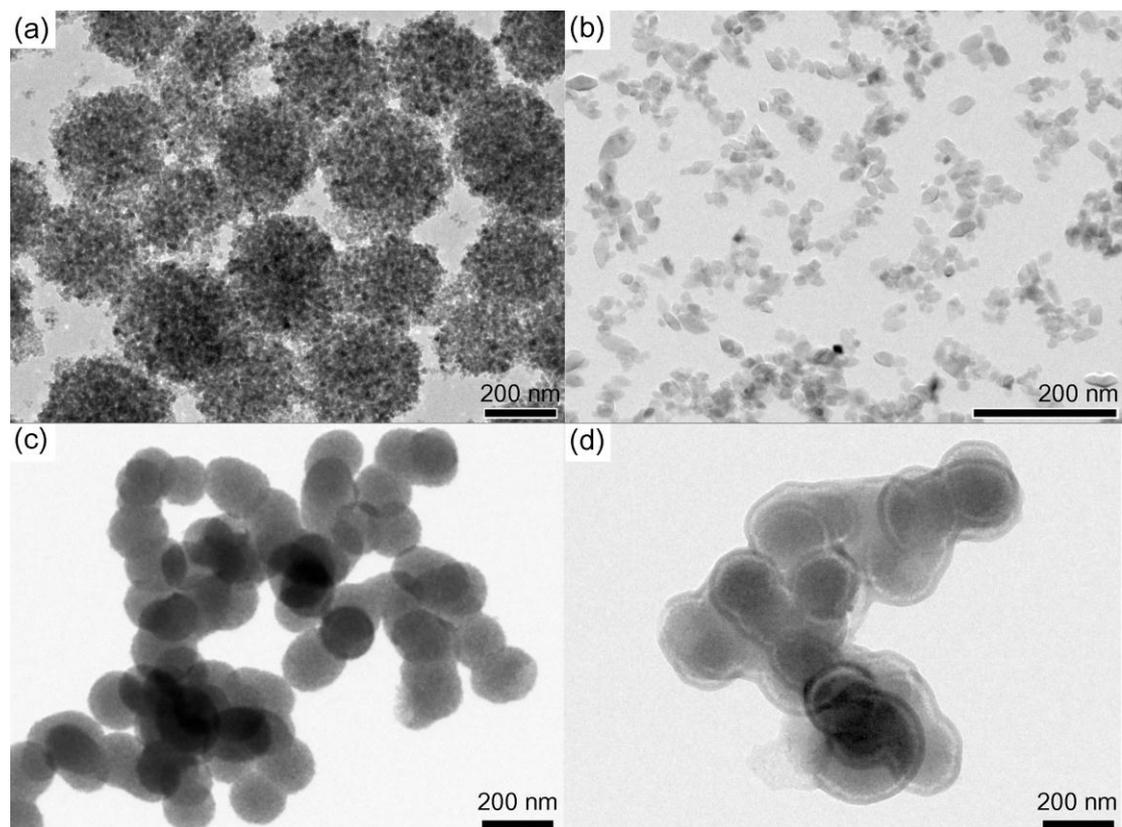


Fig. S2 TEM images of (a) crystallized TiO₂ obtained after 3 h and (b) after 12 h step I hydrothermal reaction if tin source (K₂SnO₃) was not added, (c) SnO₂ obtained after step I hydrothermal reaction if TiO₂ precursor was not added, and (d) Sn@C obtained after step III calcination process in Ar when using SnO₂ instead of TiO₂-SnO₂ in step II.

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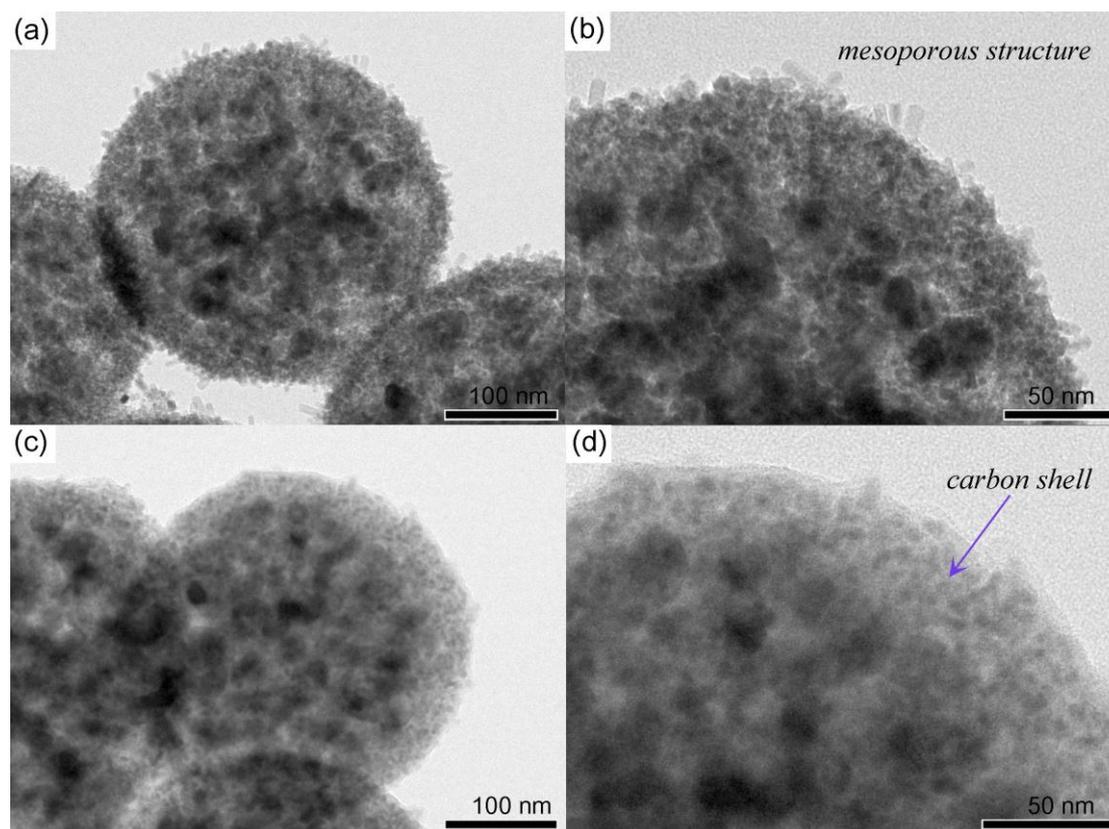


Fig. S3 TEM images of (a, b) $\text{TiO}_2\text{-SnO}_2$, and (c, d) $\text{TiO}_2\text{-Sn@C}$.

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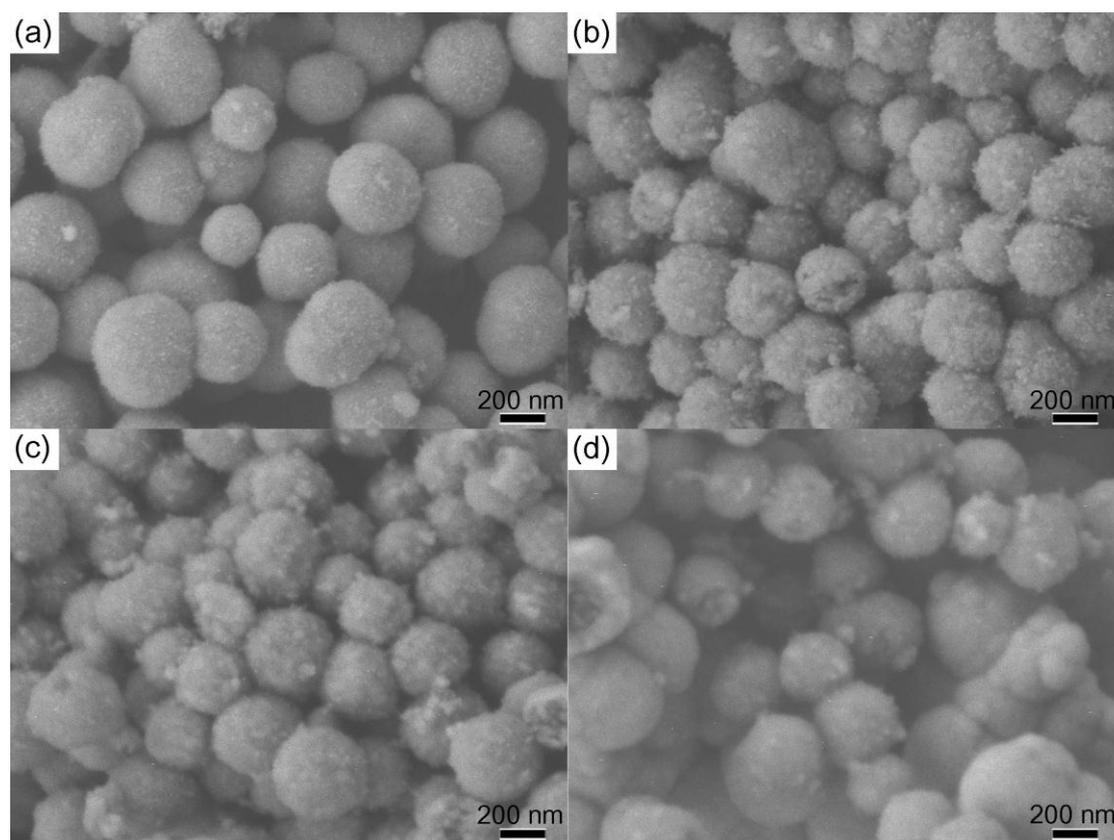


Fig. S4 SEM images of (a) TiO₂ precursor, (b) TiO₂-SnO₂, (c) TiO₂-SnO₂@C, and (d) TiO₂-Sn@C.

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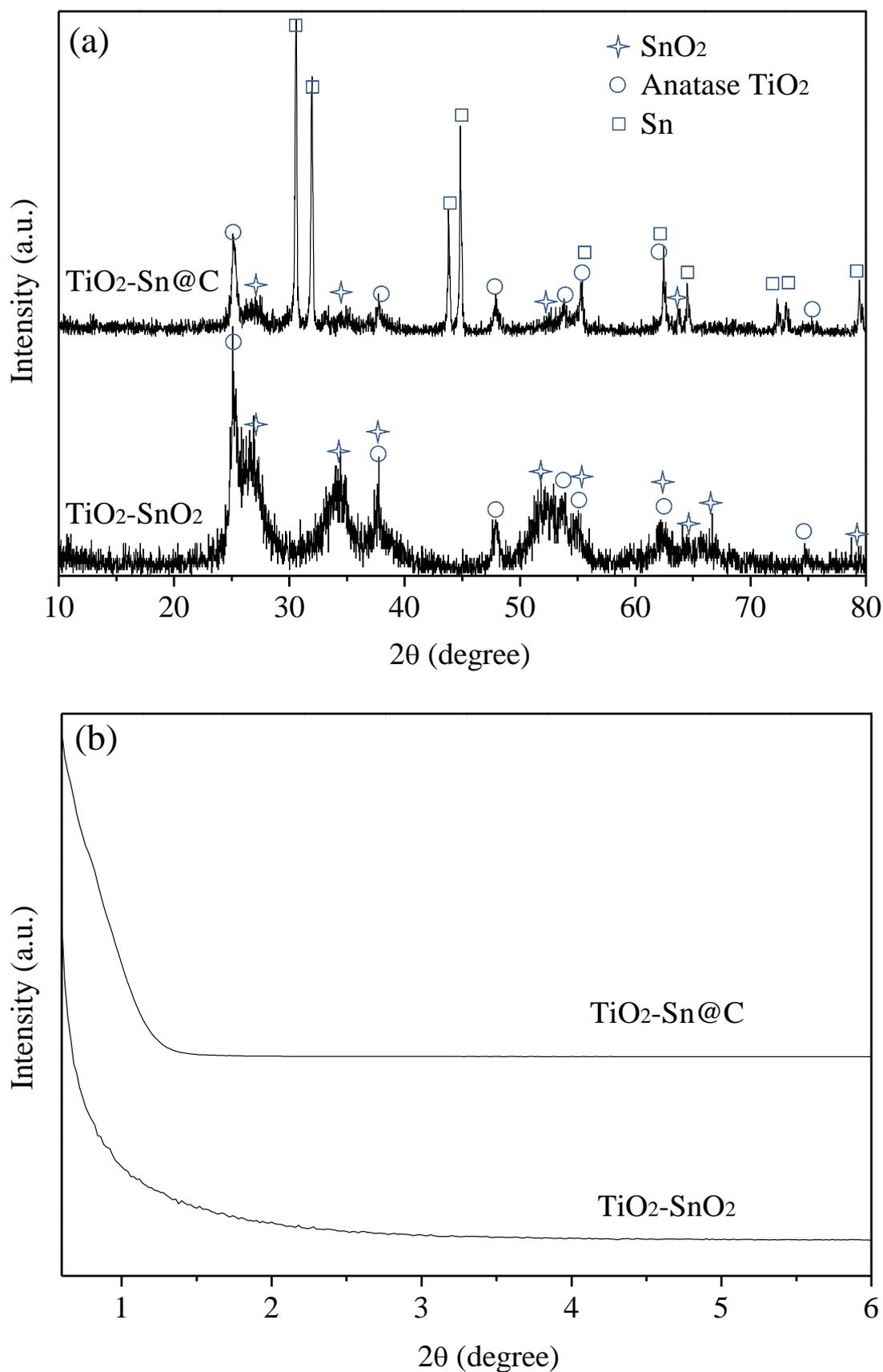


Fig. S5 (a) Wide-angle and (b) small-angle XRD patterns of $\text{TiO}_2\text{-SnO}_2$ and $\text{TiO}_2\text{-Sn@C}$.

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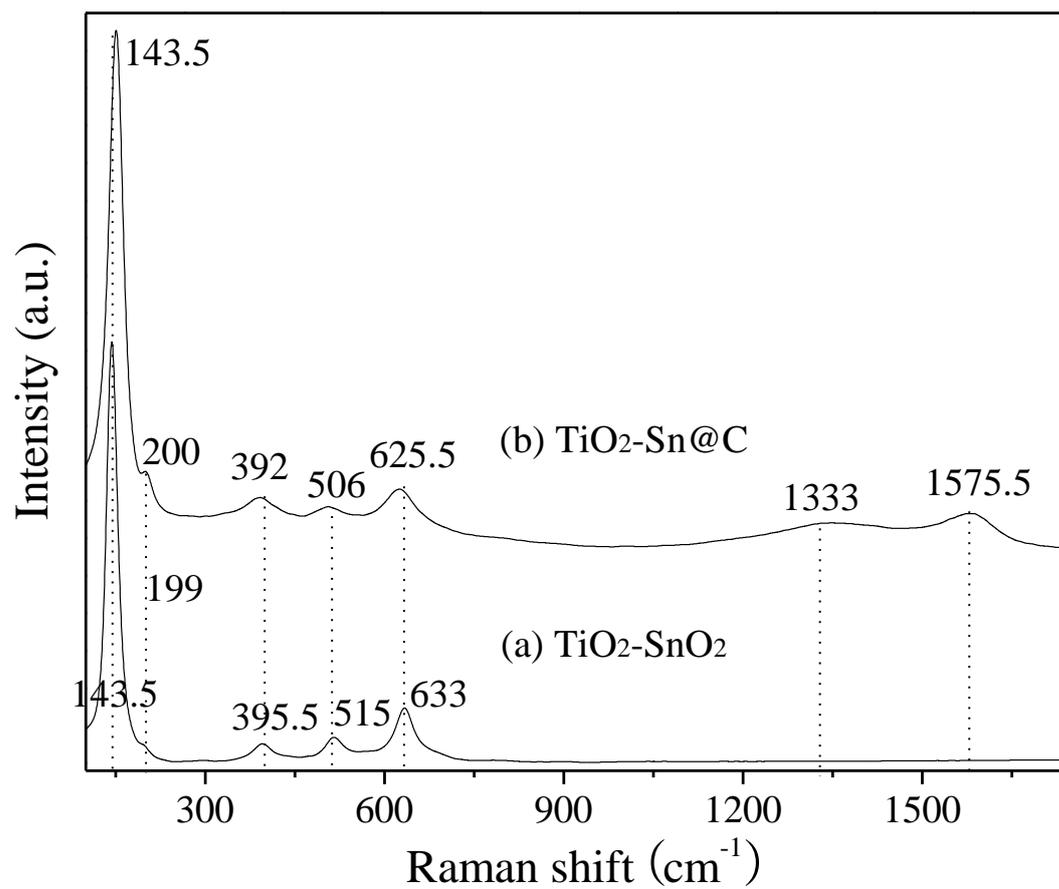


Fig. S6 Raman spectra of $\text{TiO}_2\text{-SnO}_2$ and $\text{TiO}_2\text{-Sn@C}$.

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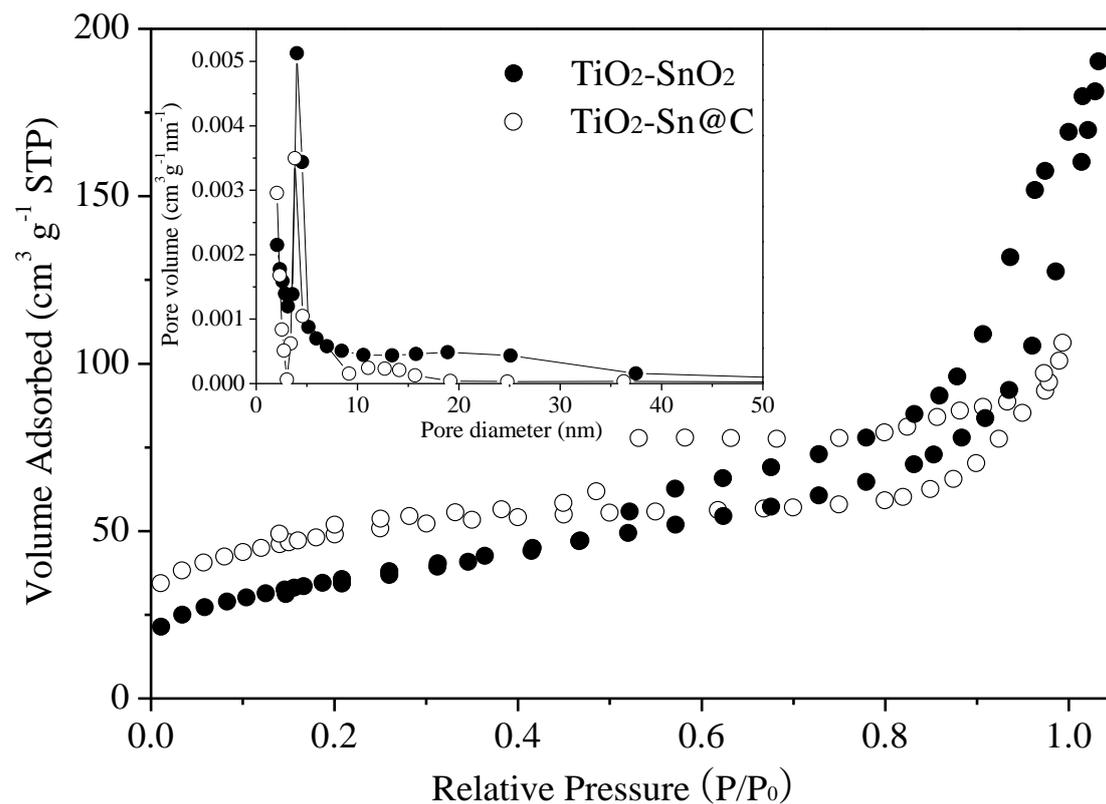


Fig. S7 N₂ adsorption and desorption isotherms of TiO₂-SnO₂ and TiO₂-Sn@C. The inset shows corresponding Barrett–Joyner–Halanda (BJH) pore-size distributions.

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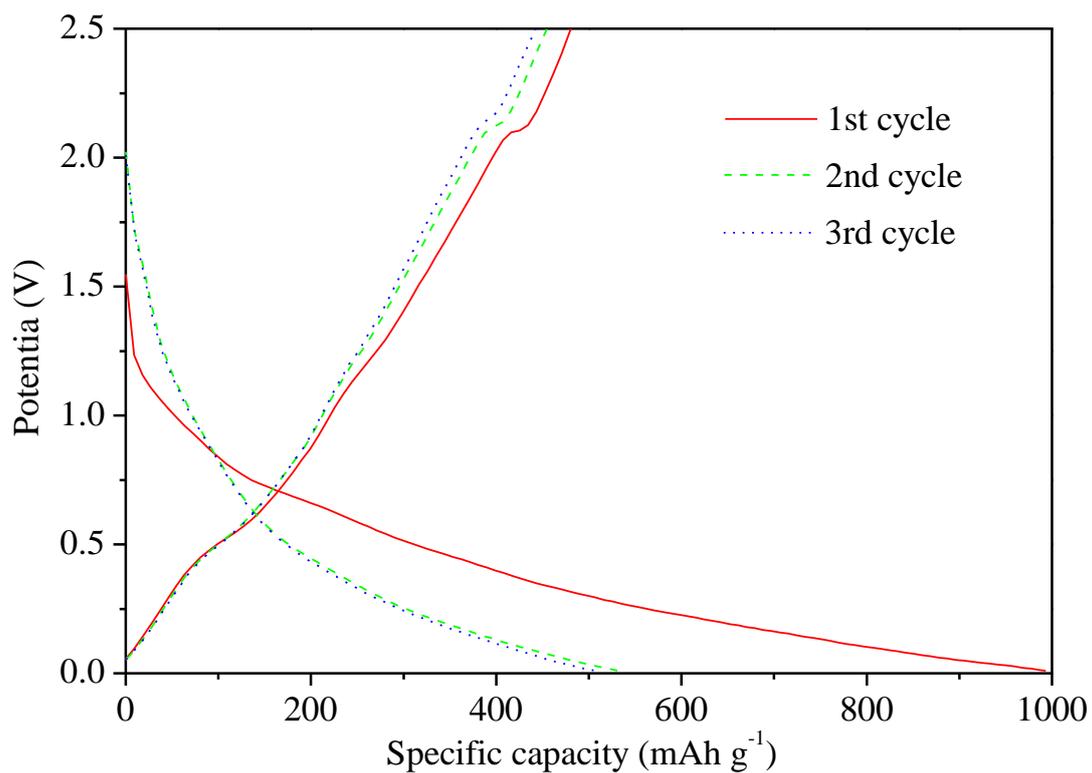


Fig. S8 Initial three discharge/charge curves of TiO₂-Sn@C at 500 mA g⁻¹.

References

- 1 J. Z. Chen, L. Yang and Y. F. Tang, *J. Power Sources*, 2010, **195**, 6893.