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## **Electronic Supplementary Information**

## A Robust Solvothermal-Driven Solid-to-Solid Transition Route from Micron SnC<sub>2</sub>O<sub>4</sub>

## to Tartaric Acid-Capped Nano SnO<sub>2</sub> Anchored on Graphene for Superior Lithium and

## **Sodium Storage**

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### **Experimental Section**

### 1. Materials

Graphite flake (~320 mesh, 99.8%), sodium nitrate (NaNO<sub>3</sub>, 99%), potassium permanganate (KMnO<sub>4</sub>, 99.0%), concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98.08%), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%), oxalic acid (HOOCCOOH, C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>, 99.0%), D-(-)-Tartaric acid (HOOCCHOHCHOHCOOH, C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>, 99.0%), tin (II) chloride dihydrate (SnCl<sub>2</sub>·2H<sub>2</sub>O, 98.0%), tin microspheres (Sn, 99.5%), potassium stannate (KSnO<sub>3</sub>•3H<sub>2</sub>O, 95.0%) and urea (CO(NH<sub>2</sub>)<sub>2</sub>, CH<sub>4</sub>N<sub>2</sub>O, 99.0%) were purchased from Aladdin Industrial Corporation. Acetylene black (99.9%) and sodium alginate ((C<sub>6</sub>H<sub>7</sub>O<sub>6</sub>Na)<sub>n</sub>, 99%) were purchased from Shanghai Macklin Biochemical Technology. Ethylene glycol (>99.0%) and Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (NVP, 98%) were purchased from DoDoChem. All the above chemicals were used as received. The ultrapure water (18.2 MW·cm) was used throughout the solution preparation and washing operation.

### 2. Material Synthesis

### 2.1. Synthesis of graphene oxide (GO) nanosheets

Graphene oxide (GO) was prepared from graphite flake (~320 mesh) via a modified Hummers method as reported in our previous work.<sup>[1]</sup> Graphite flake (5.0 g) and sodium nitrate (2.5 g) were added into 130 mL concentrated sulfur acid in a 1 L beaker placed in an ice bath. The suspension was continuously stirred by mechanical agitation for 2 h. KMnO<sub>4</sub> (15.0 g) was slowly added and stirred for another 2 h. Then, the beaker was transferred to a water bath and stirred at 35 °C for 1 h. Ultrapure water (230 mL) was added into the beaker dropwise to keep the solution temperature below 40 °C. Afterward, the beaker was transferred to a 98 °C oil-bath and kept under vigorous stirring for 30 min, followed by successive addition of ultrapure water (400 mL) and H<sub>2</sub>O<sub>2</sub> (10 mL) at room temperature. Finally, the GO solution was centrifuged with ultrapure water until achieving a neutral pH and stored in a dark brown sealed glass bottles. The concentration of GO nanosheets in the obtained concentrated GO solution was estimated by the mass of GO nanosheets, which afforded after vacuum drying of GO solutions (10 mL) at 80 °C.

### 2.2. Synthesis of SnO<sub>2</sub> NPs, SnO<sub>2</sub> SMPs, SnO<sub>2</sub> MPs, SnO<sub>2</sub> MSs and SnO<sub>2</sub>-TA MSs

SnO<sub>2</sub> nanoparticles (NPs) were synthesized by a facile one-pot solvothermal route as described below. Stannous chloride dihydrate (SnCl<sub>2</sub>·2H<sub>2</sub>O, 1 mmol) and tartaric acid (TA, 1 mmol) were dissolved in H<sub>2</sub>O (5 mL) under ultrasonication for 10 min, followed by addition of ethylene glycol (25 mL). Then, the mixture was stirred at 40 °C for 20 min. Next, the oxalic acid (OA, 3 mmol) was dissolved in H<sub>2</sub>O (10 mL) and then dropwise added into the above solution at 40 °C with vigorous stirring. After reaction completion, white suspension was obtained, and transferred to a 50 mL Teflon-lined autoclave, sealed and allowed to stand still in a thermostatic chamber at 180 °C for 15 h. Finally, the autoclave was cooled down to room temperature, and the precipitate of  $SnO_2$  NPs was collected by centrifugation in 10 mL centrifuge tube, washed with 9 mL absolute ethanol for three times, and dried at 80 °C for 12 h. Therein, for characterizations of the capping of TA on the generated  $SnO_2$  NPs, the final precipitate collected by centrifugation, which was washed with absolute ethanol (2 mL) for only one time to remove the H<sub>2</sub>O and ethylene glycol solvent with retaining most of TA capped on  $SnO_2$  NPs (denoted  $SnO_2$  NPs-TA).

Similarly,  $SnO_2$  submicron particles (SMPs) and  $SnO_2$  microparticles (MPs) were synthesized using the above procedure without the addition of TA and in the absence of TA and OA, respectively. In order to investigate the process mechanism of the interesting solid-to-solid transition from  $SnC_2O_4$  microrods (MRs) to  $SnO_2$  NPs, the intermediate products were obtained at different hydrothermal reaction times (i.e., 0, 1, 2, 5, 8, and 10 h) and then collected for characterizations.

To obviously illustrate the advantages of solvothermal driven solid-to-solid transition (SDSST) route in the size controlled synthesis of TA-capped SnO<sub>2</sub> NPs, control samples of SnO<sub>2</sub> microspheres (MSs) and SnO<sub>2</sub>-TA MSs were synthesized by the conventional solvothermal reaction of Sn salt (i.e., KSnO<sub>3</sub>•3H2O) and urea in reference to the literature.<sup>[2]</sup> In a typical experiment, KSnO<sub>3</sub>•3H<sub>2</sub>O (1 mmol) and urea (5 mmol) were dissolved in ethanol (25 mL) and H<sub>2</sub>O (15 mL) under ultrasonication for 10 min, respectively. Then, the urea solution was dropwise added into the KSnO<sub>3</sub>•3H<sub>2</sub>O solution at 40 °C (water bath) with vigorous magnetic stirring. After that, the mixture solution was transferred into a 50 mL Teflon-lined autoclave, sealed and allowed to stand still in a thermostatic chamber at 180 °C for 15 h. Finally, the autoclave was cooled down to room temperature, and the precipitate of SnO<sub>2</sub> MSs was collected by centrifugation in 10 mL centrifuge tube, washed with 9 mL absolute ethanol for three times, and dried at 80 °C for 12 h. Analogously, the SnO<sub>2</sub>-TA MSs were synthesized using the above procedure after adding TA (1 mmol) in the KSnO<sub>3</sub>•3H<sub>2</sub>O and urea reaction solution before the solvothermal treatment.

# 2.3. Fabrication of SnO<sub>2</sub> NPs-rGO, SnO<sub>2</sub> SMPs-rGO, SnO<sub>2</sub> MPs-rGO, SnO<sub>2</sub> MSs-rGO and SnO<sub>2</sub>-TA MSs -rGO composites

A high-energy planetary ball milling combined solvent evaporation strategy was used to give the SnO<sub>2</sub> NPs-rGO nanocomposite. In a typical experiment, SnO<sub>2</sub> NPs (80 mg), GO (20 mg) and H<sub>2</sub>O (15 mL) were placed in a 50 mL zirconia grinding bowl, and 100 zirconia milling balls with diameters of 3, 5 and 6.5 mm in an amount ratio of 5:3:2 were added. The ball milling was performed for 6 h at a rotation speed of 400 rpm. The obtained slurry of SnO<sub>2</sub> NPs and GO nanosheets was transferred into a 100 mL round flask and treated by ultrasonication for 30 min in an ice bath. Then, the round flask containing of the SnO<sub>2</sub> NPs and GO slurry was placed in 80 °C oil bath under vigorous magnetic stirring. Finally, SnO<sub>2</sub> NPs-rGO nanocomposite was afforded after evaporation completion of H<sub>2</sub>O and then dried under vacuum at 160°C for 4 h. Similarly, SnO<sub>2</sub> SMPs-rGO, SnO<sub>2</sub> MPs-rGO, SnO<sub>2</sub> MSs and SnO<sub>2</sub>-TA MSs-rGO composites were prepared by compositing SnO<sub>2</sub> SMPs, SnO<sub>2</sub> MPs, SnO<sub>2</sub> MSs and SnO<sub>2</sub>-TA MSs with GO nanosheets in a mass ratio of 4:1, respectively, with a similar synthesis approach to that of SnO<sub>2</sub> NPs-rGO nanocomposite.

### 2.3. In-situ Synthesis of SnO<sub>2</sub>/rGO composite

Control sample of SnO<sub>2</sub>/rGO composite was generated by in-situ adding GO in the reaction solution of SnO<sub>2</sub> NPs before the solvothermal reaction. The synthesis approach of SnO<sub>2</sub>/rGO was similar to that of SnO<sub>2</sub> NPs, except that the stannous chloride dihydrate (1.0 mmol) and tartaric acid (1.0 mmol) were dissolved in 10 mL aqueous dispersion of GO (1.1 g L<sup>-1</sup>).

### 2.4. Synthesis of SnO MRs

SnO microrods were fabricated after calcination in Nitrogen at 500 °C for 3 h of  $SnC_2O_4$  microrods, and obtained before the solvothermal reaction in the synthesis of  $SnO_2$  NPs.

### 3. Characterizations

#### 3.1 Structural Characterizations

Scanning electron microscopy (SEM) measurements were performed using a field emission source operated at an accelerating voltage of 15 kV by FEI Quanta 650. The SEM samples were prepared by dispersing the products of interest in ethanol via ultrasonication, followed by deposition and dry on a silicon substrate. Structural analysis and elemental mapping were conducted with a transmission electron microscope instrument (TEM, JEM-2100F) with energy dispersive X-ray (EDX) detector spectroscopy. Powder X-ray diffraction (XRD, Bruker AXS D8 Advance) measurements were conducted using Cu-K $\alpha$ radiation (40 kV, 120 mA) over a 2 $\theta$  range of 10-80°. Laser particle size and Zeta potential analyzer (Zetasizer ZS90) samples were prepared by dispersing products of interest in H<sub>2</sub>O via ultrasonication for 10 min before the measurement. Raman spectroscopy characterizations were performed on a Renishaw InVia Raman spectrometer equipped with a 532 nm laser. Fourier transform infrared (FTIR) spectra were collected by JASCO FTIR 6300. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific ESCALAB 250Xi electron spectrometer with Al Kα radiation (15 kV, 10 mA). Thermogravimetric analysis (TGA) was achieved using a Diamond PE TG/DTA instrument in air atmosphere at a heating rate of 10 °C min<sup>-1</sup> from room temperature to 800 °C. Brunauer-Emmet-Teller (BET) isotherms and specific surface area were obtained using a BELPREP-vac II sorptometer. After the cycling and rate performance tests, the cycled cells of interest were disassembled, and the cycled electrodes were rinsed by dimethyl carbonate (DMC), dried in the argon-filled glove box, and sealed in glass vials for subsequent TEM, SEM and XPS characterizations.

### **3.2 Electrochemical Measurements**

To make the working electrodes, after dispersion of the synthesized SnO<sub>2</sub>-based active material, acetylene black and sodium alginate at a weight ratio of 7:2:1 in ultrapure water, the resulting homogeneous slurry after grinding was pasted onto a copper foil and dried under vacuum at 80°C for 12 h. The foil was then cut into discs with a diameter of 12 mm. The average loading density of active materials in working electrodes is  $1.0 \pm 0.2$  mg cm<sup>-2</sup>. For assembling lithium coin cells, lithium foil, polypropylene (Celgard 2500, Celgard Inc., USA) and 1 mol L<sup>-1</sup> LiPF<sub>6</sub> in ethylene carbonate (EC)/DMC (volume ratio, 1:1) with 5 wt.% fluoroethylene carbonate (FEC) were used as counter electrode, separator and electrolyte, respectively. To assemble sodium coin cells, the sodium foil, glass fiber and 1 mol L<sup>-1</sup> NaClO<sub>4</sub> in EC/DMC (volume ratio, 1:1) with 5 wt.% FEC were used as counter electrode, separator and electrolyte, respectively. To assemble the LIB and SIB coin full cells with SnO<sub>2</sub> NPs-rGO as anodes, the commercial LiFePO<sub>4</sub> (LFP, DoDoChem, 98%) and Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (NVP, DoDoChem, 98%) were served as cathodes, respectively.<sup>[3]</sup> After dispersion of the LFP or NVP, acetylene black and polyvinylidene fluoride (PVDF) at a weight ratio of 8:1:1 in Nmethylpyrrolidone (NMP), the resulting homogeneous slurry after grinding was pasted onto an aluminum foil and dried under vacuum at 80 °C for 12 h which was then cut into discs with a diameter of 14 mm. The average loading density of LFP or NVP in cathode electrodes is  $6.0 \pm 0.8$  mg cm<sup>-2</sup>. Before the LIB or SIB full cell assembly, both cathodes (LFP or NVP) and anodes (SnO<sub>2</sub> NPs-rGO) were first activated by a threecycle galvanostatic charge/discharge test at 100 or 50 mA g<sup>-1</sup> in individual half-cell systems, respectively. After the electrochemical activation, the cathodes remained in the end-of-charge state and the anodes remained in the end-of-discharge state. In this case, SnO<sub>2</sub> NPs-rGO anodes were lithiated or sodiated, and the LFP or NVP cathode were delithiated or desodiated, respectively. Then, the LFP/Li or NVP/Na half cells were disassembled, the used separators were replaced with new ones, and the Li or Na side of the SnO<sub>2</sub> NPs-rGO/Li or SnO<sub>2</sub> NPs-rGO/Na half cells were replaced by the activated LFP or NVP cathode, respectively. After that, the activated cathode and anode were assembled into a coin full LIB or SIB cell for

electrochemical performance testing. Therein, the specific mass capacities of half and full cells were calculated in accord to the mass of  $SnO_2$  in the active materials. The CR2032-type coin cells were assembled in an argon-filled glove box (MIKROUNA).

Galvanostatic cycling tests were conducted using a LAND CT2001A system (Wuhan Landian) over the voltage range of 0.01-3.0 V (vs. Li<sup>+</sup>/Li or Na<sup>+</sup>/Na). Ahead of each galvanostatic cycling test at the high current rates of 1, 2, 5 and 10 A g<sup>-1</sup> for LIBs and 200 mA g<sup>-1</sup> for SIBs, the cells were first activated for three cycles at 100 mA g<sup>-1</sup> for LIBs and 50 mA g<sup>-1</sup> for SIBs, respectively. Cyclic voltammetry (CV) curves were collected on a Shanghai Chenhua electrochemical workstation at various scan rates from 0.1 to 1.0 mV s<sup>-1</sup> over the voltage range of 0.01-3.0 V (vs. Li<sup>+</sup>/Li or Na<sup>+</sup>/Na). The electrochemical impedance spectroscopy (EIS) measurements were also performed using the Shanghai Chenhua electrochemical workstation over a frequency range of 10<sup>-2</sup>-10<sup>5</sup> Hz by applying a perturbation of 0.005 V. For the prelithiation or presodiation treatments of the electrodes, in an argon-filled glove box, the active materials on the electrode sheets were directly contacted with lithium or sodium foil face to face, respectively, completely soaked together in the corresponding electrolytes, and sealed in glass vials for 12 h before assembling cells.

### **Supporting Figures and Tables**



Figure S1. (a, b) SEM and (c) TEM images of SnO<sub>2</sub> NPs. (d-e) SEM and (f-i) (HR) TEM images of SnO<sub>2</sub> NPs-rGO nanocomposite.



**Figure S2.** (a, b, d, e, g, h, j, k) SEM and (c, f, i, l) TEM images of (a-c)  $SnO_2$  SMPs obtained in the absence of TA in the synthesis of  $SnO_2$  NPs, (d-f)  $SnO_2$  SMPs-rGO, (g-i)  $SnO_2$  MPs obtained in the absence of TA and OA in the synthesis of  $SnO_2$  NPs, and (j-l)  $SnO_2$  MPs-rGO.

The SnO<sub>2</sub> SMPs (Figure S2a-S2c) are generated after the aggregation and fusion of SnO<sub>2</sub> NPs. The SnO<sub>2</sub> MPs (Figure S2g-S2i) are irregular large bulks. The large sizes of SnO<sub>2</sub> SMPs and SnO<sub>2</sub> MPs lead to their uneven composition with rGO (Figure S2d-S2f, S2j-S2l).



**Figure S3.** (a, b, d, e) SEM images and (c, f) particle size distributions estimated according to the SEM observations of (a-c) SnO<sub>2</sub> microspheres (MSs) and (d-f) SnO<sub>2</sub>-TA MSs synthesized by conventional solvothermal reaction of KSnO<sub>3</sub>.3H<sub>2</sub>O and urea in the absence and presence of TA, respectively. SEM images of (g, h) SnO<sub>2</sub> MSs-rGO and (i, j) SnO<sub>2</sub>-TA MSs-rGO obtained by ball milling combined solvent evaporation treatment of SnO<sub>2</sub> and SnO<sub>2</sub>-TA MSs with GO in a mass ratio of 4:1, respectively. (k) XRD patterns of SnO<sub>2</sub> MSs and SnO<sub>2</sub>-TA MSs. (l) TGA curves of SnO<sub>2</sub> MSs-rGO and SnO<sub>2</sub>-TA MSs-rGO obtained in air atmosphere.



**Figure S4.** (a-c, g-i) SEM images and (d, j) XRD patterns of (a-d) SnO microrods (MRs) and (g-j) Sn microspheres (MSs). Cycling performances of (e, f) SnO MRs and (k, l) Sn MSs as anodes of (e, k) LIBs and (f, l) SIBs. Therein, SnO MRs were prepared after calcination in N<sub>2</sub> at 500 °C for 3 h of the SnC<sub>2</sub>O<sub>4</sub> MRs (Figure 2a), obtained before the solvothermal reaction in the synthesis of SnO<sub>2</sub> NPs, and Sn MSs were purchased from reagent company of Aladdin Industrial Corporation.



**Figure S5.** (a, b) SEM images, (c) XRD pattern and (d) TGA curve obtained in air atmosphere of  $SnO_2/rGO$  composite synthesized by in situ addition of GO in the generation solution of  $SnO_2$  NPs before solvothermal reaction.

In the  $SnO_2/rGO$  composite (Figure S5b), quite a lot of the  $SnO_2$  particles are not encapsulated in rGO matrix. For this point, there might be two major reasons: first, GO will flocculate out of reaction solution due to its poor dispersibility in ethylene glycol; second, solvothermal leads to the reduction and then agglomeration of GO nanosheets into rGO matrix before the generation of  $SnO_2$  NPs. The mass ratio of rGO in  $SnO_2/rGO$  composite is estimated to be 22.1 wt.%, in according to the TGA measurement curve that obtained in air (Figure S5d).



**Figure S6.** (a) SEM images of intermediate precipitates in the synthesis of  $SnO_2$  SMPs obtained at different solvothermal reaction times of 0, 1, 2, 5, 8 and 10 h. (b) SEM images of intermediate precipitates in the synthesis of  $SnO_2$  MPs obtained at solvothermal reaction times of 1 and 8 h.



Figure S7. XRD patterns of intermediate precipitates obtained at different reaction times in the solvothermal synthesis of (a)  $SnO_2$  NPs, (b)  $SnO_2$  SMPs and (c)  $SnO_2$  MPs.



**Figure S8.** Representative discharge-charge profiles (left panels are corresponding dQ/dV curves of charge profiles) of (a, b) SnO<sub>2</sub> NPs-rGO, (c, d) SnO<sub>2</sub> SMPs-rGO and (e, f) SnO<sub>2</sub> MPs-rGO as anodes of (a, c, e) LIBs at 100 mA g<sup>-1</sup> and (b, d, f) SIBs at 50 mA g<sup>-1</sup>. (g) Representative charge profiles of SnO<sub>2</sub> NPs-rGO as anode of LIBs at 1000 mA g<sup>-1</sup>.

In the discharge/charge curves,  $SnO_2$  NPs-rGO delivers excellent reversibility with almost overlapped voltage profiles from the 2nd to 30th cycles at 50 mA g<sup>-1</sup>, with a stable primary charge plateaus at about 1.05 V (Figure S8b). In stark contrast, the charge plateaus in the voltage profiles of  $SnO_2$  SMPs-rGO (Figure S8d) and  $SnO_2$  MPs-rGO (Figure S8f) are short and obscure, which keep on shrinking and almost disappear after 30 cycles, demonstrating a sluggish sodium storage reactivity and reversibility due to the large sizes of  $SnO_2$  SMPs and  $SnO_2$  MPs with long sodium transfer distances.



**Figure S9.** Cycling stabilities at (a) 100, (b) 1000, (d) 50 and (e) 200 mA g<sup>-1</sup>, and (c, f) rate performances as anodes of (a-c) LIBs and (d-f) SIBs of SnO<sub>2</sub> NPs.



**Figure S10.** Cycling performances of  $SnO_2$  MSs-rGO and  $SnO_2$ -TA MSs-rGO as anodes of (a) LIBs at 1 A g<sup>-1</sup> and (b) SIBs at 50 and 200 mA g<sup>-1</sup>. Representative discharge-charge profiles of (c, e)  $SnO_2$  MSs-rGO and (d, f)  $SnO_2$ -TA MSs-rGO as anodes of (c, d) LIBs at 1 A g<sup>-1</sup> and (e, f) SIBs at 50 mA g<sup>-1</sup>.



**Figure S11.** (a, b) Cycling performances and Coulombic efficiencies of prelithiated or presodiated (green) and pristine (red) electrodes of  $\text{SnO}_2$  NPs-rGO as anodes of (a) LIBs at 100 mA g<sup>-1</sup> and (b) SIBs at 50 mA g<sup>-1</sup>. The 1st discharge-charge profiles of prelithiated/presodiated electrodes of  $\text{SnO}_2$  SMPs-rGO and  $\text{SnO}_2$  MPs-rGO as anodes of (e) LIBs and (f) SIBs. (e, f) Cycling performances and (g, h) representative discharge-charge profiles at 0-2 V of  $\text{SnO}_2$  NPs-rGO as anodes of (e, g) LIBs at 100 mA g<sup>-1</sup> and (f, h) SIBs at 50 mA g<sup>-1</sup>.



**Figure S12.** Cycling stabilities of (a) LiFePO<sub>4</sub> (LFP) in the half LIB cell at 100 mA  $g^{-1}$  in the voltage range of 3.1-3.8 V and (b) Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (NVP) in the half SIB cell at 50 mA  $g^{-1}$  in the voltage range of 2.0-4.0 V.



**Figure S13.** (a, d, g, j) CV curves at a scan rate of 0.1 mV s<sup>-1</sup>, (b, e, h, k) CV curves at various scan rates and (c, f, i, l) the corresponding log(i) versus log(v) plots at the representative redox peaks (tagged by arrows in Figure S15b, e, h and k) of (a-c, g-i) SnO<sub>2</sub> SMPs-rGO and (d-f, j-l) SnO<sub>2</sub> MPs-rGO as anodes of (a-f) LIBs and (g-l) SIBs.

As anodes of LIBs and SIBs, the  $SnO_2$  SMPs-rGO and  $SnO_2$  MPs-rGO (Figure S13a, d, g and j) exhibit similar CV curves yet weaker peak intensities in contrast to  $SnO_2$  NPs-rGO (Figure 6a and d), implying their lower reactivity.



**Figure S14.** HRTEM images of charged electrodes of (a, d) SnO<sub>2</sub> NPs-rGO, (b, e) SnO<sub>2</sub> SMPs-rGO and (c, f) SnO<sub>2</sub> MPs-rGO after 30 cycles at 100 mA g<sup>-1</sup> as anodes of LIBs.



**Figure S15.** HRTEM images of charged electrodes of (a, d) SnO<sub>2</sub> NPs-rGO, (b, e) SnO<sub>2</sub> SMPs-rGO and (c, f) SnO<sub>2</sub> MPs-rGO after 30 cycles at 50 mA g<sup>-1</sup> as anodes of SIBs.



**Figure S16.** CV curves at 0.2 mV s<sup>-1</sup> and the corresponding pseudocapacitive contributions as marked by the shaded portions of (a, c)  $SnO_2$  SMPs-rGO and (b, d)  $SnO_2$  MPs-rGO as anodes of (a, b) LIBs and (c, d) SIBs.<sup>[4]</sup>



Figure S17. CV curves at various scan rates and the corresponding pseudocapacitive contributions as marked by the shaded portions of (a)  $SnO_2$  NPs-rGO, (b)  $SnO_2$  SMPs-rGO and (c)  $SnO_2$  MPs-rGO as anodes of LIBs.<sup>[4]</sup>



**Figure S18.** CV curves at various scan rates and the corresponding pseudocapacitive contributions as marked by the shaded portions of (a) SnO<sub>2</sub> NPs-rGO, (b) SnO2 SMPs-rGO and (c) SnO<sub>2</sub> MPs-rGO as anodes of SIBs.<sup>[4]</sup>



**Figure S19.** SEM images of pristine electrodes of (a, b) SnO<sub>2</sub> NPs-rGO, (c, d) SnO<sub>2</sub> SMPs-rGO and (e, f) SnO<sub>2</sub> MPs-rGO, respectively.



**Figure S20.** Cycling stabilities at (a) 100, (b) 1000, (d) 50 and (e) 200 mA g<sup>-1</sup>, and (c, f) rate performances as anodes of (a-c) LIBs and (d-f) SIBs of SnO<sub>2</sub>/rGO composite fabricated by *in-situ* addition of GO in the solvothermal reaction solution in the synthesis of SnO<sub>2</sub> NPs.



**Figure S21.** (a) Nyquist plots and equivalent circuits of LIBs and SIBs with  $SnO_2/rGO$  as anodes. SEM images of (b) pristine and (c-f) 30th cycled electrodes of  $SnO_2/rGO$  as anodes of (c, d) LIBs at 100 mA g<sup>-1</sup> and (e, f) SIBs at 50 mA g<sup>-1</sup>.

Sample	Mass ratio of SnO <sub>2</sub>	Capacity /mAh g <sup>-1</sup>	Cycle number	C-rate /mA g <sup>-1</sup>	No.	Ref.
		1461	300	100		
	79.8 wt%	1775	800	1000		<b>TI</b> •
SnO <sub>2</sub> NPs-rGO		1680	1700	2000		I NIS
		1353	2420	5000		work
		753	4000	10000		
		1523	100	100		
SnO <sub>2</sub> @PEG-GO	84.6 wt%	1186	1000	1000	A	[1]
-		896	2000	2000		
SnO <sub>2</sub> @C/GO	55.7 wt%	1156	350	1000	В	[5]
	82.3 wt%	843	100	100	C	[6]
$C@SnO_2/KGO-90$		485	200 1000		- C	[0]
SnO <sub>2</sub> NPs/rGO-1	56.5 wt%	400	100	1000	D	[2]
3DG@SnO <sub>2</sub> @N-C	53.1 wt%	1349.5	100	100	Ε	[7]
SRG	82.3 wt%	1335.6	500	1000	_ Б	[8]
		502.1	10	5000	Г	
SnO /PGO	81.4 wt%	708	150	500	- C	[9]
51102/1000		573	420	1000	G	
SnO <sub>2</sub> /GO	87.6 wt%	492	100	200	Η	[10]
SpO-@C/rGO	90.27 wt%	844.1	1000	1000	_ I	[11]
$SIIO_2(\underline{w}C)/IOO$		525.4	1700	5000		
SnO <sub>2</sub> /RGO	81.8 wt%	263	100	100	J	[12]
SnO <sub>2</sub> NRs/GA	78.69 wt%	869	50	100	K	[13]
SnO <sub>2</sub> nanorods/Gr	71.6 wt%	815	150	100	L	[14]
3DGr/SnO <sub>2</sub>	67 wt%	974	300	100	Μ	[15]
SnO <sub>2</sub> @C@half-RGO	63.6 wt%	1034.5	200	100	Ν	[16]
$SnO_2@G@G$	90 wt%	591.9	120	80	0	[17]

Table S1. Summary of performances of graphene-based SnO<sub>2</sub> materials as anodes of LIBs . <sup>[1, 2, 5-17]</sup>

**Notes:** No.: sample number in Figure 4j; Ref.: reference number; NPs: nanoparticles; PEG: poly(ethylene glycol); NRs: nanorods; C: carbon; Gr or G: graphene; GO: graphene oxide; rGO or RGO: reduced GO; N-C: N-doped carbon; 3DG: three-dimensional graphene; SRG: SnO<sub>2</sub> nanospheres/reduced graphene oxide nanosheets; GA: 3D graphene aerogel; half-RGO: small sheets of graphene oxide.

Sample	Mass ratio of SnO <sub>2</sub>	C-rate /mA g <sup>-1</sup>	Cycle number	Capacity /mAh g <sup>-1</sup>	No.	Ref.
	70 8 mt9/	50	100	443	_	This
SIIO <sub>2</sub> NPS-100	/9.0 W170	200	250	260		work
SnO <sub>2</sub> NPs/rGO-1	56.5 wt%	100	100	212	a	[2]
SnO <sub>2</sub> @G	86.2 wt%	100	100	343	b	[18]
SnO <sub>2</sub> /rGO/CNT	78.24 wt%	50	225	248	c	[19]
SnO <sub>2</sub> /GAs	69 wt%	50	100	274	d	[20]
SnO <sub>2</sub> /NG-300	50 wt%	50	100	409.6	e	[21]
SnO <sub>2</sub> NRs/GA	78.69 wt%	50	100	232	f	[13]
SnO <sub>2</sub> QDs/GA	63.8 wt%	50	50	319	g	[22]
SnO <sub>2</sub> -N-GNS	Element ratio of Sn 20.75 at.%	50	50	294.4	h	[23]
SnO <sub>2</sub> NRs@G	30 wt%	20	100	200	i	[24]
SnO <sub>2</sub> /graphene	80 wt%	100	100	220	j	[25]
SnO <sub>2</sub> /rGO	75.5 wt%	50	80	324	k	[26]
SnO <sub>2</sub> /NG	47 wt%	20	100	283	l	[27]
SGA-2	38.5 wt%	20	100	322	m	[28]
SnO <sub>2</sub> /GDA	70 wt%	50	200	221	n	[29]
SnO <sub>2</sub> /RGO	76 wt%	100	150	330	0	[30]

Table S2. Summary of performances of graphene-based SnO<sub>2</sub> materials as anodes of SIBs . <sup>[2, 13, 18-30]</sup>

**Notes:** No.: sample number in Figure 4k; Ref.: reference number; NPs: nanoparticles; NRs: nanorods; QDs: quantum dots; Gr or G: graphene; GO: graphene oxide; rGO or RGO: reduced GO; CNT: carbon nanotube; NG: nitrogen-doped graphene; N-RGO: N-doped RGO; 3DG: three-dimensional graphene; N-GNS: nitrogen doping graphene nanosheet; SGA: SnO<sub>2</sub>/graphene aerogels; GDA: graphene dual aerogel; GA: 3D graphene aerogel.

**Table S3.** Diffusive contribution ratios in the CV curves obtained at various voltage scan rates of  $SnO_2$ NPs-rGO,  $SnO_2$  SMPs-rGO and  $SnO_2$  MPs-rGO as anodes of LIBs (Figure 7d and S16-S18).

Comulas	Voltage scan rate (mV s <sup>-1</sup> )								
Samples	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
SnO <sub>2</sub> NPs-rGO	77.9%	75.4%	73.0%	71.0%	69.2%	67.5%	63.9%	64.0%	62.1%
SnO <sub>2</sub> SMPs-rGO	57.4%	54.7%	53.0%	49.0%	46.0%	45.3%	43.8%	43.3%	42.5%
SnO <sub>2</sub> MPs-rGO	58.4%	55.1%	52.3%	49.8%	47.7%	45.7%	43.5%	41.6%	39.8%

**Table S4.** Diffusive contribution ratios in the CV curves obtained at various voltage scan rates of  $SnO_2$  NPs-rGO,  $SnO_2$  SMPs-rGO and  $SnO_2$  MPs-rGO as anodes of SIBs (Figure 7h and S16-S18).

Samples	Voltage scan rate (mV s <sup>-1</sup> )								
	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	
SnO <sub>2</sub> NPs-rGO	72.8%	69.1%	62.3%	60.0%	58.4%	57.4%	55.0%	54.8%	
SnO <sub>2</sub> SMPs-rGO	47.3%	42.6%	39.9%	36.5%	34.8%	34.2%	32.1%	29.5%	
SnO <sub>2</sub> MPs-rGO	43.9%	39.7%	37.6%	34.7%	32.0%	29.5%	29.6%	28.9%	

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