Supporting Information

Highly Reversible and Ultra-fast Lithium Storage in Mesoporous Graphene-Based TiO_2/SnO_2 Hybrid Nanosheets

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Experimental Section

Preparation of graphene oxide (GO): GO was first synthesized from natural graphite flakes based on the modified Hummers method. A homogeneous GO aqueous dispersion (3.0 mg mL^{-1}) was then ready for use.

Synthesis of graphene-based TiO_2/SnO_2 hybrid nanosheets ($TiO_2@SnO_2@GN$): GO aqueous dispersion (5 mL) was diluted in de-ionized (DI) water (100 mL) with subsequent addition of $SnCl_2 \cdot 2H_2O$ (400 mg). The resulting mixture was magnetically stirred for 0.5 h at 90 °C. Secondly, after the dispersion was cooled down to 50 ℃, HCl (4 mL) and $Ti(OBu)_4$ (400 μL) were gradually added. The mixture was further stirred at 50 ℃ for 15 h, providing a uniform suspension. Finally, ammonia was added, adjusting the pH to neutral. After the suspension was cooled down to room temperature, $TiO_2@SnO_2@GN$ was collected as black precipitate, washed several times with DI water, and dried at 50 ℃ in the air. The mass ratio of TiO2:SnO2:graphene for the $TiO_2@SnO_2@GN$ is around 1:3:0.16 and TiO_2 content is estimated to be 24 wt%, which is optimized for a full coverage of TiO_2/SnO_2 nanoparticles on graphene surface. We also prepared composites with 13 wt% and 30 wt% TiO_2 by adding $Ti(OBu)_4$ (200 μL) and $Ti(OBu)_4$ (600 μL) respectively to the system with other conditions same as above. $TiO_2@SnO_2@GN$ with 13 wt% TiO_2 shows not full coverage of nanoparticles on graphene, and for the composite with 30 wt% TiO_2 free TiO_2 nanoparticles can be found together with nanosheets. The mass ratios are calculated by EDX element analysis.

Synthesis of graphene-based SnO_2 ($SnO_2@GN$): GO aqueous dispersion (5 mL) and $SnCl_2 \cdot 2H_2O$ (400 mg) were mixed in DI water (100 mL). The mixture was magnetically stirred for 0.5 h at 90 ℃. Ammonia was added to adjust the pH value of the dispersion to neutral. After the dispersion was cooled down to room temperature, the resulting precipitate was collected, washed several times with DI water, and dried at 50 □ in the air.

Synthesis of TiO_2/SnO_2 heterostructure ($TiO_2@SnO_2$): 623 mg $SnCl_4{\cdot}5H_2O$ was dissolved in deionized water and hydrolized for 0.5 h at 90 ℃. HCl (4 mL) and $Ti(OBu)_4$ (400 μL) were gradually added, the mixture was stirred at 50 ℃ for 15 h to form a gel. Ammonia was added to adjust the pH to neutral, after the suspension was cooled down to room temperature, precipitate was collected, washed several times with DI water and dried at 50 ^{o}C in the air.

Characterizations**:** SEM micrographs were acquired using NOVA NanoSEM 230 (FEI, USA) microscope. TEM and HRTEM images, SAED pattern, elemental mapping were conducted on JEM-2100 microscope (JEOL Ltd., Japan). XRD measurements were carried out on a D/max-2500 X-ray diffractometer (Rigaku Corporation, Japan) using Cu K_α radiation (λ =0.1542 nm). Raman measurements were conducted on an Invia/Reflrx Lasser Micro-Raman spectrometer (Renishaw, England) excited by a laser beam of 532 nm. AFM images of the materials on a freshly cleaved mica surface were taken with a Multimode Nanoscope (DI, USA) in tapping mode. Nitrogen physisorption measurements were carried on ASAP 2010 M+C apparatus (Micromeritics Inc., USA). TGA curve was monitored on a Q5000IR apparatus (TA Instruments, USA), the sample is maintained at 50 ℃ to eliminate physisorption of water. FTIR spectra were recorded using Spectrum 100 spectrometer (Perkin Elmer, Inc., USA). XPS experiments were carried out on AXIS Ultra DLD system from Kratos with Al Kα radiation as X-ray source for radiation.

Electrochemical Measurements: Electrochemical tests were performed under ambient temperature using two-electrode 2032 coin-type cell. The working electrodes were prepared by mixing the samples (TiO_2@SnO_2@GN, SnO_2@GN, TiO_2@SnO_2), carbon black (Super-P), and poly(vinyl difluoride) (PVDF) at a weight ratio of 80:10:10 and pasting the mixture on pure copper foil (99.6%). The electrode was dried at 60 °C for 12 h in a vacuum oven followed by pressed at 10 MPa. Pure lithium foil was used as the counter electrode. A microporous polypropylene membrane was used as the separator. The electrolyte consisting of a solution of 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume) was obtained from Ube Industries Ltd. The cells were assembled in an argon-filled glove box with the concentrations of moisture and oxygen below 1 ppm. CV tests were conducted on a CHI760 electrochemistry workstation at a scan rate of 0.1 mV/s. Galvanostatic charge/discharge measurements were conducted on a battery tester (Land CA2001A) at various current rates in a potential range of 0.02-3.0 V vs. Li/Li^+. The specific capacities are based on the total mass of the samples.

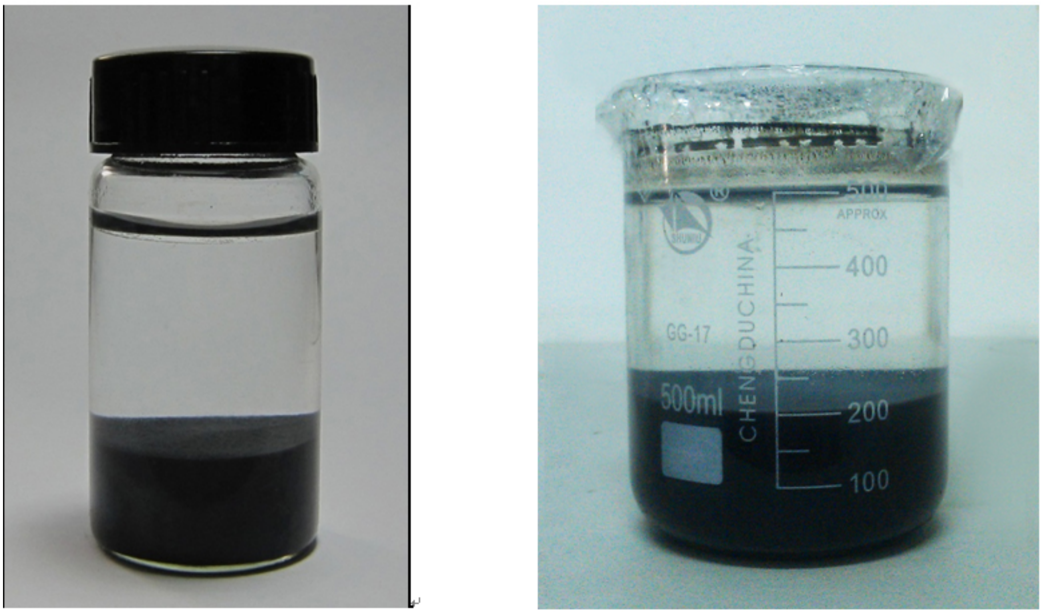


Figure S1. Photoimages of the resulting precipitate of TiO_2@SnO_2@GN.

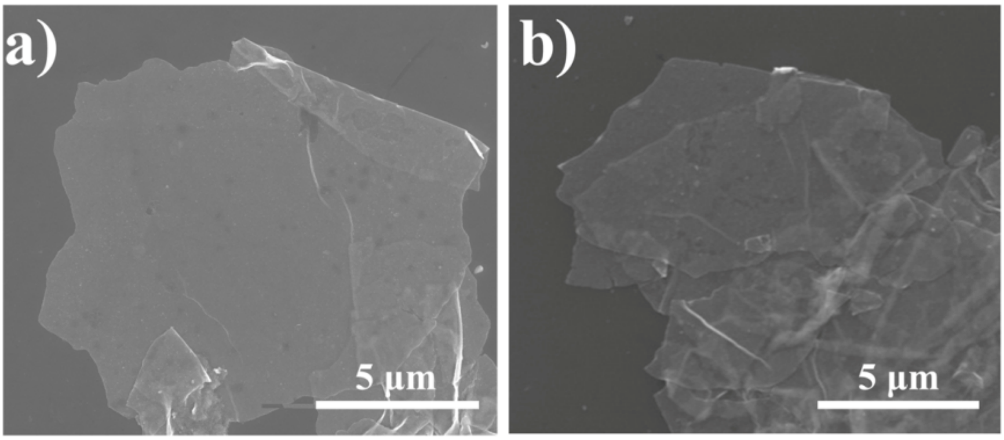


Figure S2. a) and b) SEM images of TiO_2@SnO_2@GN nanosheets.

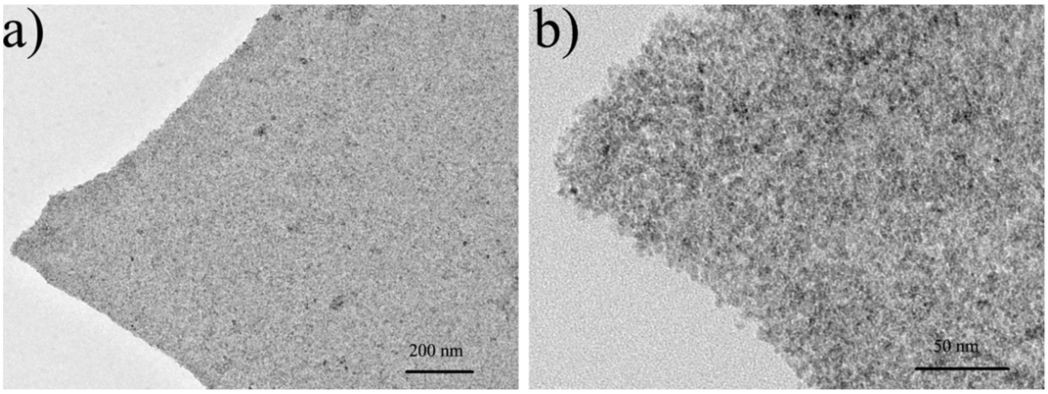


Figure S3. a) and b) TEM images of TiO_2@SnO_2@GN nanosheets with different magnifications

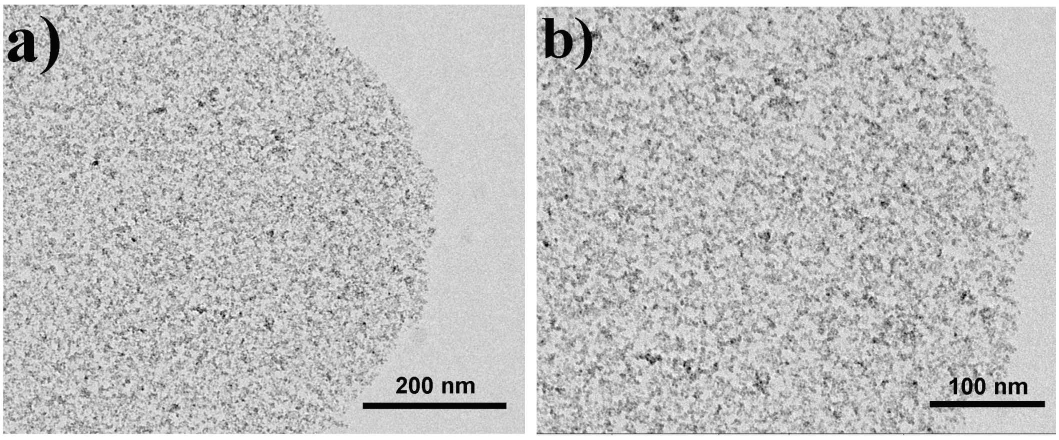


Figure S4. a) and b) TEM images of SnO_2@GN with different magnifications.

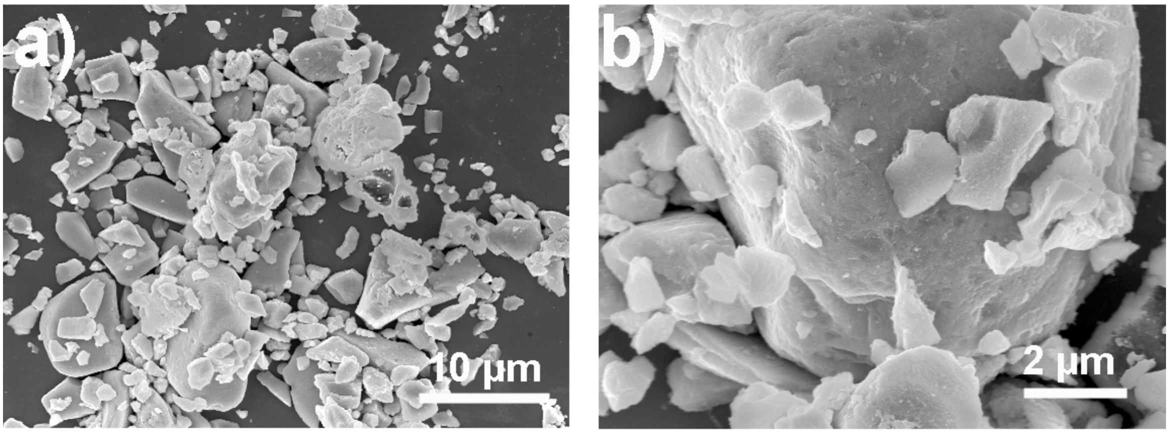


Figure S5. a) and b) SEM images of $TiO_2@SnO_2$.

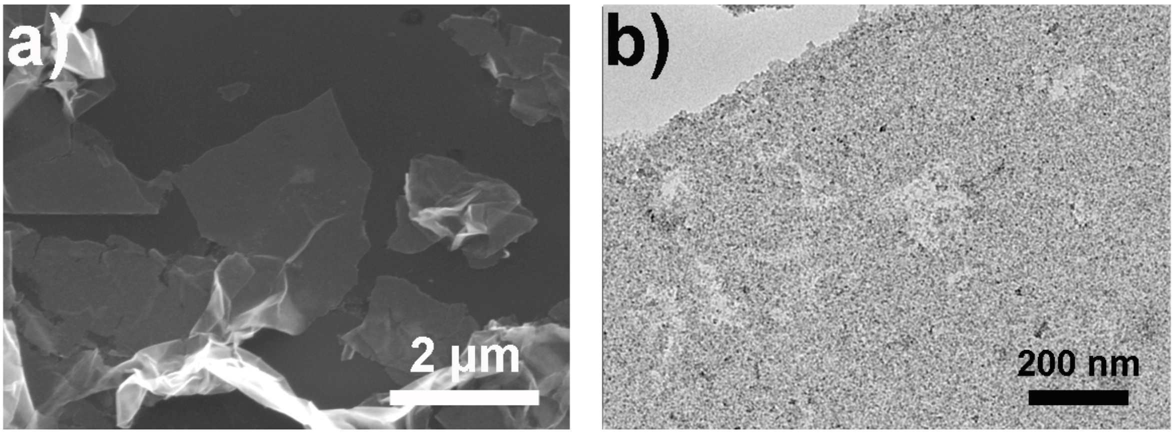


Figure S6. a) SEM b) TEM images of the $TiO_2@SnO_2@GN$ with 13 wt% TiO_2.

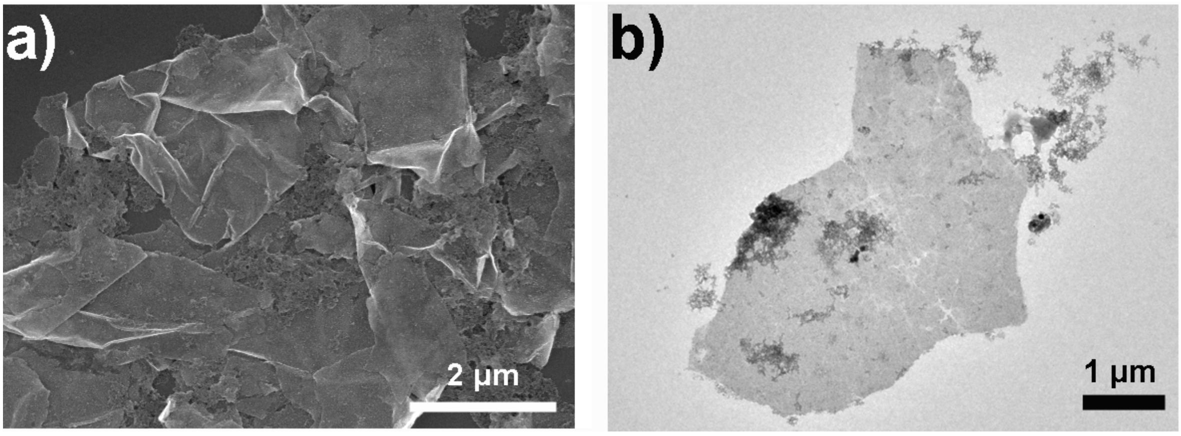


Figure S7. a) SEM b) TEM images of the composite with 30 wt% TiO_2. Free TiO_2 nanoparticles are found mixed with nanosheets.

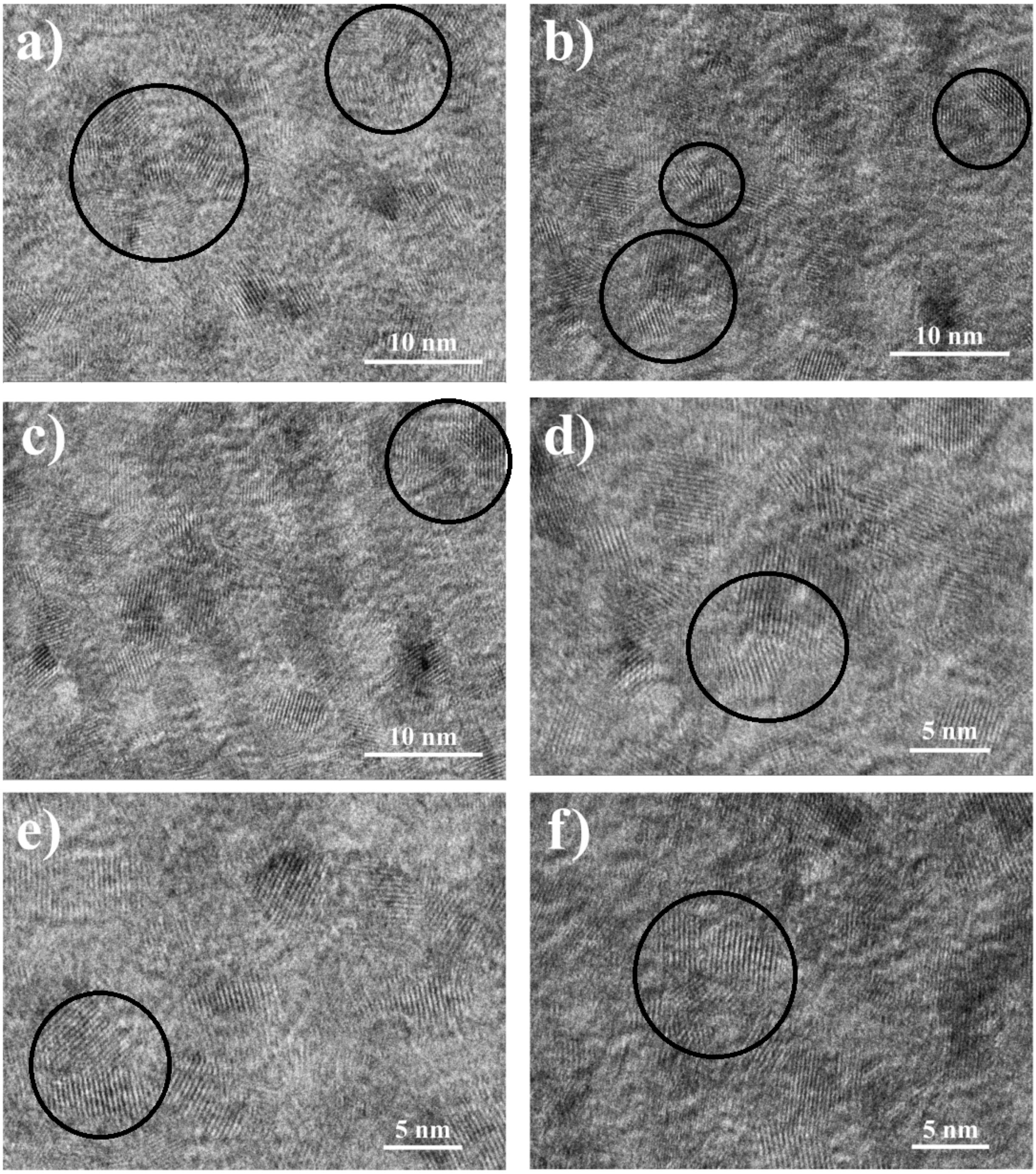


Figure S8. a-f) HRTEM images of different areas on the surface of TiO_2@SnO_2@GN.

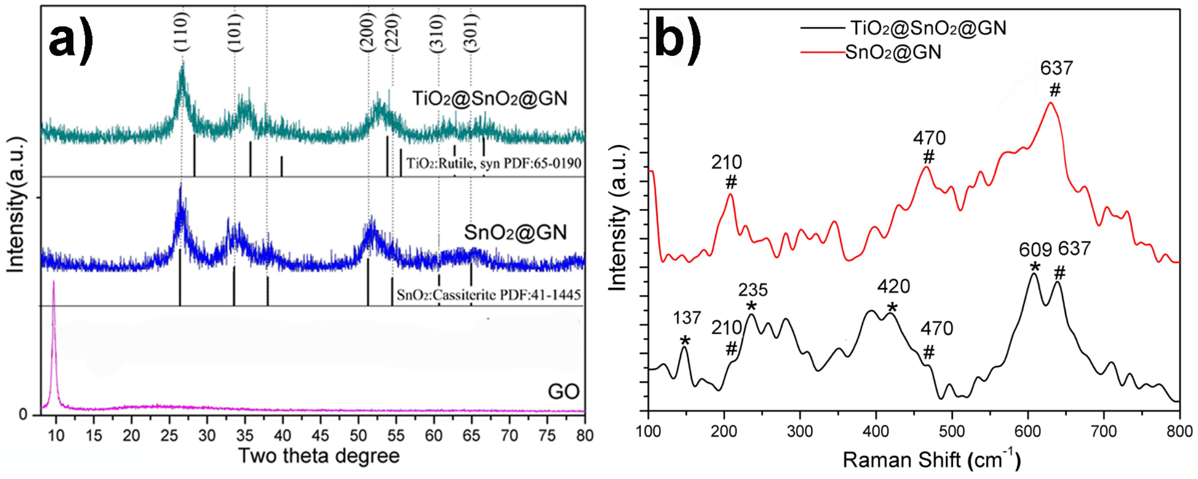
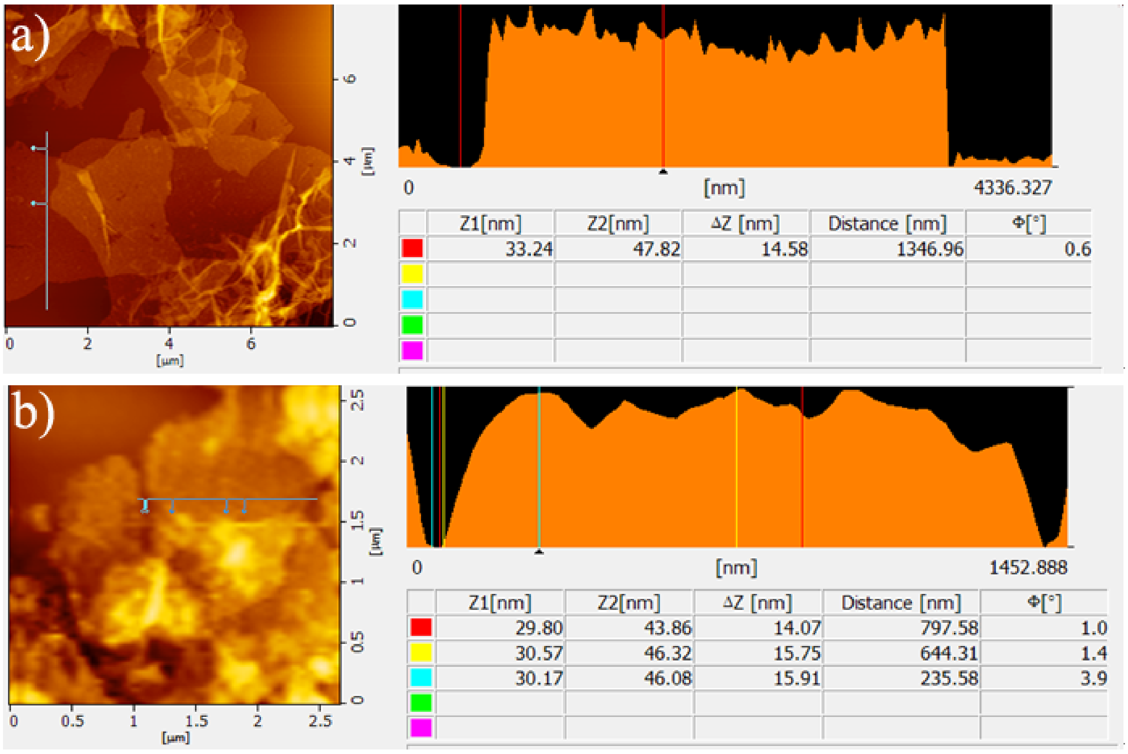


Figure S9. a) XRD patterns of GO, SnO_2@GN and TiO_2@SnO_2@GN. b) Raman spectras of SnO_2@GN and TiO_2@SnO_2@GN.



	Z1[nm]	Z2[nm]	ΔZ [nm]	Distance [nm]	Φ[°]
🟥	33.24	47.82	14.58	1346.96	0.6
🟨					
🟦					
🟩					
🟪					

	Z1[nm]	Z2[nm]	ΔZ [nm]	Distance [nm]	Φ[°]
🟥	29.80	43.86	14.07	797.58	1.0
🟨	30.57	46.32	15.75	644.31	1.4
🟦	30.17	46.08	15.91	235.58	3.9
🟩					
🟪					

Figure S10. AFM image and corresponding height profile of a) SnO_2@GN, and b) TiO_2@SnO_2@GN.

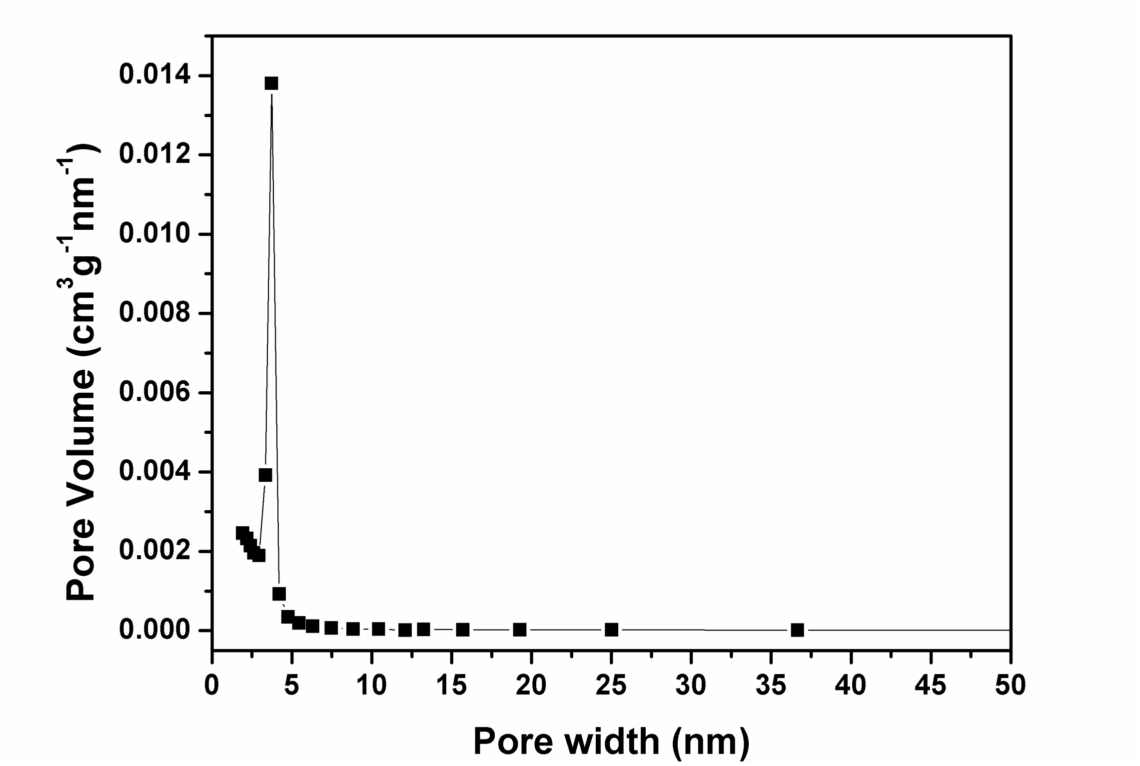


Figure S11. Pore size distribution of TiO_2@SnO_2@GN derived from the desorption branch.

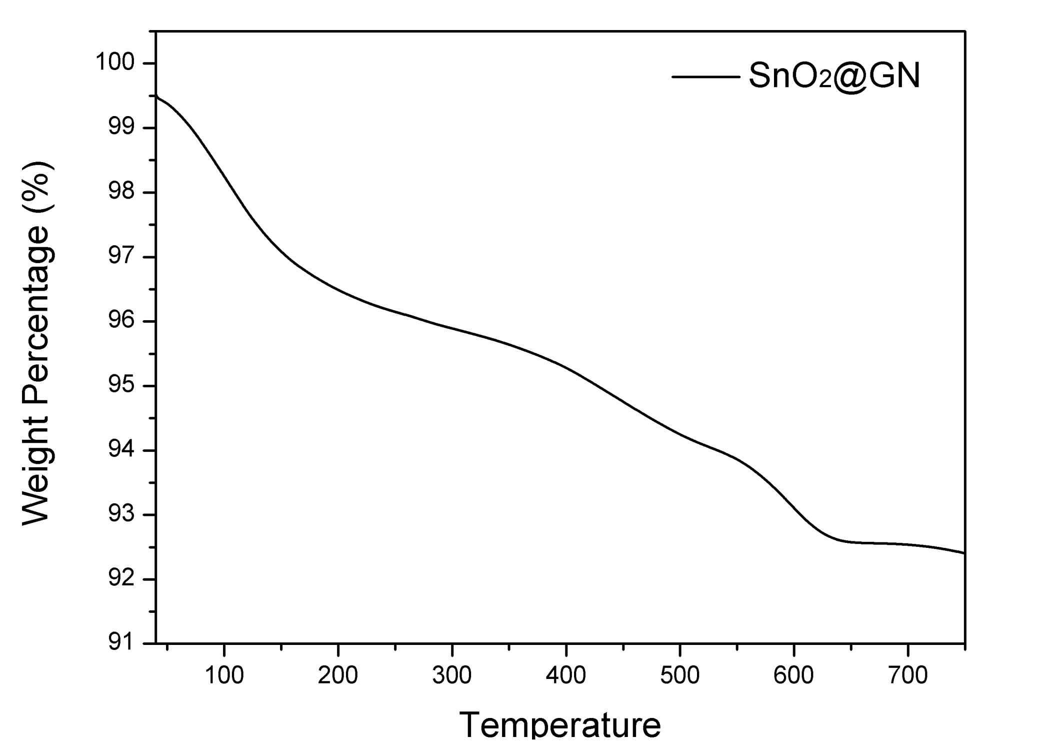


Figure S12. Thermogravimetric analysis (TGA) of SnO_2@GN under air. ~1% weight loss at 50 ℃ is due to physically adsorbed water.

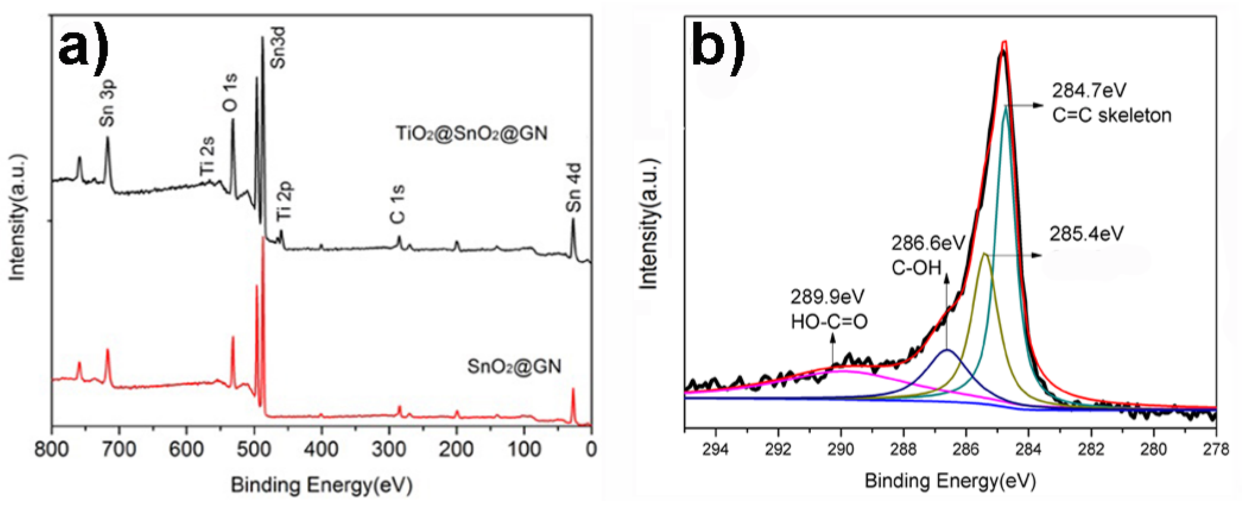


Figure S13. a) XPS spectras of SnO_2@GN and TiO_2@SnO_2@GN; b) Core-level XPS spectra of C 1s for TiO_2@SnO_2@GN.

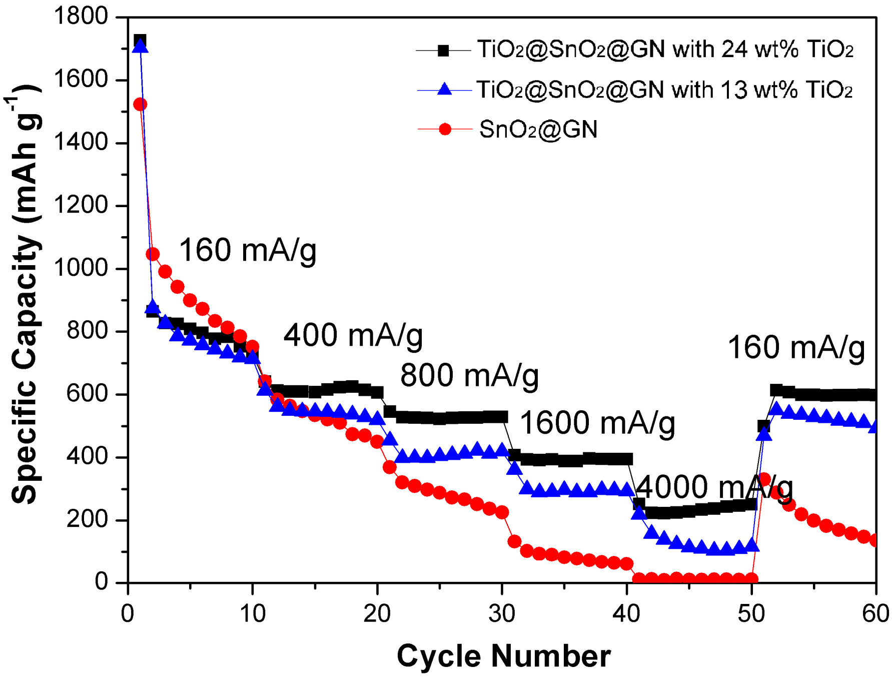


Figure S14. Specific capacity versus cycle number of SnO_2@GN, TiO_2@SnO_2@GN with 13 wt% TiO_2, TiO_2@SnO_2@GN with 24% TiO_2 at 160, 400, 800, 1600, 4000 mA g^{-1}. TiO_2@SnO_2@GN (13 wt% TiO_2) with less TiO_2 than TiO_2@SnO_2@GN (24 wt% TiO_2) exhibits enhanced rate capability than SnO_2@GN but its capacity still fades especially at 160, 400 and 4000 mA g^{-1}.

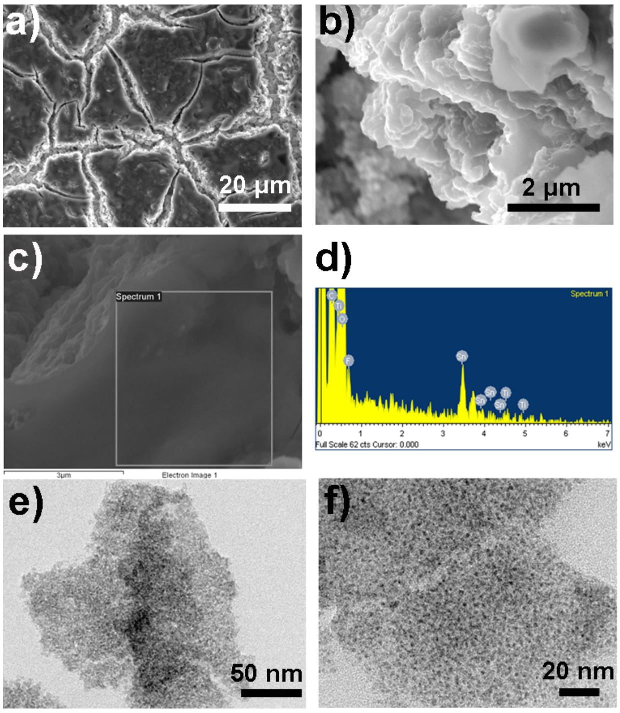


Figure S15. a-c) SEM images of TiO_2@SnO_2@GN electrode on copper foil after 300 cycles. d) The EDX spectrum of the area of image c) with Ti, Sn, O, C and F, F element is from the composition of SEI layer. e) and f) TEM images of TiO_2@SnO_2@GN hybrid after 300 cycles.

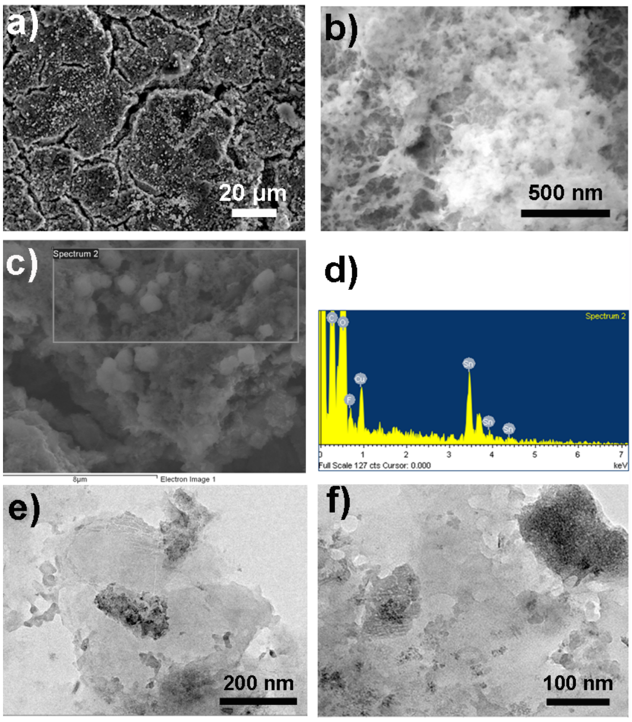


Figure S16. a-c) SEM images of SnO_2@GN electrode on copper foil after 300 cycles. d) The EDX spectrum of the area of image c) with Sn, O, C, F and Cu, Cu is from the copper foil . e) and f) TEM images of SnO_2@GN after 300 cycles.