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Supporting information

Self-assembled 3D urchin-like $Ti_{0.8}Sn_{0.2}O_2$-rGO hybrid nanostructure as anode material for high-rate and long cycle life Li-ion batteries

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Experimental section

Synthesis of graphene oxide: Graphene oxide (GO) was synthesized using the following modified Hummer's method. In specifically, graphite (2 g) was added with concentrated H_2SO_4 (69 mL), and the mixture was stirred for 30 min within an ice bath. $KMnO_4$ (8 g) was added very slowly into the dark suspension and the reaction mixture was stirred and sonicated for another 15 min. Then the ice bath was removed, and the mixture was stirred at 35 °C overnight. Distilled water was added to the pasty solution under magnetic stirring and the color of the solution turned to yellowish brown. After another 2 h of vigorous stirring, H_2O_2 (30 wt%, 25 mL) was added and the color of the solution turned to golden yellow immediately. The mixture was washed with HCl (5 %) and then deionized water for several times until the solution became acid free. After freeze-drying treatment overnight, the GO was obtained and used for the further experiments.

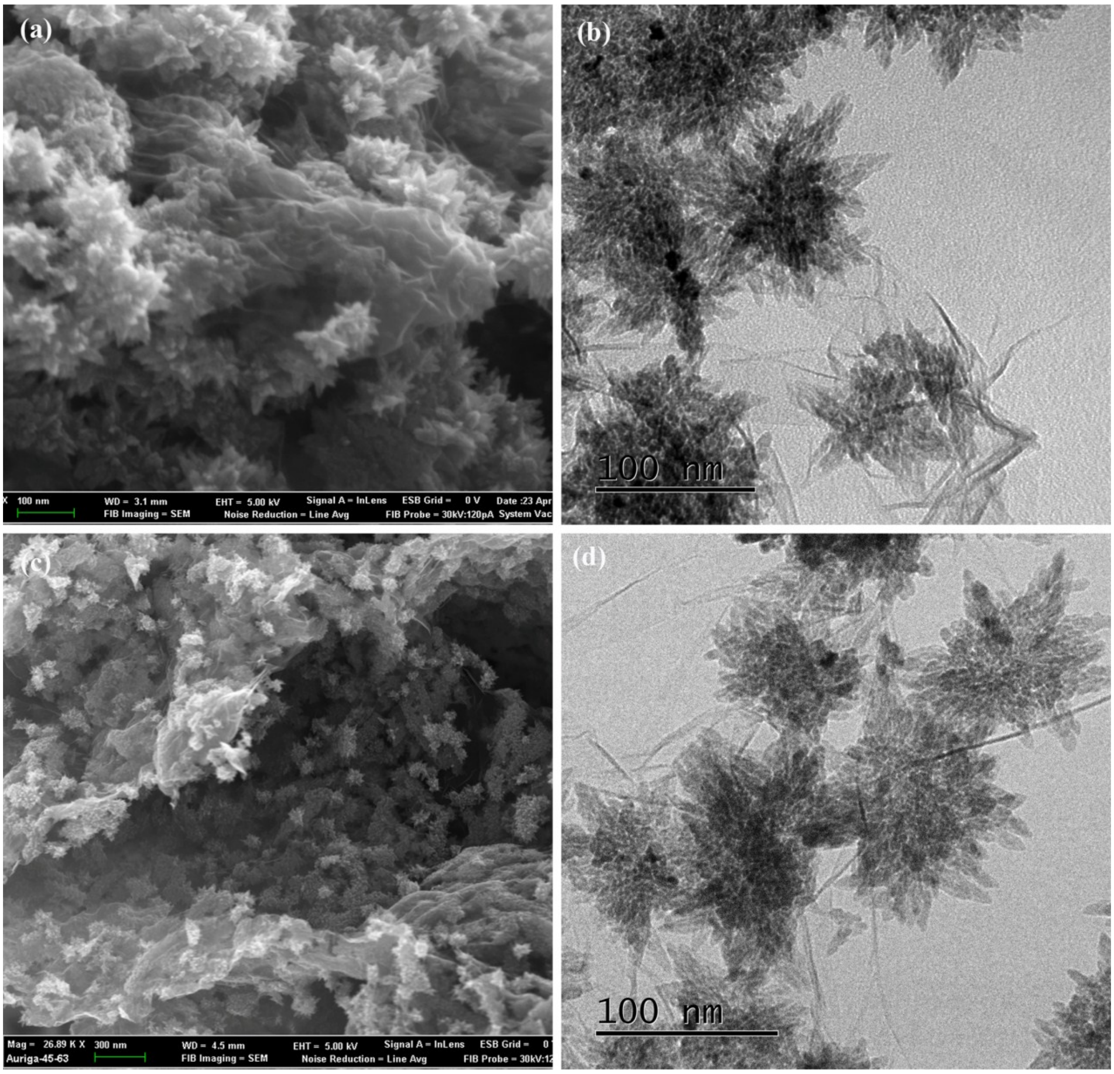

Fig. S1 The effect of GO content on the morphology of the 3D urchin-like $Ti_{0.8}Sn_{0.2}O_2$-rGO hybrid nanostructures. The total concentration of metal salts (Ti + Sn) was 0.3 M. (a) SEM and (b) TEM images of $Ti_{0.8}Sn_{0.2}O_2$ at 2 mg mL^{-1} of GO, (c) SEM and (d) TEM images of $Ti_{0.8}Sn_{0.2}O_2$ at 2.5 mg mL^{-1} of GO.

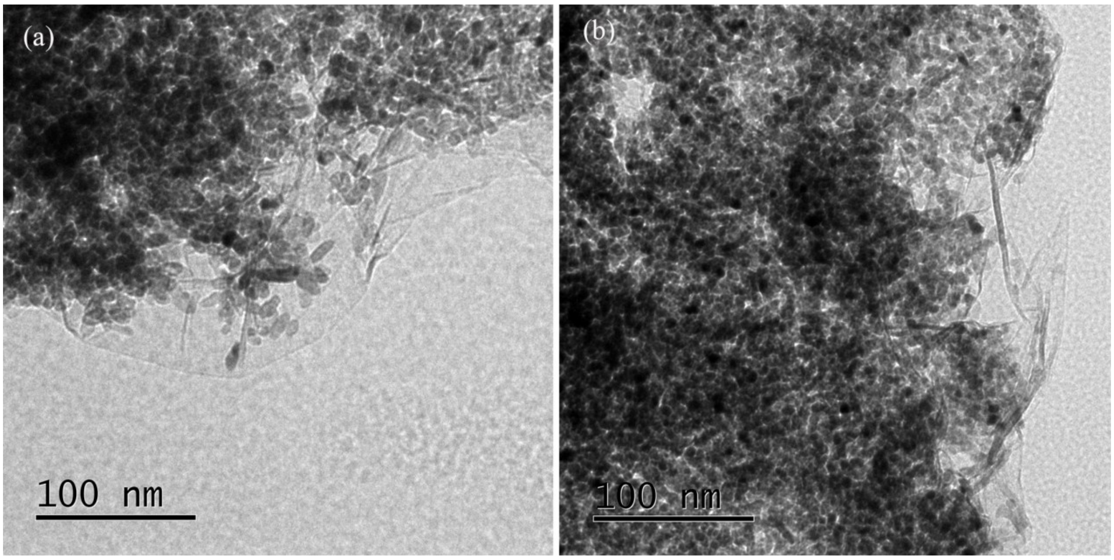

Fig. S2 The effect of metal ions ratio on morphology of the $Ti_xSn_{1-x}O_2$-rGO composites. TEM images of (a) $Ti_{0.7}Sn_{0.3}O_2$ and (b) $Ti_{0.6}Sn_{0.4}O_2$ at 1.5 mg mL^{-1} of GO.

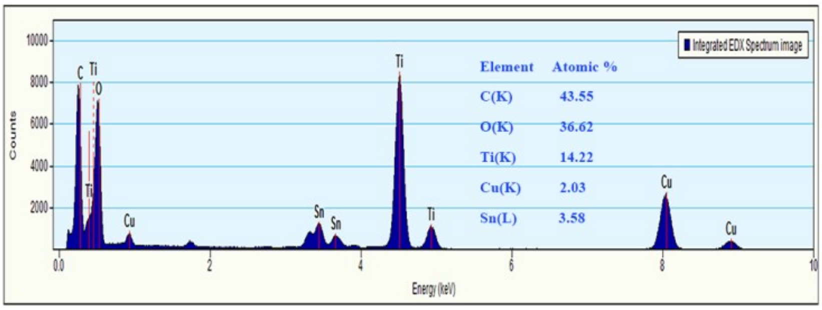

Fig. S3 EDS spectrum of the 3D urchin-like $Ti_{0.8}Sn_{0.2}O_2$-rGO hybrid.

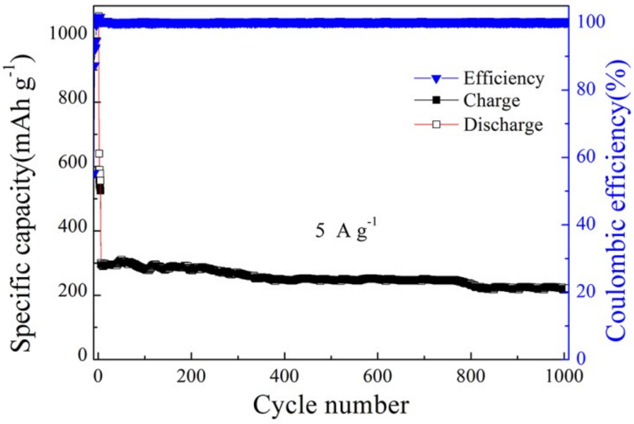

Fig. S4 Long-term cycling performance of the 3D urchin-like $Ti_{0.8}Sn_{0.2}O_2$-rGO hybrid electrode at a current density of 5 A g^{-1}.

Cycling stability is one of the most important parameter for applicability. The 3D urchin-like $Ti_{0.8}Sn_{0.2}O_2$-rGO hybrid electrode was cycled at 5 A g^{-1} for 1000 cycles to investigate its long-term cyclability. The discharge capacity of the 3D urchin-like $Ti_{0.8}Sn_{0.2}O_2$-rGO hybrid electrode still maintained at 224 mA h g^{-1} after 1000 cycles.

The excellent cycling performance at ultra-fast charging-discharging indicates the stable structure of the 3D urchin-like $Ti_{0.8}Sn_{0.2}O_2$-rGO nanostructure during Li-ion insertion-extraction.

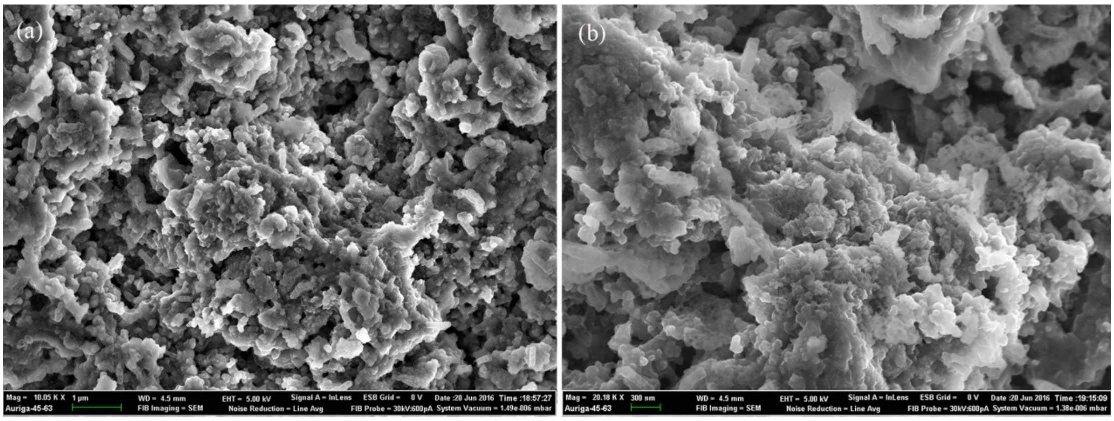

Fig. S5 SEM images of 3D urchin-like $Ti_{0.8}Sn_{0.2}O_2$-rGO hybrid electrode cycled after 500 cycles at a current rate of 1 A g^{-1}.

The structural stability of 3D urchin-like $Ti_{0.8}Sn_{0.2}O_2$-rGO hybrid electrode after 500 cycles at a current rate of 1 A g^{-1} was investigated by SEM images. It can be observed that the composite almost maintained the characters of hierarchical arrangement and multiscale pore structures (Fig. S5a). As shown in the high magnification image of Fig. S5b, some spherical (about 100 nm) appearing on the rGNs, it would indicate that the urchin-like $Ti_{0.8}Sn_{0.2}O_2$ nanostructures lost sharp corners, the urchin-like structure gradually transforms to spherical structure.

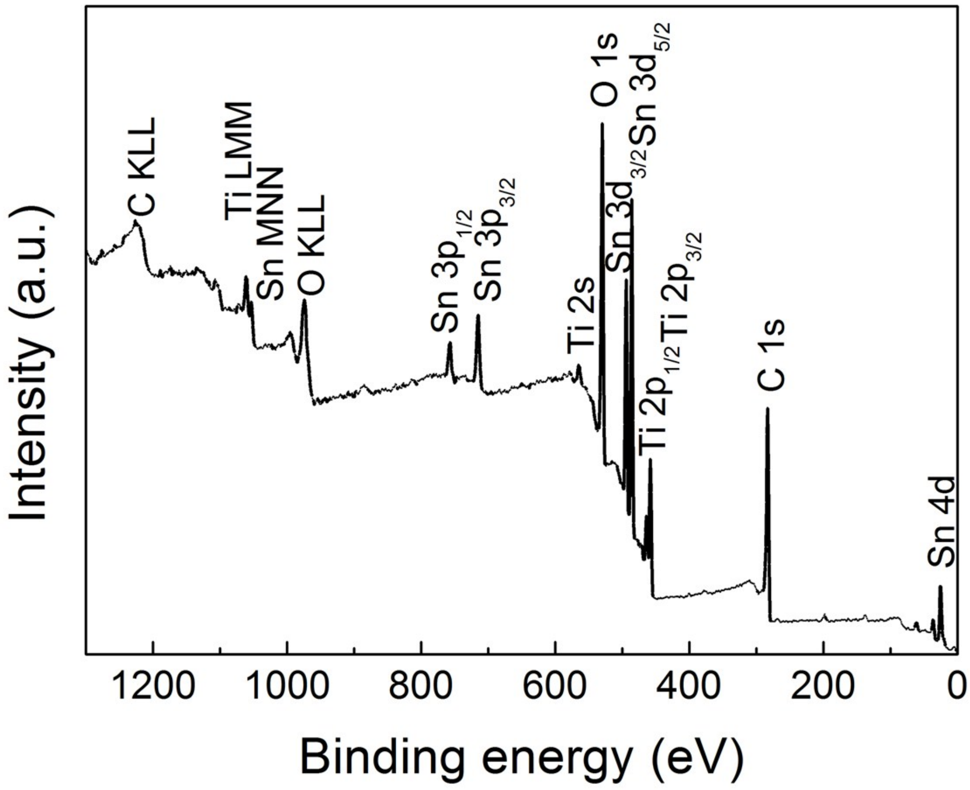

Fig. S6 XPS survey spectrum of the 3D urchin-like $Ti_{0.8}Sn_{0.2}O_2$-rGO hybrid.

To investigate the possible contribution of pseudocapacitive phenomena to the electrochemical performance, we have tested the pseudocapacitive characteristics of the $Ti_{0.8}Sn_{0.2}O_2$-rGO hybrid in coin cells with Lithium chips as the counter electrode. This approach is modeled after the Dunn et al. configuration[1] and no further in a fierce study. The results are shown as following:

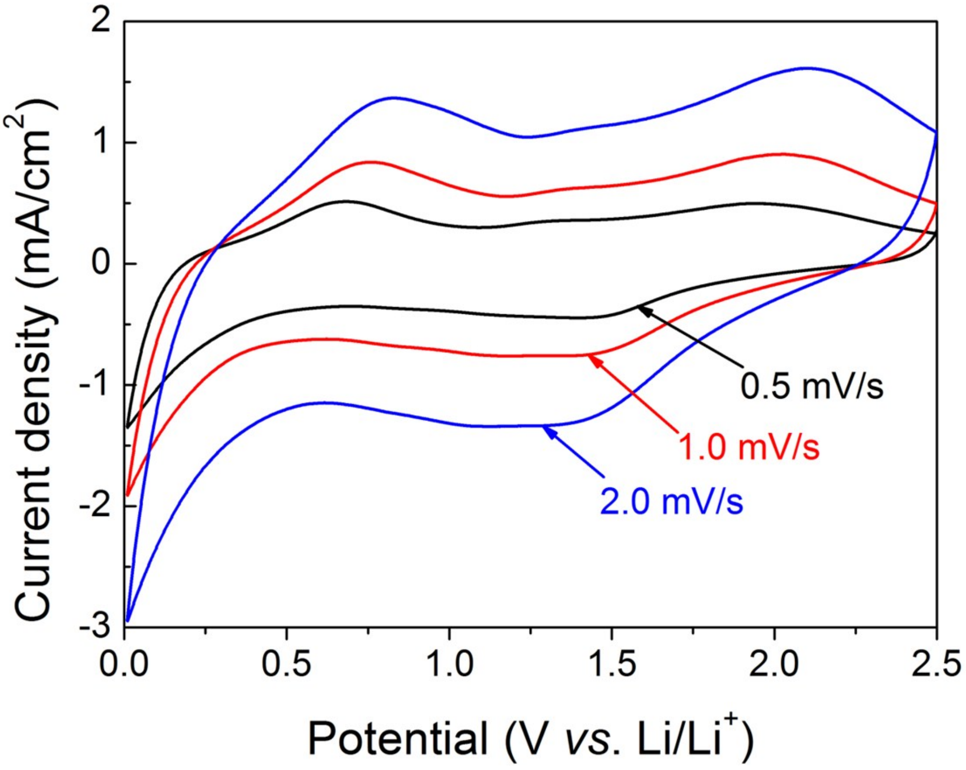

Fig. S7 Typical cyclic voltammetric responses of the 3D urchin-like $Ti_{0.8}Sn_{0.2}O_2$-rGO hybrid at various sweep rates.

Fig. S7 shows the typical cyclic voltammograms for $Ti_{0.8}Sn_{0.2}O_2$-rGO hybrid at various sweep rates. The area under the curves represents the total stored charge which arises from both faradaic and nonfaradaic processes. The cathodic/anodic peaks are in good agreement with the CV curves at a sweep rate of 0.1 mV/s. Note that for fast sweep rates, the larger peaks are observed.

The total stored charge can be separated into three components: the faradaic contribution from the Li^+ ion insertion process, the faradaic contribution from the charge-transfer process with surface atoms, referred to as pseudocapacitance, and the nonfaradaic contribution from the double layer effect. The latter two capacitive components could not be separated and characterized by analyzing the cyclic voltammetry data at various sweep rates according to

$$i = av^b \qquad (1)$$

where the measured current i obeys a power law relationship with the sweep rate v. Both a and b are adjustable parameters, with b-values determined from the slope of the plot of log i vs log v. There are two well-defined conditions: b = 0.5 and b = 1.0. For b = 0.5, the current is proportional to the square root of the scan rate, v, according to the following equation:

$$i= nFAC^*D^{1/2}v^{1/2}(anF/RT)^{1/2}\prod^{1/2}x(bt) \qquad (2)$$

where C^* is the surface concentration of the electrode material, R is the transfer coefficient, D is the chemical diffusion coefficient, n is the number of electrons involved in the electrode reaction, A is the surface area of the electrode materials, F is the Faraday constant, R is the molar gas constant, T is the temperature, and the $x(bt)$ function represents the normalized current for a totally irreversible system as indicated by the cyclic voltammetric response. The current response in eq 2 is diffusion controlled, which is indicative of a faradaic intercalation process. The other defined condition, b=1.0, is representative of a capacitive response because the capacitive current is proportional to the sweep rate, according to the following equation:

$$i = vC_dA \qquad (3)$$

where C_d is the capacitance.

According to the early work reported by Lindstrom et al.[2] and Dunn,et al., the b-values are in the range of 0.8-1 is a good indication that the majority of the currents arise from capacitive effects. Using the concepts described above, the current response at a fixed potential is the combination of two separate mechanisms, namely surface capacitive effects and diffusion-controlled Li^+ insertion as equation[3]:

$$i(v) = k_1v + k_2v^{1/2} \qquad (4)$$

or

$$i(v)/ v^{1/2} = k_1 v^{1/2} + k_2 \qquad (5)$$

In eq 4, k_1v and $k_2v^{1/2}$ correspond to the current contributions from surface capacitive effects and the diffusion controlled insertion process, respectively. Plotting the sweep rate dependence of the current allows us to determine k_1 and k_2 from the slope and the y-axis intercept point of a straight line, respectively, at each fixed potential using eq 5. This methodology thus enables us to distinguish between the currents arising from Li^+ insertion and those from capacitive effects (Fig. S8).

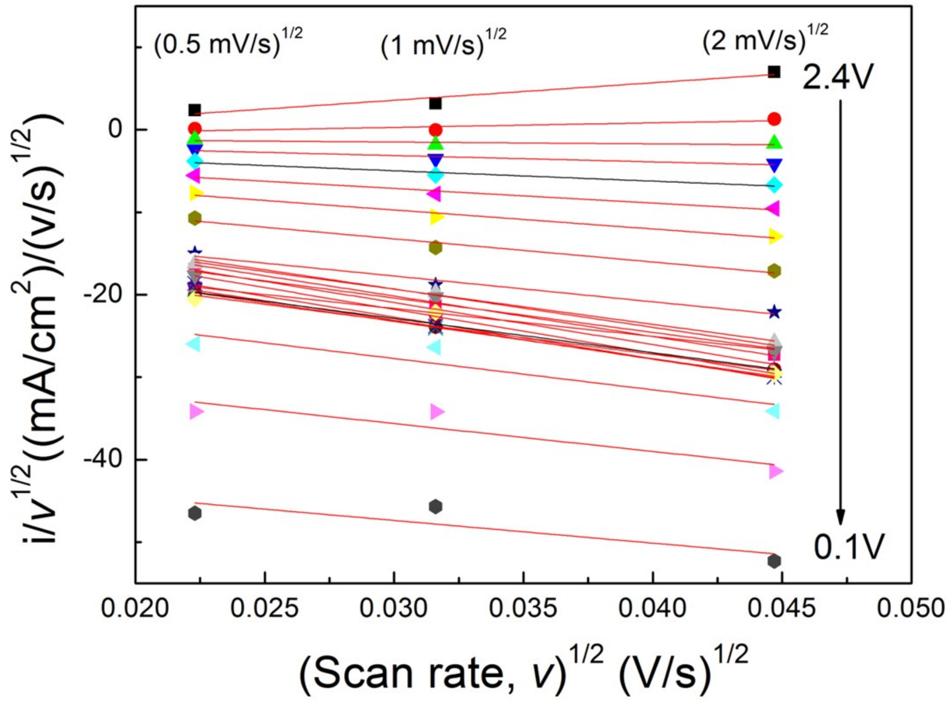

Fig. S8 Charts of the correlation between the $v^{1/2}$ and $i/ v^{1/2}$. Use of equation $i(V) / v^{1/2}) = k_1v^{1/2}+k_2$ to analyze the cathodic voltammetric sweep data for the 3D urchin-like $Ti_{0.8}Sn_{0.2}O_2$-rGO hybrid: The voltage windows were chose from 2.4 V to 0.1 V (voltage interval is 0.1 volts) and the sweep rates were varied from 0.5 to 2.0 mV/s.

Reference

1. T. Brezesinski, J. Wang, J. Polleux, B. Dunn and S. H. Tolbert, *J. Am. Chem. Soc.*, 2009, **131**, 1802-1809.
2. H. Lindstrom, S. Sodergren, A. Solbrand, H. Rensmo, J. Hjelm, A. Hagfeldt and S.-E. Lindquist, *J. Phys. Chem. B*, 1997, **101**, 7717-7722.
3. J. Wang, J. Polleux, J. Lim and B. Dunn, *J. Phys. Chem. C*, 2007, **111**, 14925-14931.