

Supporting Information

Controllable synthesis of hierarchical $\text{ZnSn}(\text{OH})_6$ and Zn_2SnO_4 hollow nanospheres and their applications as anodes for lithium ion batteries

*Ranran Zhang, Yanyan He and Liqiang Xu**

Figure Captions:

- Fig. S1 (a) XRD pattern and (b, c) TEM images of the $\text{ZnSn}(\text{OH})_6$ product obtained in the absence of PAA.
- Fig. S2 TEM images of the $\text{ZnSn}(\text{OH})_6$ synthesized in different time periods at 180 °C (PAA is 0.75 g): (a, b) 6 h; (c, d) 9 h; (e, f) 12 h; (g, h) 18 h; (I, j) 21 h; (k, l) 24 h.
- Fig. S3 TGA curves of $\text{ZnSn}(\text{OH})_6$ obtained with PAA (0.75 g) under N_2 flow.
- Fig. S4 XPS spectra: (a) survey spectrum, (b) Sn 3d, (c) Zn 2p, (d) O 1s of hierarchical Zn_2SnO_4 hollow nanospheres.
- Fig. S5 TEM images of the hierarchically hollow Zn_2SnO_4 nanospheres after 20th cycles at the current density of 500 mA/g.
- Fig. S6 Typical discharge/charge capacity and coulombic efficiency curves of the hierarchical hollow $\text{ZnSn}(\text{OH})_6$ and Zn_2SnO_4 nanospheres fabricated using different amounts of PAA: (a, b) 0.25 g, (c, d) 0.5 g, (e, f) 1.0 g at a current density of 1000 mA g⁻¹.

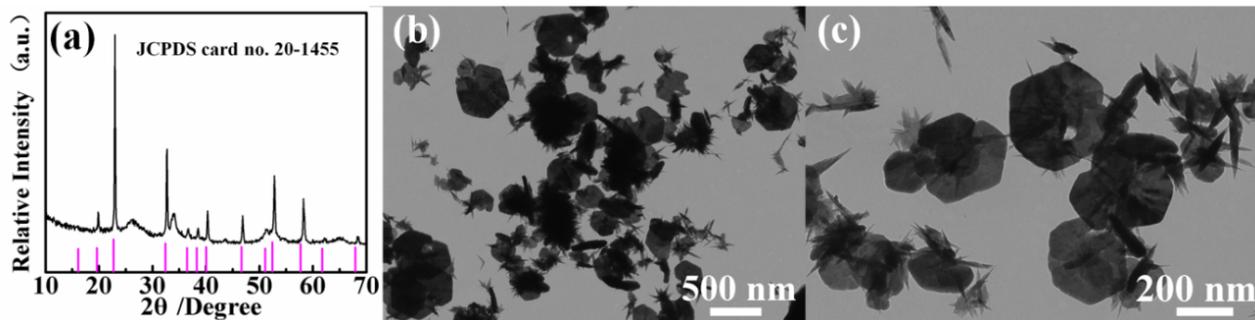


Fig. S1 (a) XRD pattern and (b, c) TEM images of the ZnSn(OH)_6 product obtained in the absence of PAA.

All the diffraction peaks in the XRD pattern (Fig. S1a) of the as-obtained product obtained in the absence of PAA evidencing the formation of the cubic ZnSn(OH)_6 (JCPDS card no. 20-1455; $a=b=c=7.800 \text{ \AA}$), while no diffraction peaks of impurities were observed from this pattern. Fig. S1(b, c) clearly display that when no PAA is added in the hydrothermal process, the products are the mixture of irregular hexagon pieces and nanoneedles.

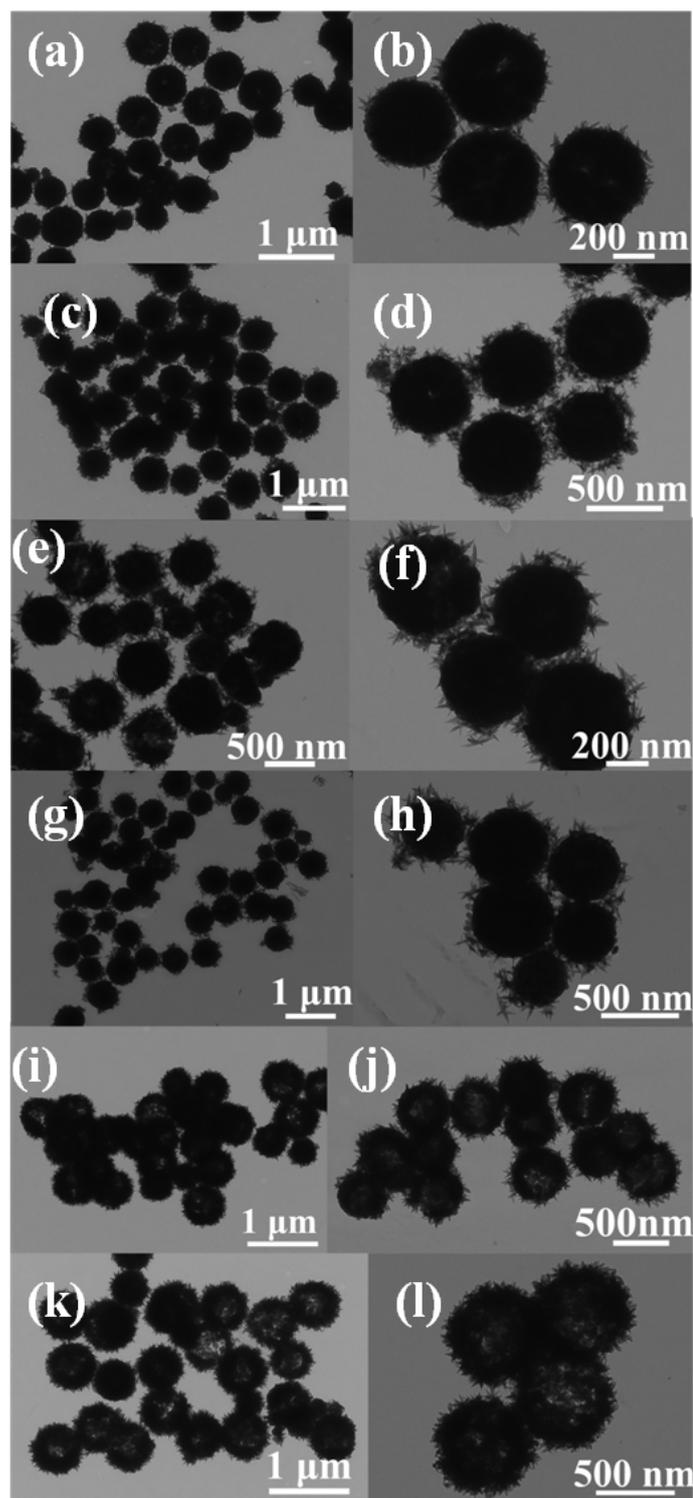


Fig. S2 TEM images of the $\text{ZnSn}(\text{OH})_6$ synthesized in different time periods at 180 °C (PAA is 0.75 g): (a, b) 6 h; (c, d) 9 h; (e, f) 12 h; (g, h) 18 h; (i, j) 21 h; (k, l) 24 h.

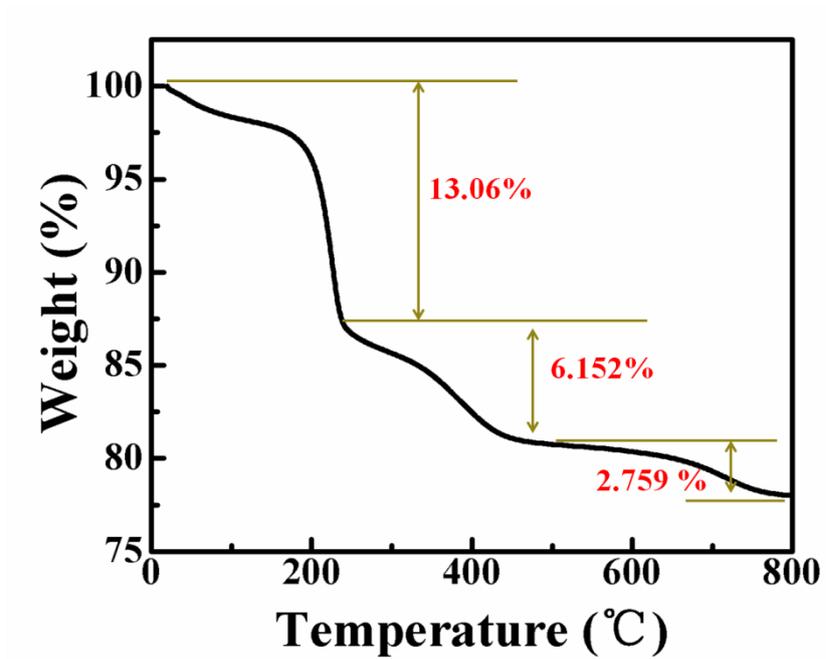


Fig. S3 TGA curves of ZnSn(OH)₆ obtained with PAA (0.75 g) under N₂ flow.

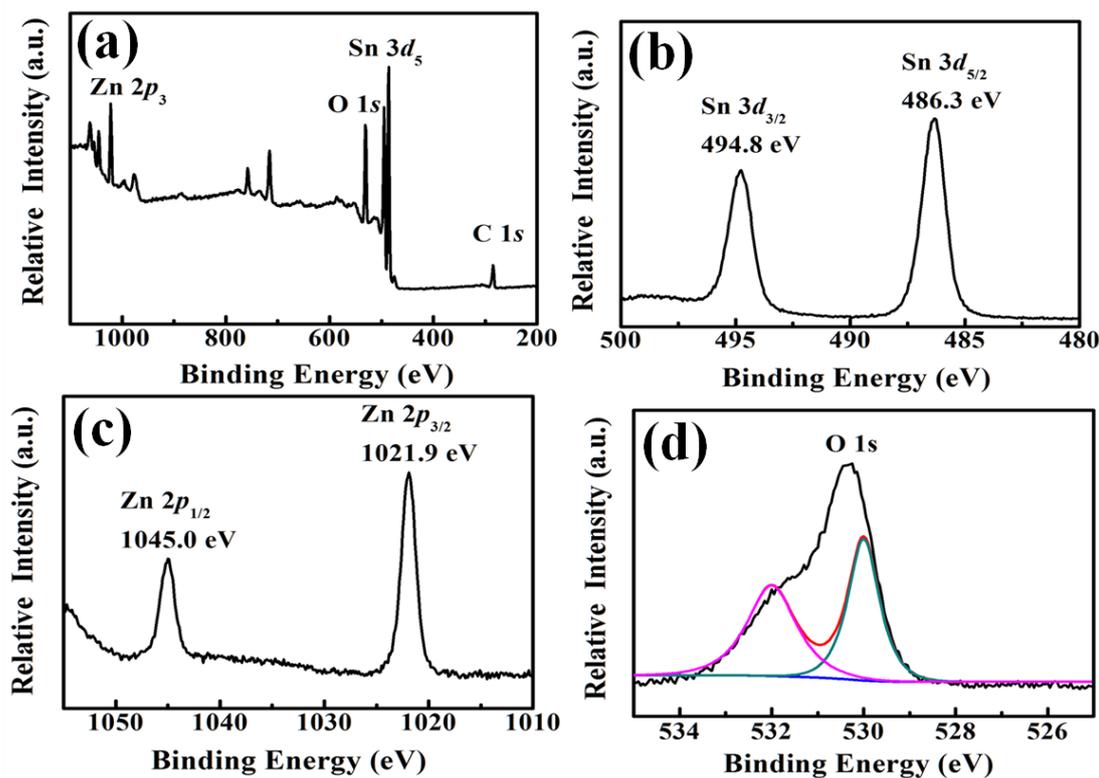


Fig. S4 XPS spectra: (a) survey spectrum, (b) Sn 3d, (c) Zn 2p, (d) O 1s of hierarchical Zn_2SnO_4 hollow nanospheres.

Fig. S4a shows the full XPS spectrum of the product, which evidences the existence of Zn, Sn, O and C elements. The peak centered at 284.8 eV in the spectrum can be assigned to carbon contamination or CO_2 adsorbed on the surface of the product when it was exposed to the air after synthesis. Fig. S4b and Fig. S4c demonstrate the existence of Sn^{4+} and Zn^{2+} , respectively. The deconvoluted O 1s spectrum in Fig. S4d displays two photoelectron peaks at 529.6, and 532.2 eV that can be assigned to the oxygen species of the Sn-O and Zn-O bonds in Zn_2SnO_4 .

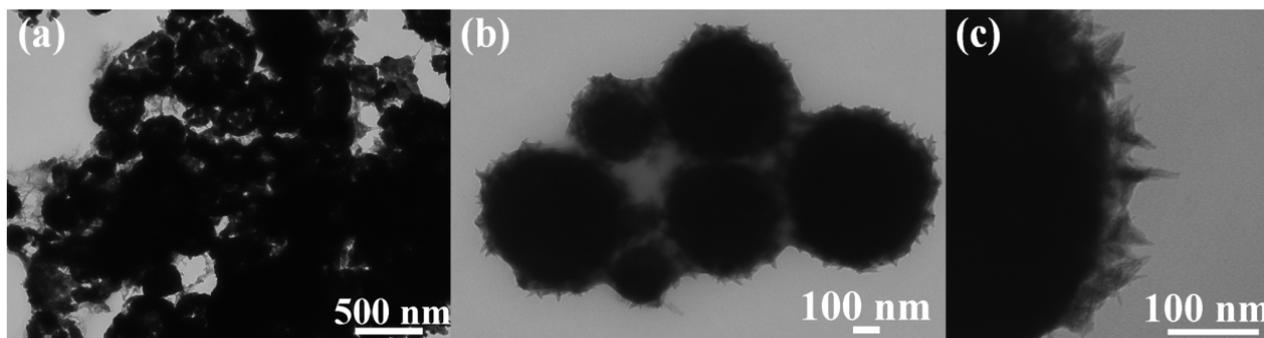


Fig. S5 TEM images of the hierarchically hollow Zn_2SnO_4 nanospheres after 20th cycles at the current density of 500 mA g^{-1} .

Typical TEM images of the hierarchically hollow Zn_2SnO_4 nanospheres after 20th cycles at the current density of 500 mA g^{-1} are shown in Fig. S5. It can be seen from Fig. S5a that majority of the product remain the spherical structures after 20th cycles at the high current density of 500 mA g^{-1} . From the magnified TEM images shown in Fig. S5b and Fig. S5c, one can see that their hierarchical spherical structure characteristics are still remained, indicating the high stable structures of the hierarchically hollow Zn_2SnO_4 nanospheres as advanced anode electrode for lithium ion batteries.

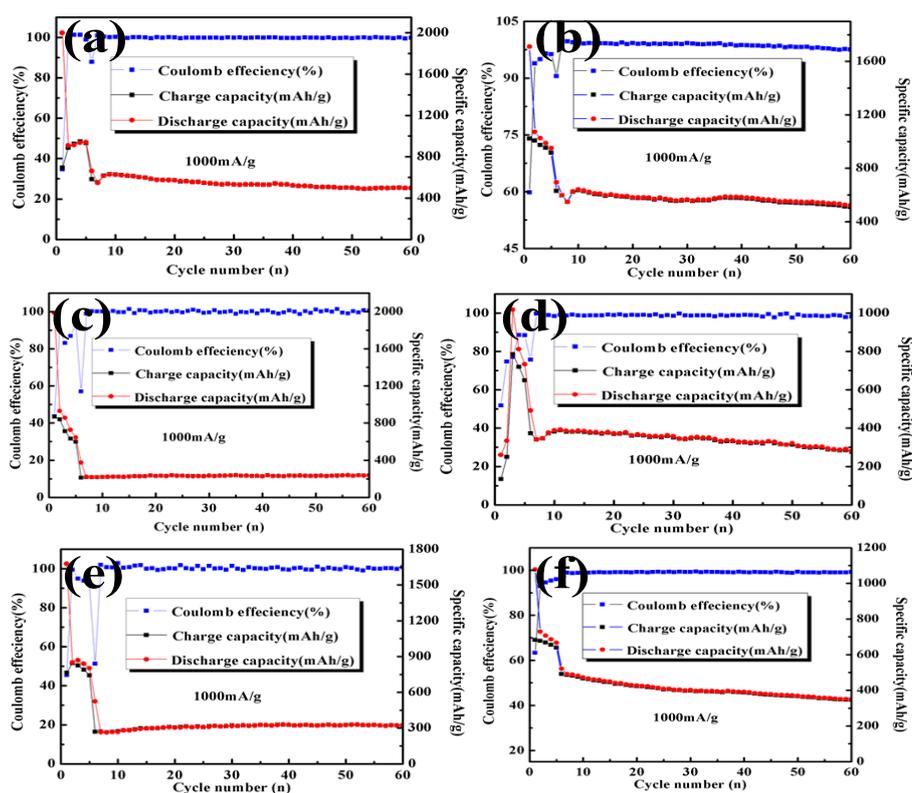


Fig. S6 Typical discharge/charge capacity and coulombic efficiency curves of the hierarchical hollow ZnSn(OH)_6 and Zn_2SnO_4 nanospheres fabricated using different amounts of PAA: (a, b) 0.25 g, (c, d) 0.5 g, (e, f) 1.0 g at a current density of 1000 mA g^{-1} .

The performance curves of the products produced by using different amounts of PAA are shown in Fig. S6, it is found that when the using amounts of PAA is 0.25g, the ZnSn(OH)_6 and Zn_2SnO_4 exhibit superior performances than those of other samples at a current density of 1000 mA g^{-1} , revealing that the as-obtained products of different sizes has different cycle performances.