

SUPPORTING INFORMATION

Pitaya-Like Microspheres Derived from Prussian Blue Analogues as Ultralong-Life Anodes for Lithium Storage

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S1. The comparison of specific capacities of encapsulated Co₃ZnC nanoparticles in pitaya-like microspheres anode and bare Co₃ZnC nanoparticle anode.

S2. Fig. S1-S21

S1. The comparison of specific capacities of encapsulated Co₃ZnC nanoparticles in pitaya-like microspheres anode and bare Co₃ZnC nanoparticle anode.

The reversible specific capacity of encapsulated Co₃ZnC nanoparticles in the pitaya-like microspheres can be calculated as follow: $C_{\text{Co}_3\text{ZnC}} \cdot \eta_{\text{Co}_3\text{ZnC}} = C_{\text{Total}} - C_{\text{Carbon}} \cdot \eta_{\text{Carbon}}$. In this equation, the C_{Total} is the overall discharge capacity of pitaya-like microsphere anode, C_{Carbon} stands for the discharge capacity of bare carbon frameworks, η_{Carbon} and $\eta_{\text{Co}_3\text{ZnC}}$ present the weight percentage of bare carbon frameworks (31.9%) and bare Co₃ZnC nanoparticles (68.1%) determined by the TGA results, respectively. To investigate the discharge capacity of bare carbon frameworks, the Co₃ZnC nanoparticles were completely removed by the etching of HF (5 wt.%) and HCl (1.0 M) successively. As shown in Fig. S16, the morphology and structure characterizations confirmed the removal of Co₃ZnC nanoparticles. The control sample of bare carbon frameworks shows a discharge capacity of about 436 mAh g⁻¹ after 20 cycles at 100 mA g⁻¹ (Fig. S18a). Therefore, the definite specific capacity of encapsulated Co₃ZnC nanoparticles in Co₃ZnC/C multicore microspheres can be calculated as follow: $C_{\text{Co}_3\text{ZnC}} = (C_{\text{Total}} - C_{\text{Carbon}} \cdot \eta_{\text{Carbon}}) / \eta_{\text{Co}_3\text{ZnC}} = (608 - 436 \times 31.9\%) / 68.1\% = 689 \text{ mAh g}^{-1}$. Compared with bare Co₃ZnC nanoparticle anode

(257 mAh g⁻¹ at 100th cycle), the encapsulated Co₃ZnC nanoparticles in pitaya-like microspheres deliver much higher specific capacity. It proves that the electrochemical performance of metal carbides can be greatly enhanced by the special architecture of well-dispersed nanoparticles embedded in 3D conductive carbon frameworks.

S2. Fig. S1-S21

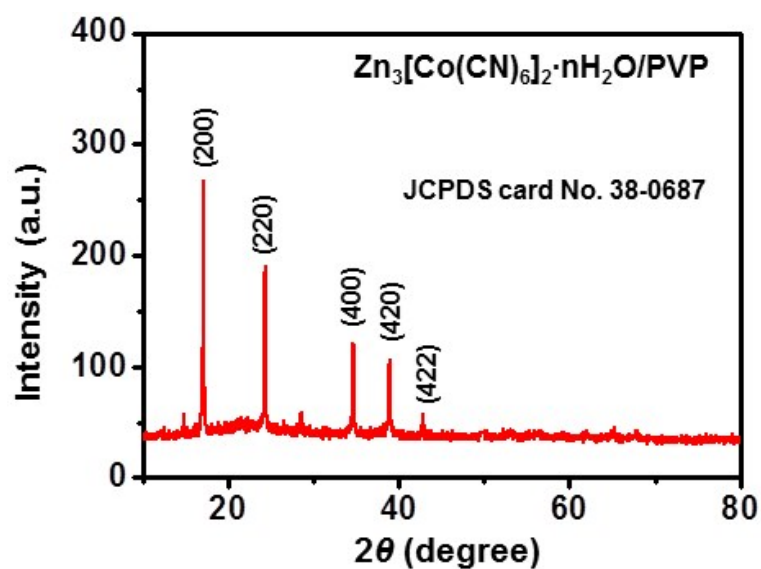


Fig. S1. XRD spectrum of Zn₃[Co(CN)₆]₂·nH₂O/PVP precursor microspheres.

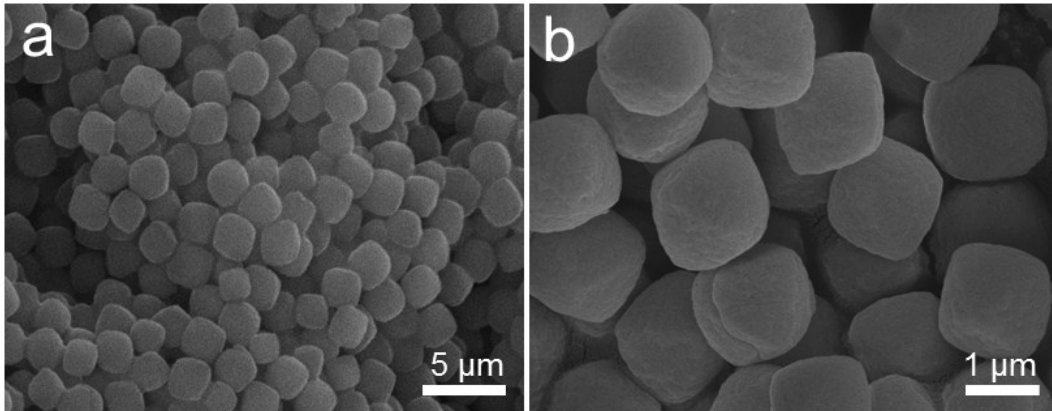


Fig. S2. (a,b) FESEM images of PBA precursor prepared with the halved amount of added PVP in the synthesis procedure.

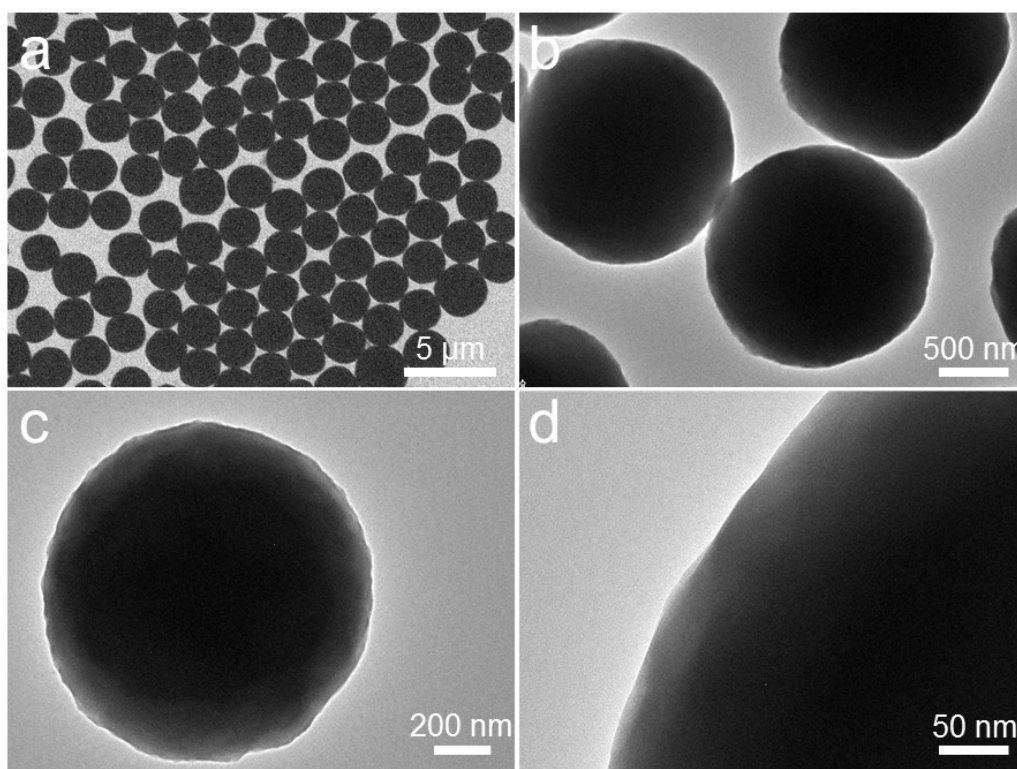


Fig. S3. Morphology characterization of the PBA precursor. (a-d) TEM images of $\text{Zn}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}/\text{PVP}$ precursor microspheres with different magnifications.

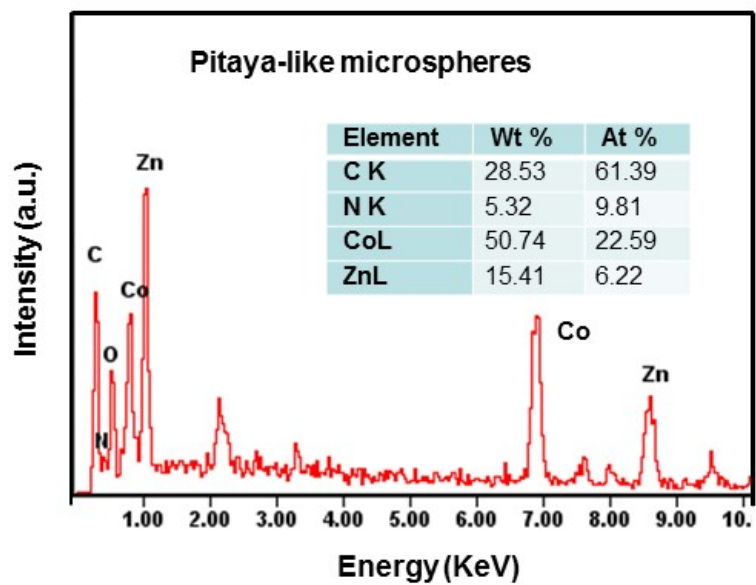


Fig. S4. EDX spectrum of the pitaya-like microspheres.

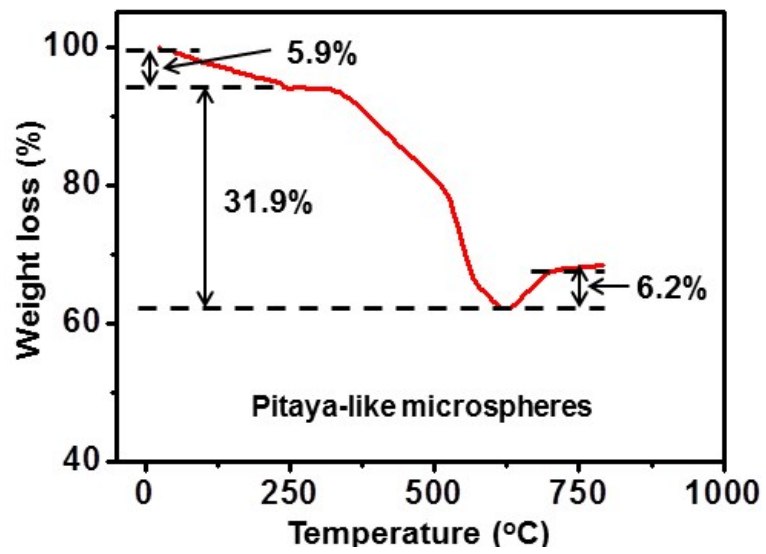


Fig. S5. Thermogravimetric analysis (TGA) curve of pitaya-like microspheres under air atmosphere with a heating rate of 10 °C/min.

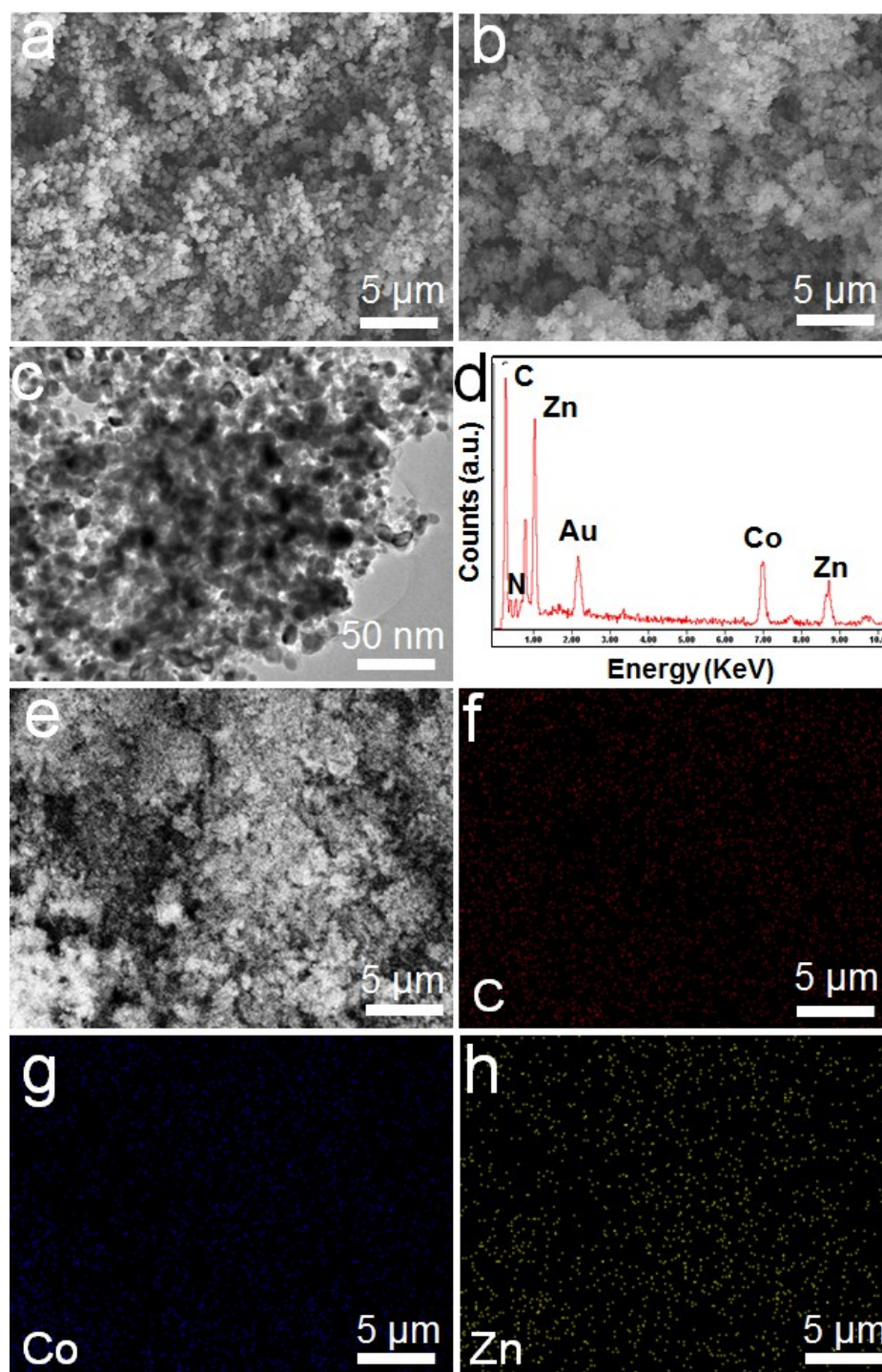


Fig. S6. FESEM images of (a) $\text{Zn}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ precursor nanoparticles without PVP and (b) bare Co_3ZnC nanoparticles. (c) TEM image of bare Co_3ZnC nanoparticles. The morphology characterizations reveal that the bare Co_3ZnC nanoparticles are composed of small particles with the size of ~ 10 nm. (d) EDX and corresponding elemental mapping of (e) raw, (f) C, (g) Co, and (h) Zn elements of

bare Co_3ZnC nanoparticles, respectively. The EDX spectrum together with the EDX elemental maps suggest the co-existence of C, Co, and Zn elements, and further demonstrate the homogeneous distribution of these elements.

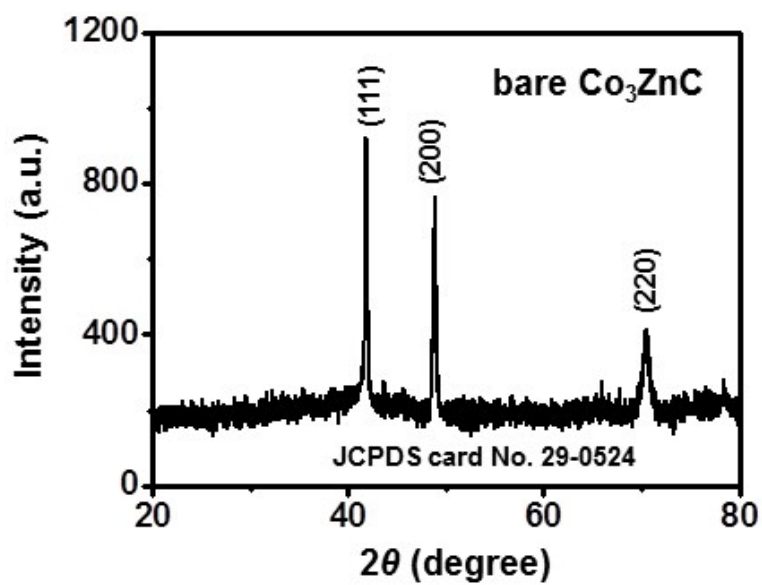


Fig. S7. XRD spectrum of bare Co_3ZnC nanoparticles.

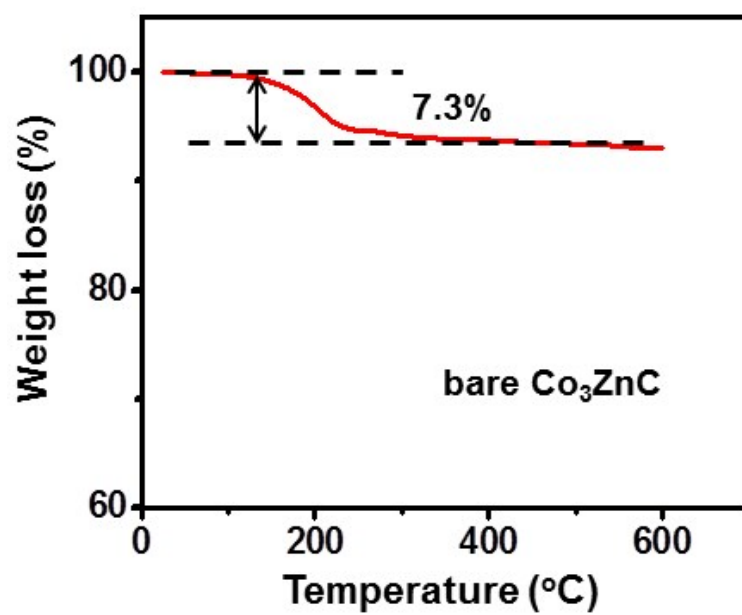


Fig. S8. TGA analysis of bare Co₃ZnC nanoparticles under air atmosphere with a heating rate of 10 °C/min.

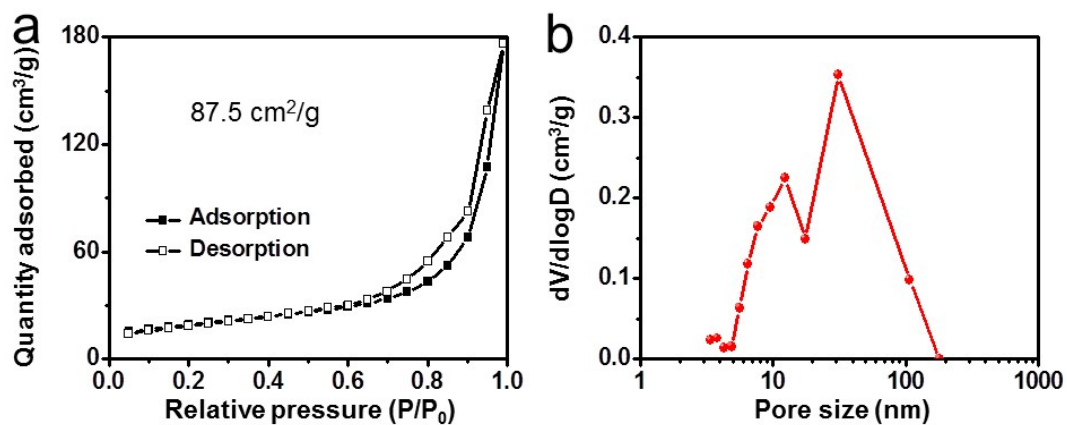


Fig. S9. (a) N₂ adsorption/desorption isotherm and (b) pore size distribution curve of bare Co₃ZnC nanoparticles.

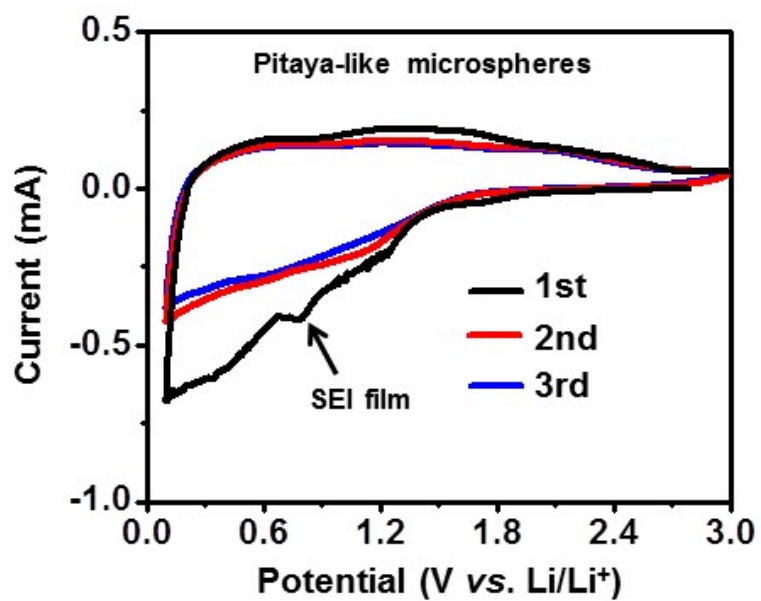


Fig. S10. CV curves of pitaya-like microsphere anode within the potential range of 0.01–3.0 V vs. Li/Li⁺ at a scan rate of 0.2 mV/s.

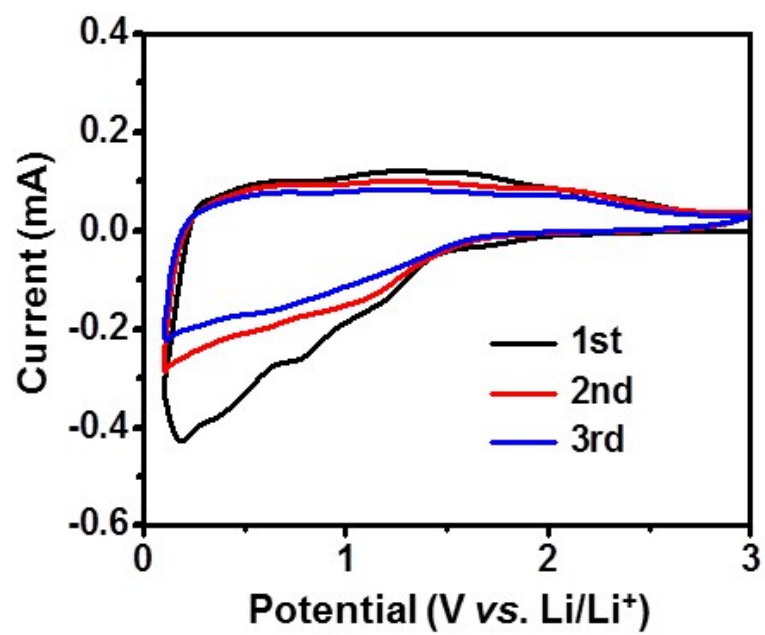


Fig. S11. CV curves of bare Co₃ZnC nanoparticle electrode within the potential range of 0.01–3.0 V vs. Li/Li⁺ at a scan rate of 0.2 mV/s.

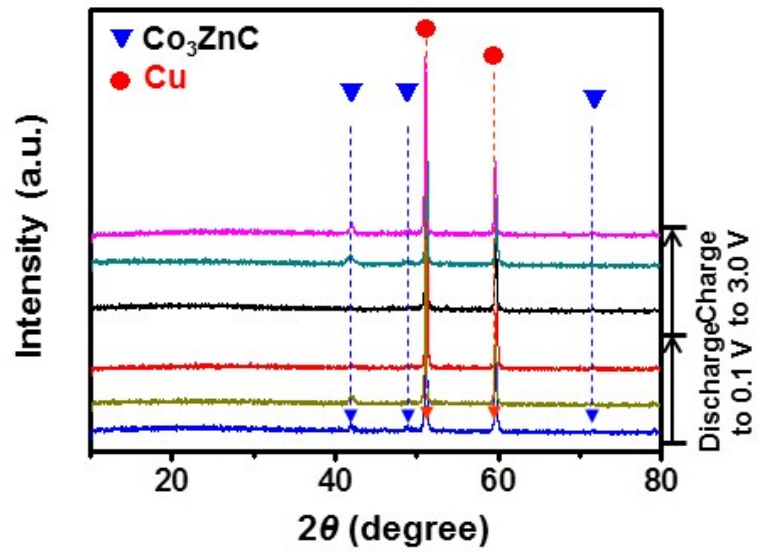


Fig. S12. *Ex-situ* XRD spectra of pitaya-like microspheres at different charge and discharge states.

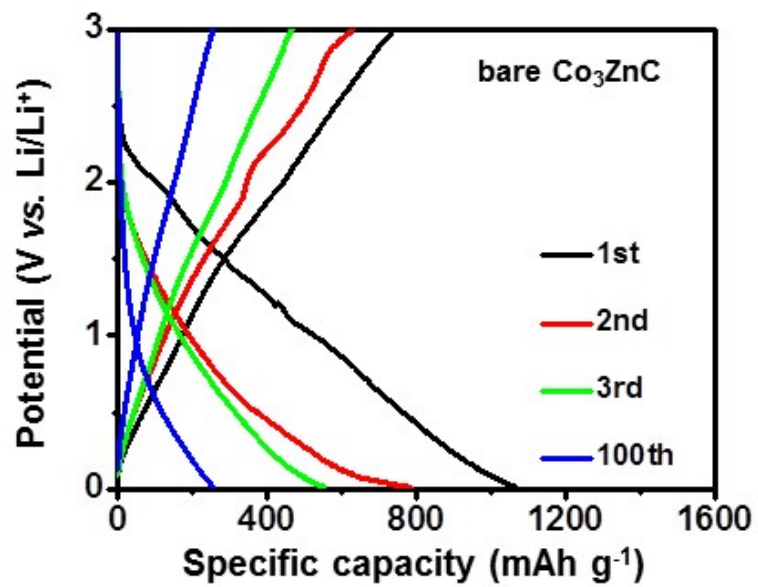


Fig. S13. Charge/discharge profiles of bare Co_3ZnC nanoparticle anode at 100 mA g^{-1} .

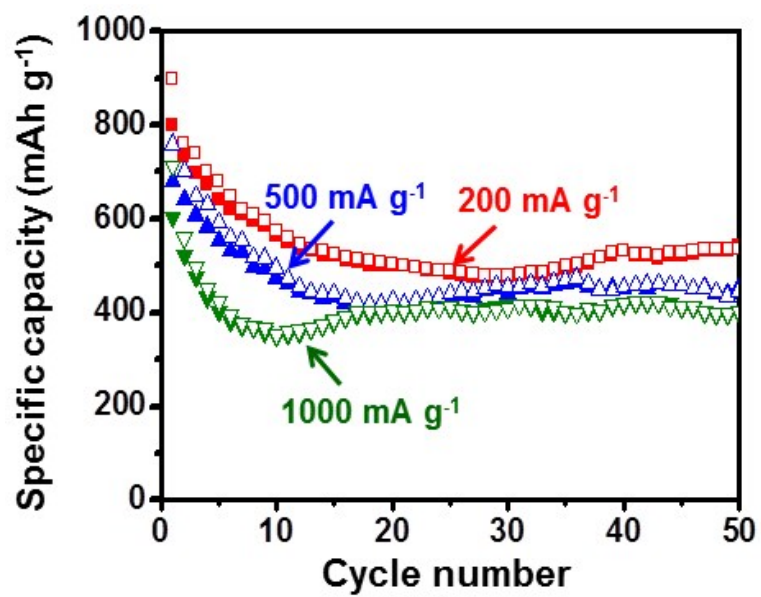


Fig. S14. Rate capability of pitaya-like microsphere electrode with different cells under various current densities.

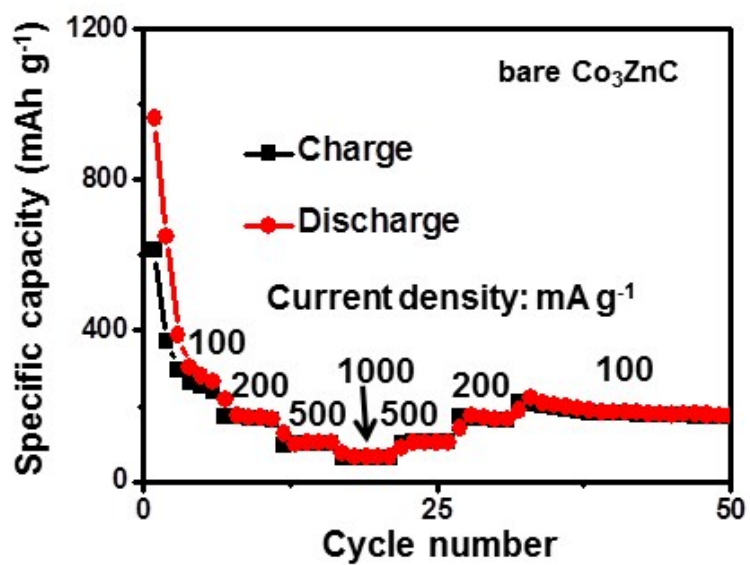


Fig. S15. Rate performance of bare Co₃ZnC nanoparticles at various current densities (100–1000 mA g⁻¹).

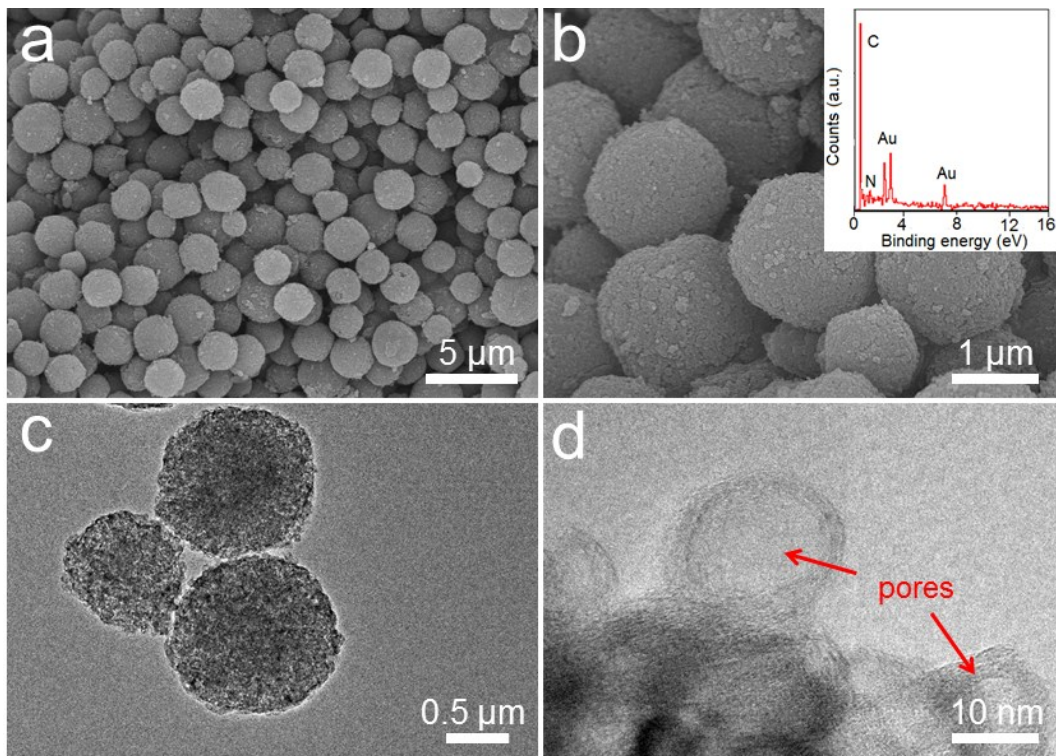


Fig. S16. (a,b) FESEM and (c,d) TEM images of bare carbon frameworks prepared by completely removing the Co_3ZnC nanoparticles in pitaya-like microspheres through the etching of HF (5 wt.%) and HCl (1.0 M) successively. The insert of (b) shows the corresponding EDX spectrum, indicating no Co or Zn element is remained in the bare carbon frameworks.

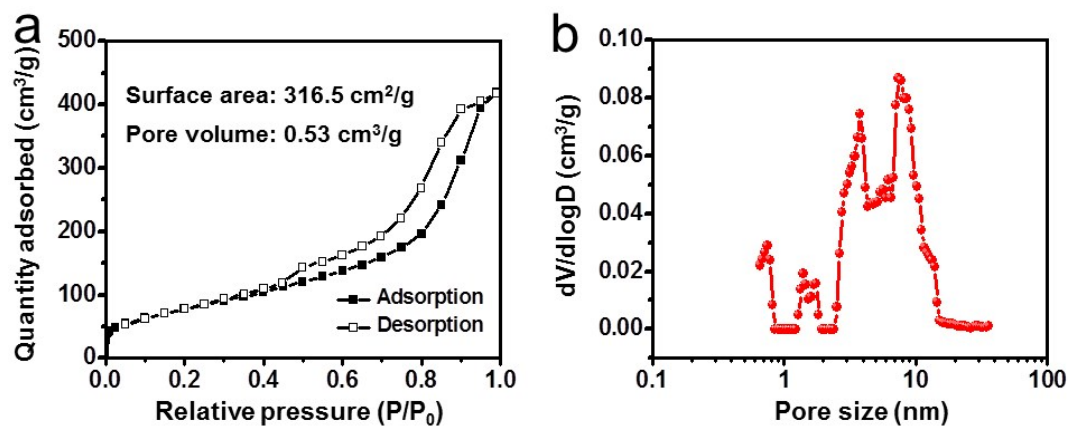


Fig. S17. (a) N₂ adsorption-desorption isotherm and (b) pore size distribution curve of bare carbon frameworks.

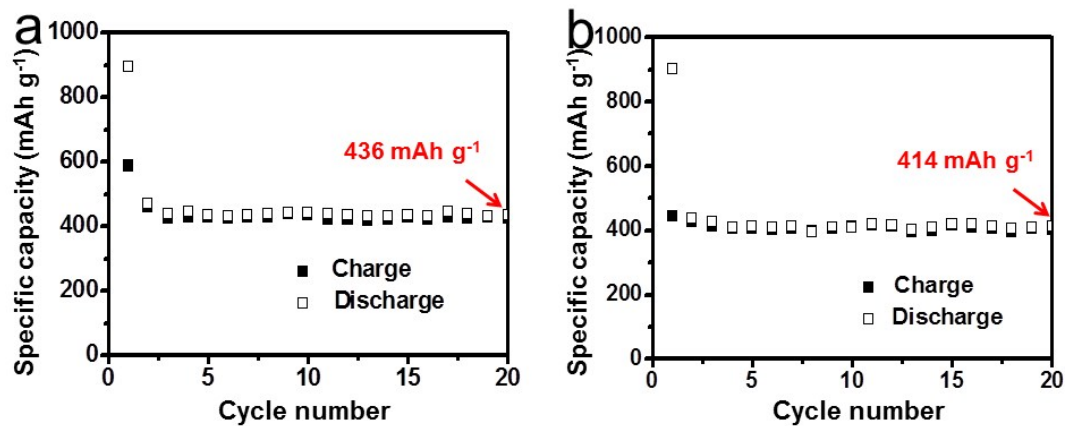


Fig. S18. Cycling performances of bare carbon frameworks before (a) and after (b) thermal annealing at 1000 °C for 6 h.

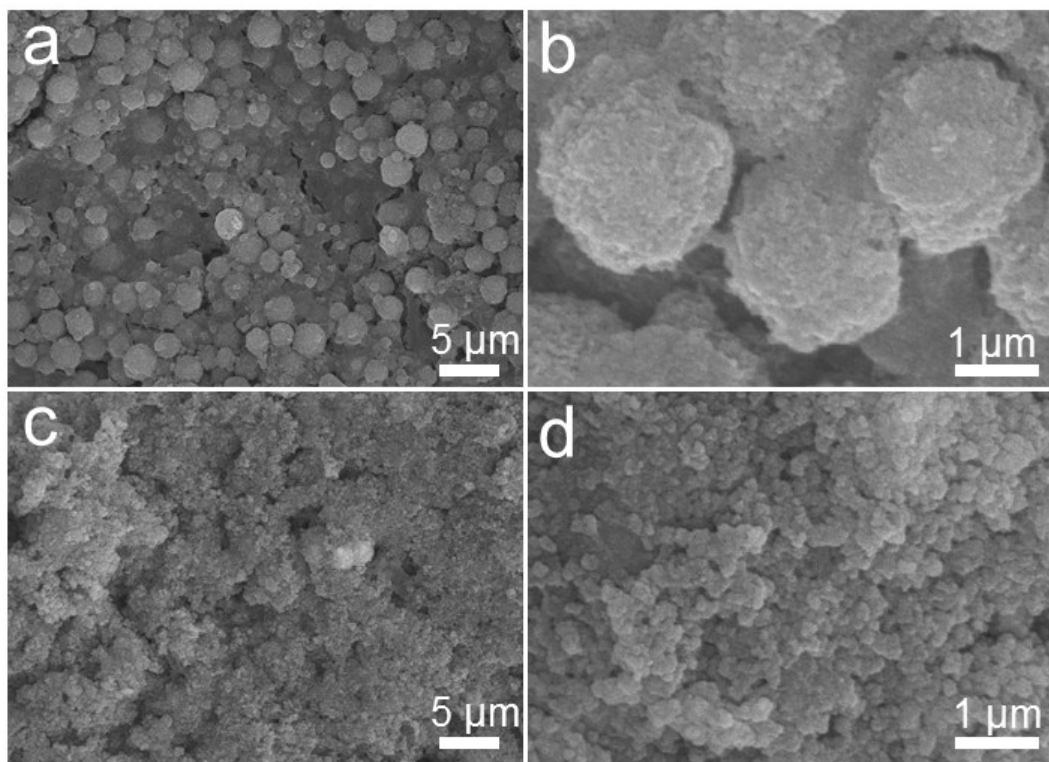


Fig. S19. (a,b) FESEM image of pitaya-like microsphere anode after 1150 cycles at 1000 mA g⁻¹. (c,d) FESEM images of bare Co₃ZnC nanoparticles after 100 cycles at 100 mA g⁻¹. The FESEM observations demonstrate that the pitaya-like microspheres can maintain excellent structural integrity without any obvious morphology change after very long-term stability tests at relatively high rate, while bare Co₃ZnC nanoparticles show structural instability and rapid capacity decay after cycling.

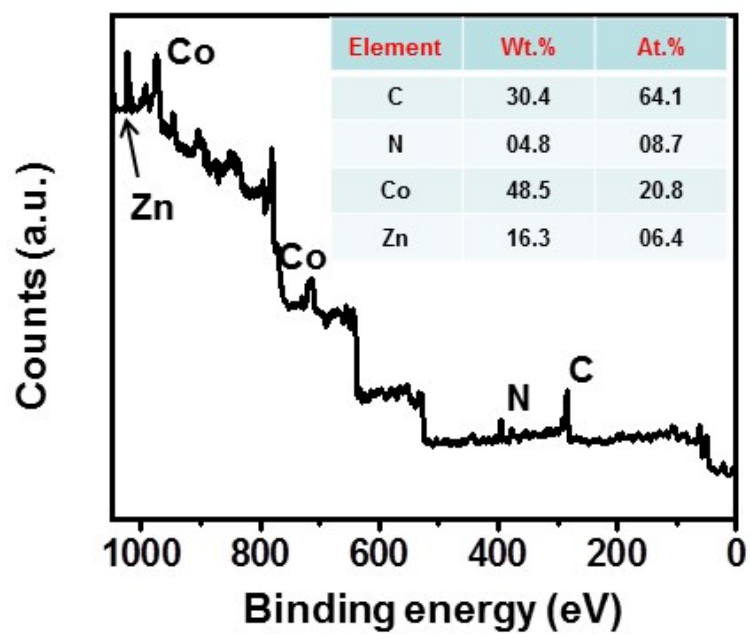


Fig. S20. XPS spectrum of pitaya-like microspheres.

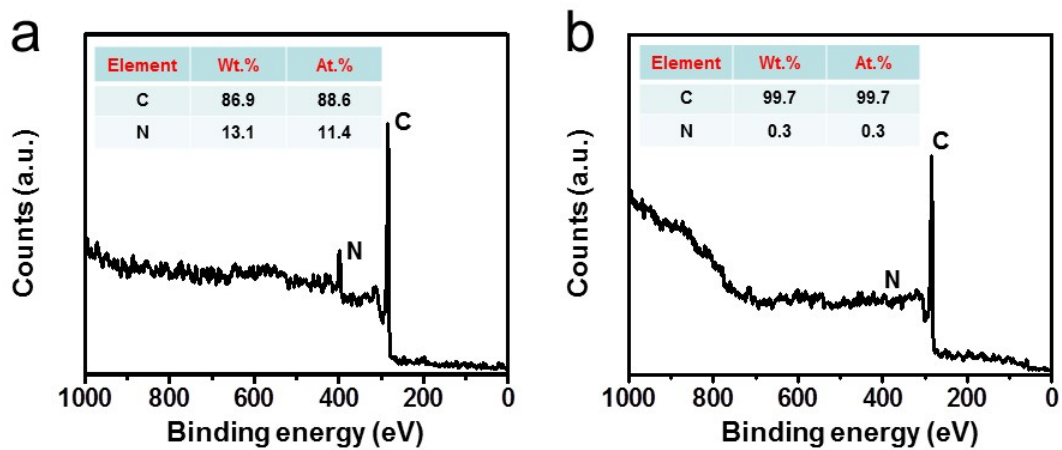


Fig. S21. XPS spectra of bare carbon frameworks (a) before and (b) after thermal annealing at 1000 °C for 6 h.