

Figure S1. (a, b) HRTEM images of the thick graphitic layers obtained by annealing of the ZIF-67 crystals at 800 °C for 48 h.

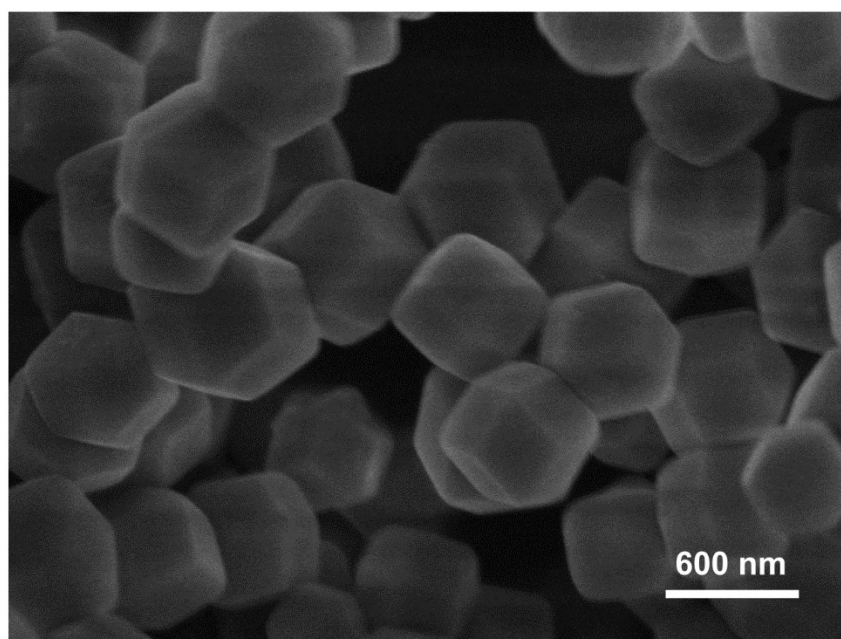


Figure S2. The SEM image of the as-prepared ZIF-67 crystals.

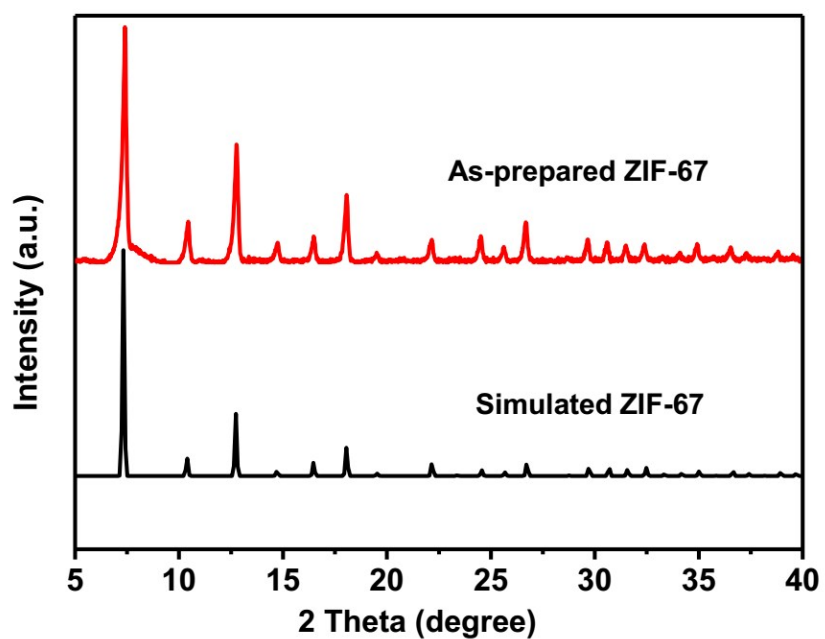


Figure S3. The PXRD pattern of the as-prepared ZIF-67 crystals and the simulated XRD pattern of ZIF-67 from CIF file.



Figure S4. The color changes of the ZIF-67 samples after annealing in N_2 at $450\text{ }^\circ\text{C}$ for different durations.

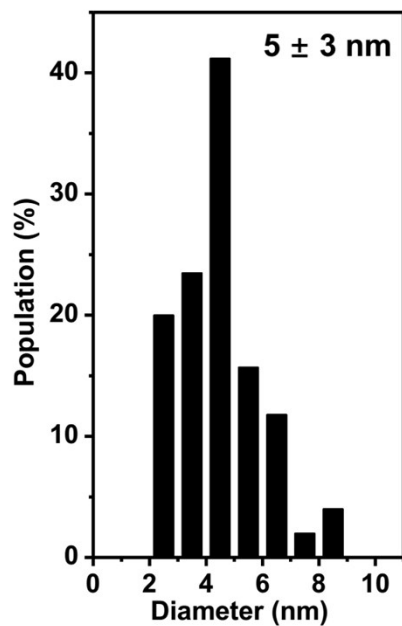


Figure S5. The size distribution of Co nanoparticles embedded in the graphitic shells networks.

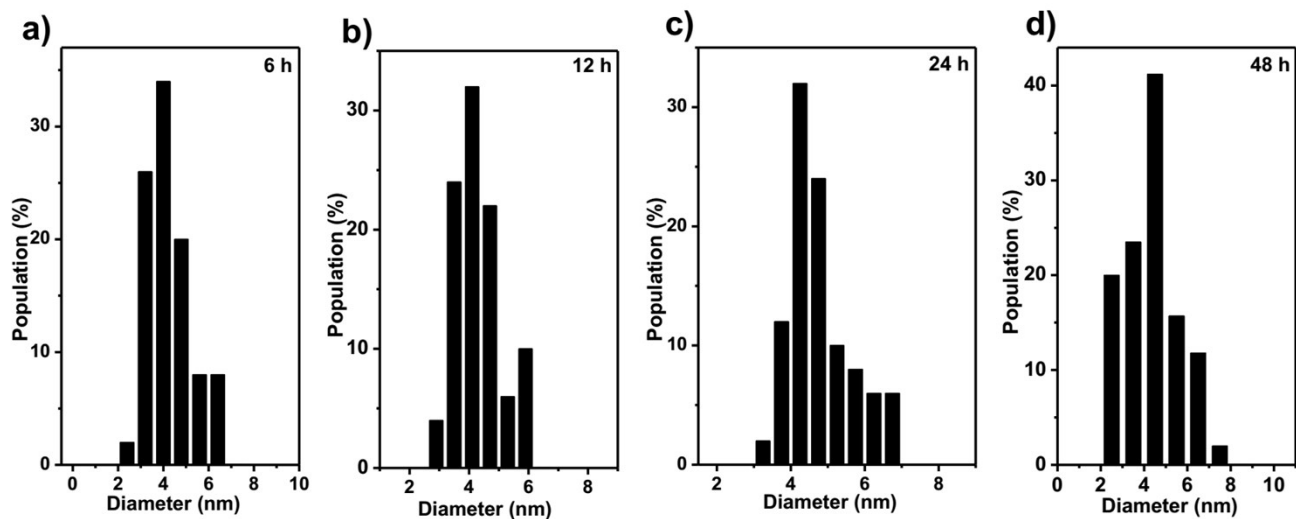


Figure S6. The size distribution histograms of Co nanoparticles embedded in the ZIF-67 samples after annealing in N_2 at $450\text{ }^\circ\text{C}$ for different durations: (a) 6 h, (b) 12 h, (c) 24 h, and (d) 48 h.

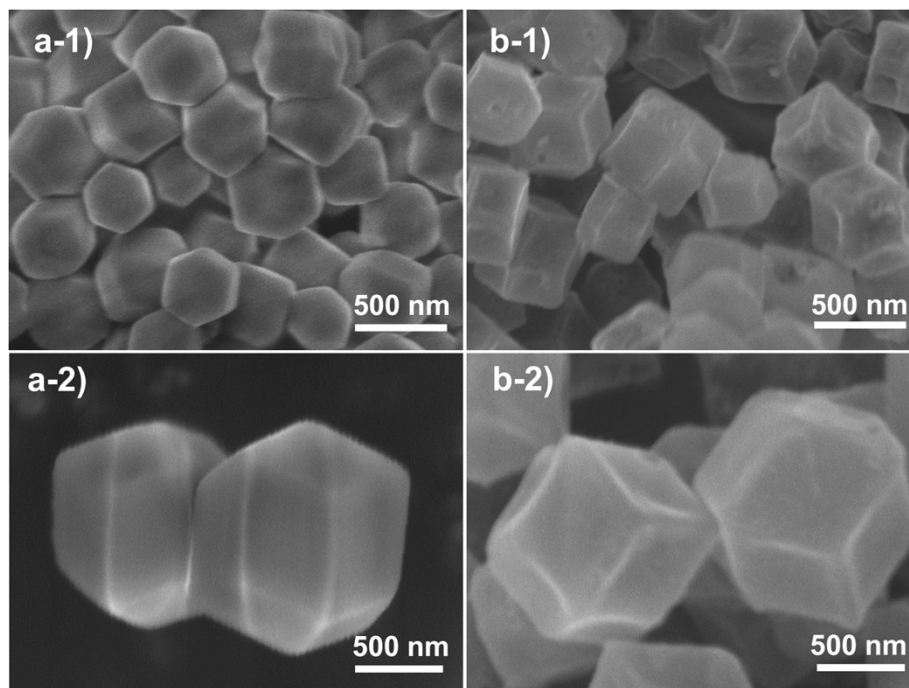


Figure S7. SEM images of the as-prepared ZIF-8 crystals (a) and the annealed ZIF-8 at 450 °C for 48 h (b).

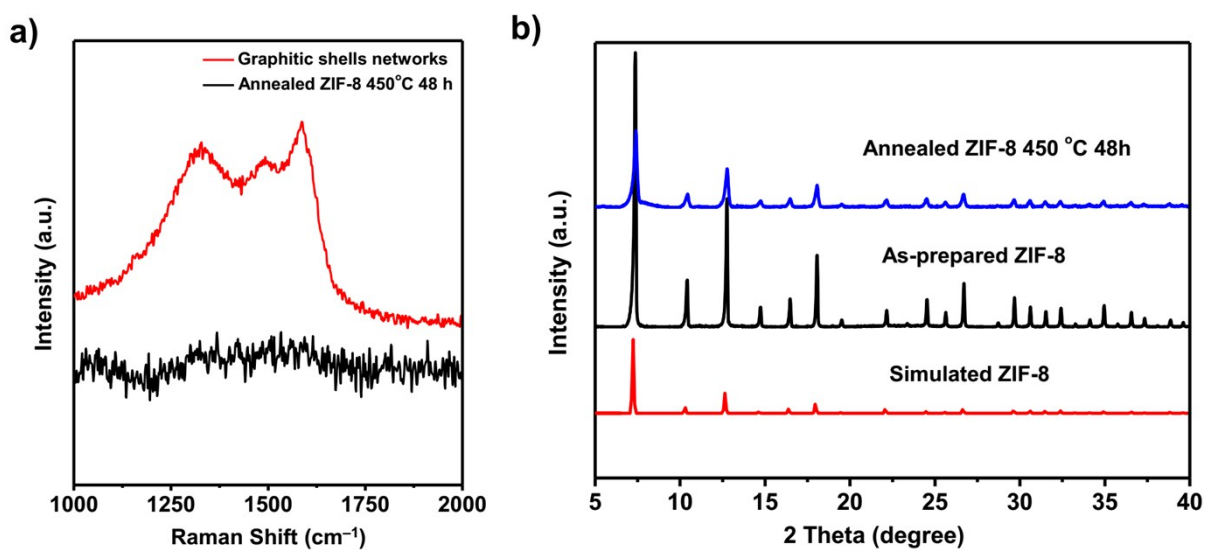
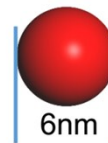


Figure S8. (a) Raman spectra of the graphitic shells networks and the annealed ZIF-8 at 450 °C for 48 h. (b) PXRD patterns of the as-prepared ZIF-8 crystals and the annealed ZIF-8 at 450 °C for 48 h.

According to the experimental average diameter of the Co nanoparticle in the networks, we set the size of the Co nanoparticles to be 6 nm,



Co nanoparticle

Herein, the volume of a Co nanoparticle is,

$$V = \frac{4}{3} \pi r^3 = \frac{4}{3} \pi \left(\frac{6}{2}\right)^3 \text{ nm}^3 = 113.1 \text{ nm}^3$$

As the density of the Co is 8.9 g/cm³, we can deduct that the molar density of the Co is $1.508 \times 10^{-22} \text{ mol/nm}^3$.

Therefore, the number of the Co atoms in a Co nanoparticle can be calculated as

$$(1.508 \times 10^{-22} \text{ mol/nm}^3) \times 113.1 \text{ nm}^3 \times N_A = 10243$$

Figure S9. The calculation procedure used to identify the total number of cobalt atoms for building up a Co nanoparticle (6 nm in size).

For a rhombic dodecahedral ZIF-67 crystal, the volume of a particle

can be calculated to be $V = \frac{16}{9} \sqrt{3} a^3 = \frac{16}{9} \sqrt{3} (0.5 b)^3 = 0.384 b^3$

For a particle with a size of 600 nm, the $b = 600 \text{ nm}$, therefore the volume

can be calculated to be $V = 0.38 \times (600 \text{ nm})^3 = 8.2 \times 10^7 \text{ nm}^3$

For a unit cell of ZIF-67, the lattice parameters is,

$$a = b = c = 1.69 \text{ nm} \quad \alpha = \beta = \gamma = 90^\circ$$

For one unit cell, 12 of Co atoms exist. The amount density of the Co atoms in ZIF-67 is,

$$\rho = \frac{12}{abc} = \frac{12}{1.69^3} \text{ nm}^{-3} = 2.44 \text{ nm}^{-3}$$

So the total number of the Co atoms in a ZIF-67 particle is,

$$N_2 = \rho V = 2.44 \times 8.2 \times 10^7 = 2.0 \times 10^8$$

Therefore, one ZIF-67 particle (600 nm in size) can yield $N_3 = \frac{N_2}{N_1} = 19542$ Co nanoparticles.

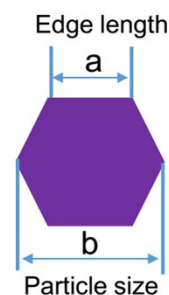
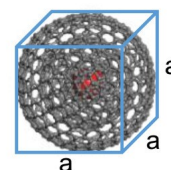


Figure S10. The calculation procedure used to identify the total number of Co nanoparticles in ZIF-67 crystals.

For a graphitic shell particle with a Co nanoparticle (6 nm) as the core and 6 layers of graphene as the shell, a cubic space ($V_1 = a^3 = 10^3 \text{ nm}^3 = 1000 \text{ nm}^3$) can be occupied (Figure 4d-4).



Because a ZIF-67 particle (600 nm in size) can yield $N_3 = \frac{N_2}{N_1} = 19542$ Co nanoparticles, we assume that a ZIF-67 particle can derive **19542** graphitic shell particles. It means that the volume of the initial ZIF-67 particle ($8.2 \times 10^7 \text{ nm}^3$) can be converted to be around $V_2 = N_3 V_1 = 1.952 \times 10^7 \text{ nm}^3$ after formation of graphitic shells networks. The volume loss is **76.2 vol%**.

Figure S11. The calculation procedure employed to determine the volume shrinkage by forming the graphitic shells networks from a ZIF-67 crystal (600 nm in size).

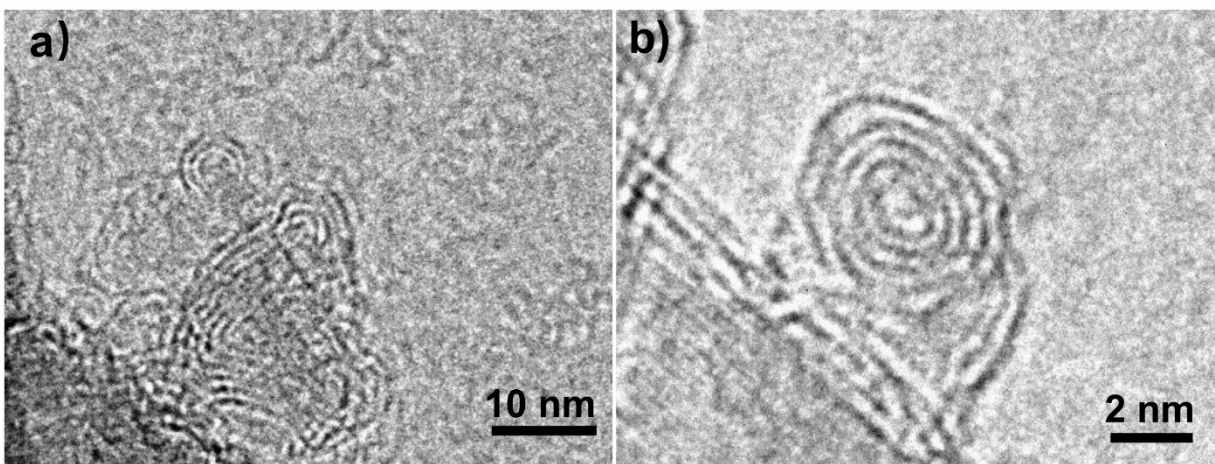


Figure S12. HRTEM images of the carbon onions particles.

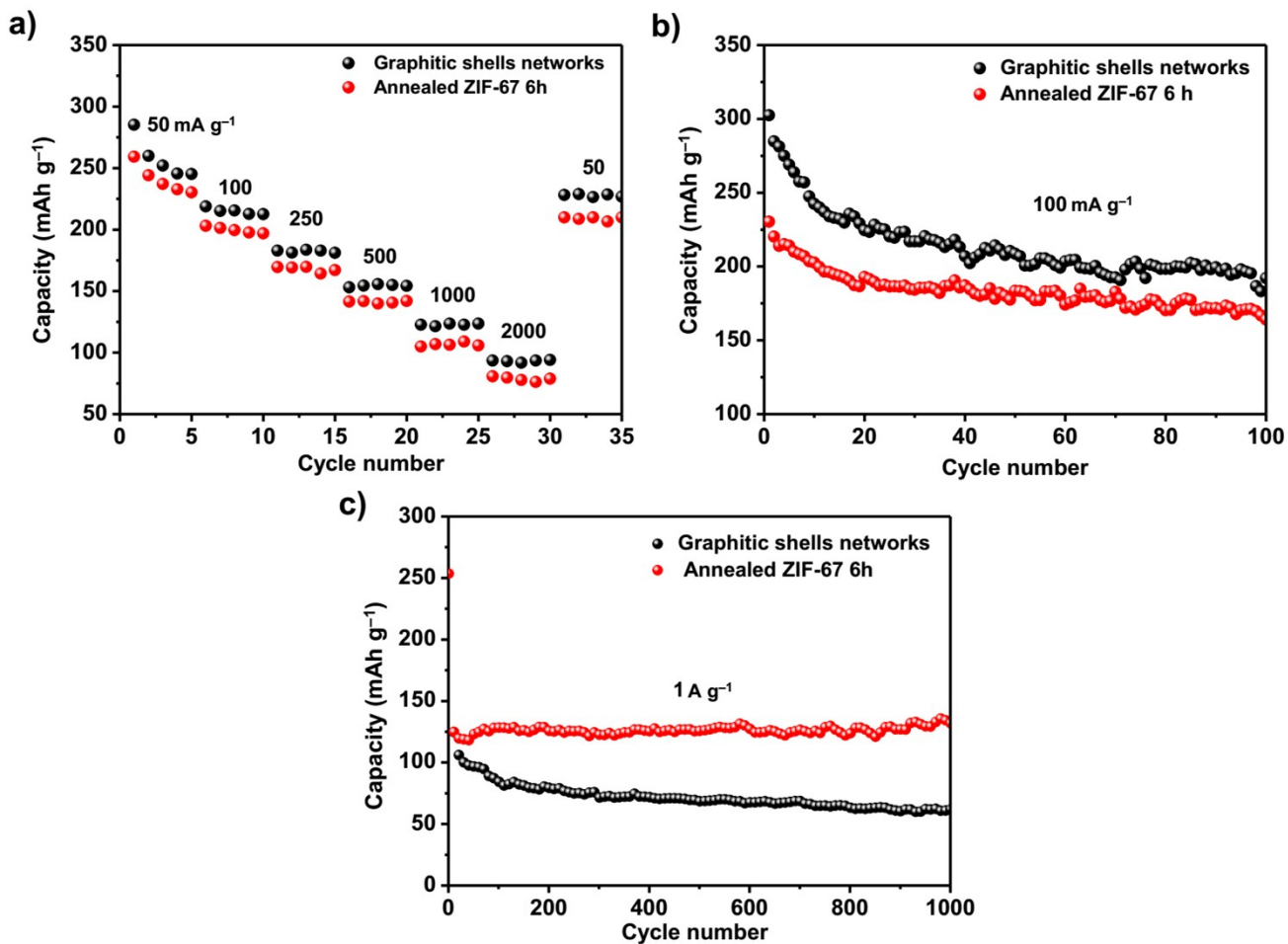


Figure S13. Rate performance (a) and cycling stability of the graphitic shells networks and the annealed ZIF-67 at 450 °C for 6 h at 100 mA g⁻¹ (b) and 1 A g⁻¹ (c).

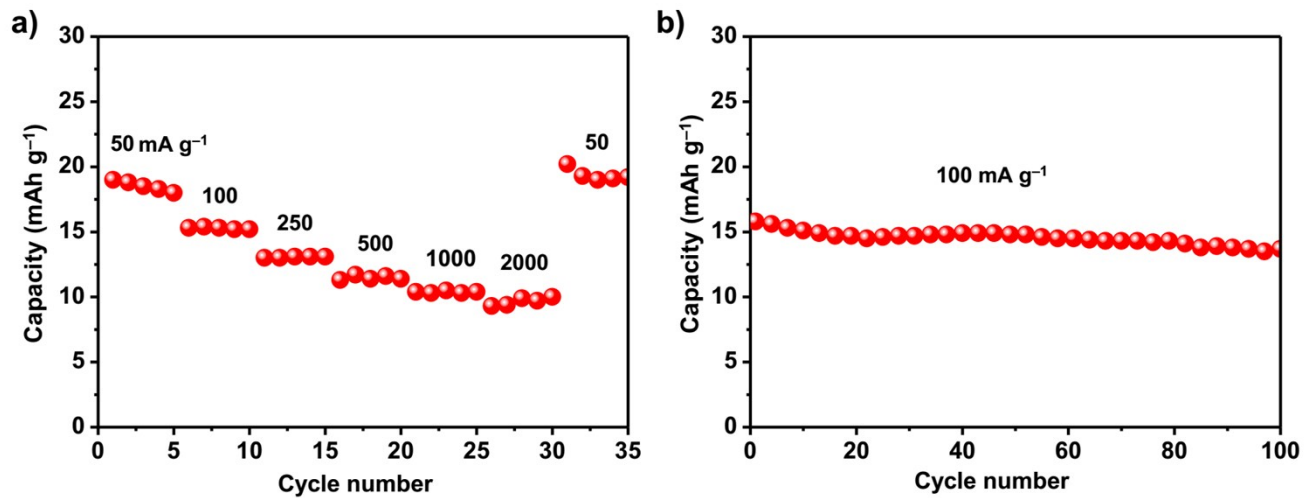


Figure S14. Rate performance (a) and cycling stability (b) of commercial graphite.

Table S1. Comparison of electrochemical performance of some carbon-based nanostructures for SIBs.

Materials	Specific capacity (mAh g ⁻¹)	Current density (mA g ⁻¹)	Cycle number	Reference
Graphitic shells networks	125	1000	1000	This work
Carbon onions particles	25	1000	1000	This work
HCNW	230	50	400	Ref. 1
NP-OPC	225	200	700	Ref. 2
CPM-1100-A	275	100	200	Ref. 3
Hollow carbon Nanospheres	160	100	100	Ref. 4
ACFs-C	243	50	100	Ref. 5
Mesoporous C/Sn	250	20	15	Ref. 6

References

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