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 °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 N₂ at 450 °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.

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

$$V = \frac{16}{9} \sqrt{3} a^2 = \frac{16}{9} \sqrt{3}(0.5 b)^2 = 0.384 b^3$$

For a particle with a size of 600 nm, the $b = 600$ 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,

$$N_2 = \rho V = 2.44 \times 8.2 \times 10^7 = 2.0 \times 10^9$$

Therefore, one ZIF-67 particle (600 nm in size) can yield

$$N_3 = \frac{N_2}{N_1} = 19542 \text{ Co nanoparticles}$$

**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 \( N_2 = \frac{N_1}{N_1} = 19542 \) 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.

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References