**Fig. S1.** XRD patterns of ZIF-8 and ZIF-8@ZIF-67.

**Fig. S2.** SEM images of (a) ZIF-8 and (b) ZIF-8@ZIF-67.

**Fig. S3.** (a), (b) XRD patterns, (c), (d) SEM and (e), (f) TEM images of ZnSe-NC and CoSe$_2$-NC.

**Fig. S4.** (a) SEM image, (b) TEM image, (c) XRD pattern and (d) HRTEM image of the mesoporous carbon polyhedron after etching.

**Fig. S5.** XRD patterns of (a) the ZIF-8@ZIF-67 processed in Ar atmosphere and (b) after subsequent selenization.

**Fig. S6.** TGA profiles of (a) ZnSe-NC and (b) CoSe$_2$-NC.

**Fig. S7.** Nitrogen adsorption/desorption isotherm of the ZIF-8@ZIF-67. The inset curve shows the corresponding BJH pore size distribution.

**Fig. S8.** Typical CV curves of the (a) ZnSe-NC and (b) CoSe$_2$-NC at a scan rate of 0.2 mV s$^{-1}$ within 0.005-3.0 V for LIBs.

**Fig. S9.** The combined third cycle CV curves of ZnSe-NC, CoSe$_2$-NC and ZnSe-NC@CoSe$_2$-NC for LIBs.

**Fig. S10.** Discharge-charge curves for the initial five cycles of (a) ZnSe-NC and (b) CoSe$_2$-NC at a current density of 0.2 A g$^{-1}$ for LIBs.

**Fig. S11.** (a) Cycling and (b) rate performance of the mesoporous carbon polyhedron obtained by etching of the ZnSe-NC@CoSe$_2$-NC.

**Fig. S12.** SEM images of the ZnSe-NC@CoSe$_2$-NC (a) after 600 discharge and (b) charge cycles. (c), (d) TEM images of ZnSe-NC@CoSe$_2$-NC after 600 cycles.
**Fig. S13.** The long-term cycling performance of the ZnSe-NC@CoSe₂-NC anode in another LIBs at a current density of 0.2 A g⁻¹.

**Fig. S14.** Non-proportional relation between the square root of scan rate and peak current for LIBs.

**Fig. S15.** Equivalent circuit used for fitting the experimental data of the ZnSe-NC@CoSe₂-NC electrode.

**Fig. S16.** GITT curves of (a) ZnSe-NC and (b) CoSe₂-NC. $D_{Li^+}$ of (c) ZnSe-NC and (d) CoSe₂-NC.

**Fig. S17.** The combined third cycle CV curves of ZnSe-NC, CoSe₂-NC and ZnSe-NC@CoSe₂-NC for SIBs.

**Fig. S18.** Ex-situ TEM/HRTEM images and corresponding SAED patterns of the ZnSe-NC@CoSe₂-NC at different discharge-charge stages in SIBs. (a) 100th discharge to 0.7 V, (b) 100th fully discharge, (c) 100th charge to 1.4 V, (d), (e) 100th fully charge.

**Fig. S19.** Ex-situ EDX spectrum of the ZnSe-NC@CoSe₂-NC electrode collected at various points in SIBs: (a) after first discharging to 0.7 V, (b) after first discharging to 0.005 V, (c) after first charging to 1.4 V, (d) after first charging to 3.0 V.

**Fig. S20.** (a) Cycling performance and (b) rate performance of ZnSe-NC, CoSe₂-NC and ZnSe-NC@CoSe₂-NC for SIBs.

**Fig. S21.** Kinetics analysis of the electrochemical behavior of the ZnSe-NC@CoSe₂-NC nanocomposite for SIBs. (a) CV curves of the ZnSe-NC@CoSe₂-NC at various sweep rates. (b) Plots (b-values) of log (scan rate) versus log (peak current) at different oxidation and reduction state. (c) Specifically b value at different oxidation and reduction state. (d) Ratio of the capacitive-controlled charge contribution (shaded area) to the total current at a scan rate of 0.4 mV s⁻¹. (e) Ratio of capacitive contribution in
ZnSe-NC@CoSe₂-Nd at different scan rates. (f) Nyquist plots before and after 50 cycles of the ZnSe-NC@CoSe₂-Nd.

**Fig. S22.** Non-proportional relation between the square root of scan rate and peak current for SIBs.

**Table S1.** Fitted electrochemical impedance parameters of ZnSe-NC, CoSe₂-Nd and ZnSe-NC@CoSe₂-Nd for SIBs.
Fig. S1.

![X-ray diffraction patterns of ZIF-8@ZIF-67 and ZIF-8.](image)

Fig. S2.

![Scanning electron microscopy images of ZIF-8@ZIF-67 and ZIF-8.](image)
Fig. S3.
Fig. S4.

Fig. S5.
When the ZnSe-NC@CoSe$_2$-NC nanocomposite was heated at the temperature range of 25 to 800 °C, the phases of the components in the composite were transformed according to the following reactions:

$$\text{ZnSe (s) + O}_2 (g) \rightarrow \text{ZnO (s) + SeO}_2 (g) \quad (1)$$

$$3\text{CoSe}_2 (s) + 8\text{O}_2 (g) \rightarrow \text{Co}_3\text{O}_4 (s) + 6\text{SeO}_2 (g) \quad (2)$$

$$\text{C (s) + O}_2 (g) \rightarrow \text{CO}_2 (g) \quad (3)$$

In the ZnSe-NC@CoSe$_2$-NC nanocomposite, the mass ratios of ZnSe, CoSe$_2$ and N-doped carbon can be denoted as $x$, $y$ and $z$, respectively and the addition of $x$, $y$ and $z$ value equals 100%. As we know, the ZnSe-NC@CoSe$_2$-NC was obtained by the selenization of ZIF-8@ZIF-67 polyhedrons. So, the N-doped carbon in the ZnSe-NC@CoSe$_2$-NC is from the ZIF-8 and ZIF-67. In order to get $x$, $y$ and $z$ value, besides the TGA curve of ZnSe-NC@CoSe$_2$-NC, the TGA curves of ZnSe-NC and CoSe$_2$-NC were also obtained. Based on the reaction (1) and the corresponding TGA of ZnSe-NC in Fig. S6a, the theoretical loss ratio of ZnSe is (100-81/144) % = 43.8% and the ratio of ZnSe to N-doped carbon is 78.13%/21.87%. Based on the reaction (2) and the corresponding TGA of CoSe$_2$-NC in Fig. S6b, the theoretical loss ratio of CoSe$_2$ is [100-240.79/(216.85 X 3)] % = 62.9% and the ratio of CoSe$_2$ to N-doped carbon is 73.49%/26.51%. According to above analysis and the data in Fig. 3b, we can get the three equations of $x$, $y$ and $z$. 
\[ x + y + z = 100\% , \]

\[ 43.8\%x + 62.9\%y + z = 58.11\% , \]

\[(21.87\%/78.13\%)x + (26.51\%/73.49\%)y = z \]

As a result, the content of ZnSe, CoSe\(_2\), N-doped carbon is 68.8\%, 8.8\% and 22.4\%, respectively.

Fig. S7.
Fig. S8.

(a) 

(b) 

Fig. S9.
Fig. S10.

(a) Potential vs. Li/Li$^+$ (V) vs. Capacity (mAh g$^{-1}$)

(b) Potential vs. Li/Li$^+$ (V) vs. Capacity (mAh g$^{-1}$)

Fig. S11

(a) Specific capacity (mAh g$^{-1}$) vs. Cycle number

(b) Specific capacity (mAh g$^{-1}$) vs. Cycle number
Fig. S13.

![Graph showing specific capacity and coulombic efficiency over cycle number.](Fig_S13)

Current density: 0.2 A g⁻¹

Fig. S14.

![Graph showing peak current vs. square root of voltage gradient.](Fig_S14)

Fig. S15.

![Diagram of equivalent circuit.](Fig_S15)
Fig. S16.

(a) Potential vs. Li/Li⁺ (V) vs. Time (min) for ZnSe-NC and CoSe₂-NC.
(b) Potential vs. Li/Li⁺ (V) vs. Time (min) for CoSe₂-NC.

(c) Log(D_x/cm² s⁻¹) vs. Voltage (V) for ZnSe-NC and CoSe₂-NC.
(d) Log(D_x/cm² s⁻¹) vs. Voltage (V) for CoSe₂-NC.

Fig. S17.

Cyclic voltammograms for ZnSe-NC, ZnSe-NC@CoSe₂-NC, and CoSe₂-NC.
Fig. S18.
Fig. S19.

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(d)  
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Fig. S20.

![Graphs showing cyclic voltammetry profiles for different materials]
Fig. S21.

Table S1.

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<th>$R_\text{ct}$ (Ω)</th>
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<th>$Z_\infty$ (mMΩ)</th>
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peaks: 

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<td>0.77</td>
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Fig. S22.