## Supporting Information

## Chain-Mail Co@C Electrocatalyst Accelerating One-step Solidphase Redox for Advanced Li–Se Batteries

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Fig. S1. Schematic design of Co nanoparticles embedded hierarchically porous carbon fibers host.



Fig. S2. SEM images of ZIF8@ZIF67@PAN fibers.



Fig. S3. SEM images of CPCFs.



**Fig. S4.** CPCFs: (a) HAADF-STEM image, (b) HR-TEM image, (c-e) EDS elemental maps: C (green), N (blue) and Co (red), (f) 3D electron tomographic reconstruction, (g and h) the orthslcies along two directions, pores indicated by the white arrows and Co nanoparticles indicated by the yellow arrows.



Fig. S5. Nitrogen adsorption/desorption isotherms of CPCFs.



Fig. S6. Pore-size distribution plots of CPCFs.



Fig. S7. XPS spectra of the Se@CPCFs.



Fig. S8. CV curve of CPCFs cathode.



Fig. S9. Discharge and charge profile of CPCFs electrode.



**Fig. S10.** (a) DFT calculations of absorption structure of Gr with  $Li_2Se$ ; (b) Charge density difference plot for  $Li_2Se$  interacting with Gr; (c) absorption structure of Co-Gr with  $Li_2Se$ ; (d) Charge density difference plot for  $Li_2Se$  interacting with Co-Gr. The yellow (blue) distribution corresponds to charge accumulation (depletion).



Fig. S11. The rate performance of the pouch cell with Se@CPCFs cathode.