

## Supplementary Information

# Coral-like CoSe<sub>2</sub>@N-doped carbon with high initial coulomb efficiency as advanced anode materials for Na- ion batteries

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## 1. Experimental

### 1.1 Synthesis of 3D coral-like $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}$ precursor

The 3D coral-like  $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}$  precursor were prepared by hydrothermal method. 1 g urea and 1g  $\text{Co}(\text{AC})_2\cdot 4\text{H}_2\text{O}$  were dissolved in 20 ml DI water. After being continuously stirred for 10 min, the obtained suspension is transferred into a 50 mL Teflonlined stainless steel autoclave, sealed and maintained at 100 °C for 5 h. The precipitates are centrifuged and washed with deionized water and ethanol several times, and then dried in vacuum at 70 °C overnight.

### 1.2 Synthesis of $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}@ \text{PDA}$ composites

100 mg coral-like  $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}$  were first dispersed into 100 mL tris-buffer solution (PH=8.5) by ultrasonication for 2 h. Then, 60 mg of dopamine hydrochloride was added into the above solution, which was kept stirring for 24 h. The resultant product hexagon  $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}@ \text{PDA}$  was collected through centrifugation and washed several times with absolute ethyl alcohol and deionized water, respectively, and dried at 70 °C overnight.

### 1.3 Synthesis of $\text{CoSe}_2$ and CL- $\text{CoSe}_2@ \text{NC}$ composites

The as-prepared  $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}$  or  $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}@ \text{PDA}$  precursors and Se powders with a weight ratio of (1:2.5) were put in a corundum boat and calcined at 450 °C in Ar atmosphere for 4 h. Then the  $\text{CoSe}_2$  and CL- $\text{CoSe}_2@ \text{NC}$  composites were obtained.

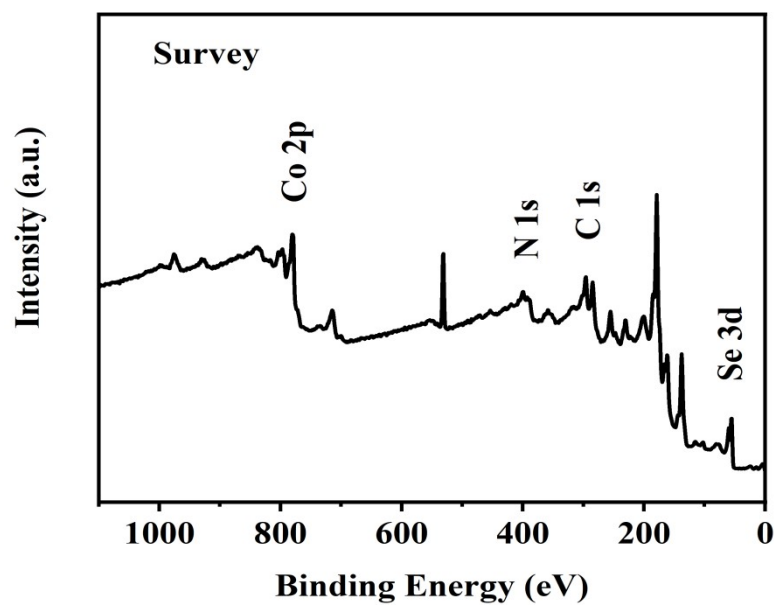
### 1.4 Materials characterization

The crystalline phase and morphology of the as-prepared  $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}$ ,  $\text{CoSe}_2$  and CL- $\text{CoSe}_2@ \text{NC}$  composites was investigated by powder X-ray diffractometry (XRD, BRUKER D8 ADVANCE) with Cu-K $\alpha$  radiation ( $\lambda=0.15406$  nm) and scanning electron microscopy (SEM, SU8010). The microstructure of  $\text{CoSe}_2$  and CL- $\text{CoSe}_2@ \text{NC}$  composites are further identified by transmission electron microscopy (TEM, TJEOL JEM 2100). The chemical composition and valence states of CL- $\text{CoSe}_2@ \text{NC}$  is analysed by X-ray photoelectron spectroscope (XPS ESCALAB 250Xi, Thermo Scientific).

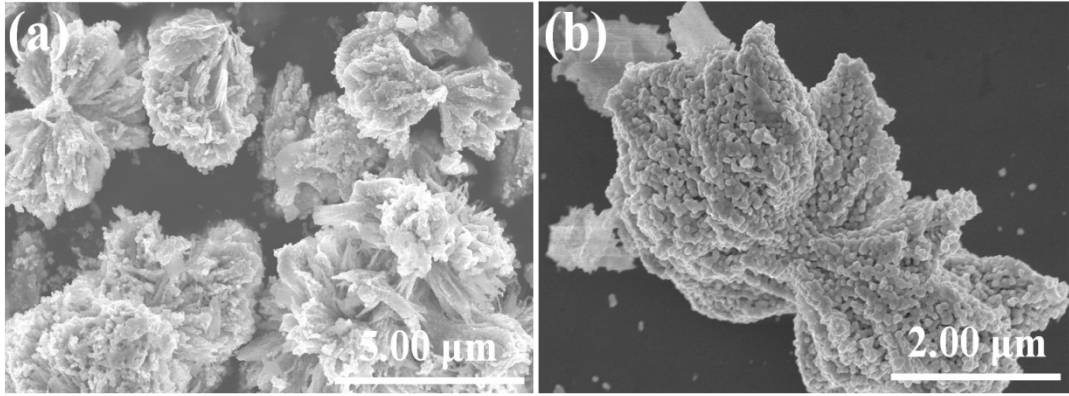
### 1.5 Cell fabrication and characterization

The sodium storage performance of  $\text{CoSe}_2$  and CL- $\text{CoSe}_2@ \text{NC}$  are evaluated with CR2025-type coin cells. The  $\text{CoSe}_2$  and CL- $\text{CoSe}_2@ \text{NC}$  are mixed with Super-P (SP) and sodium carboxymethyl cellulose (CMC) binder in a mass ratio of 7:2:1 in deionized water to form homogeneous slurry, which is then cast onto a copper foil and subsequently dried in vacuum at 110 °C for 12h. After vacuum drying at 110 °C for 12h, electrode discs with a diameter of 12.5 mm were punched out and weighed. The loading density of the active materials was ~1.4

mg/cm<sup>2</sup>. Electrochemical cells are assembled in an argon-filled glove box, in which O<sub>2</sub> and H<sub>2</sub>O contents are below 0.01 ppm. The electrolyte is 1 M NaSO<sub>3</sub>CF<sub>3</sub>/diethylene glycol dimethyl ether (DEGDME), and sodium foil is used the anode and counter electrode. A Whatman glass microfibre filter (Whatman GF/F) is utilized as the separator. The galvanostatic charge/discharge measurements are carried out in the voltage range of 0.01 to 3.0 V using a multichannel battery test system (LAND CT2001A). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) for the prepared anodes are measured with a voltage window of 0.01-3.0 V on an electrochemical workstation (MetrohmAutolab PGSTAT302N). Galvanostatic intermittent titration technique (GITT) measurements were carried out by applying a constant current of 50 mA g<sup>-1</sup> for 300 s followed by a 300 s relaxation to reach equilibrium.



**Fig. S1** The full survey scan spectrum of CL-CoSe<sub>2</sub>@NC powders.



**Fig. S2a,b** SEM of CoSe<sub>2</sub> samples.

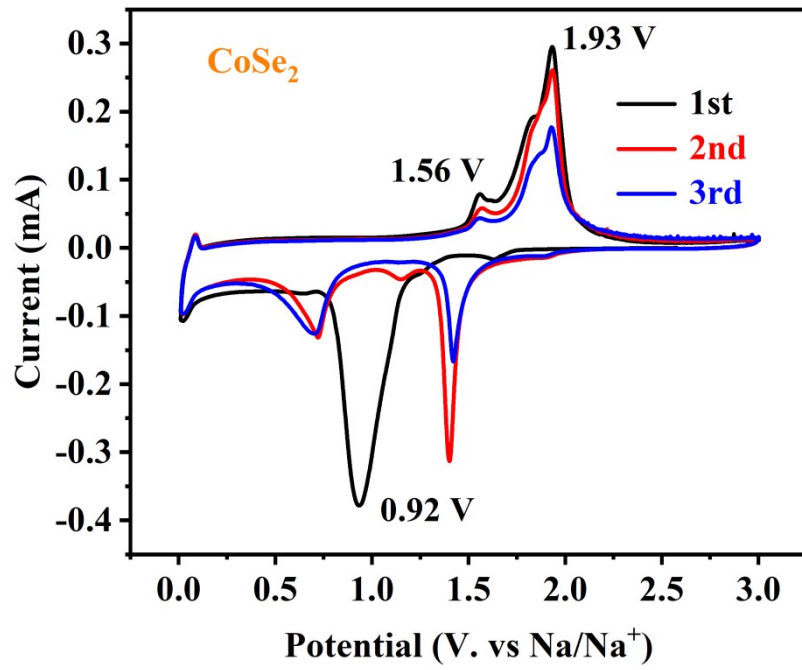
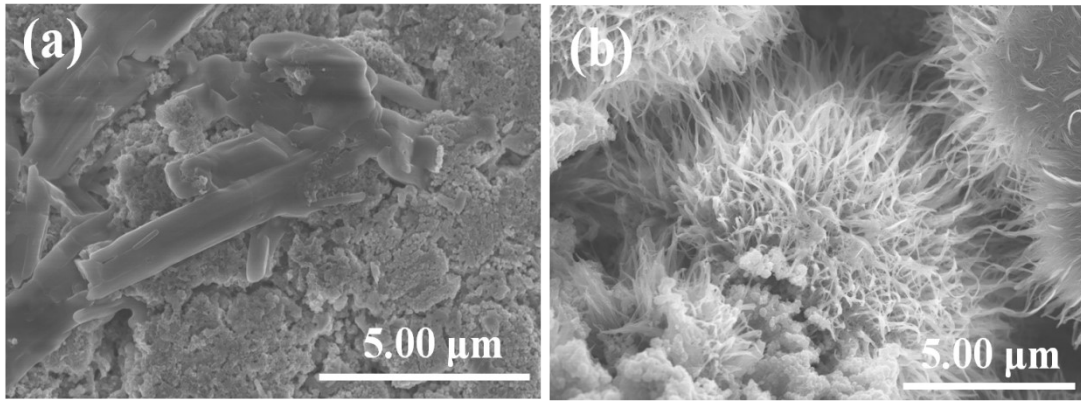
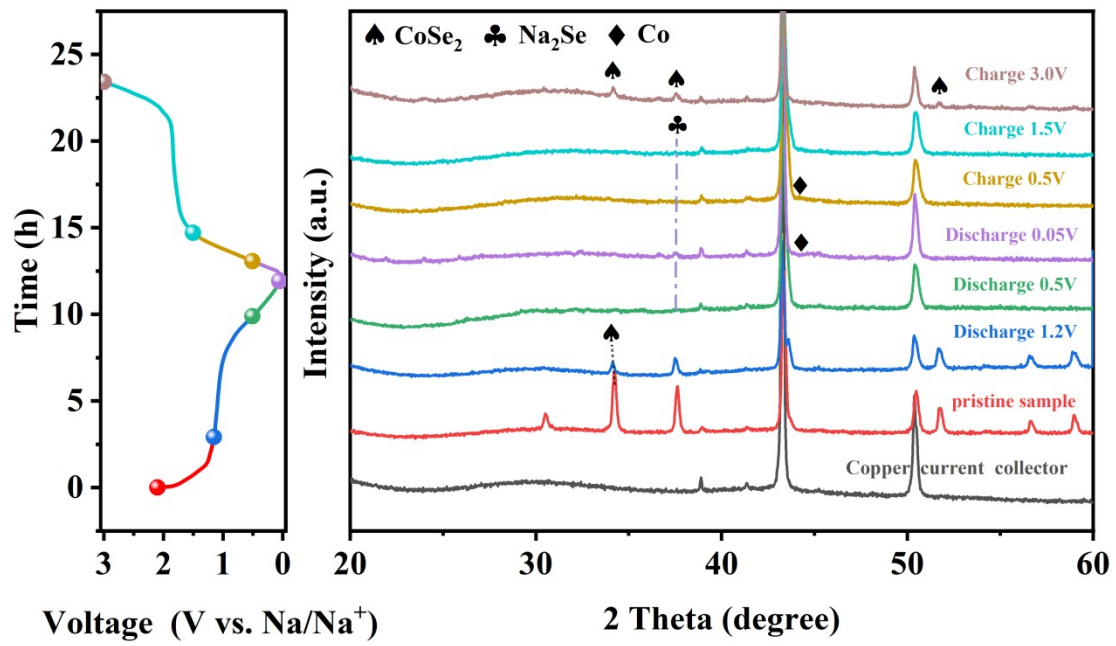


Fig. S3 The CV curve of the bare CoSe<sub>2</sub>.

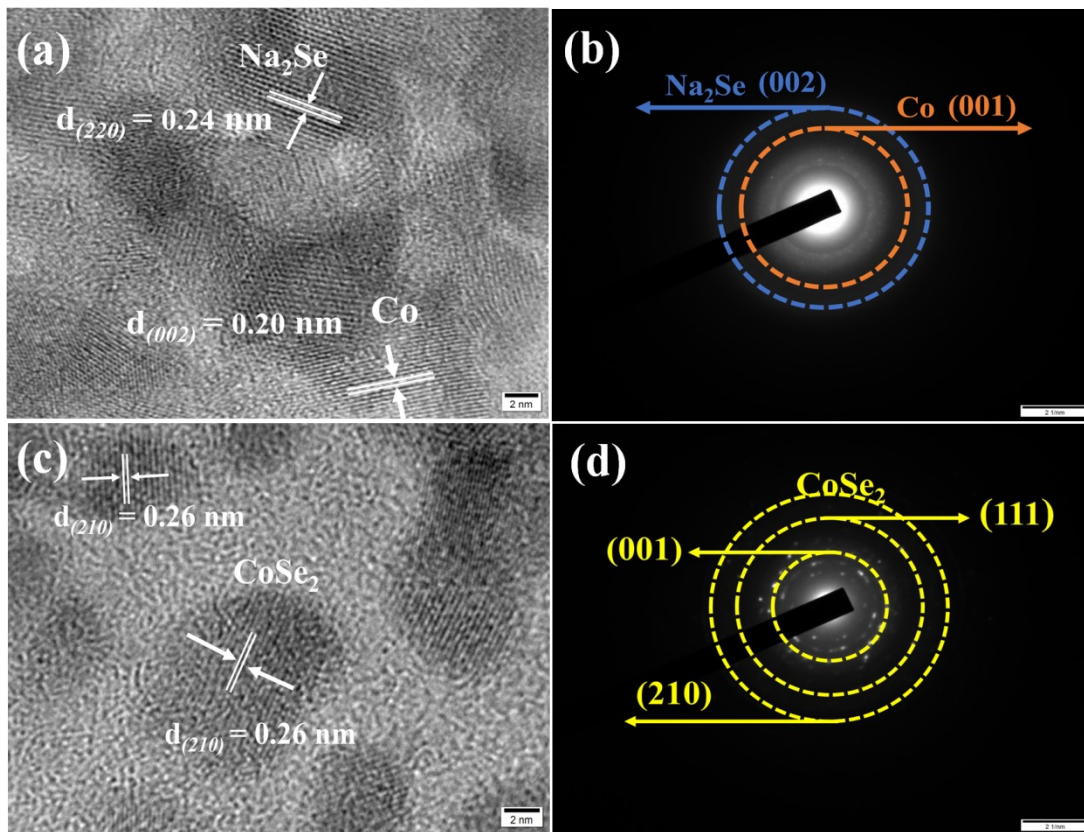


**Fig. S4** The surface morphologies of (a)  $\text{CoSe}_2$  and (b)  $\text{CL-CoSe}_2@\text{NC}$  after 50 cycles.



**Fig. S5** Ex-situ XRD patterns of CL-CoSe<sub>2</sub>@NC electrode collected during the first electrochemical cycle, with the corresponding charge/discharge profiles in NIBs.





**Fig. S6** Ex-situ HRTEM and SAED patterns of CL-CoSe<sub>2</sub>@NC (a,b) after first discharge cycle, (c,d)

after first charge cycles.