## **Supporting Information**

## **A Novel Composite Strategy to Build a Sub-zero Temperature Stable Anode for Sodium-ion Batteries**

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**Figure S1.** XRD patterns of as-synthesized  $Co<sub>9</sub>S<sub>8</sub>$  and  $Ga<sub>2</sub>S<sub>3</sub>$ 



Figure S2. XRD pattern of CoGa<sub>2</sub>S<sub>4</sub> and the corresponding Rietveld refinement.



**Figure S3.** XRD patterns of pristine CoGa<sub>2</sub>O<sub>4</sub> and the product after sulfided under 500 °C and 550 °C,

respectively.



**Figure S4.** The as-synthesized (a)  $CoGa<sub>2</sub>O<sub>4</sub>$  and (b)  $CoGa<sub>2</sub>S<sub>4</sub>$  powder.

**X-ray photoelectron spectroscopy (XPS) analysis**: the XPS survey spectrum (Figure S5a) confirms the existence of Co, Ga, S, C and O elements in the  $CoGa<sub>2</sub>S<sub>4</sub>(a)<sub>Q</sub>G$ . Co 2p spectrum fits well with two spin-orbit doublets (Figure S5b). Two peaks at 797.7 eV and 793.9 eV attribute to the binding energies of  $Co^{2+}$  and  $Co<sup>3+</sup>$  for Co 2p<sub>1/2</sub>, respectively, while those arise at 781.8 eV and 778.5 eV are ascribed to the binding energies of  $Co^{2+}$  and  $Co^{3+}$  for Co  $2p_{3/2}$ , respectively. Peaks at 802.3 eV and 786.0 eV correspond to the shakeup satellites (noted as 'Sat.'). Figure S5c shows two peaks at 1146.4 eV and 1119.2 eV, which attribute to the spin-orbit characteristics of Ga  $2p_{1/2}$  and Ga  $2p_{3/2}$ , respectively. Two fitting peaks in Figure S5d with binding energies of 163.8 eV and 162.6 eV correspond well to S  $2p_{1/2}$  and S  $2p_{3/2}$ , respectively.



**Figure S5**. (a)XPS survey spectrum of the  $CoGa<sub>2</sub>S<sub>4</sub>(a)<sub>G</sub>$  and high resolution XPS spectra of (b) Co 2p, (c) Ga

 $2p$  and (d) S  $2p$ .



**Figure S6.** Room temperature GDC profiles for the 2<sup>nd</sup> cycle of (a) CoGa2S4@G and (b)

 $Na<sub>0.7</sub>[Mn<sub>0.6</sub>Ni<sub>0.2</sub>Mg<sub>0.2</sub>]O<sub>2</sub> (NMN-2) half cells at 0.5 C, respectively.$ 

**Freezing resistance test of ether-based sodium ion batteries electrolyte**: ~5 mL electrolyte was filled in a glass bottle sealed by black tape in glovebox with ultrahigh pure argon gas. The glass bottle was then put in low temperature test chamber, setting temperature to -60 ºC. After 100 h, the electrolyte in glass bottle still remained liquid.



**Figure S7.** (a) After 100 h at -60 °C in low temperature test chamber, the glass bottle filled with electrolyte is quickly took out from the chamber, (b) after tilting the glass bottle, electrolyte still shows as well fluidity as that at room temperature.



**Figure S8.** Comparison of rate capability at different temperatures with the reported anodes for (a) SIBs and

 $(b) LIBs.$ <sup>S1-S9</sup>



**Figure S9.**  $dQ/dV$  profiles of GDC curves at 0.2 A g<sup>-1</sup> for RT, 0 °C, -20 °C, -40 °C, respectively.



Figure S10. EDX spectrum of the CoGa<sub>2</sub>S<sub>4</sub>@G electrode after (a) discharging to 0.05 V and (b) charging to 2.70 V at -20 ºC, respectively.

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