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# **Small** Micro

## Supporting Information

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Mesoporous NiS<sub>2</sub> Nanospheres Anode with Pseudocapacitance for High-Rate and Long-Life Sodium-Ion Battery

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Figure S1. Low magnification SEM image of the NiS<sub>2</sub> without PVP.



**Figure S2.** SEM images of the as-prepared  $NiS_2$  nanospheres obtained at different reaction times. (a) 30min. (b) 50min. (c) 70min.



Figure S3. XRD patterns of the NiS<sub>2</sub> nanospheres obtained at different solvents.

**S1.** Formation mechanism analysis of mesoporous NiS<sub>2</sub> nanospheres.

The formation mechanism of mesoporous  $NiS_2$  nanospheres should be a two - stage growth mechanism. The initial process is a nucleation process for primary particles, which follows the standard rapid nucleation theory.<sup>[1]</sup> When the solution becomes a supersaturated solution, resulting in the nucleation of NiS<sub>2</sub>. The nucleation process of nickel sulfide can be described as the following four steps:<sup>[2,3]</sup>

$OHCH_2CH_2OH \rightarrow CH_3CHO+H_2O$	(1)
$Ni^{2+} + CH_3CHO + 2H_2O \rightarrow CH_3CH_2OH + Ni^{4+} + 2OH^{-}$	(2)
$S_2O_3^{2^-} + Ni^{4+} \rightarrow Ni(S_2O_3)_2$	(3)
$Ni(S_2O_3)_2 + H_2O \rightarrow NiS_2 + H_2SO_4$	(4)

At high temperature, ethylene glycol is condensed to produce acetaldehyde (equation 1). The resulting acetaldehyde can be used as an oxidizing agent. Ni<sup>2+</sup> is oxidized to Ni<sup>4+</sup> (equation 2). Complexation reaction is occurred between Ni<sup>4+</sup> and  $S_2O_3^{2-}$  (equation 3). After hydrolysis, the Ni( $S_2O_3$ )<sub>2</sub> brings the formation of NiS<sub>2</sub> (equation 4).



**Figure S4.** SEM images of the products with different PVP amounts during synthesis. (a) 0.4 g, (b) 0.6 g, (c) 1 g.



Figure S5. FESEM image of the samples obtained at different solvent. (a) and (b)  $H_2O$ . (c) and (d) EG.



Figure S6. Discharge and charge curves of  $NiS_2$  electrode at different rates.



Figure S7. Discharge-charge curves of NiS<sub>2</sub> electrode after 1000 cycles.



Figure S8. Nyquist plots of mesoporous NiS<sub>2</sub> nanospheres before cycling and after 100 cycles.



Figure S9. SEM images of mesoporous  $NiS_2$  nanospheres. (a) After 1st cycle, (b) after 200 cycles.



**Figure S10.** Discharge and charge curves of different electrolytes at 0.1 A  $g^{-1}$ . (a) NaClO<sub>4</sub>/DGM, (b) NaClO<sub>4</sub>/EC-DMC, (c) NaPF<sub>6</sub>/PC-EC, (d) NaClO<sub>4</sub>/PC-DMC.



Figure S11. Nyquist plots of mesoporous NiS<sub>2</sub> nanospheres in different electrolytes.



**Figure S12.** Cycling performance of Na/NiS<sub>2</sub> batteries in different electrolytes at  $0.1 \text{ A g}^{-1}$ .



**Figure S13.** (a) Cycling performance and (b) discharge-charge curves of the mesoporous  $NiS_2$  nanospheres electrode in the voltage range of 0.01–2.9 V at 0.1 A g<sup>-1</sup>.



Figure S14. Determination of the anodic *b*-values at different potential during charging.

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