Supporting Information

A composite of CoNiP quantum dots decorating reduced graphene oxide as a sulfur host for Li-S batteries

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EXPERIMENTAL SECTION

Preparation of Materials

Graphene oxide (GO) was prepared by modified Hummer’s method. Then, cobalt nickel oxide QDs/rGO (CNOQDs/rGO) was synthesized through a unique solvothermal reaction and subsequent sintering. Homogeneous solution containing GO (30 mg) and ethylene glycol (30 mL) was prepared, firstly, and then 0.1 g CoCl$_2$, 0.1 g NiCl$_2$, and 0.5 g urea were added to the solution, followed by stirring and ultrasonic dispersion for 5 min. And then the mixture was transferred into a Teflon-sealed autoclave and performed at 200 °C for 1 h. In this solvothermal process, a gel-like film which contains Co and Ni uniformly grows on the GO surface. After being cooled to room temperature, the mixture was centrifuged and washed with ethanol and deionized water, respectively. The CNOQDs/rGO was obtained through sintering at 500 °C for 5 h in an Ar flow.$^1$

CoNiP-rGO was prepared by a phosphorization process, NaH$_2$PO$_2$H$_2$O and the prepared cobalt nickel oxide QDs/rGO as precursor (weight ratio of 15: 1), they were placed in an alumina crucible at two separate ends with the NaH$_2$PO$_2$H$_2$O at the upstream part of argon gas flow and the CNOQDs/rGO at the downstream part. They
were heated at 400 °C and kept at this temperature for 3 h.\textsuperscript{2}

Pure rGO was prepared at the same conditions except the CoCl\textsubscript{2}, NiCl\textsubscript{2} and urea addition. The CoNiP/rGO/S composites were obtained through a typical melt-diffusion approach. Sulfur powder was well-mixed with CoNiP/rGO with a weight ratio of 6:4. Then the mixture was heated at 155 °C for 15 h in an argon atmosphere. The rGO/S was also prepared through the same procedure.

**Adsorption test**

The first step of this part was successfully prepared the Li\textsubscript{2}S\textsubscript{6} solution (0.005 M), in brief, Li\textsubscript{2}S and S were first dissolved in a solution of DME/DOL (v/v = 1:1) with a molar ratio of 1:5, and then continuous stirring at 60 °C for 18 h. In the second step, two hosts with the same weight (10 mg) were added to the Li\textsubscript{2}S\textsubscript{6} solution (2 mL), respectively. In the final step, the mixed solutions were vigorous shaken for 2 min and then rested at room temperature for 10 h.\textsuperscript{3}

**Electrochemical measurements**

The active materials (CoNiP-rGO/S, rGO/S), polyvinylidene fluoride (PVDF), and acetylene black were dispersed in NMP (the weight ratio is 7:1:2) to form a uniform slurry after ball milling for 4 h. Then the slurry was coated onto an Al foil and dried at 50 °C for 12 h under vacuum. The diameter of each electrode is 1.2 cm and the sulfur loading was ~1.5 mg cm\textsuperscript{2}.

Electrochemical performances were tested in a standard CR2032 simulated batteries with Li foil as anode, and PP as separator. The electrolyte was 1.0 M LiTFSI and 1.0 % LiNO\textsubscript{3} in a solution of DME/DOL (v/v =1:1). The electrolyte dosage was accurately
controlled with electrolyte/sulfur ratio ≈57 μL mg⁻¹ under normal conditions.⁴

Galvanostatic charge/discharge measurements were performed on a Neware battery testing system with a potential window of 1.7-2.8 V. CV were conducted on a CHI760E electrochemical workstation at 0.05-0.5 mV s⁻¹ with the potential range of 1.7-2.8 V. EIS spectra were obtained on a CHI760E electrochemical workstation, the frequency ranged from 100 kHz to 0.01 Hz and the amplitude was 5 mV.

**Material Characterization**

Morphological characterization of the synthesized samples were measured with Hitachi S-4800 scanning electron microscope (SEM), and high-resolution TEM (HRTEM, Tecnai G2F30 S-Twin). The X-ray diffractometer (XRD) test of CoNiP-rGO was conducted by using Cu Ka radiation (Shimadzu XRD-6100AS). Raman spectra investigated by a LabRam HR confocal laser microRaman spectrometer at room temperature. Nitrogen adsorption isotherms and Brunauer-Emmett-Teller surface area were gained with a MicromeriticsGeminiV2380 analyzer operating at 77 K. TGA (METTLER) was conducted in air at a heating rate of 10 °C min⁻¹. X-ray photoelectron spectroscopy (XPS) analysis was obtained using an ESCALAB250 spectrometer with Mg Kα radiation as the excitation source.
Figure S1. TGA plots of CoNiP-rGO/S.

Figure S2. (a) XPS survey spectrum of CoNiP-rGO. XPS spectra of (b) N 1s, (c) P 2p. (d) XPS survey spectrum of CoNiP-rGO after Li$_2$S$_6$ adsorption. XPS spectra of (e) P 2p after Li$_2$S$_6$ adsorption.
Figure S3. Long-term cycle stability of different sulfur loading at 0.5 C.

Figure S4. CV curves of the rGO/S electrode

Figure S5. Galvanostatic charge-discharge curves of rCoNiP-rGO/S electrodes at 0.2-3 C.
Figure S6. The voltage dips curves of the CoNiP-rGO/S electrode at 0.5C and 1C at Li$_2$S nucleation point.

Figure S7. Atomic structures of S$_8$ adsorbed on CoNiP (111) surface (a) before and (b) after optimization. The yellow balls represent S atoms.

Table S1. Comparison with the CoP or NiP hosts in literature

<table>
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<tr>
<th>Sample</th>
<th>morphology</th>
<th>Loading (mg cm$^{-2}$)</th>
<th>Rate (C)</th>
<th>Cycles</th>
<th>Initial capacity (mAh g$^{-1}$)</th>
<th>capacity decay per cycle(%)</th>
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<td>NanoFlakes</td>
<td>XRD</td>
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**References:**