Ultrafine Co_{1-x}S Nanoparticles Embedded in Nitrogen Doped Porous Carbon Hollow Nanosphere Composite as Anode for Superb Sodium-Ion Batteries and Lithium Ion Batteries

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Fig. S1. Typical SEM (a) and TEM (b) images of the obtained material without of 2methylimidazole addition.

Fig. S2. EDS spectra of $Co_{1-x}S$ (a), $Co_{1-x}S@C$ (b) and $Co_{1-x}S/C$ (c).

Fig. S3. TGA curves for the $Co_{1-x}S$, $Co_{1-x}S@C$ and $Co_{1-x}S/C$ between room temperature and 650 °C measured with a heating rate of 5 °C /min under air atmosphere.

Fig. S4. Typical TEM images of the obtained materials using different amounts (mg) of 2-methylimidazole addition (a) 0, (b) 16.4, (c) 39.4, (d) 65.6, (e) 124.8, (f) 147.8 mg.

Fig. S5. The effect of different reaction time on the morphology of the materials (a) 12 h, (b) 6 h, (c) 30 min. Effect of different reaction temperature on morphology, (d) 50 °C (e) 70 °C.

Fig. S6. (a) FT-IR spectra of the materials obtained by adding different amounts (mg) of 2-methylimidazole, (I) 2-methylimidazole, (II) thiosemicarbazide, (III) 0, (IV) 39.4, (V) 124.8. (b) XRD patterns of the as-prepared samples when the amount of 2-methylimidazole was 0 mg (I), 39.4 mg, (II) and 124.8 mg (III) after reaction 72 h. **Fig. S7.** EDS spectra of adding different amounts (mg) of 2-methylimidazole, (a) 39.4 (b) 65.6 (c) 124.8.

Fig. S8. The effect of different sulfur sources on the morphology of the material when the amount of 2-methylimidazole was added 124.8 mg (a) thiourea, (b) thioacetamide. The effect of metal salt anions on the morphology of the material when the amount of 2-methylimidazole was 124.8 mg, (c) $CoSO_4 \cdot 7H_2O$, (d) $Co(CH_3COO)_2 \cdot 4H_2O$, (e) $CoCl_2 \cdot 6H_2O$.

Fig. S9. The effect of different sulfur sources on the morphologies of the solid spheres morphology (a) thiourea, (b) thioacetamide.

Tab. S1. The overview diagram of the precursors under different conditions (means using different S resource, Cobalt source, temperature, and time different amounts of 2-methylimidazole (mg)).

Fig. S10. Effect of Ni-doping on material morphology, (a) Co²⁺: Ni²⁺=15: 1, (b) Co²⁺: Ni²⁺=10: 1, (c) Co²⁺: Ni²⁺=5: 1.

Fig. S11. EDS spectra of Ni-doped precursor.

Fig. S12. TEM and SEM images of Ni-doped Co_{1-x}S precursor@PPy.
Fig. S13. (a) Electrolyte optimization of Co_{1-x}S-Na batteries. TEM images of Co_{1-x}S (b), Co_{1-x}S/C (c) and Co_{1-x}S@C (d) obtained after 30 cycles at current density of 500 mA g⁻¹.

Fig. S14. Electrochemical performance of $Co_{1-x}S$, $Co_{1-x}S/C$ and $Co_{1-x}S@C$ electrodes at 100 mA g⁻¹.

Fig. S15. TEM images of $Co_{1-x}S@C$ and $Co_{1-x}S/C$ obtained after 120 cycles at current density of 500 mA g⁻¹.

Fig. S16. Cyclic voltammetry (CV) curves of $Co_{1-x}S$ (a) and $Co_{1-x}S@C$ (b).

Tab. S2. Electrochemical performance comparisons of the $Co_{1-x}S/C$ electrode with some typical transition metal chalcogenides anode materials for SIBs.

Fig. S17. (a) Charge capacities of Ni-doped $Co_{1-x}S/C$ electrode at 500 mA g⁻¹. (b) Rate capabilities of the Ni-doped $Co_{1-x}S/C$ electrode (charge capacity).

Fig. S18. The electrochemical performance of $Co_{1-x}S/C$ (a) and Ni-doped _{Co1-x}S/C (b) in commonly used carbonate-based electrolyte (1.0 M NaClO₄-EC/PC) at the current density of 1000 mAh g⁻¹.

Tab. S3. Electrochemical performance comparisons of the $Co_{1-x}S/C$ electrode with some typical transition metal chalcogenides as anode materials for LIBs.



Fig. S1 Typical SEM (a) and TEM (b) images of the obtained material without of 2-methylimidazole addition.

Elements	Atomic presents (%)	.u.	9 9		
Со	8.72	y/a			
S	16.59	it.			
С	58.07	SUC			
0	15.82	nte			
Pt	0.81	Ţ		<u> </u>	•
			1 2 3	⁴ ⁵ ⁶ ⁷ ⁸ Energy/KeV	9 10 11
Elements	Atomic presents (%)	ı.u.			
Со	6.64	1/2	. 0		
S	10.95	Ë,	? .		
С	75.99	SU			
0	5.77	te	O		
Pt	0.66	Ξ	9 8.	• •	
		- <mark>- </mark>	1 2 3	⁴ ⁵ ⁶ ⁷ ⁷ ⁸ ⁷ ⁸	9 10 11
Elements	Atomic presents (%)	a.u.	•		
Со	4.77	y/5			
S	7.42	sit	ě		
<u>с</u>	77.64	en	<u>.</u>		
D+	9.81	nt.	Ŭ 🝙 📃	ô _	
PC	0.04			······································	(P)
			1 2 3	Énergy/KeV	9 10 11

Fig. S2 EDS spectra of $Co_{1-x}S$ (a), $Co_{1-x}S$ @C (b) and $Co_{1-x}S/C$ (c).



Fig. S3 TGA curves for the Co1-xS, Co1-xS@C and Co1-xS/C between room temperature and 650 °C measured with

a heating rate of 5 $^\circ C$ /min under air atmosphere.



Fig. S4 Typical TEM images of the obtained materials using different amounts (mg) of 2-methylimidazole addition (a) 0, (b) 16.4, (c) 39.4, (d) 65.6, (e) 124.8, (f) 147.8 mg.



Fig. S5 The effect of different reaction time on the morphology of the materials (a) 12 h, (b) 6 h, (c) 30 min. Effect of different reaction temperature on morphology, (d) 50 °C (e) 70 °C.

Time dependent experiments were carried out at 85 °C. Hollow spheres can obtain after reaction for 12 h, 6 h, even 30 min as shown in Fig. S3 a, b, c. The TEM images (Fig. S3 d, e,) exhibits also can obtain hollow spheres at 70 °C and 50 °C after reaction for 30 min. These results show the sphere morphology no obvious dependence on the reaction time and temperature.



Fig. S6 (a) FT-IR spectra of the materials obtained by adding different amounts (mg) of 2-methylimidazole, (I) 2-methylimidazole, (II) thiosemicarbazide, (III) 0, (IV) 39.4, (V) 124.8. (b) XRD patterns of the as-prepared samples when the amount of 2-methylimidazole was 0 mg (I), 39.4 mg, (II) and 124.8 mg (III) after reaction 72

h.

Elements	Atomic presents (%)	rn -
Со	5.19	
S	14.93	÷ ė
С	65.41	
0	15.67	
Pt	1.00	
		¹ Energy/KeV ⁴ ⁵
Elements	Atomic presents (%)	.
Со	6.41	(a)
S	12.72	
С	63.01	Su V
0	14.61	
Pt	1.05	
		¹ ² ² ³ ⁵ ⁵
Elements	Atomic presents (%)	a.u.
Со	4.30	<mark>·/ •</mark> •
S	10.08	
C	69.28	
0	15.59	
Pt	0.75	
		¹ E ² nergy ³ /KeV ⁴

Fig. S7 EDS spectra of adding different amounts (mg) of 2-methylimidazole, (a) 39.4 (b) 65.6 (c) 124.8.



Fig. S8 The effect of different sulfur sources on the morphology of the material when the amount of 2methylimidazole was added 124.8 mg (a) thiourea, (b) thioacetamide. The effect of metal salt anions on the morphology of the material when the amount of 2-methylimidazole was 124.8 mg, (c) $CoSO_4$ ·7H₂O, (d) $Co(CH_3COO)_2$ ·4H₂O, (e) $CoCl_2$ ·6H₂O.



Fig. S9 The effect of different sulfur sources on the morphologies of the solid spheres morphology (a) thiourea, (b) thioacetamide.

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Tab. S1 The overview diagram of the precursors under different conditions (means using different S resource, Cobalt source, temperature, and time different amounts of 2-methylimidazole (mg)).

Thioacetamide (taa), thiosemicarbazide (tsc).



Fig. S10 Effect of Ni-doping on material morphology, (a) Co²⁺: Ni²⁺=15: 1, (b) Co²⁺: Ni²⁺=10: 1, (c) Co²⁺: Ni²⁺=5:

1.

Elements	Atomic presents (%)	ı.u.			6	}				
Со	6.81	12								
Ni	1.66	t								
S	18.40	S	-							
с	46.03	IJ	\$ <u>\$</u>							
0	12.34	te	N	-		8				
Pt	0.77	l		ę	<u>X</u> .	K.				
			1		2	3		4	5	
		Energy/KeV								

Fig. S11 EDS spectra of Ni-doped precursor.



Fig. S12 TEM and SEM images of Ni-doped $Co_{1-x}S$ precursor@PPy.



Fig. S13 (a) Electrolyte optimization of $Co_{1-x}S$ -Na batteries. TEM images of $Co_{1-x}S$ (b), $Co_{1-x}S/C$ (c) and $Co_{1-x}S$ (d) obtained after 30 cycles at current density of 500 mA g⁻¹.



Fig. S14 Electrochemical performance of Co_{1-x}S, Co_{1-x}S/C and Co_{1-x}S@C electrodes at 100 mA g⁻¹.



Fig. S15 TEM images of $Co_{1-x}S@C$ and $Co_{1-x}S/C$ obtained after 120 cycles at current density of 500 mA g⁻¹.



Fig. S16 Cyclic voltammetry (CV) curves of $Co_{1-x}S(a)$ and $Co_{1-x}S@C(b)$.

Tab. S2 Electrochemical performance comparisons of the $Co_{1-x}S/C$ electrode with some typical transition metal

Electrode	Current (mA g ⁻¹)	Capacity (mA h	Cycle number	Ref/year
		g ⁻¹)		
Co ₃ S ₄ -PNS/GS	500	329	50	1/2015
Co ₉ S ₈ -carbon	500	404	50	2/2015
CNT/CoS@C	500	398	200	3/2017
Co _{1-x} S/FGNs	1000	251	200	4/2015
Co ₃ S ₄ @PANI	200	252.5	100	5/2016
CoS ₂ /CoS/GC	200	334	100	6/2016
CoS/C nanowires	100	294	100	7/2016
CoS ₂ /CNTs	100	568	100	8/2015
Co _{1-x} S/C	100	601	60	our work
	500/1000	470/326	120/130	

chalcogenides anode materials for SIBs.



Fig. S17 (a) Charge capacities of Ni-doped Co_{1-x}S/C electrode at 500 mA g⁻¹. (b) Rate capabilities of the Ni-doped

Co_{1-x}S/C electrode (charge capacity).



Fig. S18 The electrochemical performance of $Co_{1-x}S/C$ (a) and Ni-doped $Co_{1-x}S/C$ (b) in commonly used

carbonate-based electrolyte (1.0 M NaClO₄-EC/PC) at the current density of 1000 mAh g⁻¹.

Tab. S3 Electrochemical performance comparisons of the Co_{1-x}S/C electrode with some typical transition metal

chalcogenides anode materials for LIBs.

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