Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Phosphorus-doped copper sulfide microspheres with hollow structure for high-performance sodium-ion batteries

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Materials Characterization:

The morphology, microstructure and phases of the synthesized products were characterized by SEM (S4800, Hitachi, Japan), TEM (SUPRA 55, Germany) equipped with energy dispersive X-ray spectroscopy (EDS) and XRD (Bruker D8 advance, Cu) with Cu Kα of λ = 0.15417 nm. XPS was conducted using an X-ray photoelectron spectrometer (Thermo Scientific K-Alpha) with a laser source of λ = 532 nm.

Electrochemical Measurement:

The working electrode slurry was a mixture of the active material, conductivity agent (ketjen black), and CMC binder with a weight ratio of 80:10:10 using deionized water as solvents. The slurry was uniformly pasted on a copper foil and dried in vacuum at 80°C for 12 h. The coin-type cells (2032) were assembled in an Ar-filled glove box (Mikrouna), where the concentrations of H_2O and O_2 were maintained below 1 ppm. Sodium metal was used as counter/reference electrode, glass fiber (GF/D) was used as the separator, and 1 M $NaPF_6$ dissolved in dimethoxyethane (DME) solution as the electrolyte. A LAND-CT2001A battery testing system was used to test galvanostatic charge/discharge at room temperature under different current densities within a potential range of 0.01–3.0 V (vs. Na/Na+). Cyclic voltammetry was conducted on an electrochemical workstation (Chenhua, Shanghai, China) in the voltage range of 0.01–3.0 V (vs. Na/Na+). Electrochemical impedance spectroscopy (EIS) was carried out by using electrochemical workstation (Chenhua, Shanghai, China) within the frequency range of 100 kHz to 0.01 Hz under open circuit voltage.

GITT test information:

Use the following equation to calculate D_{Na^+}:

$$D_{Na^+} = \frac{4}{\pi\tau}\left(\frac{m_B V_m}{M_B S}\right)^2\left(\frac{\Delta E_S}{\Delta E_\tau}\right)^2$$

where m_B is the mass of active material, τ is the pulse duration, S is the active surface area, V_m and M_B represent the molar volume and molecular mass of carbon, respectively.

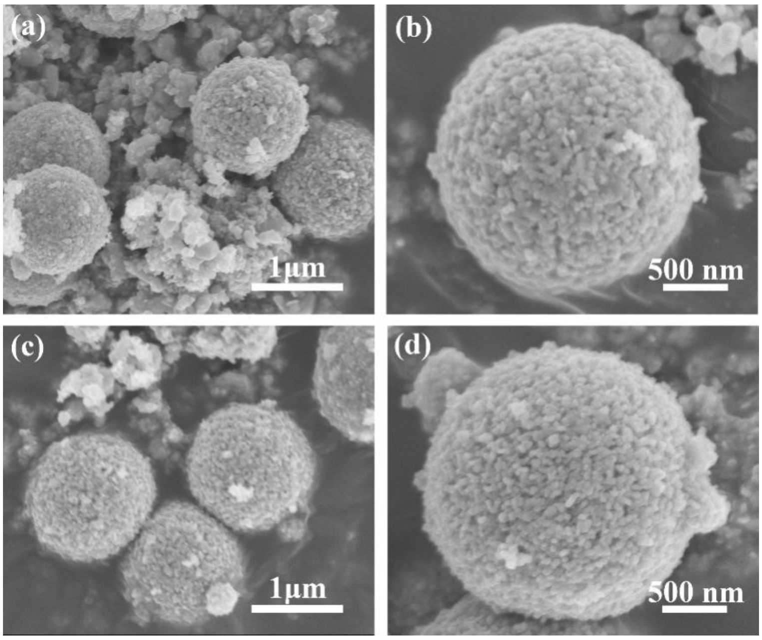

Fig. S1 SEM images of (a-b) 0.02P-CuS and (c-d) 0.04P-CuS.

Fig. S2 HRTEM images of (a) 0.03P-CuS and (b) CuS.

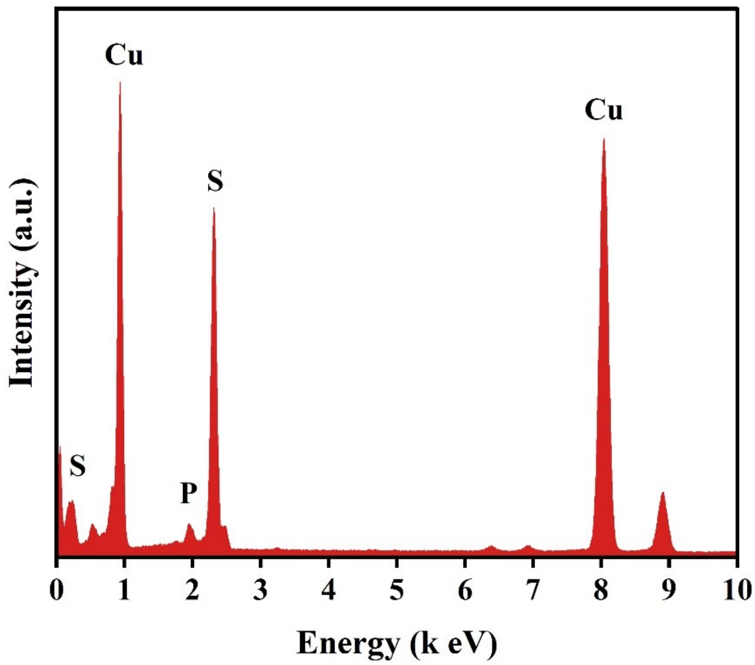

Fig. S3 Energy dispersive X-ray (EDX) spectrum of 0.03P-CuS.

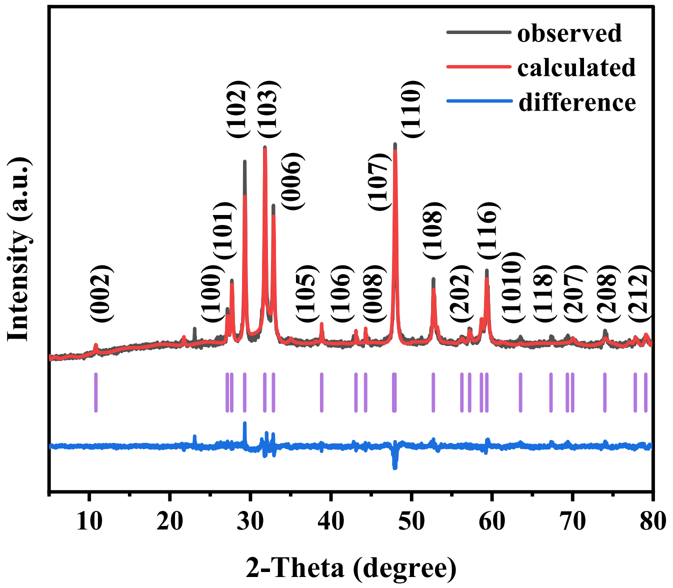

Fig. S4 XRD pattern and Rietveld refinement.

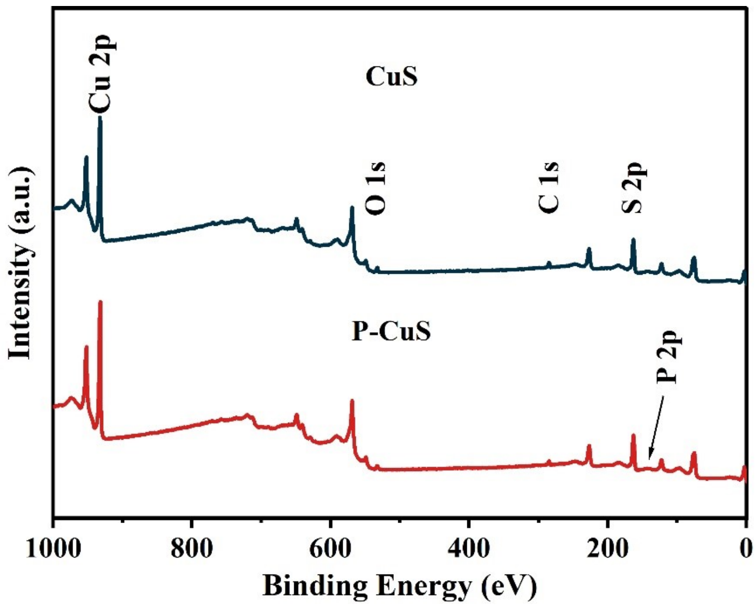

Fig. S5 XPS survey spectra of CuS and 0.03P-CuS.

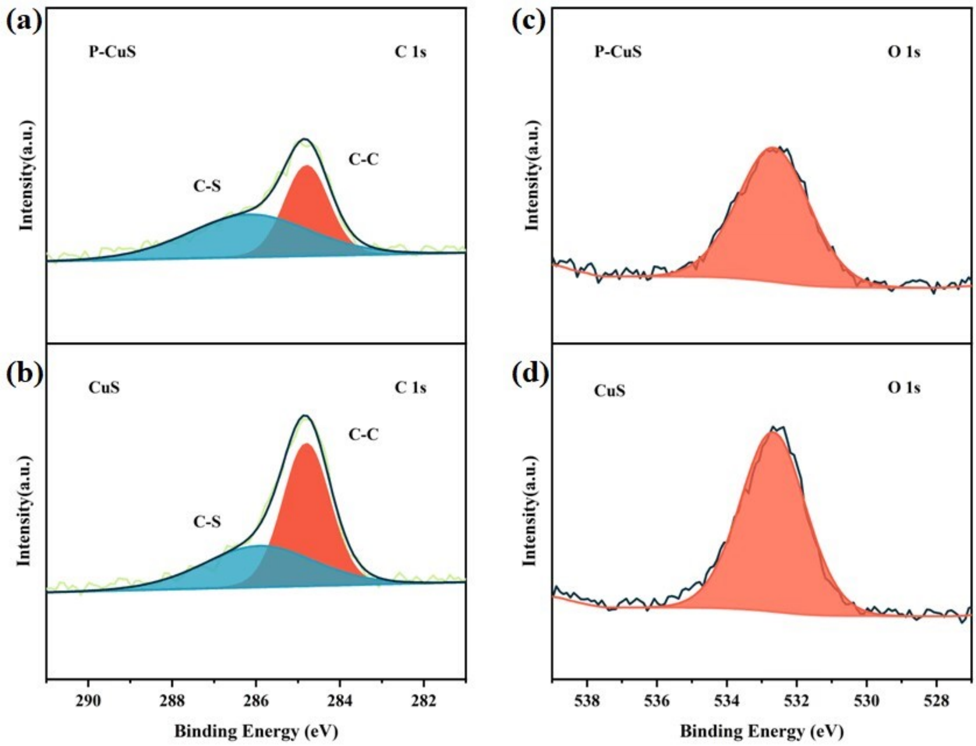

Fig. S6 High-resolution XPS spectra of (a-b) C 1s and (c-d) O 1s for 0.03P-CuS and

CuS.

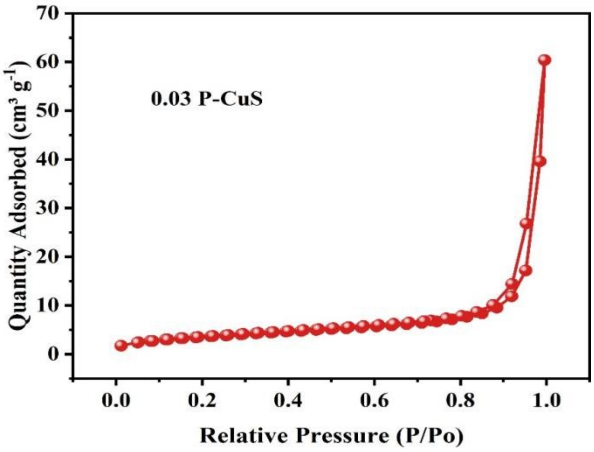

Fig. S7 N_2 adsorption-desorption isotherms of 0.03P-CuS.

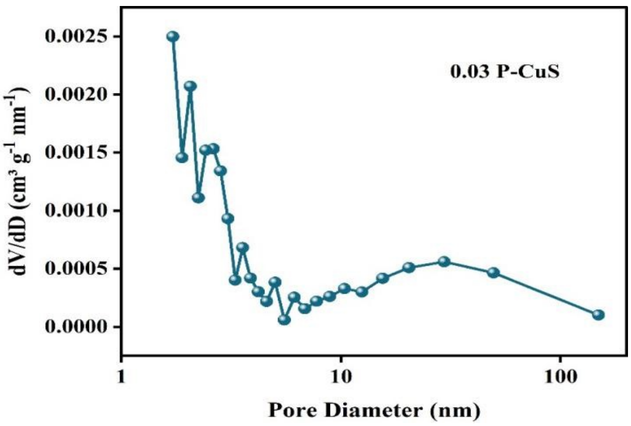

Fig. S8 Pore size distributions of 0.03P-CuS.

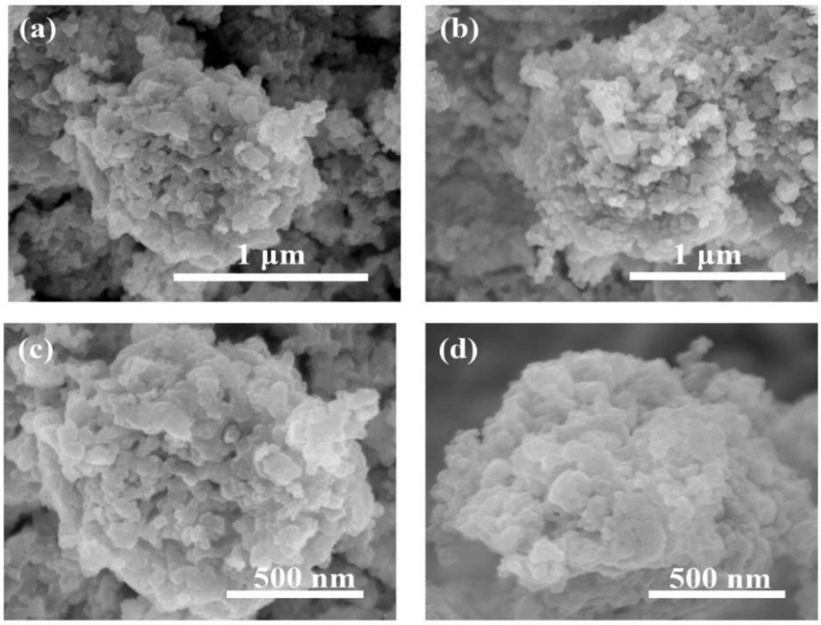

Fig. S9 SEM images of (a-b) 0.03P-CuS and (c-d) CuS after the electrochemical test.

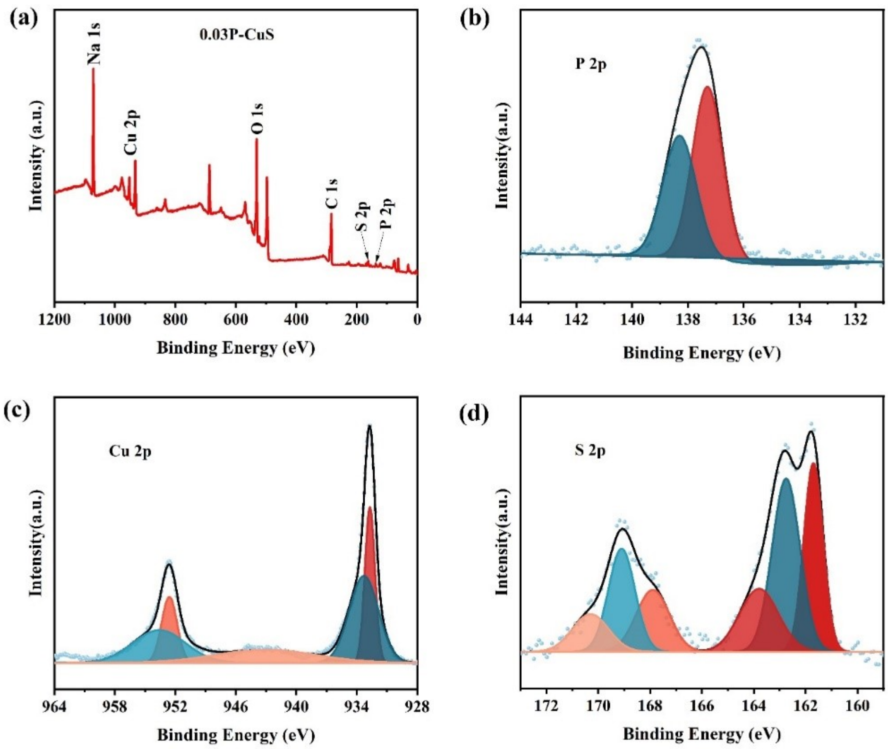

Fig. S10 (a) XPS survey spectra, high-resolution XPS spectra of (b) P 2p, (c) Cu 2p and (d) S 2p of 0.03P-CuS after the electrochemical test.

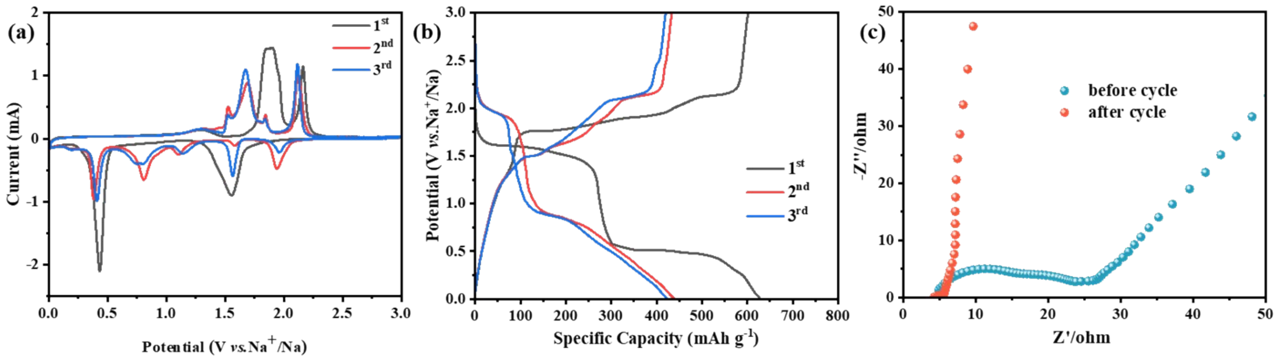

Fig. S11 (a) CV curves of CuS at 0.2 mV s^{-1}; (b) Galvanostatic charge/discharge curves of CuS at 0.2 A g^{-1}; (c) EIS of the CuS electrode before and after 3 cycles.

Table S1 Comparison of the electrochemical performance between other reports and our work of P-CuS as anode materials for SIBs.

Anode materials	Rate performance	Long-term Cycling performance	Ref.
CuS	514 mAh g^{-1} at 0.1 A g^{-1} 377.6 mAh g^{-1} at 0.5 A g^{-1} 337.3 mAh g^{-1} at 1 A g^{-1} 246.4 mAh g^{-1} at 5 A g^{-1}	361.7 mAh g^{-1} after 100 cycles at 0.1 A g^{-1}	[1]
CuS@N-C	320.2 mAh g^{-1} at 0.2 A g^{-1} 316.2mA h g^{-1} at 1 A g^{-1} 307.8 mAh g^{-1} at 2 A g^{-1} 259.4 mAh g^{-1} at 5 A g^{-1}	300.2 mAh g^{-1} after 1200 cycles at 5 A g^{-1}	[2]
CuS-Cu@CNTs	523.4 mAh g^{-1} at 0.08 A g^{-1} 478.9 mAh g^{-1} at 0.4 A g^{-1} 464.3 mAh g^{-1} at 1.2 A g^{-1} 454.8mAh g^{-1} at 2 A g^{-1} 447.3 mAh g^{-1} at 2.4 A g^{-1}	512.5 mAh g^{-1} after 1100 cycles at 2.4 A g^{-1}	[3]
NaCuS	262.0 mAh g^{-1} at 0.1 A g^{-1} 121.7 mAh g^{-1} at 2 A g^{-1}	210.9 mAh g^{-1} after 500 cycles at 1 A g^{-1}	[4]

CuS HNs	388.1 mAh g^{-1} at 1 A g^{-1} 321.4 mAh g^{-1} at 3 A g^{-1} 258.2 mAh g^{-1} at 10 A g^{-1} 193.4 mAh g^{-1} at 20 A g^{-1}	250.1 mAh g^{-1} after 2000 cycles at 20 A g^{-1}	[5]
CuS NWs@NC	546.2 mAh g^{-1} at 0.5 A g^{-1} 496.8 mAh g^{-1} at 1A g^{-1} 402.8 mAh g^{-1} at 5 A g^{-1} 350.0 mAh g^{-1} at 10 A g^{-1} 294.4 mAh g^{-1} at 20 A g^{-1}	216.7 mAh g^{-1} after 10000 cycles at 20 A g^{-1}	[6]
ZnS/CuS@C	454.4 mAh g^{-1} at 0.1 A g^{-1} 373.6 mAh g^{-1} at 1 A g^{-1} 338.2 mAh g^{-1} at 5 A g^{-1} 298.9 mAh g^{-1} at 10 A g^{-1}	282.7 mAh g^{-1} after 1750 cycles at 10 A g^{-1}	[7]
CuS@CuSe	513.4 mAh g^{-1} at 0.2 A g^{-1} 349.1mAh g^{-1} at 20 A g^{-1}	303.1 mAh g^{-1} after 1500 cycles at 20 A g^{-1}	[8]
$CuS@CoS_2$	570 mAh g^{-1} at 0.2 A g^{-1} 483 mAh g^{-1} at 0.5 A g^{-1} 360 mAh g^{-1} at 2 A g^{-1} 304 mAh g^{-1} at 5 A g^{-1}	416 mAh g^{-1} after 500 cycles at 0.5 A g^{-1}	[9]
CuS48	329.3 mAh g^{-1} at 0.1 A g^{-1} 228.6 mAh g^{-1} at 0.5 A g^{-1} 195.7 mAh g^{-1} at 1 A g^{-1} 164.6 mAh g^{-1} at 2 A g^{-1}	132.6 mAh g^{-1} after 5000 cycles at 5 A g^{-1}	[10]
PNL-CuS	522 mAh g^{-1} at 0.1 A g^{-1} 317 mAh g^{-1} at 20 A g^{-1}	420 mAh g^{-1} after 1000 cycles at 5 A g^{-1}	[11]
CuS	549 mAh g^{-1} at 1 A g^{-1} 268 mAh g^{-1} at 100 A g^{-1}	517 mAh g^{-1} after 2000 cycles at 5 A g^{-1}	[12]
CuS-150	470.6 mAh g^{-1} at 1 A g^{-1} 386 mAh g^{-1} at 5 A g^{-1} 254.7 mAh g^{-1} at 20 A g^{-1}	213mAh g^{-1} after 2000 cycles at 15 A g^{-1}	[13]

P-CuS	547.2 mAh g^{-1} at 0.2 A g^{-1} 504.3mAh g^{-1} at 1 A g^{-1} 473.3 mAh g^{-1} at 5 A g^{-1} 453.9 mAh g^{-1} at 10 A g^{-1}	442.1 mAh g^{-1} after 2000 cycles at 10 A g^{-1}	This work

References

1. L. Wu, J. Gao, Z. Qin, Y. Sun, R. Tian, Q. Zhang and Y. Gao, *J. Power Sources* 2020, **479**, 228518.
2. X. Liu, X. Li, X. Lu, X. He, N. Jiang, Y. Huo, C. Xu and D. Lin, *J. Alloys Compd.* 2021, **854**, 157132.
3. Y.-Y. Sun, Y. Li, L.-M. Sheng, T.-L. Lv, R. Guo, T.-R. Yang, Q.-S. Zhang and J.-Y. Xie, *Chem. Eng. J.* 2021, **414**, 128732.
4. Y. Sun, Z. Yu, Z. Chen, H. Wang, P. Wang, S. Han, S. Wu, W. Lu and J. Wang, *Nano Energy* 2021, **84**, 105875.
5. Y. Hu, L. Zhang, J. Bai, F. Liu, Z. Wang, W. Wu, R. Bradley, L. Li, H. Ruan and S. Guo, *ACS Appl. Energy Mater.* 2021, **4**, 8901-8909.
6. D. Zhao, M. Yin, C. Feng, K. Zhan, Q. Jiao, H. Li and Y. Zhao, *ACS Sustain. Chem. Eng.* 2020, **8**, 11317-11327.
7. W. Zhao, L. Gao, L. Yue, X. Wang, Q. Liu, Y. Luo, T. Li, X. Shi, A. M. Asiri and X. Sun, *J. Mater. Chem. A* 2021, **9**, 6402-6412.
8. W. Zhao, X. Wang, X. Ma, L. Yue, Y. Ren, T. Li, J. Xia, L. Zhang, Q. Liu, Y. Luo, N. Li, B. Tang, Y. Liu, S. Gao, A. M. Asiri and X. Sun, *J. Mater. Chem. A* 2021, **9**, 27615-27628.
9. Y. Fang, B. Y. Guan, D. Luan and X. W. Lou, *Angew. Chem. Int. Ed.* 2019, **58**, 7739-7743.
10. C. An, Y. Ni, Z. Wang, X. Li and X. Liu, *Inorg. Chem. Front.* 2018, **5**, 1045-1052.
11. D. Yu, M. Li, T. Yu, C. Wang, Y. Zeng, X. Hu, G. Chen, G. Yang and F. Du, *J. Mater. Chem. A* 2019, **7**, 10619-10628.
12. H. Kim, M. K. Sadan, C. Kim, S.-H. Choe, K.-K. Cho, K.-W. Kim, J.-H. Ahn and

H.-J. Ahn, *J. Mater. Chem. A* 2019, **7**, 16239-16248.

13. L. Zhang, Y. Hu, Y. Liu, J. Bai, H. Ruan and S. Guo, *Ceram. Int.* 2021, **47**, 14138-14145.