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Engineering of Tiny Bi_2S_3/SnS Heterostructured Nanorods *via* a Dual Polysulfide Confinement Strategy for Enhanced Alkali Metal-Ion Storage

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INTRODUCTION & AIM

Rechargeable potassium-ion batteries (PIBs) are becoming increasingly competitive in the future electric energy storage (EES) market due to their abundant natural resources and alluring potassium ion storage capacity.[1] However, sluggish reaction kinetics and rapid capacity degradation result from the large radius of potassium ions and the larger volume change during the potassiation/depotassiation reaction. Therefore, it is very important to investigate appropriate and helpful electrode materials to undergo the repeated K^+ insertion/extraction process.[2] Herein, we develop a dual polysulfide confinement strategy to produce ultra-small Bi_2S_3/SnS heterostructured nanorods coated with a polydopamine shell and followed by electrostatic assembly with MXene for durable anodes of PIBs. This strategy has the following advantages: 1) tiny Bi_2S_3/SnS nanorods (length of 35 ~ 65 nm) were synthesized by introducing OA/OeA as organic ligands. 2) a dual confinement strategy of MXene and PDA was used to suppress the shuttle effect of polysulfides and enhance their electrochemical performance. 3) the elastic polydopamine shell is used as a buffer layer to protect the active materials from pulverization and aggregation issues during cycling. Furthermore, the reliance on MXene is conducive to elevating the electronic conductivity and dispersion of Bi_2S_3/SnS nanorods. As expected, the as-synthesized BSPM-20 displays an impressive capacity of 599 mAh g^{-1} at 0.1 A g^{-1}, prominent cycle capability with a 92.6% capacity conservation after 1000 cycles at 1 A g^{-1}, for K^+ ion storage. It also delivers remarkable cycle stability and a high reversible capacity of 757 mAh g^{-1} for Li^+ ion storage and 650 mAh g^{-1} for Na^+ ion storage at a current density of 0.1 A g^{-1}, respectively.

METHOD

Synthesis of ultra-small Bi_2S_3/SnS heterostructure. Ultra-small Bi_2S_3/SnS nanorods were synthesized by a modified hydrothermal method.[1] Bismuth chloride ($BiCl_3$) and stannic chloride pentahydrate ($SnCl_4{\cdot}5H_2O$) of mass 0.3 g and 0.018 g, respectively, were added to a solution of ethanol (10 mL) and OA (20 mL). Afterwards, 4 mL of oleyl amine solution containing thioacetamide (0.225 g) was slowly added to the above solution. After vigorous stirring for 4 h, the resultant brown solution was transferred into a 50 mL Teflon-lined autoclave and maintained at 150 ℃ for 12 h. After cooling to room temperature, the brown products were washed with cyclohexane and ethanol three times, collected by centrifugation and freeze-dried to obtain Bi_2S_3/SnS nanorods. For comparison, $Bi_{1.8}Sn_{0.2}S_3$ was prepared with the same procedure except for the mass of $BiCl_3$ and $SnCl_4{\cdot}5H_2O$ were 0.3 g and 0.018 g, respectively. The pure Bi_2S_3 nanorods were synthesized with the same method with Bi_2S_3/SnS without adding $SnCl_4{\cdot}5H_2O$.

Synthesis of Bi_2S_3/SnS@PDA heterostructure. Firstly, 50 mg of the as-prepared Bi_2S_3/SnS nanorods were uniform dispersion in 50 mL deionized water by sonication for 30 min. Then, 25 mg dopamine hydrochloride (DA·HCl, 98%) was dispersed into 40 mL deionized water and drop by drop added into the Bi_2S_3/SnS colloidal solution and vigorously stirred for 24 h. Secondly, 1 mL of ammonia hydroxide was dissolved into 5 mL deionized water and added dropwise to the above solution and kept vigorously stirred for another 12 h at room temperature. Finally, the brown solution was collected by centrifugation and freeze-dried before use.

Synthesis of Bi_2S_3/SnS@PDA-PDDA/MXene nanocomposites. The Bi_2S_3/SnS@PDA-PDDA/MXene nanocomposites were synthesized by an electrostatic assembly method. Typically, 50 mg of Bi_2S_3/SnS@PDA nanorods were dispersed in 100 mL PDDA solution (0.5 mg mL^{-1}) by sonication to prepare positively charged Bi_2S_3/SnS@PDA-PDDA. The redundant PDDA was removed by centrifugation after several times rinsing. Then 25 mL of MXene suspension (0.5 mg mL^{-1}) was added into the above Bi_2S_3/SnS@PDA-PDDA suspension dropwise and vigorously stirred under Ar flow. Finally, the black precipitate was collected by centrifugation after rinsing and freeze-dried for 32 h to obtain Bi_2S_3/SnS@PDA-PDDA/MXene nanocomposites, which was named as BSPM-20. For comparison, synthesize BSPM-10 and BSPM-30 in the same manner as BSPM-20, but adjust the ratio of MXene to Bi_2S_3/SnS@PDA, for example, 90:10 or 70:30.

Synthesis of Bi_2S_3/SnS/MXene nanocomposites. The Bi_2S_3/SnS/MXene nanocomposites were synthesized by an electrostatic assembly method. Typically, 50 mg of Bi_2S_3/SnS nanorods were dispersed in 100 mL PDDA solution (0.5 mg mL^{-1}) by sonication to prepare positively charged Bi_2S_3/SnS-PDDA. The redundant PDDA was removed by centrifugation after several times rinsing. Then 25 mL of MXene suspension (0.5 mg mL^{-1}) was added into the above Bi_2S_3/SnS-PDDA suspension dropwise and vigorously stirred under Ar flow. Finally, the black precipitate was collected by centrifugation after rinsing and freeze-dried for 32 h to obtain Bi_2S_3/SnS/20%MXene nanocomposites, which were named as BSM.

RESULTS & DISCUSSION

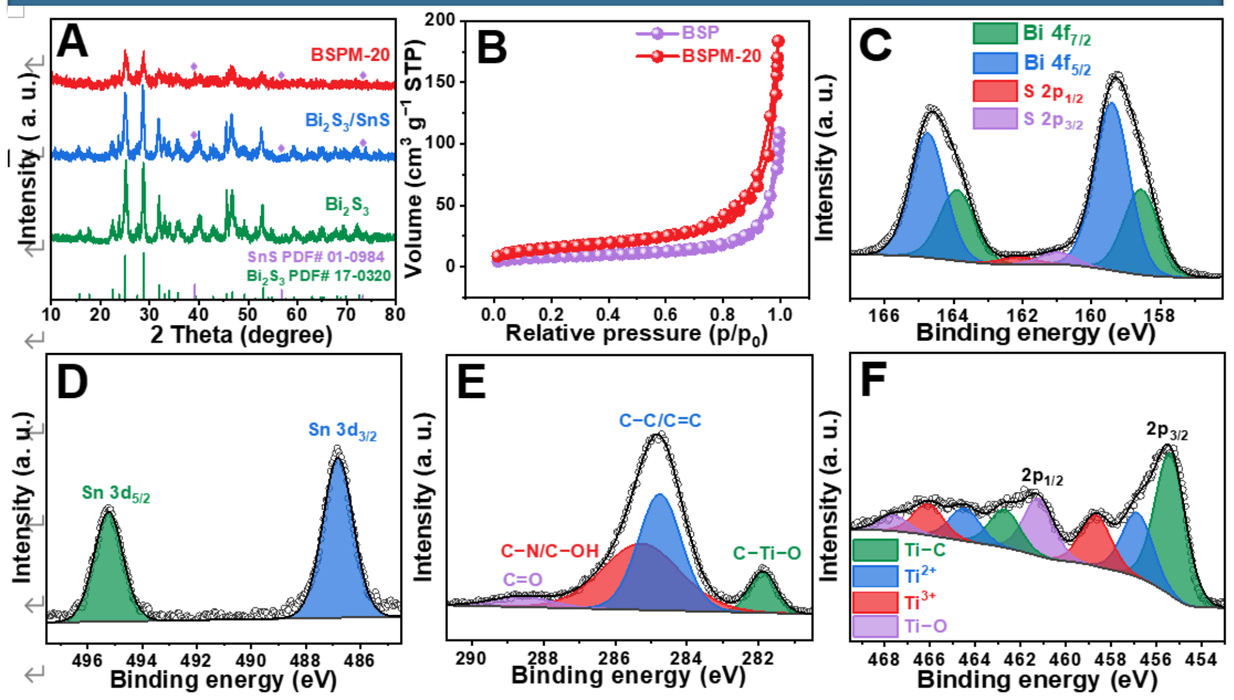

Figure 1. Phase and structural characterizations of the as-prepared samples. (A) XRD patterns. (B) Nitrogen adsorption-desorption isotherms. (C−F) High-resolution XPS spectra of Bi 4f (C), S 2p (D), Sn 3d (E) and Ti 2p (F) of BSPM-20 nanocomposites.

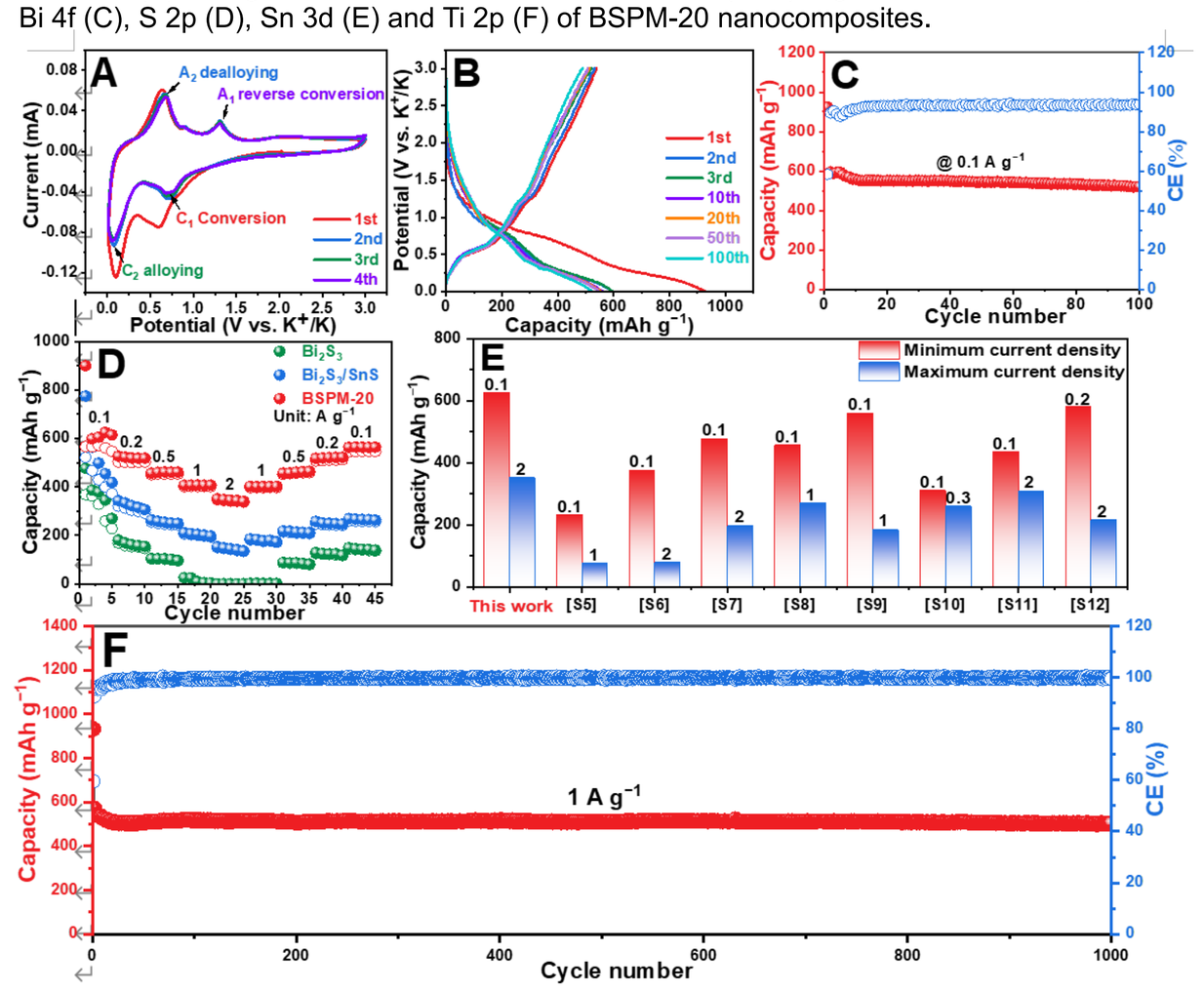

Figure 2. Electrochemical performance of BSPM-20 anode for PIBs. (A) CV plots at a sweep rate of 0.2 mV s^{-1}. (B, C) GCD curves and cycle performance of BSPM-20 under the current density of 0.1 A g^{-1}. (D) Rate capabilities at different current densities. (E) Comparison of rate performance with other Bi-based materials recently reported. Detailed references are given in the Supporting Information. (F) Long-term cycling performance and CE of BSPM-20 under the current density of 1 A g^{-1}.

CONCLUSION

In summary, we have demonstrated that the excellent potassium storage performance of BSPM-20 nanocomposite benefits from the heterojunction and dual polysulfide confinement strategy. The built-in *E*-field of p-n heterojunction could increase the electronic conductivity of B_2S_3. Furthermore, the inner MXene matrix could immobilize polysulfides via forming stable Ti-S binding and the PDA sheath owns strong chemical adsorption for confining polysulfides. In addition, the PDA shell can facilitate charge transfer and protect the huge volume expansion during cycling.

FUTURE WORK / REFERENCES

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