Fabrication of S,N-Doped Carbon-Coated SnS₂/SnS Heterostructures Supported by Hollow Carbon Microspheres for Sodium-Ion Storage

Suning Gao,¹ Zaichun Liu,² Liangtao Yang,^{3,4} Jie Shao,⁵ Qunting Qu,⁵ Yuping Wu,^{2,z} Philipp Adelhelm,^{3,4} and Rudolf Holze^{1,2,6,z}

¹Institute of Chemistry, Chemnitz University of Technology, AG Elektrochemie, 09111 Chemnitz, Germany

²State Key Laboratory of Materials-oriented Chemical Engineering, School of Energy Science and Engineering, Nanjing Tech University, Nanjing, 211816, Jiangsu Province, People's Republic of China

³Institute of Technical Chemistry and Environmental Chemistry, Friedrich-Schiller University Jena, 07749 Jena, Germany

⁴Institute of Chemistry, Humboldt-University Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany

⁵College of Energy, Soochow Institute for Energy and Materials Innovation, Soochow University, Suzhou, 215006, People's Republic of China

⁶St. Petersburg State University, Institute of Chemistry, St. Petersburg, 199034, Russia

Developing novel anode materials containing electroactive heterostructures which boost ion and charge transfer kinetics in a carbon matrix is still a great challenge. Here we report on a new smartly designed material: SnS₂/SnS p-n heterostructures embedded in S,N-doped carbon layer supported by hollow carbon spheres (C@SnS_x@C) by a facile method and applied as negative electrode material in sodium ion batteries. The C@SnS_x@C (at optimized carbon ratio) negative electrode can deliver an initial reversible capacity of 636.5 mAh·g⁻¹ at 0.1 A·g⁻¹, superior rate capability (265.1 mAh·g⁻¹ at rate of 10.0 A·g⁻¹) and long cycle life (capacity retention of 96.3 % at 1.0 A·g⁻¹ after 150 cycles). The SnS₂/SnS p-n heterojunctions provide a lower sodium ion diffusion energy barrier (0.38 eV), higher Na⁺ adsorption energy (−4.66 eV) and higher electronic conductivity due to an internal electric field according to density functional theory calculations compared to plain SnS. Moreover, S,N-doped carbon facilitates electronic conductivity and buffers the volume changes during the conversion reaction-based SnS_x upon sodium insertion and extraction process. Porous hollow carbon spheres contribute to prevent the agglomeration of SnS₂/SnS nanosheets and keep the structural integrity. Our findings on this unique material might be extended to other ion battery technologies.

© 2021 The Author(s). Published on behalf of The Electrochemical Society by IOP Publishing Limited. This is an open access article distributed under the terms of the Creative Commons Attribution Non-Commercial No Derivatives 4.0 License (CC BY-NC-ND, <http://creativecommons.org/licenses/by-nc-nd/4.0/>), which permits non-commercial reuse, distribution, and reproduction in any medium, provided the original work is not changed in any way and is properly cited. For permission for commercial reuse, please email: permissions@iopublishing.org. [DOI: 10.1149/1945-7111/abf5f6]

Manuscript submitted February 11, 2021; revised manuscript received March 26, 2021. Published May 19, 2021.

Supplementary material for this article is available [online](#)

The increasing use of renewable electricity (wind, solar, tide etc.) and the need for its storage call for extensive research efforts on rechargeable and low-cost batteries. Sodium ion batteries (SIBs) are considered as a promising replacement for lithium ion batteries (LIBs) because of abundant sodium resources and the physiochemical properties of sodium similar to those of lithium.^{1–4} Among current challenges, one urgent issue is the exploration of suitable negative electrode materials because of inevitable capacity decay and sluggish kinetics.^{5,6} Thus, it is of great urgency to develop novel anode materials with high specific capacity, long cycling life and high power capability, which matches the performance of already established positive electrode materials.

Typical anode materials including insertion type,^{7,8} alloy reaction-based⁹ and conversion materials^{10,11} have been widely investigated for SIBs. Among them, tin sulfides (SnS or SnS₂)^{12–14} are appealing because of their unique layered crystal structures which is beneficial for accommodation of Na⁺. SnS_x (x = 1,2) exists in several crystal phases because of the versatile oxidation states of Sn and sulfur.¹⁵ The sodium storage reactions of SnS_x can be represented as intercalation and conversion reactions (SnS_x + 2x Na⁺ + 2x e[−] → Sn + x Na₂S, x = 1,2) with a subsequent alloying reaction (Sn + 3.75 Na⁺ + 3.75 e[−] → Na_{3.75}Sn), which contributes to a high theoretical capacity (1022 mAh·g^{−1} in orthorhombic SnS and 1136 mAh·g^{−1} in hexagonal SnS₂, respectively).^{16,17} However, intrinsically poor electrical conductivity and large volume variation (343% in SnS₂ and 315% in SnS) when reacting with sodium ions, which inevitably results in sluggish kinetics of electron transport and pulverization of electrode upon sodium storage, hamper their use.¹⁸ In addition, the conversion reaction and the subsequent alloying reaction

typically cause a high initial irreversibility. Ideally, the Sn⁰/Na₂S will be fully converted to SnS_x in the reverse conversion reaction. However, the internal stress-induced force of recrystallization will result in coarsening of Sn nanograins with a loss of contact interfaces in Sn⁰/Na₂S, thus resulting in an incomplete Sn⁰/Na₂S reverse conversion reaction during charging process along with a resulting capacity loss and low initial Coulombic efficiency (ICE).^{19,20}

To address these concerns, numerous attempts, such as designing nanosized electroactive materials with the aim to shorten ion diffusion length,²¹ incorporating carbon matrix as protective layer or support for improving the electric conductivity and buffering volume variation,²² and constructing hollow structures²³ have been developed. Specifically, hollow structures provide a high surface-to-volume ratio that can ensure sufficient electrode-electrolyte solution contact.²⁴ On the other side, recent studies^{25,26} have aimed at establishing electroactive materials involving p-n heterostructures to minimize the irreversibility and boost the rate capability. Some reports revealed that heterostructures obtained via combining p-type and n-type semiconductors with distinct band gaps will reinforce electron transport and facilitate the electrochemical reaction kinetics because of the built-in internal electric field around heterointerfaces.²⁷ Furthermore, heterostructures can provide higher Na⁺ adsorption energy according to DFT calculations as well as support fast Na⁺ diffusion along the boundaries of coupled nanocrystals.²⁸

To date, constructing uniformly distributed and highly integrated heterostructured electrode materials still faces a series of challenges. In addition, to our current knowledge, there is no study of fabrication of SnS₂/SnS heterostructures through a solid-state reaction by partial phase transformation from SnS₂ to SnS, and their application as negative electrode material in SIBs. The fundamentals and mechanisms of ion storage remain to be understood more deeply. Herein, we report for the first time on a novel

^zE-mail: wuyup@njtech.edu.cn; rudolf.holze@chemie.tu-chemnitz.de

SIB negative electrode material SnS_2/SnS p-n heterostructures embedded in S,N-doped carbon layer supported by hollow carbon spheres ($\text{C}@\text{SnS}_x\text{@C}$) and present our understanding of the reasons resulting in excellent electrochemical performance of $\text{C}@\text{SnS}_x\text{@C}_2$ electrode by microscopic techniques (SEM and HRTEM), XRD, XPS and first-principles density functional theory (DFT) calculations. Based on analysis of CV data and previous contributions,^{29,30} a possible reaction mechanism for charging and discharging process is proposed. The $\text{C}@\text{SnS}_x\text{@C}_2$ electrode exhibits an initial reversible capacity of $636.5 \text{ mAh}\cdot\text{g}^{-1}$ at $0.1 \text{ A}\cdot\text{g}^{-1}$, superior rate capability ($265.1 \text{ mAh}\cdot\text{g}^{-1}$ at rate of $10.0 \text{ A}\cdot\text{g}^{-1}$) and long cycle life (a high capacity retention of 96.3% at $1.0 \text{ A}\cdot\text{g}^{-1}$ after 150 cycles). It is expected that this electrode material can be employed as host for other charge carrier ions too.

Experimental

Materials synthesis.—*Synthesis of hollow carbon spheres.*—Monodisperse silica nanospheres (550 nm in diameter) are synthesized by the Stöber's method. Briefly, 1 ml TEOS (Tetraethyl orthosilicate) is added into a mixture which contains 1 ml of $\text{NH}_3\cdot\text{H}_2\text{O}$, 4 ml of deionized H_2O , and 20 ml 2-propanol at room temperature followed by stirring. After reacting for 2 hours, a white powder is obtained by centrifugation, re-dispersion, and drying. Hollow carbon spheres (HCS) are synthesized by a multistep process via polymerization-annealing-etching. First, 100 mg silica are dispersed in 100 ml of Tris buffer aqueous solution ($\text{pH} \approx 8.5$) followed by adding 50 mg of dopamine under stirring at room temperature for 24 h. Next, the obtained $\text{SiO}_2\text{@PDA}$ ($\text{SiO}_2\text{@polydopamine}$) brown powder is annealed at 500°C for 3 h at a rate of 2°C min^{-1} under argon to obtain $\text{SiO}_2\text{@C}$. Finally, HCS black powder is obtained after dissolving $\text{SiO}_2\text{@C}$ in a 2 M NaOH solution at 50°C for 8 h followed by centrifugation and drying.

Synthesis of HCS@SnS_2 and pure SnS_2 .—HCS@ SnS_2 is synthesized by hydrothermal reaction. 20 mg HCS is dispersed in 30 ml absolute ethanol through ultrasonication, thereafter 100 mg $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 100 mg thioacetamide (TAA) are added into the solution and stirred for 2 h. Finally, HCS@ SnS_2 powder is obtained after 24 h reaction at 180°C with subsequent washing and drying. Plain SnS_2 samples are synthesized under the same conditions without adding HCS.

Synthesis of $\text{HCS@SnS}_2\text{@PDA}$ and $\text{SnS}_2\text{@PDA}$.—100 mg HCS@ SnS_2 , 100 mg SnS_2 and 100 mg of dopamine hydrochloride are dispersed into a Tris buffer solution (10 mM, 100 ml), and reacted for 24 h. HCS@ $\text{SnS}_2\text{@PDA}$ and $\text{SnS}_2\text{@PDA}$ are collected by centrifugation and drying at 60°C in vacuum. In order to obtain different PDA layer thicknesses, 50 mg of dopamine hydrochloride is added under the same conditions in a separate run.

Synthesis of $\text{C}@\text{SnS}_x\text{@C}$, $\text{SnS}_x\text{@C}$ and C@SnS@C_2 .— $\text{C}@\text{SnS}_x\text{@C}$ and $\text{SnS}_x\text{@C}$ are obtained by annealing HCS@ $\text{SnS}_2\text{@PDA}$ and $\text{SnS}_2\text{@PDA}$ under protective argon gas at 500°C for 3 h at a rate of 2°C min^{-1} . Designations $\text{C}@\text{SnS}_x\text{@C}_1$ and $\text{C}@\text{SnS}_x\text{@C}_2$ correspond to the different amounts of dopamine (50 and 100 mg) in the previous step. $\text{SnS}_x\text{@C}$ is prepared by $\text{SnS}_2\text{@PDA}$ with 100 mg dopamine. C@SnS@C_2 is obtained by annealing HCS@ $\text{SnS}_2\text{@PDA}$ under protective argon gas at 600°C for 3 h at a rate of 2°C min^{-1} .

Materials characterization.—Crystal structures of the prepared samples were established by X-ray powder diffraction (XRD) on a Bruker D2 Phaser X-ray diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at a voltage of 30 kV and a current of 10 mA. The XPS measurements were done with an ESCALAB 250 Xi XPS Microprobe (Thermo Scientific) equipped with a monochromatized $\text{Al K}\alpha$ X-ray source (1486.6 eV). The pass energy was 200 eV for survey spectra and 20 eV for high-resolution spectra. The

morphologies of the samples were examined by field-emission scanning electron microscopy (FEI Nova NanoSEM 200) at 10 kV, and high-resolution transmission electron microscopy (Tecnai G2 F30) with energy dispersive X-ray spectroscopy. Thermogravimetric analysis was performed on a Mettler Toledo 1600 system with an MX1 balance with a heating rate of $10^\circ\text{C min}^{-1}$. N_2 sorption isotherms were collected on an Autosorb IQ Station 3 apparatus. The samples were degassed in vacuum at 120°C for 3 h and then N_2 sorption isotherms were measured at 77 K.

Electrochemical measurements.—The electrochemical tests were carried out using CR2016 coin-type cells. For electrochemical measurements, a slurry was prepared by mixing active materials with conductive carbon black and a carboxymethyl cellulose binder at a mass ratio of 8:1:1 in deionized water to obtain a uniform dispersion, followed by drop-casting onto copper foils. The average areal mass loading of the active materials on electrodes was about $0.8\text{--}1.0 \text{ mg cm}^{-2}$. The used electrolyte solution was 1.0 M NaClO_4 dissolved in a mixture of ethylene carbonate and dimethyl carbonate (EC/DMC, 1:1, v/v) with 5 wt % fluoroethylene carbonate (FEC). CR2016 coin cells were assembled with sodium foil as the counter electrode and a glass fiber GF/C filter (Whatman) as the separator inside an Ar-filled glovebox (H_2O and $\text{O}_2 < 1 \text{ ppm}$). Galvanostatic discharge and charge tests at various current densities were conducted between 0.01 and 3.0 V vs Na^+/Na on a battery test system (BioLogic Science Instrument EC Lab) at room temperature 25°C , the mass specific capacity was calculated based on the mass of the active material. Cyclic voltammetry (CV, $0.2\text{--}1.0 \text{ mV s}^{-1}$, $0.01\text{--}3.0 \text{ V}$ vs Na^+/Na) and electrochemical impedance spectroscopy (EIS, 100 kHz – 0.01 Hz, 10 mV) measurements were conducted with the same device.

Na^+ ion diffusion coefficient calculation.—The calculation is based on the equations shown below, R is the gas constant $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, T is the room temperature of 298 K, A is the surface area of the electrode of 0.785 cm^2 , n is the number of electrons per reaction species, it is estimated by different ratios of SnS_2 to SnS from Table SI (available online at stacks.iop.org/JES/168/050527/mmedia) in different electrodes and the values ranged from 2 to 4. F is the Faraday constant 96500 C mol^{-1} , c is the bulk concentration of Na in the electrode material of 1 mmol ml^{-1} , σ_ω is the Warburg factor obtained from the slope of the fitted lines of Z_{re} vs $\omega^{-1/2}$. Details of the DFT calculations can be seen in the Supporting information (SI).

Results and Discussion

Scheme 1a presents the preparation process of $\text{C}@\text{SnS}_x\text{@C}$. First, uniform silica particles acted as hard templates in the formation of hollow carbon spheres (HCSs). In the next step, Sn^{4+} -ions easily attached on the surface of the obtained HCSs due to the strong electrostatic attraction between negatively charged oxygen-containing functional groups and Sn^{4+} , allowing the assembly of a compact and dense honey-comb-like SnS_2 layer covered on the surface of HCSs (HCSs@SnS_2) through a hydrothermal process. Finally, $\text{C}@\text{SnS}_x\text{@C}$ were collected by a polymerization-carbonization process under argon at 500°C . Following a reaction mechanism is suggested 1–3³¹

Noticeably, according to Eq. 3, the orthorhombic SnS phase is formed driven by the evaporation of sulfur transported away by the inert carrier gas during the annealing reaction. The phase

Scheme 1. (a) The schematic procedure for preparing C@SnS_x@C, (b) Na⁺-ion intercalated C@SnS_x@C.

transformation reaction is not completed at 500 °C. This partial phase transformation results in the successful formation of SnS₂/SnS. According to our knowledge, SnS₂/SnS has been prepared hydrothermally³² but not yet obtained through a solid-state reaction with a direct phase transformation process. Scheme 1b shows the model of Na⁺-intercalated C@SnS_x@C.

The crystalline structures of obtained samples are studied by X-ray diffraction (XRD). To confirm the successful fabrication of the SnS₂/SnS heterostructure in the C@SnS_x@C2 composite, C@SnS@C2 is also examined by XRD for comparison. Figure 1a presents the diffraction pattern of C@SnS@C2 which is in good agreement with that of the orthorhombic-SnS (ICDD 39-0354). All significant diffraction peaks of C@SnS_x@C1, C@SnS_x@C2 and SnS_x@C samples in Figs. 1b and S1 are assigned to two phases: orthorhombic SnS (ICDD 39-0354) and hexagonal SnS₂ (ICDD 23-0677). Specifically, diffraction peaks located at $2\theta = 15.0^\circ, 28.20^\circ, 32.10^\circ, 49.96^\circ, \text{ and } 52.45^\circ$ are assigned to the (001), (100), (101), (110), and (111) planes of hexagonal-SnS₂, respectively. The peaks at $2\theta = 22.00^\circ, 26.10^\circ, 30.49^\circ, 31.54^\circ, 39.06^\circ, 44.75^\circ \text{ and } 51.30^\circ$ can be attributed to the (110), (120), (101), (111), (131), (141) and (151) planes of orthorhombic-SnS, respectively.

The chemical composition of different samples and the atomic ratio of different elements are obtained by thermogravimetric analysis and elemental analysis, results are shown in Table SI and Fig. 1c. Specifically, the weight percentages of carbon in C@SnS_x@C1, C@SnS_x@C2 and SnS_x@C nanocomposites are 26, 39 and 37 wt. %, respectively. The mass fractions of SnS in SnS₂/SnS of these samples are calculated to be around 29, 71 and 62 wt. %, respectively. In addition, slight weight losses of as-prepared samples below 350 °C revealed by TGA curves in Fig. 1c are attributed to the desorption of absorbed water. Sharp weight losses beyond 350 °C of 28.8, 41.1 and 38.8 wt. %, respectively, are caused by simultaneous oxidation of SnS₂/SnS to SnO₂ and carbon to CO₂ in the air atmosphere.

Barrett–Joyner–Halenda (BJH) pore-size analysis and nitrogen adsorption-desorption isotherm measurements are performed to measure the pore size distribution and specific surface area of these samples; results are exhibited in Figs. 1d–1e. C@SnS_x@C2 and SnS_x@C present typical type IV isotherms according to the IUPAC criteria,³³ this proves that mesopores have been created in these samples. Specifically, pore size distributions of these samples range from 3 to 6 nm as determined by BJH pore-size analysis. The specific surface areas of C@SnS_x@C2 and SnS_x@C are 41 and 33 m²·g^{−1}, respectively. As a result, the mesopores ensure large contact area between electroactive material and electrolyte solution and provide shorter ion diffusion lengths limited by nanosized pore walls, which are beneficial to achieve high electrochemical performance.

The valence state and surface chemical composition of these samples are investigated by X-ray photoelectron spectroscopy (XPS). A deconvolution procedure including Gaussian profiles and Shirley background have been implemented. According to Fig. 2a, Sn, C, N, O, and S are detected in the survey spectrum of C@SnS_x@C2, no other elements were found. The high-resolution XP spectra of Sn 3d, S 2p, N 1s and C 1s in C@SnS_x@C2 are further investigated. The deconvoluted peaks at 487.2 and 495.6 eV from Fig. 2b are attributed to Sn 3d_{3/2} and Sn 3d_{5/2} of Sn⁴⁺, respectively. Peaks located at 486.7 and 495.1 eV are associated with Sn 3d_{3/2} and Sn 3d_{5/2} of Sn²⁺, this confirms successful formation of SnS₂/SnS heterostructures.³⁴ In contrast, Fig. S1 depicts the XPS of Sn 3d of C@SnS@C2. It can be noticed that the characteristic peaks of Sn 3d of C@SnS_x@C2 (495.4 and 486.9 eV for Sn 3d_{3/2} and Sn 3d_{5/2}) shift to higher binding energies compared to those of C@SnS@C2 (495.2 and 486.8 eV for Sn 3d_{3/2} and Sn 3d_{5/2}).³⁵ The S 2p spectra are shown in Fig. 2c, the peaks fitted at 162.7 and 161.9 eV are ascribed to S 2p_{1/2} and S 2p_{3/2} of S^{2−} originating from SnS₂ and SnS, respectively. The peaks at 164.9 and 163.8 eV are assigned to sulfur covalently bonded to carbon,

Figure 1. (a)–(c) XRD patterns and TGA curves of C@SnS_x@C2, C@SnS_x@C1, C@SnS_x@C2 and SnS_x@C, respectively, (d)–(e) N₂ adsorption/desorption isotherms and pore size distributions of C@SnS_x@C2 and SnS_x@C, respectively.

Figure 2. (a) XP survey spectrum and fitted high-resolution spectra of (b) Sn 3d, (c) S 2p, (d) C 1s and (e) N 1s of C@SnS_x@C2.

which indicates sulfur doped carbon has been formed.³⁶ An additional peak at 168.5 eV might be traced to oxidized sulfur from SO_x²⁻ formed during XPS measurements.³⁷ The high-resolution C 1s spectrum of C@SnS_x@C2 is presented in Fig. 2d. Five fitted peaks located at 289.0, 286.8, 285.8, 285.2 and 284.8 eV correspond to C=O, C-OH, C-N/C-S, O-C-O, and C-C bonds, respectively.³⁸ In detail, the deconvoluted peak of C-N bond confirms N-atoms are doped into carbon matrix, which further proves S,N-doped carbon has been prepared. Sp²-hybridized graphitic structures related to the main peak at 284.8 eV are advantageous for fast electron transport.³⁹

Moreover, four N contributions can be fitted well to the high-resolution N 1s (Fig. 2b) spectrum: 403.0, 400.8, 400.0, 398.7 eV. They are associated with oxygenated N, graphitic N, pyrrolic N and pyridinic N, respectively.^{40–42} From XPS analysis mentioned above, the coupling effect of SnS and SnS₂ in heterostructures as well as chemical bonds formed between carbon and SnS_x are assumed to greatly enhance the electronic conductivity of d C@SnS_x@C2 during Na⁺ storage process.

Figures 3a–3c shows the SEM images of HCS, HCS@SnS₂, C@SnS_x@C2 to observe their morphologies. Figure 3a presents

Figure 3. (a)–(c) SEM images of HCS, HCS@SnS₂ and C@SnS_x@C₂, and the inset SEM and TEM images at a high magnification, respectively, (d) TEM images of C@SnS_x@C₂, (e)–(f) HRTEM images and corresponding SAED of the selected red circle area marked in the inset image of figure d of C@SnS_x@C₂, (g)–(l) elemental mapping of a single C@SnS_x@C₂ sphere.

uniform hollow spheres with a size of around 600 nm after removal of the interior silica by chemical etching. The hollow carbon layer is about 50 nm thick according to the observation of the inset high magnification TEM image. As displayed in Fig. 3b, HCS@SnS₂ exhibits a highly monodisperse spherical morphology with an average size of about 800 nm after hydrothermal reaction. Ultrathin SnS₂ nanosheets are crosslinked with each other and homogeneously covered on the surface of HCS as exhibited in the inset. According to Fig. 3c, the spherical morphology of C@SnS_x@C₂ of around 850 nm size is retained with a rough surface after annealing. The inset reveals PDA-derived carbon sheath layer is homogeneously coated on the surface of SnS_x nanosheets.

Transmission electron microscopy (TEM) has been performed to view microstructural features of C@SnS_x@C₂. According to Fig. 3d SnS_x nanosheets embedded in a carbon sheath layer supported by hollow carbon spheres have been prepared. In detail, it is easily seen that carbon-covered SnS_x nanosheets have been attached on both external and internal surface of HCSs. The carbon sheath layers can efficiently buffer the volume changes of SnS_x nanosheets, and the supporting hollow carbon sphere can function as electronically conducting bridges between adjacent C@SnS_x@C₂ nanoparticles. Figures 3e–3f presents HRTEM results of the selected area e and f marked in the inset of Fig. 3d. As seen in Fig. 3e, SnS_x nanosheets are coated with a S,N-doped carbon layer of around 8 nm thickness, and the lattice fringes with d-spacing of 0.403 and 0.278 nm are

assigned to the (110) plane of SnS and the (101) plane of SnS₂, respectively. Notably, distinct grain boundaries around SnS and SnS₂ can be observed which confirms the formation of SnS₂/SnS heterojunctions. Figure 3f reveals the HRTEM image enlarged from the selected area f with a marked red circle in Fig. 3d. In detail, distinct heterointerfaces between SnS and SnS₂ are noticed and analyzed. The well-defined lattice fringes with interplanar distance of 0.278 and 0.283 nm correspond to the (101) plane of SnS₂ and the (111) plane of SnS, respectively. The formed heterojunctions are advantageous to enhance the electronic conductivity and Na⁺-diffusion kinetics when applied in metal-ion batteries according to previous reports.^{38,39} In contrast, the morphologies of C@SnS_x@C₁ and SnS_x@C are presented in Figs. S2 and 3. Figure S2a–c exhibits the same microstructure apart from different thicknesses of carbon coating layers at different magnifications. Figures S2d–S2f presents the flower-like morphology of core-shell SnS_x@C without the support of HCS. Figures. 3g–3l exhibit energy-dispersive X-ray spectroscopy (EDX) element mappings of a single separated C@SnS_x@C₂ nanoparticle. A homogenous distribution of present elements in C@SnS_x@C₂ is clearly noticed, verifying that heterostructured SnS_x nanosheets are uniformly dispersed in the carbon matrix.

CVs were recorded to monitor reaction of the C@SnS_x@C₂ electrode with Na⁺-ions in a voltage window range from 0.1 to 3.0 V at a scan rate of 0.2 mV s⁻¹. Obtained plots are presented in

Figure 4. (a) The initial five CV curves of a C@SnS_x@C2 electrode at a scan rate of 0.2 mV·s⁻¹, (b) first five galvanostatic charge and discharge profiles at a rate of 100 mA·g⁻¹ of C@SnS_x@C2 anode, (c) rate capability of C@SnS_x@C1, C@SnS_x@C2, C@SnS@C2 and SnS_x@C electrodes at rates ranging from 0.1 to 10 and then gradually backed to 0.1 A·g⁻¹, respectively, (d) galvanostatic charge and discharge profiles at rates from 0.1 to 10.0 A·g⁻¹, respectively, (e) rate capability of C@SnS_x@C2 anode vs current density compared with some other Sn-based SIB anode materials, (f)–(g) cycling life and Coulombic efficiencies of C@SnS_x@C1, C@SnS_x@C2, C@SnS@C2 and SnS_x@C electrodes, respectively, (h) Nyquist plots of C@SnS@C2, C@SnS_x@C2 and SnS_x@C electrodes after 10 cycles at a rate of 0.5 A·g⁻¹, (j) Nyquist plots of C@SnS_x@C2 anode after certain charge-discharge cycles.

Fig. 4a. In the first negative-going scan, the weak cathodic peak located at about 1.6–1.8 V is ascribed to Na⁺ intercalation into SnS_x.⁴³ A broad reduction peak at around 0.8–1.1 V is attributed to the conversion reaction along with SEI film formation as a result of the reduction of electrolyte solution.^{44,45} Another broad peak situated at around 0.42 V is associated with the alloying reaction between Sn and Na⁺ during the further electrode potential scanning.⁴⁶ In the reverse, positive-going scan the anodic peaks at about 0.27 and 0.73 V are attributed to the dealloying reaction. In subsequent scans, the oxidation peak at around 1.12 V can be traced to the conversion back-reaction. Subsequently, the less obvious anodic peak at 2.27 V corresponds to the extraction of Na⁺.²⁹ In the following repeated scans, the CV curves strongly coincide which demonstrates a high stability and reversibility of the C@SnS_x@C2 electrode. In detail, two couples of redox peaks at about 0.24/0.27 V and 0.62/0.72 V are assigned to the alloying/de-alloying reaction, a pair of redox peaks situated about at 0.97/1.12 V is associated with typical conversion/conversion back-reaction and a couple of redox peaks at around 1.75/2.36 V is attributed to intercalation/extraction process.

From CV observations, a six-stage mechanism during sodium storage process can be described in the following Eqs. 4–9:

Stage I (OCV–1.1 V), intercalation reaction:

Stage II (1.1–0.6 V), conversion reaction:

Stage III (0.6–0.1 V), alloying reaction:

Stage IV (0.01–1.0 V), de-alloying reaction:

Stage V (1.0–2.0 V), reverse conversion reaction:

Stage VI (2.0–3.0 V), extraction reaction:

The galvanostatic charge-discharge plots of a C@SnS_x@C2 electrode are presented in Fig. 4b in a voltage range from 0.01 to 3.0 V vs Na⁺/Na at a current density of 0.1 A·g⁻¹. The initial charge capacity of the electrode reached 611 mAh·g⁻¹ with Coulombic efficiency (CE) of 76.8% in the first cycle. The irreversible capacity loss can be ascribed to the irreversible conversion reaction of Sn⁰/Na₂S as well as SEI formation.³⁰ In order to reveal the capacity contribution of carbon in a C@SnS_x@C2 electrode, the cycling performance of plain carbon electrode is examined at the current density of 0.5 A·g⁻¹ as presented in Fig. S4. The initial reversible capacity of plain carbon electrode is 95 mAh·g⁻¹ (according to the result of TGA, it can be calculated that the capacity contribution of SnS_x in C@SnS_x@C2 is 859 mAh·g⁻¹). It should be noticed that this calculation is based on the assumption that the specific capacities of hollow carbon and carbon sheath are the same after exposure to the annealing temperature of carbon-derived PDA. Two plateaus appear in the first discharge plot at about 1.0 V and 0.42 V, demonstrating that a conversion reaction occurred between SnS_x and Na⁺ followed by an alloying reaction between formed Sn and Na⁺, respectively. In the reverse charge process, plateaus situated at about 0.3, 0.7, 1.1 and 2.3 V can be assigned to the de-alloying reaction, reverse conversion and extraction process, respectively. This is in a good agreement with the CV observations. The coinciding curves in following cycles confirm high reversibility of the C@SnS_x@C2 electrode with CE values around 100% after the first cycle. In contrast, first five galvanostatic charge-discharge curves of C@SnS@C2, C@SnS_x@C1 and SnS_x@C electrodes are collected in Fig. S5. In detail, discharge capacity values of these electrodes are 626, 1080, 775 mAh·g⁻¹, respectively, with charge capacity values of 450, 860, 596 mAh·g⁻¹, thus leading to CE values of 71.8, 80.36, and 76.90%, respectively. Noticeably, the plateaus in the charge-discharge measurements of C@SnS@C2 electrode have changed somehow due to a different sodium storage mechanism which is in line with the CV observations as presented in Fig. S6.

The rate capability of these electrodes is tested; results are displayed in Fig. 4c. The C@SnS_x@C2 electrode delivers a high reversible capacity of 636.5, 590.0, 561.0, 519.0, 471.0, 389.0 and 265.1 mAh·g⁻¹ at current rates 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 A·g⁻¹, respectively. When the current density is set back to 0.1 A·g⁻¹, the specific capacity recovers quickly to 610 mAh·g⁻¹, which indicates a superb rate capability. In contrast, the C@SnS_x@C1 electrode reaches a specific capacity of 896.0, 825.0, 757.0, 685.0, 588.0, 311.0 and 88.0 mAh·g⁻¹, and the SnS_x@C electrode exhibits 610.0, 569.0, 511.0, 442.0, 313.0, 182.0 and 36.0 mAh·g⁻¹, respectively, while that of C@SnS@C2 electrode is only 489.0, 429.0, 371.0, 329.0, 290.0, 239.0 and 185.0 mAh·g⁻¹ at rates of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, and 10.0 A·g⁻¹, respectively. The reasons behind the excellent rate performance of C@SnS_x@C2 electrode are a synergistic effect involving building blocks of a nanosized dimension, p-n SnS₂/SnS heterojunctions and a favorable carbon fraction, which extremely improve electrical conductivity and certainly assure fast sodium ion diffusion. A minimal increase in polarization at rates growing from 0.1 to 10.0 A·g⁻¹ of C@SnS_x@C2 electrode in the GCD plots is noticed, as shown in Fig. 4d. Figure 4e shows a comparative diagram of specific capacity vs current density of our C@SnS_x@C2 electrode and some other current state-of-the-art Sn-based SIB negative electrodes.^{47–51} Our C@SnS_x@C2 electrode delivers superior rate capability due to the synergistic effects mentioned above.

Galvanostatic charge/discharge profiles and corresponding CE values at a fixed current density are recorded and calculated to evaluate the cycling stability of C@SnS_x@C2, C@SnS_x@C1, C@SnS@C2 and SnS_x@C electrodes, results are presented in Figs. 4f–4e. Figure S7 illustrates the cycling stability of C@SnS_x@C2 and C@SnS_x@C1 electrodes at a low rate of 0.2 A·g⁻¹. The C@SnS_x@C2 electrode

delivers a reversible capacity of 463 mAh·g⁻¹ after 150 cycles at a rate of 1.0 A·g⁻¹ (a high capacity retention of 96.3%). However, the C@SnS_x@C1 electrode undergoes dramatic capacity decay after 30 cycles and has a low capacity retention of 27.3% of its initial capacity (636 mAh·g⁻¹) after 150 cycles. In contrast, the SnS_x@C and C@SnS@C2 electrodes fall to 206 mAh·g⁻¹ after 100 cycles and 230 mAh·g⁻¹ after 150 cycles at a current density of 1.0 A·g⁻¹, respectively. Accordingly, C@SnS_x@C2 is an appealing SIB electrode material based on these electrochemical analyses.

In addition, the reaction kinetics of these as-prepared electrodes have been investigated by electrochemical impedance measurements (EIS). All Nyquist plots as shown in Figs. 4h–4i reveal two parts: a distorted semicircle and an inclined line. The first part in the high-medium frequency region is ascribed to the combination of capacitance and resistance of the SEI film ($C_{\text{SEI}} + R_{\text{SEI}}$), double layer capacitance and the charge transfer resistance ($C_{\text{dl}} + R_{\text{ct}}$). The inclined line in the low frequency region is associated with a semi-infinite diffusion process.⁵² Figure 4h depicts Nyquist plots of these electrodes after 10 cycles at a rate of 0.5 A·g⁻¹. Obviously, the diameter of the semicircle of the C@SnS_x@C2 electrode is the smallest one, which indicates the lowest internal resistance of the C@SnS_x@C2 electrode. The low internal resistance might be in part caused by the presence of S,N-doped carbon and well-coupled p-n SnS₂/SnS heterostructures. In addition, Nyquist profiles after 50 cycles are also collected and presented in Fig. S8; they exhibit similar trends. The internal resistance values are shown in Table SII. Nyquist plots after certain numbers of cycles are also recorded to trace the reaction kinetics of C@SnS_x@C2 electrode; the results are presented in Fig. 4i. The internal resistance values gradually increase due to some unwelcome side reactions during continued cycling, the data are collected in Table SIII. The Na⁺ diffusion coefficient is a direct index reflecting the transport kinetics in electrode materials during the sodium ion storage. The sodium ion diffusion coefficient (D) can be calculated from the EIS results according to the following Eqs. 10–11:^{52–54}

$$D_{\text{Na}^+} = R^2 T^2 / 2 A^2 n^4 F^4 c^2 \sigma_{\omega}^2 \quad [10]$$

$$Z_{\text{re}} = R_s + R_{\text{ct}} + \sigma_{\omega} \omega^{-1/2} \quad [11]$$

where in R corresponds to the gas constant, n is the number of electrons transferred in the electrode reaction, T is the room temperature, A is the surface area of the electrode, F is the Faraday constant, c is the bulk concentration of Na in the electrode material, σ_{ω} is the Warburg factor deduced from the slope of the fitted lines of Z_{re} vs $\omega^{-1/2}$. Results are exhibited in Fig. S9, the calculation can be found in the SI. The calculated D values of SnS_x@C, C@SnS@C2 and C@SnS_x@C2, are 5.37×10^{-15} , 1.56×10^{-14} , and 8.48×10^{-14} cm²·s⁻¹ respectively. The higher D_{Na^+} value of C@SnS_x@C2 electrode compared to those of other electrodes demonstrating faster Na⁺ diffusion might be attributed to the three-dimensional structures, coupling effect of p-n SnS₂/SnS heterostructures and shorter Na⁺ diffusion length caused by nanosized building blocks.

It should be highlighted that the p-n SnS₂/SnS heterointerface could give rise to a built-in internal electric field which promotes charge transport, which results in better rate capability.⁵⁵ In addition, mesopores can offer sufficient electrode-electrolyte contact areas, thus ensuring abundant reaction electroactive material, which leads to high specific capacity. In addition, S,N-doped carbon sheath layer and the hollow carbon sphere substrate can not only buffer the volume variations of SnS and SnS₂ during cycling but also enhance the electric conductivity, which contributes to long cycling stability.

Density functional theory (DFT) calculations are implemented to investigate the density of states (DOS), Na⁺ diffusion energetics and the energy band structures in SnS₂/SnS heterostructures. Carbon in C@SnS_x@C2 is neglected in DFT calculations. Figure S10 presents

Figure 5. Band structures and electronic density of states for SnS_x (a), (b) and SnS (c), (d), charge density difference isosurfaces for NaSnS_x (e) and NaSnS (f) (isosurface value is 0.005 eV Å⁻³, + and - induced charges are represented in cyan/yellow solid spheres, respectively), migration energy barrier for Na⁺ in SnS_x and SnS (g), schematic illustration of the (h) superior performance mechanism and (i) induced internal electric field in the SnS₂/SnS p-n heterojunctions.

atomic migration pathways for Na⁺ in SnS₂/SnS and SnS. The Na⁺ adsorption energy (E_{ads}) of SnS₂/SnS is -4.66 eV compared to that of SnS (-2.55 eV) which confirms an enhanced Na⁺ accommodation capacity. According to Figs. 5b and 5d, SnS and SnS₂/SnS heterostructures exhibit similar DOS patterns. However, a consecutive distribution of DOS pattern of SnS₂/SnS heterostructures is calculated indicating that SnS₂/SnS heterostructure is changed to metallic type from semiconducting type.⁵⁶ In addition, it can be seen in Fig. 5a that the electronic orbitals of Sn, Na, and S overlap in the SnS₂/SnS heterostructure, while a widened band gap (0.823 eV) of SnS is shown in Fig. 5c. These findings illustrate that SnS₂/SnS heterostructure can strongly lower the Na⁺ adsorption energy and enhance the electrical conductivity during sodium ion storage. Furthermore, Fig. 5g shows the diffusion energy barrier for SnS₂/SnS heterostructure of 0.38 eV, which is much lower than that of SnS (0.72 eV), and which certainly suggests Na⁺ diffusion is more welcome and favored in C@SnS_x@C2.

Figures 5e and 5f reveal the charge distribution in SnS and SnS₂/SnS heterostructures after Na⁺ intercalation. An induced

internal electric field and an obvious charge separation of SnS₂/SnS heterostructure which greatly facilitates Na⁺ diffusion during sodium ion storage can be noticed in Fig. 5e. Furthermore, it can be concluded that the charge transfer and exchange between Na⁺ ion and SnS₂/SnS is much stronger than in SnS (Fig. 5f). Figures 5h and 5i illustrate an induced internal electric field crossing p(SnS)-n(SnS₂) heterojunctions and how Na⁺ transfers between p-n heterojunctions under the internal electric field during a charge and discharge process. Na⁺ diffusion kinetics are highly promoted in the SnS₂/SnS heterostructure which is confirmed by the lower Na⁺ diffusion energy barrier.

DFT results are strongly endorsed and supported by experimental data. Overall, the above results indicate that an advanced and superior sodium ion storage performance has been achieved in our newly designed negative electrode material for a SIB by successfully constructing SnS₂/SnS p-n heterojunctions embedded in a carbon sheath layer supported by a hollow carbon sphere substrate. This novel negative electrode material can be extended to other metal ion battery technologies.

Conclusions

In summary, SnS_2/SnS p-n heterostructures embedded in a S,N-doped carbon sheath layer and supported by a hollow carbon sphere have been prepared for the first time. The characteristic properties of $\text{C}@\text{SnS}_x/\text{C}2$ have been investigated by microscopies (SEM and HRTEM), XRD and XPS. The $\text{C}@\text{SnS}_x/\text{C}2$ (optimized carbon ratio) negative electrode can deliver an initial reversible capacity of $636.5 \text{ mAh}\cdot\text{g}^{-1}$ at $0.1 \text{ A}\cdot\text{g}^{-1}$, superior rate capability ($265.1 \text{ mAh}\cdot\text{g}^{-1}$ at rates of $10.0 \text{ A}\cdot\text{g}^{-1}$) and long cycle life (a high capacity retention of 96.3% at $1.0 \text{ A}\cdot\text{g}^{-1}$ after 150 cycles). Specifically, the formed SnS_2/SnS p-n heterostructure can improve the electrical conductivity through inducing a built-in electric field promoting Na^+ diffusion, which results in high rate performance further evidenced by EIS analysis and supported by first-principle DFT calculations. In addition, S,N-doped carbon sheath can accommodate the volume variation during sodium ion storage, and the internal hollow carbon substrate can assure structural integrity by alleviating the aggregation of SnS_2/SnS nanosheets. Furthermore, the mesoporous structure might facilitate transport along with ensuring sufficient electrode-electrolyte solution contact, overall leading to high specific capacities even at high rates. It is believed that the outstanding electrochemical characteristics of $\text{C}@\text{SnS}_x/\text{C}2$ electrode make it an appealing anode material for SIBs and also for other metal ion batteries.

Acknowledgments

The authors gratefully acknowledge SEM data by C. Tegenkamp (the Solid Surface Analysis group at the Institute of Physics); S. Barth provided XRD data, and R. Oleksandra performed XPS measurements. S. G. and L.Y. thank the CSC council for PhD scholarships. RH received financial support provided within a research project at St. Petersburg State University grant № 26455158, Y.W. financial support of NSFC (51425301 and U1601214). We also appreciate High Performance Computing Center of Nanjing Tech University for the computational resources generously provided.

ORCID

Rudolf Holze <https://orcid.org/0000-0002-3516-1918>

References

- J. W. Choi and D. Aurbach, *Nat. Rev. Mater.*, **1**, 16013 (2016).
- Z. C. Liu et al., *NPG Asia Mater.*, **11**, 12 (2019).
- K. X. Lei, C. C. Wang, L. J. Liu, Y. W. Luo, C. N. Mu, F. J. Li, and J. Chen, *Angew. Chem. Int. Ed.*, **130**, 4777 (2018).
- C. C. Wang, L. B. Wang, F. J. Li, F. Y. Chen, and J. Chen, *Adv. Mater.*, **29**, 1702212 (2017).
- B. Dunn, H. Kamath, and J.-M. Tarascon, *Science*, **334**, 928 (2011).
- P. Adelhelm, P. Hartmann, C. L. Bender, M. Busche, C. Eufinger, and J. Janek, *J. Nanotechnol.*, **6**, 1016 (2015).
- Y. Wen, K. He, Y. Zhu, F. Han, Y. Xu, I. Matsuda, Y. Ishii, J. Cumings, and C. Wang, *Nat. Commun.*, **5**, 4033 (2014).
- Y. J. Fang, D. Y. Luan, Y. Chen, S. Y. Gao, and X. W. Lou, *Angew. Chem. Int. Ed.*, **59**, 7178 (2020).
- L. Wu, X. Hu, J. Qian, F. Pei, F. Wu, R. Mao, X. Ai, H. Yang, and Y. Cao, *Energy Environ. Sci.*, **7**, 323 (2014).
- Y. J. Fang, D. Y. Luan, Y. Chen, S. Y. Gao, and X. W. Lou, *Angew. Chem. Int. Ed.*, **59**, 2644 (2020).
- Y. J. Fang, B. Y. Guan, D. Y. Luan, and X. W. Lou, *Angew. Chem. Int. Ed.*, **58**, 7739 (2019).
- D. Chao et al., *ACS Nano*, **10**, 10211 (2016).
- Y. Liu, X.-Y. Yu, Y. Fang, X. Zhu, J. Bao, X. Zhou, and X. W. Lou, *Joule*, **2**, 725 (2018).
- X. Jin, H. Huang, A. Wu, S. Gao, M. Lei, J. Zhao, X. Gao, and G. Cao, *ACS Nano*, **12**, 8037 (2018).
- J.-H. Ahn, M.-J. Lee, H. Heo, J. H. Sung, K. Kim, H. H. Wang, and M.-H. Jo, *Nano Lett.*, **15**, 3703 (2015).
- C. Rao, H. R. Matte, and U. Maitra, *Angew. Chem. Int. Ed.*, **52**, 13162 (2013).
- Y. C. Liu, N. Zhang, L. F. Jiao, and J. Chen, *Adv. Mater.*, **27**, 6702 (2015).
- Y. Zhao, L. Wang, M. T. Sougrati, Z. X. Feng, Y. Leconte, A. Fisher, M. Srinivasan, and Z. C. Xu, *Adv. Energy Mater.*, **7**, 1601424 (2017).
- R. Hu, Y. Ouyang, T. Liang, X. Tang, B. Yuan, J. Liu, L. Zhang, L. Yang, and M. Zhu, *Energy Environ. Sci.*, **10**, 2017 (2017).
- J. Wang, L. Wang, C. Eng, and J. Wang, *Adv. Energy Mater.*, **7**, 1602706 (2017).
- S. N. Gao, F. Liao, S. Z. Ma, L. L. Zhu, and M. W. Shao, *J. Mater. Chem. A*, **3**, 16520 (2015).
- S. Gao, L. Zhu, L. Liu, A. Gao, F. Liao, and M. Shao, *Electrochim. Acta*, **191**, 908 (2016).
- C. C. Yec and H. C. Zeng, *J. Mater. Chem. A*, **2**, 4843 (2014).
- X. J. Wang, J. Feng, Y. C. Bai, Q. Zhang, and Y. D. Yin, *Chem. Rev.*, **116**, 10983 (2016).
- X. Xie, M.-Q. Zhao, B. Anasori, K. Maleski, C. E. Ren, J. Li, B. W. Byles, E. Pomerantseva, G. Wang, and Y. Gogotsi, *Nano Energy*, **26**, 513 (2016).
- C. Huang, S. Wu, A. Sanchez, J. Peters, R. Beanland, J. Ross, P. Rivera, W. Yao, D. Cobden, and X. Xu, *Nat. Mater.*, **13**, 1096 (2014).
- X. Chang, T. Wang, P. Zhang, J. Zhang, A. Li, and J. Gong, *J. Am. Chem. Soc.*, **137**, 8356 (2015).
- W. Wen, J.-M. Wu, Y.-Z. Jiang, L.-L. Lai, and J. Song, *Chem*, **2**, 404 (2017).
- X. Ou, L. Cao, X. H. Liang, F. H. Zheng, H. S. Zheng, X. F. Yang, J. H. Wang, C. H. Yang, and M. L. Liu, *ACS Nano*, **13**, 3666 (2019).
- C. H. Yang, X. H. Liang, X. Ou, Q. B. Zhang, H.-S. Zheng, F. H. Zheng, J.-H. Wang, K. Huang, and M. L. Liu, *Adv. Funct. Mater.*, **29**, 1807971 (2019).
- T. Zhou, W. K. Pang, C. Zhang, J. Yang, Z. Chen, H. K. Liu, and Z. Guo, *ACS Nano*, **8**, 8323 (2014).
- J. M. Lu, S. Y. Zhao, S. X. Fan, Q. Lv, J. Li, and R. T. Lv, *Carbon*, **148**, 525 (2019).
- J. C. Groen, L. A. A. Peffer, and J. Pérez-Ramírez, *Microporous Mesoporous Mater.*, **60**, 1 (2003).
- B. Li, P. Gu, G. Zhang, Y. Lu, K. Huang, H. Xue, and H. Pang, *Small*, **14**, 1702184 (2018).
- P. L. Zheng et al., *Nanoscale*, **9**, 14820 (2017).
- J. Shi, Y. Wang, Q. Su, F. Cheng, X. Kong, J. Lin, T. Zhu, S. Liang, and A. Pan, *Chem. Eng. J.*, **353**, 606 (2018).
- L. Fan, X. Li, X. Song, N. Hu, D. Xiong, A. Koo, and X. Sun, *ACS Appl. Mater. Interfaces*, **10**, 2637 (2018).
- Y. C. Du, X. S. Zhu, X. S. Zhou, L. Y. Hu, Z. H. Dai, and J. C. Bao, *J. Mater. Chem. A*, **3**, 6787 (2015).
- J. Y. Long, Y. Gong, and J. H. Lin, *J. Mater. Chem. A*, **5**, 10495 (2017).
- H. Wang, X. Lu, L. Li, B. Li, D. Cao, Q. Wu, Z. Li, G. Yang, B. Guo, and C. Niu, *Nanoscale*, **8**, 7595 (2016).
- S. N. Gao, L. T. Yang, J. Shao, Q. T. Qu, Y. P. Wu, and R. Holze, *J. Electrochem. Soc.*, **167**, 100525 (2020).
- S. N. Gao, L. T. Yang, Z. C. Liu, J. Shao, Q. T. Qu, M. Hossain, Y. P. Wu, P. Adelhelm, and R. Holze, *Energy Technol.*, **8**, 2000258 (2020).
- Y. Zhao, B. Guo, Q. Yao, J. Li, J. Zhang, K. Hou, and L. Guan, *Nanoscale*, **10**, 7999 (2018).
- S. Wu et al., *Nature Commun.*, **7**, 13318 (2016).
- Z. Zeng, X. Jiang, R. Li, D. Yuan, X. Ai, H. Yang, and Y. Cao, *Adv. Sci.*, **3**, 1600066 (2016).
- M. G. Park, D. H. Lee, H. Jung, J. H. Choi, and C. M. Park, *ACS Nano*, **12**, 2955 (2018).
- S. B. Wang, Y. J. Fang, X. Wang, and X. W. Lou, *Angew. Chem. Int. Ed.*, **58**, 760 (2019).
- H. D. Bian, Z. B. Li, X. F. Xiao, P. Schmuki, J. Lu, and Y. Y. Li, *Adv. Funct. Mater.*, **29**, 1901000 (2019).
- S.-W. Zhang, W. Lv, D. Qiu, T. F. Cao, J. Zhang, Q. W. Lin, X. R. Chen, Y.-B. He, F. Y. Kang, and Q.-H. Yang, *J. Mater. Chem. A*, **7**, 10761 (2019).
- Y. Zheng, T. F. Zhou, C. F. Zhang, J. F. Mao, H. K. Liu, and Z. P. Guo, *Angew. Chem. Int. Ed.*, **55**, 3408 (2016).
- P. L. He, Y. J. Fang, X.-Y. Yu, and X. W. Lou, *Angew. Chem. Int. Ed.*, **56**, 12202 (2017).
- G. Gao, D. Tie, H. Ma, H. Yu, S. Shi, B. Wang, S. Xu, L. Wang, and Y. Zhao, *J. Mater. Chem. A*, **6**, 6675 (2018).
- M. V. Reddy, R. Jose, A. L. Viet, K. I. Ozoemena, B. V. R. Chowdari, and S. Ramakrishna, *Electrochim. Acta*, **128**, 198 (2014).
- F. X. Wang et al., *Adv. Mater.*, **32**, 1905361 (2019).
- T. Zhou, W. Lv, J. Li, G. Zhou, Y. Zhao, S. Fan, B. Liu, B. Li, F. Kang, and Q.-H. Yang, *Energy Environ. Sci.*, **10**, 1694 (2017).
- C. Wang, F. Wang, Z. Liu, Y. Zhao, Y. Liu, Q. Yue, H. Zhu, Y. Deng, Y. Wu, and D. Zhao, *Nano Energy*, **41**, 674 (2017).