A general polymer-assisted spinodal decomposition strategy is used to prepare hierarchically porous sodium super ionic conductor (NASICON)-structured polyanion-type materials (e.g., Na$_3$V$_2$(PO$_4$)$_3$, Li$_3$V$_2$(PO$_4$)$_3$, K$_3$V$_2$(PO$_4$)$_3$, Na$_4$MnV(PO$_4$)$_3$, and Na$_2$TiV(PO$_4$)$_3$) in a tetrahydrofuran/ethanol/H$_2$O synthesis system. Depending on the boiling point of solvents, the selective evaporation of the solvents induces both macrophase separation via spinodal decomposition and mesophase separation via self-assembly of inorganic precursors and amphiphilic block copolymers, leading to the formation of hierarchically porous structures. The resulting hierarchically porous Na$_3$V$_2$(PO$_4$)$_3$ possessing large specific surface area ($\approx 77$ m$^2$ g$^{-1}$) and pore volume ($\approx 0.272$ cm$^3$ g$^{-1}$) shows a high specific capacity of 117.6 mAh g$^{-1}$ at 0.1 C achieving the theoretical value and a long cycling life with 77% capacity retention over 1000 cycles at 5 C. This method presented here can open a facile avenue to synthesize other hierarchically porous polyanion-type materials.

1. Introduction

The sodium super ionic conductor (NASICON)-structured polyanion-type materials Na$_x$M$_2$(NO$_4$)$_3$ (N = P$^{5+}$, Mo$^{6+}$, S$^{6+}$, and Si$^{4+}$; M = V, Ti, Zr, Mn, etc.) with 3D large open framework are of significant interest because they allow the reversible and rapid Na$^+$ diffusion.[1–3] In particular, Na$_3$V$_2$(PO$_4$)$_3$ (NVP) has been regarded as excellent cathode materials for sodium-ion batteries (SIBs) due to its high theoretical energy density of 400 Wh kg$^{-1}$ and reversible capacity over 117.6 mAh g$^{-1}$.[4] Unfortunately, it is very difficult to realize the theoretical capacity as a result of the poor electronic conductivity of phosphates.[5] Furthermore, the large bulk structure of NVP with dense frameworks is bad for transportation of Na$^+$ and the uniform deposition of discharge products, thus resulting in the poor performance.[6] Up to now, many strategies, primarily including coating NVP active materials with conductive materials to improve the electronic conductivity and downsizing NVP particles to reduce the electron and Na$^+$ diffusion paths, have been proposed to address these issues.[7] In this case, encapsulation of NVP nanoparticles into 3D porous carbon skeleton has been demonstrated to be an acceptable attempt for
increasing the electronic conductivity of NVP.\textsuperscript{[8,9]} Although the properties have been improved in some aspects such as rate performance and cycling stability, it also leads to some adverse impacts such as low tap density and volumetric energy density.

Recently, hierarchically porous materials with the combination of periodic mesopores (2–50 nm) and macropores (>50 nm) hold significant potential in energy storage fields owing to their advanced physical and chemical properties as well as superior structural properties such as ultrahigh surface areas, interconnected hierarchical porosity, low density, large accessible space, and micrometer-scale particle size.\textsuperscript{[10–14]} Such characteristics both offer the rapid transportation of electrons and ions and high tap density due to close contact among nanocrystalline particles in the micrometer-sized hierarchical architecture. In the past few years, the synthesis of hierarchically macro/mesoporous materials is mainly based on the use of surfactants as soft templates to produce mesopores and the preformed colloidal crystals (e.g., polymer beads, silica beads, and foams) as hard templates to create macropores.\textsuperscript{[15–18]} However, this method usually involves laborious and complicated steps, low yields, high cost, and the resulting structural compositions are still limited to a small range, such as metal oxides, silica, and carbon.

Up to now, it is still an enormous challenge to synthesize hierarchically porous NASICON-structured polyanion-type materials, for instance NVP, using traditional synthesis methods for porous materials including nanocasting and molecular self-assembly methods. As an ionic compound, NVP is easy to be dissolved in common solvents during the process of nanocasting, which makes it extremely difficult to maintain the porous structure of product during removal of the hard template process. When using the molecular self-assembly method, it is really of hardship to regulate the deposition of inorganic precursors to the hydrophilic part of surfactant templates and co-assemble into porous structure due to the high reactivity of negatively charged phosphate anions (PO$_4^{3-}$) and positively charged metal ions (V$^{n+}$).\textsuperscript{[19]} Moreover, after the high-temperature treatment (≈700 °C), NVP particles have a strong tendency to sinter into irregular or bulk structure during crystallization process.\textsuperscript{[20]} Therefore, the development of a versatile method for the synthesis of porous NVP is highly desirable but remains a great challenge.

With this aim in mind, we develop a general polymer-assisted spinodal decomposition strategy for the synthesis of a series of hierarchically porous NASICON-structured polyanion-type materials (e.g., Na$_3$V$_2$(PO$_4$)$_3$, Li$_3$V$_2$(PO$_4$)$_3$, K$_3$V$_2$(PO$_4$)$_3$, Na$_3$MnV(PO$_4$)$_3$, and Na$_3$TiV(PO$_4$)$_3$) in a tetrahydrofuran (THF)/ethanol (EtOH)/H$_2$O synthesis system (Scheme 1). Depending on their boiling point, the selective evaporation of the solvents induces both mesophase separation via self-assembly of inorganic precursors and polymers and macrophase separation via spinodal decomposition, resulting in the formation of unique
3D-interconnected porous structures. The polymers such as amphoteric poly(ethylene oxide)-b-polystyrene (PEO-b-PS) diblock copolymer are used as the structure-directing agent (SDAs) for mesopores and carbon source to form carbon layer coating active nanocrystals and maintain the stability of porous structure during annealing process. The resulting 3D-interconnected porous carbon-coated NVP (abbreviation as 3DP-NVP@C) nanocomposites possess an open macro/mesoporous structure with large specific surface areas (up to 77 m² g⁻¹) and pore volumes (0.272 cm³ g⁻¹). Owing to their special features, the 3DP-NVP@C cathode shows a high specific capacity of 117.6 mAh g⁻¹ at 0.1 C, approaching the theoretical value, a remarkable rate capability of 96.8 mAh g⁻¹ at 10 C, and a prominent cyclic stability with 77% capacity retention over 1000 cycles at 5 C.

2. Results and Discussion

Figure S1a, Supporting Information, displays the detailed fabrication steps of hierarchically porous NVP. NVP precursor was prepared by adding phosphoric acid and sodium carbonate into the as-obtained VOSO₄ aqueous solution. After introducing the SDA of PEO₁₁₇-b-PS₁₉₀ into NVP precursor (Figure S2, Supporting Information), a transparent blue NVP precursor/PEO₁₁₇-b-PS₁₉₀/THF/EtOH/H₂O mixture was obtained. Then, the mixture could slowly evaporate the volatile components at 40 °C (THF and EtOH) and aged at 100 °C to remove solvents completely. Finally, the resulting composites were preheated at 350 °C and pyrolyzed over 700 °C in inert atmosphere, leading to highly crystalline 3DP-NVP@C. The samples obtained at different calcination temperatures are denoted as 3DP-NVP@C-T, where T refers to the calcination temperatures.

The pore structure of 3DP-NVP@C was investigated by nitrogen adsorption–desorption analysis and mercury intrusion porosimetry (Figure S1, Supporting Information). Withincreasingthecalcination temperatures from 800 to 900 °C, the BET surface areas and pore volumes of 3DP-NVP@C-700 are as high as 77 m² g⁻¹ and 0.272 cm³ g⁻¹, respectively (Table S1, Supporting Information). With increasing the calcination temperatures from 800 to 900 °C, the BET surface areas and pore volumes gradually decrease from 51 to 20 m² g⁻¹, and from 0.205 to 0.151 cm³ g⁻¹, respectively. Mercury intrusion porosimetry further reveals that 3DP-NVP@C-800 consists of multiple levels of macropore sizes ranging from 100 to 600 nm and the average pore diameter is 270 nm (Figure 1h), which agrees with the observations in TEM and SEM images.

The nanoscale X-ray computed tomography (nanoCT) was further employed to characterize the 3D macroporous structure of 3DP-NVP@C-800, which cannot destroy the structure of the sample and can reconstruct a relatively large volume of ±65 µm (Figure S5, Supporting Information). After pretreatment, the 3D-reconstructed images of 3DP-NVP@C-800 show a disordered macrostructure (Figure 2a; Figure S6a and Videos S1 and S2, Supporting Information). To unveil the characteristics of complex macrostructure, we use a pore network extraction method based on the maximal ball algorithm to simplify the 3D images and analyze the composition of macrostructure.[22] The ball-and-stick model displays that the porous structure of 3DP-NVP@C-800 is composed of pore represented by red ball and throat represented by green stick (Figure S6b, Supporting Information). Moreover, the skeletal networks for the material region (blue) and porous region (red) are established by simplifying the corresponding zoomed 3D images, which keep the topological structure and geometrical characteristic of 3DP-NVP@C-800 and exhibit a highly interconnected and co-continuous macrostructure (Figure 2b–e). The skeletal network analyses provide the detailed information of macrostructure, such as the pore size distribution (e.g., pore radius, throat radius, and throat length) and the degree of complexity (coordination number and shape factor). The main population of pore radius for 3DP-NVP@C-800 ranges from 50 to 250 nm and the average pore radius is calculated, based on the correction principle of pore and throat (see the Experimental Section, Supporting Information), to be 130 nm (Figure 2f; Table S2, Supporting Information), which is consistent with SEM images and mercury intrusion porosimetry. The throat radius is mainly distributed in the range below 150 nm and the efficient throat length can reach 50–600 nm range (Figure S6c,d, Supporting Information). We also calculate the average coordination number that refers to the number of throats connected to a pore and plays a crucial role in the pore continuity and transport properties.[23] The average coordination numbers predicted for the sample is 5, further confirming the well-interconnected macroporous structure (Figure 2g). We approximate the shape of pores and throats with arbitrary capillaries of cross-sectional shape due to the complex and highly irregular geometric profiles. The pore shape factor and throat shape factor are widely distributed in the range of 0–0.045, indicating the shapes of pore and throat are cross-sectional triangle (Figure 2h). The highly interconnected macroporous structure enables the increased interfacial area of electrolyte/electrode and fast diffusion.
of ions, which is beneficial for the applications in electrochemical systems.

The phase purity and crystallinity of 3DP-NVP@C were characterized by wide-angle X-ray diffraction (WXRD) analysis. All the diffraction peaks can be assigned to rhombohedral phase with $R-3c$ space group (JCPDS no. 53-0018), suggesting the good crystal structure of 3DP-NVP@C. And increasing the calcination temperatures from 700 to 900 °C improves the crystallinity of the samples (Figure 3a). The structural properties and composition of 3DP-NVP@C were elucidated by various spectroscopic measurements and thermogravimetric (TG) analysis. The Raman spectra of 3DP-NVP@C show the characteristic modes of NVP in the range from 50 to 1200 cm$^{-1}$, which can be attributed to the stretching vibrations of PO$_4^{3-}$. There are two types of carbon bands, including the G (graphite band) bands and D (disorder-induced phonon mode) situated at 1594 and 1342 cm$^{-1}$,
Figure 2. Macrostructure characterization of 3DP-NVP@C-800. a) Isosurface visualization of the 3D tomographic reconstruction of macrostructure of 3DP-NVP@C-800 obtained from nanoCT data. b–e) Macroporous structure is analyzed with a pore network extraction method based on the maximal ball algorithm, which simplifies the complicated 3D image into skeletal representations. The zoomed images of b) material (blue) and c) porous (red) regions, the skeletal networks for the d) material (blue) regions and the e) porous (red) regions. f) Population distribution of pore radius, g) coordination number, and h) shape factor. Note: the definitions of pore, throat, and shape factor are shown in Figures S7 and S8, Supporting Information.

respectively (Figure 3b). The intensity ratios of D band to G band ($I_D/I_G$) for 3DP-NVP@C-700, 3DP-NVP@C-800, and 3DP-NVP@C-900 are 1.01, 0.98, and 0.89, respectively, indicating the relatively higher graphitization degree of 3DP-NVP@C-900. X-ray photoelectron spectroscopy (XPS) reveals the presence of C, Na, O, P, and V signals in all samples (Figure S9, Supporting Information). The existence of two valence states ($V^{3+}$ and $V^{4+}$) of V can be observed in V 2p high-resolution XPS spectra of 3DP-NVP@C (Figure 3c). The presence of $V^{4+}$ may be ascribed to the oxidation of the samples in air. The C 1s high-resolution XPS spectra (Figure 3d) of 3DP-NVP@C can be deconvoluted into four types of carbon, namely, sp$^2$-hybridized carbon (C–C, C=O) and sp$^3$-hybridized carbon (C–O, O–C=O). The high content of C–C in 3DP-NVP@C-800 and 3DP-NVP@C-900 suggests the superior conductivity (Table S3, Supporting Information).

Determined from TG analysis and CHN elemental analysis, the 3DP-NVP@C-900 possesses minimal carbon content (1.9%) as compared with 3DP-NVP@C-700 (4.2%) and 3DP-NVP@C-800 (2.7%) (Figure S10 and Table S4, Supporting Information). Due to the low carbon content and large crystalline grains of 3DP-NVP@C-900, it possesses the highest tap density of 1.02 g cm$^{-3}$, followed by 3DP-NVP@C-800 (0.93 g cm$^{-3}$) and 3DP-NVP@C-700 (0.81 g cm$^{-3}$).

Based on the above results, we propose a polymer-assisted spinodal decomposition strategy for the synthesis of 3DP-NVP@C (Scheme 1). First, the PEO$_{117}$-b-PS$_{190}$/THF solution is introduced in NVP precursor/H$_2$O/EtOH solution to form a transparent blue solution with an obvious Tyndall effect. The dynamic light scattering (DLS) experiments reveal the micellar sizes of 45 nm in the mixture are larger than those of PEO$_{117}$-b-PS$_{190}$ unimer ($\approx$ 33 nm) (Figure S11, Supporting Information), indicating the NVP precursor can interact with the PEO block in PEO$_{117}$-b-PS$_{190}$ by favorable enthalpic interactions (e.g., hydrogen bonding, ionic interactions) and self-assemble into spherical core–shell composite micelles with the core of PS block and the shell of PEO block/NVP precursor. In the initial stage of solvent evaporation at 40 °C for 4 h, these composite micelles can self-assemble and gradually flock together to form uniform mesostructures driven by the interfacial force of THF and water (Figure 4a; Figure S12, Supporting Information). Along with the further evaporation of solvents at 40 °C for 24 h, the removal of highly volatile solvents (THF and EtOH) leads to NVP
precursor/PEO\textsubscript{117}-b-PS\textsubscript{190} composites more insoluble owing to the strong hydrophobicity of the PS block, and thus the stable mixture enters a supersaturated state-thermodynamically unstable state. It functions as a driving force to trigger the macrophase separation through spinodal decomposition to form macro pores (Figure S13, Supporting Information).\textsuperscript{[28,29]} Meanwhile, the composite micelles are gradually destroyed and the NVP precursor grows and gathers, which results in the collapse of pore walls and the combination of mesopores and macropores, thus forming a hierarchically porous structures (step 1, Figure 4b,c; Figure S14, Supporting Information).\textsuperscript{[30]} Subsequent removing H\textsubscript{2}O at 100 °C for 24 h further enhances the destruction of mesophases and the growth of NVP precursor, and forms the inorganic–organic hybrid composites (step 2, Figure 4d; Figure S15, Supporting Information). By preheating at 350 °C in N\textsubscript{2} atmosphere, SEM images indicate the obtained sample possesses a porous structure constituted of small nanoparticles (Figure 4e,f). FT-IR spectrum of the product reveals the peaks in the range of 1200–2000 cm\textsuperscript{−1}, corresponding to the monosubstituted benzene rings in PEO\textsubscript{117}-b-PS\textsubscript{190}, almost disappear, which confirms the most decomposition of PEO\textsubscript{117}-b-PS\textsubscript{190} (Figure S16, Supporting Information). The residual PEO\textsubscript{117}-b-PS\textsubscript{190} can be carbonized into rigid carbon to form the carbon coating layer and be in situ used as stabilizer to prevent the uncontrolled aggregation of NVP nanoparticles and maintain the stability of porous structure. After further pyrolysis over 700 °C, NVP precursor can be crystallized without the structure collapse (step 3). Finally, the highly crystalline NVP with hierarchically porous structures is obtained.

The effect of polymers and types of solvents on the porous structure of NVP were also investigated to demonstrate the formation mechanism of 3DP-NVP@C. In a comparative experiment without PEO\textsubscript{117}-b-PS\textsubscript{190}, when H\textsubscript{2}O is directly used as the solvent (Figure S1b, Supporting Information), the evaporation of single solvent (H\textsubscript{2}O) cannot be used as the stimulus for macrophase separation, the nonporous bulk NVP (denoted as NPB-NVP) is obtained (Figure S17a, Supporting Information), suggesting the multicomponent solvents are vital for the macrophase separation. When using EtOH/H\textsubscript{2}O or THF/EtOH/H\textsubscript{2}O as solvents without any polymers (Figure S1c, Supporting Information), the selective evaporation of three solvents at 40 °C for 24 h can act as a trigger to induce macrophase segregation between the H\textsubscript{2}O-rich phase and the NVP precursor-rich phase (Figure S18a, Supporting Information). Subsequent thoroughly removing H\textsubscript{2}O at 100 °C for 24 h leaves highly interconnected macro pores (Figure S18b,c, Supporting Information). After pyrolysis at 700 °C in N\textsubscript{2} atmosphere, SEM and TEM images exhibit the porous bulk NVP only possesses the macroporous structures with low pore volumes (Figure S17b–i, Supporting Information), confirming that PEO\textsubscript{117}-b-PS\textsubscript{190} is the decisive factor for mesophase segregation.

Under the guidance of the synthesis of 3DP-NVP@C, the poly mer assisted-spinodal decomposition strategy can be extended...
to prepare other hierarchically porous NASICON-structured polyanion-type materials (e.g., Li$_3$V$_2$(PO$_4$)$_3$, K$_3$V$_2$(PO$_4$)$_3$, Na$_4$MnV(PO$_4$)$_3$, and Na$_2$TiV(PO$_4$)$_3$) by introduction of corresponding inorganic precursors into the reaction system (Figure S19, Supporting Information). Moreover, the porous polyanion-type materials can also be synthesized by using other polymers as SDAs, such as triblock copolymer (Pluronic P127 and P123) and poly(ethylene oxide) (PEO-5000), and so forth, and the corresponding results are shown in Figure S20 and Table S5, Supporting Information. These extending results suggest that our proposed strategy can be generalized for synthesizing hierarchically porous polyanion-type materials of other topologies by rationally selecting the polymers and inorganic precursors.

The electrochemical properties of 3DP-NVP@C obtained at different calcination temperatures and NPB-NVP-900 (the sample calcined at 900 °C in N$_2$ atmosphere) were evaluated by the assembly of half-cells with metallic Na as anode. Cyclic voltammetry (CV) measured at different scan rates were performed to investigate the electrochemical behaviors. A pair of well-defined redox peaks in the range of 2.3–3.8 V are observed in CV curves measured at 0.1 mV s$^{-1}$ for the samples, which can be attributed to the V$^{4+}$/V$^{3+}$ redox couple reaction accompanied by Na$^+$ insertion/extraction from the NVP lattice matrix (Figure 5a). Compared with the other samples, the current of 3DP-NVP@C-900 highest, and the reduction and oxidation peaks of 3DP-NVP@C-900 shift toward higher and lower potentials, respectively, suggesting its low polarization, which may be ascribed to the high crystallinity, improved conductivity, and porous framework of 3DP-NVP@C-900. The well-defined redox peaks are still maintained even at a high scan rate of 1 mV s$^{-1}$, indicating the excellent rate performance of 3DP-NVP@C-900 (Figure S21, Supporting Information). The well linear relationship between $v^{1/2}$ (the square root of scan rate) and $I_p$ (the peak current density) confirms the diffusion-controlled reaction during the sodium storage in NVP electrodes (Figure 5b). According to Randles–Sevcik equation, the sodium-ion diffusion coefficient ($D$) of 3DP-NVP@C-900 is calculated to be 4.07 × 10$^{-11}$ cm$^2$ s$^{-1}$, higher than those of 3DP-NVP@C-800 (2.51 × 10$^{-11}$ cm$^2$ s$^{-1}$) and NPB-NVP-900 (8.87 × 10$^{-13}$ cm$^2$ s$^{-1}$), which indicates the fast charge transfer.
transfer kinetics and improved rate capability of 3DP-NVP@C-900.

The galvanostatic discharge/charge measurements of the products were carried out at the dis-/charge rate of 1 C (1 C = 117 mA g\(^{-1}\)) over a potential range of 2.3–3.8 V (vs Na\(^+\)/Na). The distinct charge and discharge plateaus at around 3.4 V, assignable to the redox pair of V\(^{3+}/V^{4+}\), is observed for 3DP-NVP@C (Figure 5c), which is consistent with the CV profiles. Among these samples, the designed 3DP-NVP@C-900 shows a smallest voltage gap between charge and discharge plateaus and decreased potential slope before the cutoff voltages, suggesting the lowest polarization. As expected, the 3DP-NVP@C-900 exhibits the highest capacity of 116.4 mAh g\(^{-1}\), followed by 3DP-NVP@C-800 (110.1 mAh g\(^{-1}\)), 3DP-NVP@C-700 (99.2 mAh g\(^{-1}\)), and then NPB-NVP-900 (60.1 mAh g\(^{-1}\)) (Figure 5c). After 100 cycles, the capacity retention of 3DP-NVP@C-900 remains 95%, which is much higher than those of 3DP-NVP@C-800 (80%) and NPB-NVP-900 (40%) (Figure S22, Supporting Information). The superior performance of 3DP-NVP@C-900, compared with 3DP-NVP@C-700 and 3DP-NVP@C-800, can be ascribed to the improved conductivity and crystallinity. Moreover, the hierarchically porous structure is beneficial for the increased interfacial area of electrolyte/electrode and guarantees the fast transportation of electrons.\(^{[34]}\) Thus, the performance of 3DP-NVP@C-900 is much higher than that of NPB-NVP-900.

The rate performances of the samples were also studied and shown in Figure 5d. The introduction of porous structure and conductive carbon coating into the bulk NVP greatly enhances the rate performance. The 3DP-NVP@C-900 electrode delivers an improved discharge capacity of 117.6 mAh g\(^{-1}\) at the initial rate of 0.1 C, achieving the theoretical value. With increasing the current rate to 0.2, 0.5, 1.0, and 2.0 C, 5 C, and, 10 C, the discharge
3. Conclusion

In summary, we develop a facile and general polymer-assisted spinodal decomposition strategy to synthesize a series of hierarchically porous NASICON-structured materials. Based on the boiling point of solvents, the controlled solvent evaporation induces the multiscale phase separation in both the mesoscopic and macroscopic ranges. During this process, the polymers such as PEO_{117}-b-PS_{190} are used as SDAs and carbon sources to form carbon-coated active nanocrystals and prevent the collapse of porous structure during the crystallization of inorganic precursors. So, this method can be generalized for synthesizing other hierarchically porous polyanion-type materials with defined porosity and interconnectivity by rationally selecting the polymers and inorganic precursors. Combining the advantages of the porous framework and inherent NASICON structure of NVP, the obtained 3DP-NVP@C electrodes exhibit the excellent sodium storage performances. The method may open new horizons in constructing advanced hierarchically porous materials, such as NaFePO_4, NaTi_2(PO_4)_3, NaV_{1-x}M_xPO_4F, Na_4(VO_1-xPO_x)_2F_{1+2x} (0 < x < 1), and so on.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

hierarchically porous structures, macro/mesoporous materials, NASICON-structured materials, self-assembly, spinodal decomposition

[1] D. Wang, X. Bie, Q. Fu, D. Dixon, N. Bramnik, Y.-S. Hu, F. Fauth, Y. Wei, H. Ehrenberg, G. Chen, F. Du, Nat. Commun. 2017, 8, 15888.
[2] Z. Jian, Y.-S. Hu, X. Li, W. Chen, Adv. Mater. 2017, 29, 1601925.
[3] Y. Qi, Z. Tong, J. Zhao, L. Ma, T. Wu, H. Liu, C. Yang, J. Lu, Y.-S. Hu, Joule 2018, 2, 2348.
[4] Q. Zheng, H. Yi, X. Li, H. Zhang, J. Energy Chem. 2018, 27, 1597.
[5] Q. An, F. Xiong, Q. Wei, J. Sheng, L. He, D. Ma, Y. Yao, L. Ma, Adv. Energy Mater. 2015, 5, 1401963.
[6] X. Cao, A. Pan, B. Yin, G. Fang, Y. Wang, X. Kong, T. Zhu, J. Zhou, G. Cao, S. Liang, Nano Energy 2019, 60, 312.
[7] W. Ren, X. Yao, C. Niu, Z. Zheng, K. Zhao, Q. An, Q. Wei, M. Yan, L. Zhang, L. Mai, Nano Energy 2016, 28, 216.
[8] Y. Jiang, Z. Yang, W. Li, L. Zeng, F. Pan, M. Wang, X. Wei, G. Hu, L. Gu, Y. Yu, Adv. Energy Mater. 2015, 5, 1402104.
[9] Y. Fang, L. Xiao, X. Ai, Y. Cao, H. Yang, Adv. Mater. 2015, 27, 5895.
[10] L. Chen, M. Sun, Z. Wang, W. Yang, Z. Xie, B.-L. Su, Chem. Rev. 2020, 120, 11194.
[11] L. Wu, Y. Li, Z. Fu, B.-L. Su, Natl. Sci. Rev. 2020, 7, 1667.
[12] J. Jin, L. Wu, S. Huang, M. Yan, H. Wang, L. Chen, T. Hasan, Y. Li, B.-L. Su, Small Methods 2018, 2, 1800171.
[13] Y. Boyjoo, H. Shi, Q. Tian, S. Liu, J. Liang, Z. Wu, M. Jaroniec, J. Liu, Energy Environ. Sci. 2021, https://doi.org/10.1039/D0EO03316B.
[14] S. Yu, G. Xing, L. Chen, T. Ben, B.-L. Su, Adv. Mater. 2020, 32, 2003270.
[15] R. Zhang, D. Shen, M. Xu, D. Feng, W. Li, G. Zheng, R. Che, A. Elzatahry, D. Zhao, Adv. Energy Mater. 2014, 4, 1301725.
[16] Y. Liu, K. Lan, A. Bagabas, P. Zhang, W. Gao, J. Wang, Z. Sun, J. Fan, Small 2016, 12, 860.
[17] T. Zhao, Y. Ren, J. Yang, L. Wang, W. Jiang, A. Elzatahry, A. Alghamdi, Y. Deng, D. Zhao, W. Luo, J. Mater. Chem. A 2016, 4, 16446.
[18] T. Sun, N. Shan, L. Xu, J. Wang, J. Chen, A. A. Kakhidov, R. H. Baughman, Chem. Mater. 2018, 30, 1617.
[19] B. Bastakoti, Y. Li, S. Guragain, M. Pramanik, S. Alshehri, T. Ahamad, Z. Liu, Y. Yamauchi, Chem. - Eur. J. 2016, 22, 7463.
[20] D. Yang, Z. Lu, X. Rui, X. Huang, H. Li, J. Zhu, W. Zhang, Y. Lam, H. Hng, H. Zhang, Q. Yan, Angew. Chem. Int. Ed. 2014, 53, 9352.
[21] H. Xiong, L. Wu, Y. Liu, T. Gao, K. Li, Y. Long, R. Zhang, L. Zhang, Z. Qiao, Q. Huo, X. Ge, S. Song, H. Zhang, Adv. Energy Mater. 2019, 9, 1901634.
[22] H. Dong, M. Blunt, *Phys. Rev. E* **2009**, *80*, 036307.
[23] C. Jo, J. Hwang, W. Lim, J. Lim, K. Hur, J. Lee, *Adv. Mater.* **2018**, *30*, 1703829.
[24] Y. Cai, X. Cao, Z. Luo, G. Fang, F. Liu, J. Zhou, A. Pan, S. Liang, *Adv. Sci.* **2018**, *5*, 1800680.
[25] J. Guo, P. Wang, X. Wu, X. Zhang, Q. Yan, H. Chen, J. Zhang, Y. Guo, *Adv. Mater.* **2017**, *29*, 1701968.
[26] E. Wang, M. Chen, X. Liu, Y. Liu, H. Guo, Z. Wu, W. Xiang, B. Zhong, X. Guo, S. Chou, S. Dou, *Small Methods* **2018**, *3*, 1800169.
[27] W. Luo, Y. Li, J. Dong, J. Wei, J. Xu, Y. Deng, D. Zhao, *Angew. Chem. Int. Ed.* **2013**, *52*, 10505.
[28] J. Hwang, C. Jo, K. Hur, J. Lim, S. Kim, J. Lee, *J. Am. Chem. Soc.* **2014**, *136*, 16086.
[29] W. Lim, C. Jo, A. Cho, J. Hwang, S. Kim, J. Han, J. Lee, *Adv. Mater.* **2019**, *31*, 1806547.
[30] T. Inoue, *Prog. Polym. Sci.* **1995**, *20*, 119.
[31] S. Li, Y. Dong, L. Xu, X. Xu, L. He, L. Mai, *Adv. Mater.* **2014**, *26*, 3545.
[32] Y. Xu, Q. Wei, C. Xu, Q. Li, Q. An, P. Zhang, J. Sheng, L. Zhou, L. Mai, *Adv. Energy Mater.* **2016**, *6*, 1600389.
[33] J. Fang, S. Wang, Z. Li, H. Chen, L. Xia, L. Dinga, H. Wang, *J. Mater. Chem. A* **2016**, *4*, 1180.
[34] T. Wei, G. Yang, C. Wang, *Nano Energy* **2017**, *39*, 363.
[35] H. Xiong, H. Zhou, G. Sun, Z. Liu, L. Zhang, L. Zhang, F. Du, Z. Qiao, S. Da, *Angew. Chem., Int. Ed.* **2020**, *59*, 11053.
[36] P. Wang, S. Sun, Y. Jiang, Q. Cai, Y. Zhang, L. Zhou, S. Fang, J. Liu, Y. Yu, *ACS Nano* **2020**, *14*, 15577.