Energy Storage



S-Doped TiSe₂ Nanoplates/Fe₃O₄ Nanoparticles Heterostructure

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2D Sulfur-doped TiSe₂/Fe₃O₄ (named as S-TiSe₂/Fe₃O₄) heterostructures are synthesized successfully based on a facile oil phase process. The Fe₃O₄ nanoparticles, with an average size of 8 nm, grow uniformly on the surface of S-doped TiSe₂ (named as S-TiSe₂) nanoplates (300 nm in diameter and 15 nm in thickness). These heterostructures combine the advantages of both S-TiSe₂ with good electrical conductivity and Fe₃O₄ with high theoretical Li storage capacity. As demonstrated potential applications for energy storage, the S-TiSe₂/Fe₃O₄ heterostructures possess high reversible capacities (707.4 mAh g⁻¹ at 0.1 A g⁻¹ during the 100th cycle), excellent cycling stability (432.3 mAh g⁻¹ after 200 cycles at 5 A g⁻¹), and good rate capability (e.g., 301.7 mAh g⁻¹ at 20 A g⁻¹) in lithium-ion batteries. As for sodium-ion batteries, the S-TiSe₂/Fe₃O₄ heterostructures also maintain reversible capacities of 402.3 mAh g⁻¹ at 0.1 A g⁻¹ after 100 cycles, and a high rate capacity of 203.3 mAh g⁻¹ at 4 A g⁻¹.

In recent years, titanium-based compounds have attracted great interests for various applications including thermoelectronics,^[1] charge density wave devices,^[2] intelligent solar control,^[3] photo-thermal cancer therapy,^[4] catalysis,^[5,6] and energy storages.^[7,8] Among them, TiO₂ has been explored as a promising electrode material for lithium-ion batteries (LIBs) or sodium-ion batteries

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(SIBs) due to its safe and stable working plateau potential (about 1.5-1.75 V vs Li/Li⁺), good structural stability, long lifespan, excellent rate capability as well as the low processing cost and simplicity of syntheses.^[9,10] However, TiO₂ possesses a low theoretical capacity (335 mAh g^{-1}), which is less than that of commercial graphite (372 mAh g⁻¹).^[11] Moreover, the reported capacity of TiO₂ is sometime far below its theoretical value. For example, Wang and co-workers reported a reversible capacity of 237 mAh g⁻¹ after 100 cycles at a current rate of 1 C for the multishelled TiO₂ hollow microspheres;^[12] and anatase TiO_2 nanosheets with the first charge capacity of 169 mAh g⁻¹ at a current rate of 5 C can be achieved as reported by Lou and co-workers.^[13] This is possibly due to the low ion diffusion coefficient and

intrinsic low electrical conductivity,^[14] which limits its application in LIBs and SIBs. Similar challenge is encountered for TiS₂ with a low theoretical capacity of 240 mAh g⁻¹ due to the insertion mechanism.^[15,16] Nevertheless, it is reported that TiS₂ suffers from the irreversible changes at the surface and distorted structures to form Li dendrites, resulting in rapid capacity fading upon cycling, especially in the high potential region.^[17,18] On the other hand, modifications of the typical anode materials, such as graphene,^[19–21] transition-metal dichalcogenides,^[22] and MXenes^[23] have been successfully identified, and their improved performances as an anode material of Li/Na-ion batteries are expected to be explored.

Transition metal selenide, such as titanium selenide, shows much lower optical bandgap and much higher electrical conductivity compared to their sulfide counterparts or oxide.^[24] TiSe₂ can be a good candidate in LIBs and SIBs because of the relatively high electrical conductivity and theoretical capacity (520 mAh g⁻¹ based on conversion reaction). In addition, sulfur doping in selenides has been demonstrated to effectively increase the charge carrier concentration and electrical conductivity due to the bonding defects induced by sulfur doping.^[25–27] These are the remarkable advantages for sulfur doped TiSe₂ as an active material for high-rate and high-capacity lithium storage applications, which has not been explored. In addition, further increasing the Li storage capacities of TiSe₂-based electrodes is desired as the theoretical capacity of TiSe₂ is relatively lower than many transition-metal oxide anodes.^[28–31] Thus,

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Figure 1. a) XRD pattern of the $TiSe_2$ and S- $TiSe_2$, b) XPS high-resolution spectrum of the S 2p of S- $TiSe_2$.

 $TiSe_2$ can be considered as a framework that incorporates a secondary phase with high specific capacities to form heterostructures. In this regard, Fe_3O_4 is a good choice to couple with $TiSe_2$ due to its high theoretical capacity (e.g., 926 mAh g⁻¹), natural abundance, and environmental benignity.^[32] Combination of these two materials with a rationally designed heterostructure and the complementary features may lead to improved Li/Na storage properties.

Herein, we report a two-step facile oil phase process to prepare heterostructures with Fe₃O₄ nanoparticles anchored on S-TiSe₂ hexagonal nanoplates. The S-TiSe₂ nanoplates were obtained in oil phase with an average lateral size of 300 nm and a thickness of 15 nm. The heterostructure is obtained by using the S-TiSe₂ nanoplates as the heterogeneous nucleation supports to grow Fe₃O₄ nanoparticles with an average size of ≈8 nm. The obtained heterostructured S-TiSe₂ nanoplates/Fe₃O₄ nanoparticles (S-TiSe₂/Fe₃O₄) exhibit improved performance in Li/Na storage versus the bare S-TiSe₂ nanoplates. Serving as lithium-ion battery electrodes, the S-TiSe₂/Fe₃O₄ exhibits a large reversible capacities of 707.4 mAh g^{-1} at 0.1 A g^{-1} during the 100th cycle, which is higher than those of the S-TiSe₂ nanoplates (168.8 mAh g^{-1}) and the pure Fe_3O_4 (487.7 mAh g⁻¹). Besides, good rate capability (e.g., 301.7 mAh g^{-1} at 20 A g^{-1}) and excellent cycling stability (432.3 mAh g⁻¹ after 200 cycles at 5 A g⁻¹) can be achieved during the Li⁺ intercalation and deintercalation process. As for Na storage, the S-TiSe₂/Fe₃O₄ heterostructures also maintain high reversible capacities of 402.3 mAh g^{-1} at 0.1 A g^{-1} during the 100th cycle and a high rate capacity 203.3 mAh g^{-1} at 4 A g^{-1} .

For comparison purpose, the pure TiSe_2 nanoplates are first synthesized by reacting TiCl_4 and selenium powder in a hot oleylamine/trioctylphosphine solution. The crystalline phase of TiSe_2 was first investigated by X-ray diffraction (XRD) and the result is shown in **Figure 1a**. By comparing the XRD pattern of the sample and standard data from the Joint Committee on Powder Diffraction Standards (JCPDS), all the diffraction peaks are in good agreement with the hexagonal type TiSe_2 (JCPDS no. 71-4828). The scanning electron microscope (SEM) images of the as-prepared TiSe_2 reveal that uniform nanoplates with an average lateral size of a few µm can be obtained (Figure S1a,b, Supporting Information). Without addition of the trioctylphosphine (TOP), flower-shaped TiSe_2 nanoclusters are obtained with obvious agglomeration of the nanocrystals (Figure S2, Supporting Information). This indicates that the TOP can serve as a capping ligand, which is supposed to bind strongly to Se.^[33] The S-doping is introduced by addition of the sulfur powder during the synthesis of TiSe₂ nanoplates. The XRD pattern (Figure 1a) of S-TiSe₂ reveals that the diffraction peaks can also be indexed to hexagonal TiSe₂ (JCPDS no. 71-4828). Compared to the pure TiSe₂, the XRD pattern of S-TiSe₂ reveals the diffraction peaks with a slight displacement to higher angles. This right shift is probably due to the smaller ionic radius of S atoms. In the Raman spectroscopy, both nanoplate samples exhibit two peaks, which are related to the composition-dependent vibration modes (Figure S3a, Supporting

Information). The observed peaks from pure TiSe2 at 185 and 354 cm⁻¹ are attributed to the out-of-plane vibrational mode A_{1g} and in-plane vibrational mode E_{2g} of Ti-Se bond, respectively.^[34] The S-TiSe₂ features the evident band broadening and the two peaks shift to lower frequency range, implying a possible structural disorder due to the S-doping.^[35] The UV-vis-NIR absorption of the TiSe2 and S-TiSe2 samples is shown in the inset of Figure S3b (Supporting Information). From the spectroscopy, the optical bandgaps of TiSe₂ and S-TiSe₂ can be calculated to 0.38 and 0.31 eV, respectively (Figure S3b, Supporting Information). The bandgap narrowing of the S-TiSe₂ may lead to higher electrical conductivity.[36-38] The chemical state of the S-TiSe₂ sample is investigated by X-ray photoelectron spectroscopy (XPS). The high-resolution Ti 2p XPS spectrum (Figure S4a, Supporting Information) exhibits the major Ti $2p_{3/2}$ peak at 457.8 eV and the Ti $2p_{1/2}$ peak at 464.1 eV, which reveals the predominant valence state of the Ti is Ti^{4+,[39]} As shown in Figure S4b (Supporting Information), the 3d peaks of selenium at around 54.0 eV can be divided into two well-defined peaks: Se $3d_{5/2}$ at 53.8 eV and Se $3d_{3/2}$ at 55.2 eV, confirming the existence of Se²⁻ in the sample.^[40] Two XPS peaks of S 2p are observed at 160.8 and 166.7 eV, respectively, in the S-TiSe₂ (Figure 1b). They were assigned to the Ti-S and S-Ti-Se bonding due to the S dopants, respectively.^[41,42] From the XPS peaks, the atomic ratio of S/Se can be calculated to be 0.19. These results demonstrate the successful preparation of TiSe₂ with S doping.

Figure 2a shows the SEM image of S-TiSe₂, and it can be clearly seen that uniform nanoplates can be obtained after the addition of sulfur. The lateral size of these nanoplates was 300 nm, which is much smaller than that of pristine TiSe₂. This indicates S anions can act as a growth-control agent and lead to a decrease of the nanostructure size as previously reported.^[43,44] The transmission electron microscope (TEM) image (Figure 2b) the S-TiSe₂ indicate that the product is hexagonal nanoplates with the edge length of about 150 nm. The high-resolution transmission electron microscope (HRTEM) image (Figure 2c) of a single S-TiSe₂ plate shows it is single crystalline. The observed lattice fringes with interplanar distance of 0.17 nm can be indexed to the (110) planes of TiSe₂. Notably, the TEM image of the side view (Figure 2d) of the nanoplates exhibits that the thickness is about 15 nm. The scanning TEM image and the corresponding energy dispersive X-ray spectroscopy (EDX) elemental mapping images (Figure S5, Supporting



Figure 2. a) SEM image and b) TEM images of S-TiSe₂, c) HRTEM images of S-TiSe₂, and d) sectional TEM image of S-TiSe₂.

Information) reveal the uniform distribution of Ti, Se, S elements in the nanoplate. The different molar ratio of S/Se is applied to adjust the doping content of the S and consequently influence the nucleation and growth of S-TiSe₂ nanocrystals (Figure S6, Supporting Information). With the increased S content, the lateral dimension of individual nanoplate increases, and finally nanosheets can be obtained with the molar ratio of S/Se = 1:1.

S-TiSe₂/Fe₃O₄ heterostructures were prepared by decomposing iron–oleate complex in oleyamine with the presence of S-TiSe₂ nanoplates. **Figure 3**a shows the XRD pattern of S-TiSe₂/ Fe₃O₄ composites, and it can be seen that all the major diffraction peaks can also be assigned to hexagonal TiSe₂ (JCPDS no. 71-4828). Additionally, the prominent peak at 35.5° can be indexed to (311) planes of cubic Fe₃O₄ (JCPDS no. 07-0322). The XPS result was used to further analyze the samples. The XPS spectrums of Ti 2p, S 2p, and Se 3d (Figure S7a–c, Supporting Information) are almost the same as the above mentioned S-TiSe₂. Figure S7d (Supporting Information) shows the XPS result of the Fe 2p regions, and the peak of Fe 2p_{3/2} at 710.8 eV indicates the existence of both Fe²⁺ and Fe³⁺. The satellite peak located at 718.8 eV is proven to be a characteristic peak of Fe³⁺ in γ -Fe₂O₃, which suggests that the Fe₃O₄ is partly oxides.^[45]

Figure 3b shows the SEM image of S-TiSe₂/Fe₃O₄ heterostructures, where Fe₃O₄ nanoparticles anchored on hexagonal nanoplates. The TEM images (Figure 3c) show that the size of Fe₃O₄ nanoparticles is around 8 nm. The HRTEM image (Figure 3d) reveals the interplanar distance of 0.30 nm in the nanodomain corresponds to the (311) planes of Fe₃O₄, and the interplanar distances of 0.30 nm can be assigned to (002) planes of TiSe₂. Further EDX analysis (Figure S8, Supporting Information) shows the atomic ratio of Ti:Fe = 0.28:0.13. Thereafter, the weight percentage of Fe_3O_4 in the composite material is calculated to be 14.9%. For comparison, pure Fe₃O₄ nanoparticles can be obtained by directly decomposing iron-oleate complex in oleyamine. The XRD pattern (Figure S9a, Supporting Information) of the pure Fe₃O₄ shows that all the diffraction peaks can also be assigned to the cubic Fe₃O₄ (JCPDS no. 07-0322). The TEM image (Figure S9b, Supporting Information) indicates the Fe₃O₄ is uniform nanoparticles with an average diameter of ≈8 nm. Based on the N2 gas adsorption/ desorption measurements (Figure S10a, Supporting Information), the Brunauer-Emmett-Teller (BET) surface area of S-TiSe₂ (51.1 m² g⁻¹) is much higher than that of the pure TiSe₂ $(8.8 \text{ m}^2 \text{ g}^{-1})$, which may be related to the smaller size of S-TiSe₂. The BET surface area of S-TiSe₂/Fe₃O₄ heterostructures is calculated to be 45.9 m² g⁻¹, which is slightly lower than that of the S-TiSe₂ nanoplates (51.1 $m^2 g^{-1}$). This possibly due to the growth of Fe₃O₄ nanoparticles on the S-TiSe₂ nanoplates that may block some pores. In addition, the pore size distribution of







Figure 3. a) XRD pattern, b) SEM image and c) TEM image of S-TiSe₂/Fe₃O₄, and d) HRTEM images of S-TiSe₂/Fe₃O₄.

 $S-TiSe_2/Fe_3O_4$ heterostructures falls in the range of 18–40 nm (Figure S10b, Supporting Information).

The LIBs performance of S-TiSe₂/Fe₃O₄ heterostructures was evaluated by assembling the sample into coin cells with lithium foil as both the counter and reference electrodes. Figure 4a shows the cyclic voltammetry (CV) curves of S-TiSe₂/Fe₃O₄ heterostructures obtained between 0.005 to 3.0 V at a scan rate of 0.2 mV s⁻¹. The Li⁺ insertion and desertion mechanisms of TiSe₂ have not been identified in the previous studies, which are considered to be similar to those of transition metal selenide because of their similar crystal structure. The electrochemical reaction of TiSe₂ for Li-ion storage is proposed based on those of transition metal selenide.^[46-48] In the first cycle, three dominating cathodic peaks are observed at 0.56, 1.35, and 1.54 V, respectively. The reduction peak at 1.35 and 1.54 V can be attributed to Li insertion into the interlayers of TiSe₂, producing Li_xTiSe₂ (Equation (1)).^[49] Additionally, the peak at 0.56 V is assigned to formation of metal Ti and Li₂Se (Equation (2)), and is accompanied by the formation of a solid electrolyte interphase (SEI) layer.^[50,51] During the first anodic process, two peaks located at 1.95 and 2.23 V correspond to the conversion reaction of Li₂Se and Ti to Ti ion (Equations (3) and (4)).^[52] The discharge and charge processes can be summarized below.

Discharge process:

$$TiSe_2 + xLi^+ + xe^- \to Li_xTiSe_2 \tag{1}$$

$$\operatorname{Li}_{x}\operatorname{Ti}\operatorname{Se}_{2} + (4 - x)\operatorname{Li}^{+} + (4 - x)e^{-} \to \operatorname{Ti} + 2\operatorname{Li}_{2}\operatorname{Se}$$
(2)

Charge process:

$$Ti + 2Li_2Se \rightarrow Li_xTiSe_2 + (4 - x)Li^+ + (4 - x)e^-$$
 (3)

$$\mathrm{Li}_{x}\mathrm{Ti}\mathrm{Se}_{2} \to \mathrm{Ti}\mathrm{Se}_{2} + x\mathrm{Li}^{+} + xe^{-}$$
(4)

Upon subsequent cycling, the cathodic peaks shift slightly to the higher voltage range than that in the first cycle, probably because of the microstructure alteration after the first lithiation/ delithiation cycle. This is commonly observed in other conversion reaction-based anode materials.^[53,54] The CV curves of the S-TiSe₂/Fe₃O₄ electrode are almost overlapped during the subsequent cycles, indicating a highly reversible electrochemical process. For comparison, the CV curves of S-TiSe₂ and S-TiSe₂/ Fe₃O₄ between 0.005 and 3.0 V at a scan rate of 0.2 mV s⁻¹ are shown in Figure S11 (Supporting Information). It can be seen obviously that the area of CV curves for S-TiSe₂/Fe₃O₄ is much larger than that of the S-TiSe₂, indicating the significantly improved capacity.

Figure 4b shows the charge–discharge voltage profiles of S-TiSe₂/Fe₃O₄ heterostructures at a current density of 0.1 A g⁻¹. In the first cycle, the S-TiSe₂/Fe₃O₄ electrode delivers discharge capacities of 1150.6 mAh g⁻¹ and charge capacities of







Figure 4. Electrochemical performance for LIBs at room temperature (25 °C). a) Cyclic voltammograms of S-TiSe₂/Fe₃O₄ between 0.005 and 3.0 V at a scan rate of 0.1 mV s⁻¹. b) Charge–discharge voltage profiles of S-TiSe₂/Fe₃O₄ at a current density of 0.1 A g⁻¹. c) Cycling performance and Coulombic efficiency of S-TiSe₂ and S-TiSe₂/Fe₃O₄ at 0.1 A g⁻¹. d) Rate capability of S-TiSe₂/Fe₃O₄ at various current rates, e) long-term cycling performance of the S-TiSe₂/Fe₃O₄ and pure Fe₃O₄ at a current density of 2.0 A g⁻¹.

780.7 mAh g⁻¹, with a Coulombic efficiency of 67.9%. All the potential plateaus in the discharge–charge curves match the redox peaks observed in the CV curves. During the subsequent cycle, The S-TiSe₂/Fe₃O₄ shows discharge capacities of 789.3 mAh g⁻¹ and a charge capacities of 763.2 mAh g⁻¹, corresponding to a Coulombic efficiency of 96.7%. The cycling performances of the S-TiSe₂, pure Fe₃O₄ and S-TiSe₂/Fe₃O₄ are shown in Figure 4c. The pure Fe₃O₄ and S-TiSe₂ electrodes give initial discharge capacities of 1251.3 and 411.2 mAh g⁻¹ at 0.1 A g⁻¹, respectively. But the capacities drop rapidly to 487.9 and 168.8 mAh g⁻¹, respectively, after 100 cycles. By contrast, the S-TiSe₂/Fe₃O₄ heterostructures shows higher reversible capacities of 707.4 mAh g⁻¹ at 0.1 A g⁻¹ after 100 discharge/ charge cycles.

For comparison, the rate capability of S-TiSe₂ and pure TiSe₂ is provided in Figure S12 (Supporting Information). It can be observed that S-TiSe₂ has better rate capability than pure TiSe₂ due to the significantly enhanced electrical conductance with S-doping (Figure S13, Supporting Information). Therefore, we choose S-TiSe₂ as a framework that incorporates Fe_3O_4 nanoparticles to form S-TiSe₂/Fe₃O₄ heterostructures to further improve the capacity of S-TiSe₂. The

rate capability of the as prepared S-TiSe₂/Fe₃O₄ heterostructures is evaluated at various current densities from 0.1 to 20 A g⁻¹. As demonstrated in Figure 4d, the reversible capacities of the composite are 739.8, 671.8, 623.6, 565.3, 495.4, 435.7, 360.7, and 301.7 mAh g⁻¹ at current densities of 0.1, 0.2, 0.5, 1, 2, 5, 10, and 20 A g⁻¹. After changing the current density from 20 to 0.1 A g⁻¹, the specific capacity returns to 724.4 mAh g⁻¹. The S-TiSe₂/Fe₃O₄ and Fe₃O₄ electrodes were charged/discharged at a high current density of 2 A g⁻¹ for a long-term cycling test (Figure 4e). The S-TiSe₂/Fe₃O₄ electrode maintains a high specific capacities of 432.3 mAh g⁻¹ after 200 cycles. The Fe₃O₄ electrode shows a specific capacities of 318.7 mAh g⁻¹ after 200 cycles.

Electrochemical impedance spectroscopy (EIS) is carried out to describe charge-transfer mechanisms of the S-TiSe₂/ Fe₃O₄ heterostructures in LIBs. Figure S14 (Supporting Information) shows the Nyquist plots of S-TiSe₂ and S-TiSe₂/ Fe₃O₄ after 1 and 100 cycles. Each Nyquist plot comprises a depressed semicircle at medium frequency and a sloping line in the low frequency region.^[55] The semicircle is defined as the charge-transfer impedance (R_{ct}), and straight line represents the Warburg impedance (Wo). Additionally, the high frequency



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region is related to the ohmic resistance (Re). It is obviously seen that the R_{ct} of S-TiSe₂/Fe₃O₄ electrode (126 Ω) is much smaller than that of S-TiSe₂ (292 Ω), which manifests lower charge-transfer resistance exists in the S-TiSe₂/Fe₃O₄ electrode/ electrolyte interface. This is possibly due to the better infiltration of the electrolyte into Fe₃O₄, resulting in a faster Faradaic reaction in the S-TiSe₂/Fe₃O₄ heterostructures.^[56,57] Moreover, the heterostructures may also aid in reducing polarization during the Li⁺ intercalation and deintercalation process.^[58] The R_{ct} of S-TiSe₂/Fe₃O₄ electrode increases a little bit after 100 cycles (171 Ω), revealing the excellent structural stability of the electrode. Furthermore, the higher slope of the low-frequency line of the S-TiSe₂/Fe₃O₄ cell at low frequency means the faster lithium-ion diffusion process can be achieved. For the S-TiSe₂/Fe₃O₄ sample after 50 cycles at 0.1 A g^{-1} , the SEM image (Figure S15, Supporting Information) indicates the nanoplate structure can be partially retained, suggesting its good structural durability.

The sodium storage abilities of the S-TiSe₂/Fe₃O₄ heterostructures are further evaluated. **Figure 5**a shows the galvanostatic charge–discharge profiles of the S-TiSe₂/Fe₃O₄ electrode at a current density of 0.1 A g⁻¹ for the first three cycles. Several voltage plateaus occur in the first discharge curve, which are attributed to the intercalation reaction of Na⁺ into S-TiSe₂ and Fe₃O₄.^[59] In the subsequent oxidation curve, the plateaus are associated with the desodiation process. The initial discharge and charge capacities of 984.6 and 497.5 mAh g⁻¹ are delivered by the S-TiSe₂/Fe₃O₄, resulting in an initial Coulombic efficiency of 50.5%. The large irreversible capacity loss in the initial cycle can be mainly attributed to the irreversible SEI formation, electrolyte decomposition, and possibly electrochemical pulverization.^[60] Except for the initial cycle, the following charge/discharge curves are overlapped well. The rate capability of the S-TiSe₂/Fe₃O₄ is shown in Figure 5b. It is observed that high specific capacities of 430.0, 373.2, 332.7, 300.4, 260.3, 228.4, and 203.3 mAh g⁻¹ can be obtained at the current densities of 0.1, 0.2, 0.5, 1, 2, 3, and 4 A g⁻¹, respectively. After the current density changing from 4 to 0.1 A g⁻¹, the specific capacity returns to 410.0 mAh g⁻¹. In addition, the cycling performances of the S-TiSe₂/Fe₃O₄ and Fe₃O₄ are further tested at a current density of 0.1 A g⁻¹ for up to 100 cycles. As shown in Figure 5c, the specific capacity of S-TiSe₂/Fe₃O₄ during the 100th cycle is 402.3 mAh g⁻¹, which suggests good electrochemical stability for Na storage. The reversible capacities of pure Fe₃O₄ electrode drop rapidly to 233.5 mAh g⁻¹ after 100 cycles.

In summary, an oil phase synthesis of uniform S-TiSe₂/Fe₃O₄ nanoplates is reported. The heterostructure with enhanced electrical conductivity shows improved Li/Na storage properties. Therefore, compared with S-TiSe₂ nanoplates (168.8 mAh g⁻¹ at 0.1 A g^{-1} during the 100th cycle), the as-prepared S-TiSe₂/Fe₃O₄ nanoplates deliver larger reversible capacities of 707.4 mAh g⁻¹ at 0.1 A g⁻¹ during the 100th cycle, and also higher than that of the pure Fe₃O₄ (487.7 mAh g⁻¹). Besides, superior rate capability (e.g., 301.7 mAh g⁻¹ at 20 A g⁻¹) and excellent cycling stability (432.3 mAh g^{-1} after 200 cycles at 5 A g^{-1}) can be achieved during the Li⁺ intercalation and deintercalation process. For the SIBs application, the S-TiSe2/Fe3O4 nanoplates also show excellent Na storage properties with high reversible capacities (402.3 mAh g^{-1} at 0.1 A g^{-1} during the 100th cycle), and excellent rate capabilities (203.3 mAh g⁻¹ at 4 A g⁻¹). This fascinating electrochemical performance is attributed to the unique



Figure 5. Electrochemical performance for SIBs at room temperature (25 °C). a) Galvanostatic charge–discharge profiles of the S-TiSe₂/Fe₃O₄ at a current density of 0.1 A g⁻¹. b) Rate performance of the S-TiSe₂/Fe₃O₄. c) Cycling performance of the S-TiSe₂/Fe₃O₄ and pure Fe₃O₄ at a current density of 0.1 A g⁻¹.

heterostructure and the strong synergistic effects of the combined contributions from the S-TiSe_2 nanoplates and the Fe_3O_4 nanoparticles.

Experimental Section

Synthesis of S-Doped TiSe₂ Nanoplates: In a typical synthesis, 500 mg selenium powder (\approx 6 mmol) was first dissolved in 3 mL of TOP in a three-neck flask. After vigorous stirring for 5 min, the solution become clear, then 200 mg sulfur powder (\approx 6 mmol) and 15 mL of oleylamine (OLA) were adding in the flask. The solution was heated to 120 °C and staying at this temperature for 30 min with magnetic stirring and under argon gas protection to eliminate the moisture. After the solution being cooled down to room temperature, 3 mL of TiCl₄ was injected into the flask. It can be seen clearly that the color of solution become brown. Subsequently, the solution was heated to 300 °C at 10 °C min⁻¹, and maintained at this temperature for 90 min. After being cooled down, S-doped TiSe₂ nanoplates product was collected by centrifugation at a rotating speed of 9800 for 5 min, and washed by hexane for three times, and then dried in a vacuum oven at 60 °C overnight. The pure TiSe₂ can be obtained using the same method without adding the sulfur powder.

Synthesis of Heterostructured S-Doped TiSe₂ Nanoplates/Fe₃O₄ Nanoparticles Composites: The iron-oleate complex was synthesized according to a reported procedure with minor modification. FeCl₃·6H₂O (2 mmol) and Na-oleate (4 mmol) were dispersed in 10 mL ethanol, 10 mL deionized (DI) water, and 20 mL hexane. After stirring for 60 min, the upper organic layer containing the iron-oleate complex was collected by separatory funnel, and washed three times with DI water to remove the residual sodium salts, and then stored in a vacuum oven at 60 °C overnight to evaporate the solvent completely, resulting in ironoleate complex with waxy solid form. S-doped TiSe₂ nanoplates/Fe₃O₄ nanoparticles composites were prepared through second oil phase synthesis. First, 100 mg S-doped TiSe₂ nanoplates product and 5 mg iron-oleate complex were dissolved in 10 mL of OLA in a three neck round-bottom flask, and degassed at 120 °C under argon gas protection for 30 min to get rid of the moisture. After that, the temperature was raised to 300 °C within 30 min and maintained for 30 min. The mixture was cooled to room temperature naturally. The final product was washed with hexane several times, followed by drying at 60 °C in a vacuum oven overnight. Finally, the as-prepared samples were annealed under the protection of argon at 400 °C for 2 h with a heat rate of 3 °C min⁻¹. The pure Fe_3O_4 can be obtained by the same method without adding the S-doped TiSe₂ nanoplates.

Characterization: The morphology of all the samples was investigated by field-emission scanning electron microscope (JEOL, Model JSM-7600F) and TEM (JEOL, Model 2100F, operating at 200 kV), including capturing HRTEM images and EDX mapping. Samples for TEM analysis were prepared by drop casting the sample dispersed in hexane onto carbon-coated copper grids, then followed by the evaporation of solvent. The crystal structure characterization of the samples was taken on a Shimadzu powder or thin film 6000 X-ray diffractometer with the 2θ range from 10° to 80° by using Cu K α_1 (λ = 0.15406 nm) radiation. Surface area and porosimetry distribution system (ASAP 3020) were used for the survey of nitrogen adsorption/desorption isotherms at -196 °C, and all samples were degassed at 120 °C for 8 h under vacuum before testing. The specific surface area was calculated by the Brunauer-Emmett-Teller method. XPS was performed by AXIS-His (Kratos Analytical). UV-vis-NIR absorption analysis was measured on a Cary 5000 mode with the wavelength range of 1000-3000 nm.

Electrochemical Measurements: The working electrode was fabricated by mixing 80% wt of the samples with 10% wt of conductive carbon black and 10% wt of polyvinylidene fluoride binder in *N*-methylpyrrolidone solvent. After homogeneous dispersing, the slurry was coated on a copper foil and dried in a vacuum oven at 60 °C overnight. The lithium-ion batteries performance was carried out using two-electrode coin cells with pure lithium foil as both the counter and the reference electrodes. Celgard 2400 membrane was used as the separator, and the electrolyte was 1.0 M LiPF₆ in the 1:1 (volume) mixture of ethylene carbonate/dimethyl carbonate. As for sodium-ion batteries, Na foil was used as a counter electrode and a glass fiber was used as the separator. The electrolyte was 1.0 M NaClO₄ in propylene carbonate with 5% fluorinated ethylene carbonate. Cell was assembled in an Ar-filled glovebox with concentrations of moisture and oxygen below 1.0 ppm. All the cells of galvanostatic charge and discharge curves were tested in NEWARE battery test system in the voltage range of 0.005–3.0 V. The CV was used by Solartron analytical equipment (model 1470E) with a scan rate of 0.2 mV s⁻¹. EIS measurements were performed on an impedance spectrum analyzer (Solatron, SI 1255B impedance/gain-phase analyzer; software: ZView) at open-circuit potential with the frequency range from 10 kHz to 0.01 Hz at an AC perturbation of 5 mV. The electrode loading for each battery is about 0.5 mg \pm 0.1 mg cm⁻².

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.

Keywords

heterostructures, lithium-ion batteries, S-doped TiSe_2 nanoplates, sodium-ion batteries

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