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Degenerate doping S_2 in Ni_3S_2 lattice into chemically homogeneous superlattice $Ni_3(S)_{1,1}(S_2)_{0,9}$ multi-storey micropyramids array on Ni foam towards excellent electrical conductivity and high-rate capability.

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Towards excellent electrical conductivity and high-rate capability:

A degenerate superlattice Ni₃(S)_{1.1}(S₂)_{0.9} micropyramids electrode

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Abstract: Degenerate semiconductor is very highly desired in energy conversion and storage technologies due to its metal-like conduction behaviors. This is the first time the doping S_2 in Ni₃S₂ lattice into chemically homogeneous Ni₃(S)_{1.1}(S₂)_{0.9} superlattice structure is proposed to induce a degenerate characteristic towards excellent electrical conductivity and high-rate capability. In this study, a series of the chemically homogeneous S₂-doped Ni₃(S)_{1.8}(S₂)_{0.2}, Ni₃(S)_{1.6}(S₂)_{0.4}, Ni₃(S)_{1.3}(S₂)_{0.7}, and Ni₃(S)_{1.1}(S₂)_{0.9} micropyramid arrays on Ni foam were synthesized by reacting the Ni foam and alkaline sulfur aqueous solution in different S₂²⁻ concentrations. The perfect

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Ni₃(S)_{1.1}(S₂)_{0.9} superlattice structure corresponds to the periodic S–Ni–S₂ atom arrangements in whole crystal lattice, which endows a degenerate characteristic of metal-like electrical conductivity to significantly improve the electrochemical performance. The bulk series resistance (R_s) value is only 0.62 Ω , while the chargetransfer resistance (R_{ct}) is nearly 0 Ω in the superlattice Ni₃(S)_{1.1}(S₂)_{0.9} electrode. As a cathode material for application in lithium ion batteries (LIBs), a very high specific capacity of 874 mAh g⁻¹ is achieved at current density of 200 mA g⁻¹. Remarkably, it still holds a high capacity of 565 mAh g⁻¹ at current density of 500 mA g⁻¹, indicating its superior high-rate capability. This study reveals that the periodic S–Ni–S₂ atom arrangements in crystal lattice is a key factor in determining the superlattice structure, high specific capacity, and the dynamic behaviors of electron/ion transport.

Keywords: degenerate semiconductor; electrical conductivity; S₂-doping; superlattice; lithium ion batteries.

1. Introduction

The increasing market demands of advanced energy storage devices have promoted the development of advanced electrode materials.^[1-5] In the past years, carbon materials have been widely used in the lithium ion batteries (LIBs) and supercapacitors because of their special advantages in high electrical conductivity, reusability, and environment benignity. However, the low specific capacity of carbon materials is a serious defect, and hinders their large-scaled application. The more effort is currently focused on various advanced electrode materials, including carbon-based hybrid materials and inorganic nanostructured materials for supercapacitors, LIBs and next-generation batteries, such as Li-S batteries, Li–air batteries and aqueous batteries.^[6-10] Among them, Ni₃S₂ has been extensively explored as the most promising electrode materials for application in supercapacitors, LIBs and next-generation batteries due to their good electroactivity and low cost. In particular, the theoretical specific capacity of Ni_3S_2 for LIBs is 472 mAh g⁻¹, which is obvious higher than that of the mostly used carbon materials. Up to now, various Ni₃S₂ nanostructures (e.g. nanosheets, nanowires and nanotubes)^[11-14] and their heterostructure nanomaterials (e.g. $Ni_3S_2@carbon, Ni_3S_2@MoS_2, V_2O_5@Ni_3S_2, Ni_3S_2@NiMoO_4)^{[15-18]}$, have been extensively studied. However, compared to the carbon materials, their electrical conductivity are much lower, resulting in their damaged structure and poor ratecapability, thus device performance is still unsatisfactory.

Towards excellent electrical conductivity and high-rate capability, the degenerate semiconductor materials are very highly desired due to their metallike conduction behaviours. It is well known that, when a n-type semiconductor is

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heavily doped with donors, it could be converted into degenerate semiconductor, its Fermi level lies within its conduction band, and a metal-like conduction occurs, namely doping-induced degenerate state.^[19, 20] Similarly, with heavy doping by acceptor in a p-type semiconductor, when Fermi level crosses its valence band, the doping-induced degenerate state also arises.^[19, 20] To date, some efforts on the doping nanostructures have achieved many outstanding results, such as V,^[21] Zn,^[22] Mo,^[23] Sn,^[24] or Fe^[25] doped Ni₃S₂. In this case, the doping metal atoms can form local impurity energy level within forbidden band to induce the staggered alignment of band edges, and increase charge carrier concentration correspondingly.^[26, 27] However, it is difficult to obtain a periodic arrangement of the doping atoms in whole crystal, thus the mobility of charge carrier is not high enough and still hinder its electrical conductivity. Therefore, it is very important to develop a new strategy toward the degenerately doping nanostructures with the desired metal-like electrical conductivity.

In this work, we address this issue by doping S_2 in Ni_3S_2 lattice to fabricate the chemically homogeneous S_2 -doped Ni_3S_x crystals on nickel foam. By reacting nickel foam with appropriate amounts of sulfur powders in a NaOH aqueous solution, a series of S_2 -doped Ni_3S_x crystals were obtained. The key of this reaction design is the use of the alkaline sulfur aqueous solution of NaOH. It is well known that NaOH is very efficient to activate sulfur powders into high active polysulfide ions $(S_n^{2^2}, n > 8)$, and finally generate S^{2^2} and additional species, such as $S_2^{2^2}$ and $S_3^{2^2}$. Using homologous $S_2^{2^2}$ species in appropriate amounts to displace the bridging sulfur (S^{2^2}) in Ni_3S_2 units allows us to fabricate the S_2 -doped Ni_3S_x crystals, such as $Ni_3(S)_{1.8}(S_2)_{0.2}$, $Ni_3(S)_{1.6}(S_2)_{0.4}$, $Ni_3(S)_{1.3}(S_2)_{0.7}$, and $Ni_3(S)_{1.1}(S_2)_{0.9}$. It was found that the doping $S_2^{2^-}$ species in Ni_3S_2 lattice are favorable for significantly increasing electrical conductivity. This is mainly due to the following natural characteristics:

(i) The doping $S_2^{2^-}$ species can enhance donor energy level and narrow's band gap, and correspondingly increase charge carrier concentration, because the energy level of the highest occupied molecular orbital (HOMO) of S_2 is higher than that of S due to orbital hybridization and electron delocalization in the sulfur dimer ($S_2^{2^-}$).

(ii) The heterocontacts in the S_2 -doped Ni_3S_2 crystals can resist the charges recombination, which hinder the neutralization of ions, resulting in high electron mobility ratio.

Importantly, by tuning the S₂/S atomic ratios to ~1:1, the S₂-doped Ni₃S_x crystal structure could be converted to the chemically homogeneous Ni₃(S)_{1,1}(S₂)_{0.9} superlattice structure, consisting of the periodic alternate of Ni–S and Ni–S₂ atom layers. We found that the Ni₃(S)_{1,1}(S₂)_{0.9} superlattice structure with the periodic S–Ni–S₂ atom arrangements has the degenerate doping induced metal-like behaviors for excellent electrical conductivity and high-rate capability, which were systematically investigated by electrochemical measurements and electrochemical impedance spectroscopy (EIS) analyses. The bulk series resistance (R_s) value is only 0.63 Ω , while the charge-transfer resistance (R_{ct}) is nearly 0 Ω in the superlattice Ni₃(S)_{1.1}(S₂)_{0.9} electrode. To exploit its potential application, LIBs were assembled with the superlattice Ni₃(S)_{1.1}(S₂)_{0.9} electrode as a working electrode. A very high specific capacity of 874 mAh g⁻¹ has been achieved at current density of 200 mA g⁻¹. Remarkably, it still holds a capacity as

high as 565 mAh g^{-1} at current density up to 500 mA g^{-1} , indicating its superior high-rate capability.

The article describes the formation, morphology, microstructure and electrochemical properties of the degenerate $Ni_3(S)_{1.1}(S_2)_{0.9}$ superlattice electrode material, which is illustrated in **Scheme 1**. This work will encourage more study on the degenerately doped nanostructures for potential electrochemical, photoelectric and photocatalytic applications.

2. Experimental

2.1 Materials and methods.

All reagents were of analytical grade and used without further purification. To start the synthesis, 0.1 mol NaOH and appropriate amounts of S power (2.0, 3.0, 5.0, 7.0 mmol) were dissolved in 30 mL deionized water by magnetic stirring at 90°C for 3 h to make an alkaline sulfur aqueous solution. Different amounts of S power were used to control the composition of the resulting alkaline sulfur aqueous solution. Then, the 2mL of resulting alkaline sulfur aqueous solution was transferred into a 15 mL Teflon-lined stainless steel autoclave. After that, the 1×2 cm² piece of Ni foam with a thickness of 0.2 mm was enclosed in the alkaline sulfur reaction solution and heated at 180°C for 12 h. After cooling to the room temperature, the Ni foam was taken out and washed with deionized water and then dried in a vacuum oven at 60°C for 6h. For comparison, the undoped Ni₃S₂ nanowires array grown on Ni foam was also prepared by reacting Ni foam with thioacetamide (TAA) in the aqueous solution of NaOH under the same conditions (See the Supporting Information). The resulting Ni foam was weighed, and the mass loading of Ni₃S_x on Ni foam was calculated by the equation follow.

$$m$$
 (Ni₃S_x) = $\Delta m \times M$ (Ni₃S_x) / $x \div M$ (S)

Where Δm is the weight difference of the Ni foam before and after the hydrothermal sulfidation, M (Ni₃S_x) and M (S) is the molar mass of Ni₃S_x and S, respectively.

2.2 Physical Characterizations.

X-ray diffraction (XRD) patterns were collected on a Philips MPD 18801 diffractometer with Cu-K α radiation ($\lambda = 1.54178$ Å). Scanning electron microscopy (SEM) micrographs were observed using field emission scanning electron microscopy (FE-SEM, Nova NanoSEM 450) equipped with energydispersive X-ray spectroscopy (EDS, OXFORD X-Max 50). The high resolution TEM (HRTEM) images and the select-area electron diffraction (SAED) patterns were obtained by a JEOL JEM 2100 high-resolution transmission electron microscope operated at 200 kV. The Raman spectrum was recorded by a LABRAM-1B confocal laser micro-Raman spectrometer with an excitation wavelength of 532 nm. Ultraviolet visible (UV-vis) absorption spectrum was obtained using a Shimadzu UV-3600 UV-vis-NIR spectrophotometer.

2.3 Electrochemical measurements.

The electrochemical measurements were conducted in 2M KOH electrolyte on CHI760E electrochemical workstation with a three-electrode system, where the Ni_3S_x/Ni foam electrode was used as the working electrode, Pt foil and standard Hg/HgO electrode as the counter electrode and reference electrode, respectively. The electrochemical impedance spectroscopy (EIS) analyses were performed in the frequency range of 100 kHz to 1 Hz with an AC oscillation of 5 mV. The CR2025-type coin cells were assembled in a high-purity argon filled glove box ($H_2O < 0.5$ ppm, $O_2 < 0.5$ ppm, MBraun, Unilab). The as-prepared Ni₃S_x on Ni foam were used as the working electrode, lithium metal foil as the counter and reference electrode, and Celgard 2320 as the separator membrane. The electrolyte was 1 M LiPF₆ dissolved in EC:EMC:DMC = 1:1:1 in volume ratio. Cyclic voltammogram (CV) tests were performed on a electrochemical workstation (Autolab PGSTAT 302N) between 0.02 V and 3.00 V at a scanning rate of 0.1 mV s⁻¹. Charge–discharge measurements were performed with a multichannel battery tester (Neware BTS-610) between 0.02 V and 3.00 V at room temperature.

3. Results and discussion

3.1 Preparation and structure characterizations.

In this reaction design, sulfur powers were first activated in the aqueous solution of NaOH at 90°C for 3 h to make an alkaline sulfur aqueous solution. We observed that the solution color subsequently turns from yellow to orange and then red within 1 h, and finally returns to pale yellow within 2 h. The color change originates from the formation of polysulfide ions $(S_n^{2-}, n > 8)$ by the following well-known reaction (eqn (1)).

$$(2n+1)S + 6OH \rightarrow 2S_n^{2} + SO_3^{2} + 3H_2O$$
 (1)

With *n* value increasing, the polysulfide ions (S_n^{2-}) solution color changes from yellow to orange and then to red. Obviously, the polysulfide ions (S_n^{2-}) with long S chains are more reactive than their yellow and orange counterparts, because the S–S bond in long sulfur chains is much weaker due to electron delocalization along the whole S_n^{2-} chain. Thus, the red polysulfide (S_n^{2-}) precursors are highly

active to generate S^{2-} and additional species, such as S_2^{2-} and S_3^{2-} (eqn (2)), resulting in the final pale yellow solution.

$$S_n^{2-} \rightarrow S^{2-} + S_2^{2-} + S_3^{2-} + \dots$$
 (2)

The final pale yellow sulfur solution was tested by a UV-vis spectrophotometer. As shown in **Fig. 1**, the high absorbance in the 260–280 nm regions is mainly derived from S^{2-} species. The absorption band at 297 nm stem from $S_2^{2^-}$, while the absorption about 370 nm is originated from $S_3^{2^-}$. This assignment of spectral bands is consistent with previous reports.^[28-30] From this UV-vis absorption experiment, we observed that the increasing sulfur reactant content leads to increased absorbance at all three wavelengths, and generates considerable amounts of S^{2-} and more $S_2^{2^-}$, and a few $S_3^{2^-}$ species in the alkaline aqueous solution. No other $S_n^{2^-}$ species are produced in the final pale yellow sulfur solution, such as $S_4^{2^-}$ (absorption of 420 nm), $S_5^{2^-}$ (absorption of 438 nm), and $S_6^{2^-}$ (absorption of 450 nm).

The final pale yellow sulfur solution was used to react with Ni foam through a hydrothermal process at 180°C (eqn (3)).

$$Ni + S^{2-} + S_2^{2-} \rightarrow Ni_3S_{2-y}(S_2)_y$$
 (3)

This simple method leads to the self-sulfidation of nickel foam, thus the $S_2^{2^-}$ species were combined into Ni₃S₂ lattice to produce the S₂ -doped Ni₃S_{2-y}(S₂)_y samples on the Ni foam. The $S_3^{2^-}$ species cannot be combined into Ni₃S₂ lattice at 180°C due to its steric bulkiness or decomposition to S²⁻ and S₂²⁻. The composition of the resulting S₂ -doped Ni₃S_{2-y}(S₂)_y samples was controlled by using the different amounts of S power reactants in the alkaline aqueous solution. The Ni /S atomic ratio in the Ni₃S_{2-y}(S₂)_y series were validated by energy-

dispersive X-ray spectroscopy (EDS), and the obtained samples were marked as $Ni_3S_{2.2}$, $Ni_3S_{2.4}$, $Ni_3S_{2.7}$, and $Ni_3S_{2.9}$, respectively (Figure S3 in the Supporting Information). Just taking the obtained $Ni_3S_{2.9}$ sample as an example (Figure S3e), the EDS data validate that the atomic ratio (at. %) of Ni and S in the $Ni_3S_{2.9}$ crystals is 50.81:49.19, which is very close to the marked 3.0:2.9 ratio. Thus, according to the $Ni_3S_{2.9}(S_2)_y$ form, the composition of $Ni_3S_{2.9}$ can be calculated (by 2-y+2y=2.9, namely, y=0.9) and formally represented as $Ni_3(S)_{1.1}(S_2)_{0.9}$. Similarly, the other samples can be formally represented as $Ni_3(S)_{1.8}(S_2)_{0.2}$, $Ni_3(S)_{1.6}(S_2)_{0.4}$ and $Ni_3(S)_{1.3}(S_2)_{0.7}$. The increasing S_2 content is due to a considerable number of $S_2^{2^2}$ species substituting the S^{2^2} in the Ni_3S_2 units, which was further validated by the below Raman investigation.

Fig. 2a shows the Raman spectra of all the obtained samples, for comparison. For the undoped Ni₃S₂ sample (**Pattern a in Fig. 2a**), the observed Ni–S vibration modes show six strong signal at 188, 202, 224, 304, 325 and 350 cm⁻¹, respectively, which can be readily indexed to six Raman-active modes (2A1 + 4E) of the heazlewoodite-phase Ni₃S₂, consistent with those reported earlier.^[31,32] For all the S₂²⁻-doped samples, the Raman spectra exhibit distinct vibration signals in two groups: S–S vibration mode at 478 cm⁻¹,^[33] and the six Ni–S vibration modes in the broad range from 350 cm⁻¹ to 188 cm⁻¹. For the Ni₃(S)_{1.8}(S₂)_{0.2} sample (**Pattern b in Fig. 2a**), the weaker S–S stretching signal at 478 cm⁻¹ indicates only a few sulfur dimers (S₂²⁻) in the crystal lattice, because the S–S vibration mode typically produces a strong Raman signal.^[33] With the increasing S₂ doping ratio, for all the S₂²⁻-doped samples, the S–S stretching signal at 478 cm⁻¹ displays a systematic intensity increase, implying the introduction of more sulfur dimers $(S_2^{2^-})$ in the lattice. Moreover, for all the $S_2^{2^-}$ doped samples, the Raman peaks from the Ni-S vibration modes obviously shift downward in Raman frequency with the increasing S_2 doping ratio (Fig. 2b). The frequency shift is closely related to the induced strain/stress in crystal structure.^[34,35] If the Raman frequency is shifted downward, the induced-strain is present in the crystal, the converse for induced-stress.^[34,35] In our cases, the $Ni_3(S)_{1,1}(S_2)_{0,9}$ sample shows the maximum downward shift in Raman frequency (Pattern e in Fig. 2b), indicating the greatest induced-strain in the $Ni_3(S)_{1,1}(S_2)_{0,9}$ crystals. We propose that the frequency shift is a result of the anion exchange between S^{2-} and S_2^{2-} in the Ni₃S₂ units. Doping S_2^{2-} in the Ni₃S₂ host lattice could undoubtedly vary the force constants, because of the bond strength of S-Ni-S₂ being different from the pure S-Ni-S bond. Thus, the varying bond strengths of S–Ni–S₂, depending on the S₂ ratios in the lattice, induce the strain in the entire crystals. It is worth noting that, for all the $S_2^{2^2}$ -doped samples, the Raman intensity of the six Ni-S vibration modes is reduced, while the full width at half maximum (fwhm) is increased (Fig. 2b), indicating the smaller polarizability of sulfur atoms in the these S_2^{2-} -doped Ni₃S₂ samples. This result is originated from the strong covalent nature of S-atom π -donation to the Ni metal center. In the S-Ni-S₂ case, the orbital hybridization and electron delocalization of sulfur dimer (S_2^{2-}) with its π -donation to neighboring Ni atoms could result in some degree of electron delocalization over the S-Ni-S₂ atom layer, increasing the bond strength and force constant in the whole lattice, and thus decreasing the polarizability of S atoms.

The crystallographic structures of the $S_2^{2^2}$ -doped Ni₃S_x series are further investigated by XRD analysis. Fig. 3 shows a representative XRD pattern of the obtained Ni₃(S)_{1.1}(S₂)_{0.9} sample scratched from Ni foam for eliminating the backdrop of Ni foam. The diffraction pattern is in agreement with the feature of the heazlewoodite Ni₃S₂ in hexagonal phase (JCPDS No. 44-1418). All of the diffraction peaks can be readily indexed to the (101), (110), (003), (202), (113), (211), (104), (303) and (214) planes of heazlewoodite hexagonal Ni_3S_2 . No other diffraction peaks were observed in the XRD pattern, which indicates that the obtained $Ni_3(S)_{1,1}(S_2)_{0,9}$ crystal is chemically homogeneous solid solution. Importantly, the diffraction angles of the all diffraction peaks are bigger than those of normal Ni_3S_2 (JCPDS No. 44-1418), indicating a lattice contraction in the Ni₃(S)_{1.1}(S₂)_{0.9} crystal. *Considering* the stronger electronic effects of $S_2^{2^-}$ with its π -donation to neighboring Ni atoms, we believe that the S₂ species have entered the Ni₃S₂ host lattice and further tuned the electronic structure of chemical bonds, increasing bond strength and force constant, and thus resulting in the lattice contraction. This XRD result is well consistent with the Raman results explained above. For all of the $S_2^{2^2}$ -doped Ni₃S_x series, there are just negligible differences in their crystal structure of heazlewoodite hexagonal phase (FigureS4 in the Supporting Information).

Fig. 4 shows a representative SEM image of the obtained $Ni_3(S)_{1.1}(S_2)_{0.9}$ samples grown on Ni foam. As seen in **Fig. 4a** from a distant view, the SEM image shows a net-like open 3D porous structure, namely, the skeleton structure of Ni foam is completely retained after the hydrothermal process. From the close views (**Fig. 4b and c**), it is clear that the Ni foam surface is uniformly covered

with the pyramid-like $Ni_3(S)_{1.1}(S_2)_{0.9}$ arrays. It can be seen that the micropyramids are well-distributed aslant or perpendicular to the Ni foam support with an average height of about 1.2 µm. In the high magnification SEM image (**Fig. 4d**), it appears that each of the micropyramids is a multi-storey schistous structure along its entire height, consisting of many triangle nanosheets of about 30 nm in thickness.

To obtain more detailed structural information of the $Ni_3(S)_{1,1}(S_2)_{0,9}$ micropyramids, high-resolution TEM (HRTEM) and select area electron diffraction (SAED) were measured. The SAED pattern in inset of Fig. 5a shows a set of diffraction spots corresponding to the hexagonal Ni₃S₂ structure. The spots indexed as spot (110) and spot (021) correspond to a plane distance of 2.81 Å and 2.29 Å, respectively, which is a slight deviation from the normal value (2.8730 Å and 2.3498 Å, respectively) of hexagonal Ni₃S₂ structure (JCPDS No. 44-1418). Interestingly, these diffraction spots are comprised of primary diffraction spots with some subcell spots toward an almost continuous line, which is indeed a characteristic of superlattice structures.^[36-38] As shown in Fig. 5b, the HRTEM image clearly reveals a novel superlattice structure. The superlattice structure has a short alternate period of two atom layers interleaved by the alternate bright and dark lattice fringes in the same spacing of 3.98 Å, which are highlighted by the white lines and yellow dots in the HRTEM image. In addition, the distance for two adjacent lattice fringes is about 1.99 Å, corresponding to the (202) plane, smaller than that (2.04 Å) in the normal Ni_3S_2 structure (JCPDS No. 44-1418). Typically, this is a chemically homogeneous superlattice structure, in which the S_2/S atomic ratio is near to 1:1 in lattice. So the bright and dark contrast fringes should correspond to the Ni–S and Ni–S₂ atom layers.

In our experiments, only 2 mL of the alkaline sulfur aqueous solution containing the S^{2-} and S_2^{2-} in different concentration were used to feed the nucleation and growth of S_2^{2-} -doped Ni₃S_x crystals on Ni foam at180°C with enough time intervals of 12 h. In this case, the final structure strongly depends on the feeding amounts of S^{2-} and S_2^{2-} . Typically, the well-defined Ni₃(S)_{1,1}(S₂)_{0,9} superlattice structure were prepared in the high concentration of the S^{2-} and S_2^{2-} resources. With the decreasing amounts of the S^{2-} and S_2^{2-} in the alkaline sulfur aqueous solution, those comparative $Ni_3(S)_{1.8}(S_2)_{0.2}$, $Ni_3(S)_{1.6}(S_2)_{0.4}$ and $Ni_3(S)_{1,3}(S_2)_{0,7}$ samples were produced, and the obtained SEM images (Figure S5) and SAED patterns (Fig. 6) reveal the detailed evolution process of the superlattice $Ni_3(S)_{1,1}(S_2)_{0,9}$ micropyramids. As seen in Figure S5, the different SEM images shows the morphology evolution from the $Ni_3(S)_{1.8}(S_2)_{0.2}$ pyramidlike bases to the final $Ni_3(S)_{1,1}(S_2)_{0,9}$ schistous multi-storey micropyramids, implying an Ostwald ripening growth process. As to the multi-storey schistous structure of the superlattice $Ni_3(S)_{1,1}(S_2)_{0,9}$ micropyramids, many forces could cause its overgrowth, which follow Ostwald ripening kinetics, such as dipolar and electrostatic fields associated with the crystal-face attraction, hydrophobic interactions, aggregate, hydrogen bonds, and vander Waals forces.^[39,40]

Significantly, the relevant SAED patterns explore the detailed structural evolution of the $Ni_3(S)_{1.1}(S_2)_{0.9}$ superlattice. As shown in **Fig. 6a-c**, for all the comparative samples, the corresponding SAED pattern is comprised of primary diffraction spots with some subcell spots adjacent to primary spots, and the trend

is from separate spots toward a continuous line with the increasing S₂ ratios. This is a natural characteristic during the formation of a superlattice structure, tuned by adjusting the atom ratio of S_2 to S in lattice configuration. Hence, the structural evolution of $Ni_3(S)_{1.1}(S_2)_{0.9}$ superlattice could be a result of the anion exchange between S^{2-} and S_2^{2-} . Kinetically, the anion exchange between the S_2^{2-} and S^{2-} can easily occur because of the higher electronegativity of S_2 ($3s^23p^5$) than that of S atom $(3s^23p^4)$ due to orbital hybridization and electron delocalization in the S₂ dimer. Crystallographically, the crystal phase systems of undoped Ni_3S_2 and S_2 -doped $Ni_3(S)_{1,8}(S_2)_{0,2}$, $Ni_3(S)_{1,6}(S_2)_{0,4}$ and the $Ni_3(S)_{1.3}(S_2)_{0.7}$ crystals all are the same heazlewoodite hexagonal phase, which facilitate the bulky S₂ to enter the host lattice at the hydrothermal condition. Also, the Raman results above provide some support for the anion exchange mechanism. For the well-defined superlattice $Ni_3(S)_{1,1}(S_2)_{0,9}$ structure, about 50% S₂ ratios in lattice, the Raman results demonstrate the greatest induced-strain in its crystal structure. This means that the greatest induced-strain best cater to the needs of the periodic S–Ni–S₂ even arrangements in whole crystal lattice.

3.2 Electrochemical performance.

To investigate the electrochemical performance of the superlattice $Ni_3S_{2.9}$ micropyramids array grown on Ni foam, a series of electrochemical measurements were carried out by directly using the architecture as the working electrode in a three-electrode system with 2 M KOH as electrolyte.

Fig. 7a shows the cyclic voltammetry (CV) curves within a potential window of 0–0.6 V (versus SCE) at scan rates from 5 to 20 mV s⁻¹. A pair of battery-like redox peaks is found in each curve with the cathodic peak around 0.25 V and the

anodic peak around 0.50 V, which can be attributed to the reversible electrochemical reaction of Ni₃S_{2.9}/Ni₃S_{2.9}(OH)₃ based on a battery-like diffusioncontrolled process.^[41] Significantly, with the increasing scan rate, the peak currents in both the cathode and anode are linearly increased with the square root of the scan rate (Fig. 7b), indicating that the redox reactions of the superlattice Ni₃S_{2.9} electrode are perfectly reversible and ultra-fast. This means an excellent electron/ion transport behavior in the superlattice Ni_3S_2 electrode. Fig. 7c displays its galvanostatic charge-discharge (GCD) curves at various current densities. The observed nonlinear curves confirm its typical battery-like behavior, while the stable charge/discharge platform match well with the potential positions of redox peaks in the CV curves. Based on the GCD curves, the rate performances from 5 mA cm⁻² to 100 mA cm⁻² were illustrated in FigureS6. As shown in FigureS6, the specific capacity is up to $1.02C \text{ cm}^{-2}$ at current density of 5 mA cm⁻². Increasing the current density to 100 mA cm⁻², a high capacity of 0.63 C cm⁻² (~ 61.8 % of the maximum value) still retains, demonstrating its superior high-rate capability.

Such superior electrochemical performance of the superlattice $Ni_3S_{2.9}$ electrode is expected to be a result of the degenerate doping S_2 in Ni_3S_2 lattice. In order to explore the influence, the electrochemical impedance spectroscopy (EIS) measurements were carried out, and several control experiments reveal some interesting impedance changes. **Fig. 8** shows the Nyquist plot of all the obtained Ni_3S_x series electrode after 10th cycle in the frequency range from 100 kHz to 1 Hz, where Z' and Z'' are the real and imaginary parts of the impedance, respectively. Usually, the Nyquist impedance plot display a small semicircle in

the high-frequency region and a straight line in the low-frequency region. In the high frequency region, the first intercept at the real axis (Z') represents a bulk series resistance (R_s) , including the inherent resistance of electroactive material, the bulk resistance of electrolyte, and the contact resistance between the active material and the current collector.^[42, 43] The small semicircle corresponds to the charge-transfer resistance (R_{ct}) , which is associated with the electron/ion transport behaviors in the electrochemical redox process of the electroactive materials. For the undoped Ni₃S₂ nanowires (**Fig. 8a**), the R_s value is 0.87 Ω , while the R_{ct} value is 2.12 Ω , which is consistent with the result of early reported 3D Ni₃S₂ nanosheet arrays on Ni foam.^[13] Comparatively, the measured R_s value for the four $S_2^{2^2}$ -doped Ni₃S_{2.2}, Ni₃S_{2.4}, Ni₃S_{2.7} and Ni₃S_{2.9} samples was 0.70, 0.55, 0.64 and 0.62 Ω , respectively (Fig. 8b-e). The general trend is that the R_s value is decreased with the increasing S_2 ratios. Obviously, this is a typical dopinginduced degenerate process, and the Ni₃S_{2.9} superlattice structure has the degenerate-induced metal-like characteristic for excellent electrical conductivity at $R_s = 0.62 \ \Omega$. While the radius of the high frequency semicircles is decreased systematically with the increasing S₂ ratios, until disappeared in the superlattice $Ni_3S_{2.9}$ electrode (inset in Fig. 8), which demonstrate the improving chargetransfer kinetics with the increasing S_2 ratios. For the superlattice $Ni_3S_{2.9}$ electrode, the charge-transfer resistance (R_{ct}) is nearly 0 Ω (Fig. 8e). Such R_s and $R_{\rm ct}$ value in the superlattice Ni₃S_{2.9} electrode is much smaller than most of recently reported values, such as hierarchical $V_2O_5@Ni_3S_2$ hybrid arrays (R_s =1.25 Ω , $R_{\rm ct}$ =0.92 Ω),^[17] Ni₃S₂ wrapped by rGO on carbon cloth ($R_{\rm s}$ =1.1 Ω),^[44] hierarchical urchin-like Ni₃S₂ ($R_s = 1.15\Omega$, $R_{ct} = 1.02\Omega$),^[45] honeycomb-like Ni₃S₂

Ω),^[46] $R_{\rm ct}$ =4.5 nanosheet arrays $(R_{\rm s}$ =0.92Ω, and Hierarchical carbon@Ni₃S₂@MoS₂ double core-shell nanorods ($R_s=0.68\Omega$, $R_{ct}=4.8\Omega$).^[47] Besides, the line in low-frequency region is described as Warburg resistance (Zw), demonstrating the impeded diffusion/transport process of electrolyte inside the electrode. Cdl and Cl are the double layer capacitance and the limit capacitance, respectively.^[22, 48, 49] For all the Ni_3S_x series electrode (Fig. 8a-e), the impedance plot tends to become vertical line with the increasing S_2 ratios, where the largest slope degree is achieved in the Ni₃S_{2.9} superlattice electrode, indicating its excellent ion diffusion activity in the electrochemical process.^[44] The excellent electron/ion transport behavior of the Ni₃S_{2.9} superlattice could be attributed to its unique structures. First, First-principle calculations indicate that the doping S_2 species could naturally tune the whole electronic structure by orbital hybridization and electron delocalization over its adjacent S atoms, thus its Fermi level lies within its valence band, and a metal-like electrical conductivity occurs (See First-principle calculations in the Supporting Information). Secondly, the alternate S-Ni-S₂ atomic arrangement could act as the periodic heterojunction to resist the charges recombination, which hinder the neutralization of ions, resulting in high electron mobility ratio and high-rate capability. Moreover, the multi-storey schistous structure can provide efficient pathways for ions transport and electrolyte diffusion along its whole surface, and also provide some flexible space to accommodate the volume change in the ion/electrolyte diffusion processes.

To demonstrate further applications, the superlattice $Ni_3S_{2.9}$ architecture as the working electrode was assembled into a CR2025 coin cell with lithium metal

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foil as the counter electrode. Also, we assembled the undoped Ni₃S₂ nanowirws architecture into a CR2025 coin cell under the same conditions, for comparison. The mass loading of the superlattice Ni₃S_{2.9} micropyramids and the undoped Ni₃S₂ nanowirws on Ni foam was calculated to be 4.28 mg.cm⁻² and 5.70 mg.cm⁻², respectively.

Cyclic voltammetry (CV) curves for the superlattice Ni₃S_{2.9} sample are shown in Fig. 9a, which are recorded in the potential range of 0.02-3.0 V (vs. Li⁺/Li) with a scan rate of 0.1 mV s⁻¹. At the first scan, two cathodic peaks around 0.90 and 0.62 V is evident, which can attribute to the insertion of Li^+ in the Ni₃S_{2.9} active materials { $Ni_{3}S_{1.1}(S_{2})_{0.9} + 4Li^{+} + 4e \rightarrow 3Ni + 1.1Li_{2}S + 0.9Li_{2}(S_{2})$ } and the formation of a solid electrolyte interface (SEI) film on the active material surface ^[22, 49]. In contrast, there are four anodic peaks at about 1.05, 1.71, 1.94 and 2.26 V due to the extraction of Li^+ from the Ni₃S_{2.9} active materials and other side reactions.^[22, 49] There are several obvious differences in subsequent cycles compared to the first scan. The reduction peak shifts to 1.28 V, then to 1.33 V, while three anodic peaks around 2.26, 1.71 and 1.05 V are loosening from the second cycle due to the activation of the $Ni_3S_{2,9}$ materials.^[22, 49] The CV curves well overlap each other in the subsequent cycles, demonstrating the good reversibility of the $Ni_3S_{2,9}$ electrode. However, it is noticeable that the current intensity in Li⁺ insertion process is continually decreasing with the increased cycling number in the CV curves. This means the diffusion-controlled Li⁺ insertion process becomes to be easier with the increasing cycles. Fig. 9b presents the galvanostatic charge-discharge profiles recorded for different cycles at a current density of 500 mA g⁻¹. It is evident that the discharge and charge

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plateaus match well with the respective peaks on the CV curves. Remarkably, the discharge curves display a constant discharge plateaus at ~1.94 V with the increasing cycle number, revealing the excellent discharge stability at ~1.94 V.

Fig. 10 shows the discharge–charge cycling performance between 0.02 and 3.0 V. For the undoped Ni₃S₂ sample, at the current density of 200 mA g^{-1} , the discharge-charge cycles show a continuous capacity decay process, which is a common phenomenon for pure Ni_3S_2 nanocrystals due to its structural degradation in the lithium insertion/extraction reactions. Comparatively, for the superlattice Ni₃S_{2.9} sample, at the current density of 200 mA g^{-1} , the first discharge–charge cycle has a discharge capacity of 944 mAh g⁻¹ and a charge capacity of 669 mAh g⁻¹. The irreversible capacity in the initial cycle is well consistent with the initial CV scan, which has been widely referred to the formation of SEI film and other side reactions.^[49, 50] The reversible capacity are observed at the 3th cycle for 646 mAh g⁻¹, and then gradually increase until the 80th cycle up to 874 mAh g⁻¹. Subsequently, a capacity decay phenomenon appears similar to that of the undoped Ni₃S₂ sample, however, a high capacity of 824 mAh g⁻¹ still holds at the 100th cycle. Importantly, the superlattice Ni₃S_{2.9} sample has the superior high-rate capability. As seen in Fig. 10, at the current density of 500 mA g⁻¹, the reversible capacity continuously increase up to 565 mAh g⁻¹ at the 100th cycle, which is consistent with the level of discharge–charge profile measurements above. Such a capacity increase phenomenon could be attributed to the presence of sulfur dimer (S_2) in Ni₃S_{2.9} structure, in which the S₂ species could provide higher electronegativity $(3s^23p^5)$ and additional sulfur active sites to store more Li^+ ions. At the same time, the morphology of $Ni_3S_{2,9}$

micropyramids could be changed during the cycling reaction of $2Li^+ + S_2^{2-} \leftrightarrow$ $Li_2(S_2)$. As seen in **Figure S10**, after 100 cycles at current density of 500 mA g⁻¹, the micropyramid-like Ni₃S_{2.9} structure is transformed into graphene-like irregular nanosheets with the unchanged crystallization phase. This means more $S_2^{2^2}$ active sites with higher electronegativity could be gradually exposed during the cycling reactions, convenient for the Li^+ storage. Also, the exposed $\text{S}_2^{2^-}$ species would finally dissolve to generate the S²⁻ species in the tricky electrochemical processes. Therefore, the reversible discharge-charge capacity is gradually increased to a maximum value, then gradually decayed accompanied with the structural degradation in the cycling tests. On the other hand, the higher electronegativity of sulfur dimer (S_2) has great effect on the extraction behavior of Li^+ ions, so that the rate-capacity at the higher current density of 500 mA g⁻¹ is reduced, not well match with the excellent electrical conductivity of $Ni_3S_{2,9}$. However, the actual rate-capacity up to 565 mAh g^{-1} is really better than the previously reported nickel sulfide [11-14, 50], also almost matched to the carbonbased Ni₃S₂ hybrid materials.^[51-53] Moreover, It is worth noting that the Coulombic efficiency for the superlattice $Ni_3S_{2,9}$ has been maintained above 97% with the prolonged cycles except the initial two cycles for 71% and 94%, respectively. These results indicate that the $Ni_3S_{2,9}$ superlattice is indeed a promising candidate for application in LIBs.

4. Conclusions

In this paper, we demonstrate a simple wet-chemical S_2 doping method to construct a novel S_2 -tuned chemically homogeneous $Ni_3(S)_{1.1}(S_2)_{0.9}$ superlattice multi-storey micropyramid arrays on Ni foam as a battery-type

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electrode material. The homogeneous superlattice $Ni_3(S)_{1.1}(S_2)_{0.9}$ structure is composed of the alternate S-Ni-S₂ atom arrangements in whole crystal lattice, which is different from the chemically heterogeneous and nonhomogeneous superlattice, and has the doping induced metal-like electrical conductivity. The R_s value is only 0.62 Ω , while the R_{ct} is nearly 0 Ω , indicating an excellent electron/ion transport behavior in the superlattice $Ni_3(S)_{1,1}(S_2)_{0,9}$ electrode. As a cathode material for application in LIBs, a very high specific capacity of 874 mAh g⁻¹ has been achieved at current density of 200 mA g⁻¹. Remarkably, it still holds a high capacity of 565 mAh g^{-1} at current density of 500 mA g^{-1} , indicating its superior high-rate capability. The superior specific capacity and high-rate capability benefit from the periodic alternate arrangements of S₂ species in $Ni_3(S)_{1,1}(S_2)_{0,9}$ superlattice, which could naturally improve band structure and spatial field effect over the whole crystal to optimize the charge transfer kinetics for much lower resistance, also provide higher electronegativity and additional sulfur active sites to store more Li⁺ ions. Moreover, the schistous multi-storey micropyramid structure could facilitate the electrolyte diffusion and ion transport along its entire surface, and also accommodate the volume change in ion diffusion processes. The convenient and successful degenerate doping S₂ strategy could be large-scale applied to other metal sulfides with novel superstructures for material chemists and physicists to further study on electrochemical, photoelectric and photocatalytic applications.

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Figure Captions:

Scheme 1. Schematic illustration of the S_2 -tuned superlattice $Ni_3(S)_{1.1}(S_2)_{0.9}$ multistorey micropyramids array on Ni foam with its application for LIBs.

Fig. 1 UV-vis absorption spectrum of the final pale yellow alkaline sulfur aqueous solution diluted 30 times with distilled water. The content of sulfur in the reactants is (a) 2.0 mmol, (b) 3.0 mmol, (c) 5.0 mmol, and (d) 7.0 mmol.

Fig. 2 Raman spectra of a) all the obtained samples, and b) an expanded view from the Ni–S vibration modes. Patterns of (a) pure Ni₃S₂, (b) Ni₃(S)_{1.8}(S₂)_{0.2}, (c) Ni₃(S)_{1.6}(S₂)_{0.4}, (d) Ni₃(S)_{1.3}(S₂)_{0.7}, and (e) Ni₃(S)_{1.1}(S₂)_{0.9}.

Fig. 3 XRD pattern of the obtained S_2 -doped Ni₃(S)_{1.1}(S₂)_{0.9} sample scratched from the Ni foam for eliminating the backdrop of Ni foam.

Fig. 4 SEM images in different magnifications of the $Ni_3(S)_{1.1}(S_2)_{0.9}$ micropyramids array grown on Ni foam.

Fig. 5 TEM image (a) and HRTEM image (b) of the $Ni_3(S)_{1.1}(S_2)_{0.9}$ superlattice. Inset in TEM image is the corresponding SAED pattern of the $Ni_3(S)_{1.1}(S_2)_{0.9}$ superlattice.

Fig. 6 Selected area electron diffraction (SAED) patterns of (a) $Ni_3(S)_{1.8}(S_2)_{0.2}$, (b) $Ni_3(S)_{1.6}(S_2)_{0.4}$, (c) $Ni_3(S)_{1.3}(S_2)_{0.7}$, and (d) $Ni_3(S)_{1.1}(S_2)_{0.9}$.

Fig.7 Electrochemical evaluation of the superlattice $Ni_3S_{2.9}$ electrode in the threeelectrode system: (a) CV curves in different scan rates. (b) linear relation of peak current density to the square root of scan rate. (c) Galvanostatic charge–discharge curves at various current densities.

Fig.8 Nyquist plots of the obtained Ni_3S_x series electrode after 10th cycle of (a) undoped Ni_3S_2 , (b) $Ni_3S_{2.2}$, (c) $Ni_3S_{2.4}$, (d) $Ni_3S_{2.7}$, and (e) $Ni_3S_{2.9}$ in the frequency range from

100 kHz to 1 Hz. The inset is the equivalent electrical circuit and resistance values (in Ω). An enlargement for the high frequency region is also shown in the inset.

Fig. 9 The electrochemical performance of the $Ni_3S_{2.9}$ superlattice as a working electrode in coin cell. (a) CV curves in a potential range of 0.02–3.0 V for the initial five cycles, (b) Galvanostatic charge–discharge profiles at current density of 500 mA g⁻¹.

Fig. 10 The discharge–charge cycling performance between 0.02 and 3.0 V of the undoped Ni_3S_2 at current density of 200 mA g⁻¹, and the superlattice $Ni_3S_{2.9}$ at current density of 200 and 500 mA g⁻¹, respectively.

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Scheme 1.



S2-tuned Ni3(S)1.1(S2)0.9 superlattice electrode





Fig. 2



Fig. 3



Fig. 4







Fig. 6





Fig. 7











Credit author statement:

All authors have the same status and contributions to the work reported in the manuscript, including the interpretation of data, editing and writing assistance.

Journal Prevention

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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