NiMn layered double hydroxides derived multiphase Mn-doped Ni sulfides with reduced graphene oxide composites as anode materials with superior cycling stability for sodium ion batteries

Chen, Jingwei; Li, Shaohui; Qian, Kai; Lee, Pooi See

2018

Chen, J., Li, S., Qian, K., & Lee, P. S. (2018). NiMn layered double hydroxides derived multiphase Mn-doped Ni sulfides with reduced graphene oxide composites as anode materials with superior cycling stability for sodium ion batteries. *Materials Today Energy*, 9, 74-82. doi:10.1016/j.mtener.2018.02.008

<https://hdl.handle.net/10356/140444>

<https://doi.org/10.1016/j.mtener.2018.02.008>

© 2018 Elsevier. All rights reserved. This paper was published in *Materials Today Energy* and is made available with permission of Elsevier.

Downloaded on 26 Apr 2023 19:30:48 SGT

NiMn Layered Double Hydroxides derived Multiphase Mn-doped Ni Sulfides with Reduced Graphene Oxide Composites as Anode Materials with Superior Cycling Stability for Sodium Ion Batteries

*Jingwei Chen, Shaohui Li, Kai Qian and Pooi See Lee**

School of Materials Science and Engineering, Nanyang Technological University, 639798,
Singapore

Corresponding Author

*Pooi See Lee, email: pslee@ntu.edu.sg

ABSTRACT: Sodium ion batteries have been drawing attention in recent years as the next generation batteries, due to the even distribution and abundance of sodium source. Metal sulfides as the promising sodium ion battery anode materials have the advantages of relatively high electronic conductivity than the metal oxides and high theoretical capacity. However, the accompanied severe volume changes upon de/sodiation often lead to fast capacity decay, poor rate capability and unsatisfactory cycling stability. In our work, multiphase Mn-doped Ni sulfides (NMS) nanoparticles were obtained by sulfidation process, the NMS nanoparticles deliver higher electronic conductivity and larger sodium diffusion coefficient than the multiphase Ni sulfides (NS) nanoparticles, resulting in a better rate performance. With the addition of reduced graphene oxide (rGO), NMS nanoparticles anchored on the surface of reduced graphene oxide (NMGS) were obtained. The optimized NMGS can deliver specific capacity of 460.9 mAh/g at a current density of 50 mA/g, while retaining a capacity of 169.4 mAh/g at an increased current density of 5000 mA/g, demonstrating good rate performance. In addition, when the ether-based electrolyte (1M NaCF₃SO₃ in diethylene glycol dimethyl ether) is used, the NMGS can maintain a capacity of 229.2 mAh/g at high current density of 5000 mA/g, and retain capacity of 206.1 mAh/g at 500 mA/g after 2000 cycles. The high specific capacity, great rate performance with excellent cycling stability emphasizes the promising potential of NMGS as sodium ion battery anodes.

Keywords: Mn doping; sulfide; anode; sodium ion battery.

TOC GRAPHICS

1. Introduction

Sodium ion battery (SIB) has been drawing much attention due to the abundance and even distribution of sodium resources. With similar electrochemical behaviors, SIB often suffers from compromised energy density and slower electrochemical kinetics than Lithium ion battery (LIB), due to the higher standard potential ($E^0_{\text{Na/Na}^+} = -2.71 \text{ V}$, $E^0_{\text{Li/Li}^+} = -3.04 \text{ V}$ versus standard hydrogen electrode), heavier and larger Na ions.[1-3] However, compared to LIB, SIB has higher cost effectiveness with 10 times lower cost/Ah, resulting in great potential in stationary applications.[1-5] Interesting materials including sodium layered oxides,[6] phosphates,[7-9] Prussian blue analogues,[10, 11] etc. have been explored as SIB cathode materials with good electrochemical performance. However, efforts should be made to obtain superior SIB anode materials as the typical graphitic carbon anode used in LIB is incapable of Na^+ ions intercalation.[1, 12, 13] Although progress has been made to enable sodium intercalation in graphite by co-intercalation phenomenon,[14, 15] the capacity realized based on carbon materials are still generally within the range of less than 300 mAh/g.[16-18]

Compared with metal oxides counterparts, metal sulfides often possess higher electronic conductivity, better thermal and mechanical stability as well as better electrochemical reversibility.[19, 20] In addition, metal sulfides have higher theoretical capacity compared to the conventional intercalation-based electrode materials, thus metal sulfides have been regarded as the promising SIB anode materials.[20] However, the accompanied volume change induced by repeated de/sodiation often resulted in unsatisfactory electrochemical performance.[21, 22] [23] As a result, some approaches have been introduced to overcome this problem including nanostructure design, compositional design and incorporation of functional materials, etc.[24-28] It has been demonstrated that downsizing of conversion-based electrode materials to nanoscale

can relieve the volume expansion/shrinkage, facilitate Na^+ diffusion, thus enhancing the utilization rate of electrode materials and the rate performance.[29-33] It was reported by Jun. et al. that anatase TiO_2 with the smallest size of 80 nm can realize superior rate performance due to the enhanced Na^+ diffusion kinetics and electron transfer.[29] The other way is to introduce conductive and stable carbon materials, which could facilitate not just the electron transfer but also buffer the stress caused by volume changes, thus enhancing the rate performance and cycling retention.[34-36] By incorporating carbon layers, MoS_2/C composite can deliver superior sodium storage performance than the MoS_2 alone, due to more active sites and higher stability.[37] Also, when interconnected with graphene and carbon nanotubes, the WS_2/C nanocomposites delivered better rate capability with extended cycling stability due to the stable structure and accommodated volume change.[23] In addition, hetero-doping has been found to be effective in enhancing electrochemical performance by introducing extra redox behaviors with improved electronic conductivity.[38] For example, $\text{Bi}_{0.94}\text{Sb}_{1.06}\text{S}_3$ solid solution was synthesized with nanorod cluster morphology. When coupled with graphite, the $\text{Bi}_{0.94}\text{Sb}_{1.06}\text{S}_3$ -graphite composite exhibits superior sodium-ion storage performance as compared to Bi_2S_3 -graphite and Sb_2S_3 -graphite due to reduced polarization and improved reversibility.[39] The Mo-doped SnS_2 grown on carbon cloth was found to enhance capacity with higher rate performance and cycling stability than the SnS_2 grown on carbon cloth, which can be ascribed to the increased interlayer spacing and more defects generated.[25]

Based on the above discussions, we design and synthesize multiphase Mn-doped Ni sulfides nanoparticles anchored on the surface of reduced graphene oxide (rGO) as a hetero-doped sodium anode composite. This is achieved by sulfidizing the NiMn layered double hydroxide/graphene oxide composites. Layered double hydroxides are a group of multi-metal clay materials that are

constituted by positive host layers and charge compensating intercalated anions/water. With general formula of $[M^{2+}_{1-x} M^{3+}_x (OH)_2][A^{n-}]^{x/n} \cdot zH_2O$, LDHs have the merit of tunable composition, high specific capacitance, layered structure, and high dispersion of cations in host layers.[40] Among them NiMn LDH was reported to have semi-metal behavior with increased carrier mobility and reduced surface hydrogen desorption energy due to the incorporation of Mn element.[41] Upon sulfidation of the NiMn LDH, we show that the multiphase Mn-doped Ni sulfides (NMS) possess higher electronic conductivity, smaller charge transfer resistance and higher diffusion coefficient, leading to improved rate performance compared to pure multiphase Ni sulfides. Upon formation of rGO, the resultant multiphase Mn-doped Ni sulfides/rGO composites (NMGS) exhibit higher surface area and further reduced charge transfer resistance, resulting in a high capacity 460.9 mAh/g at a current density of 50 mA/g, high rate performance (169.4 mAh/g at 5 A/g), and good cycling stability (240.6 mAh/g after 150 cycles at 500 mA/g). When applied as anode material in ether based electrolyte (1M NaCF₃SO₃ in diethylene glycol dimethyl ether), NMGS delivers further improved rate performance (229.2 mAh/g at 5 A/g) and excellent cycling stability with capacity of 206.1 mAh/g after 2000 cycles at 500 mA/g.

2. Experimental

2.1 Materials Preparation

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$, hexamethylenetetramine (HMTA) and thioacetamide were used as purchased without further purification. Graphite oxide (GO) was prepared by modified Hummer's method using graphite powders.[22] multiphase Mn-doped Ni sulfides (NMS) were prepared by two-step hydrothermal reactions. Firstly, NiMn layered double hydroxides (LDH) were prepared as the precursors. In the first step, 30 mM $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 10 mM $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 20 mL deionized (DI) water by stirring. Afterwards, 0.56 g HMTA was added in the solution and stirred for 10 minutes. The solution was then transferred into a Teflon liner of 45 ml for hydrothermal treatment at 80 °C for 14 hours. The product was washed and collected by centrifugation at 10000 rpms for 5 minutes three times using DI water. In the second step, the NiMn LDH collected was firstly dispersed in 20 mL DI water by magnetic stirring, followed by adding 25 mM thioacetamide into the solution. The solution was subsequently transferred into 45 mL Teflon liner for hydrothermal reactions at 160 °C for 8 hours. The black products were washed and collected by centrifugation at 10000 rpms for 5 minutes three times using DI water and ethanol. After being freeze-dried overnight, the final products of NMS were collected and denoted as NMS. In the same process, without adding $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$, 40 mM $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added instead in the first step, the final products were denoted as NS after the two step hydrothermal reactions. In order to prepare NMGS, 1.0 mg/mL GO was dissolved in 20 mL deionized water first prior to the addition of 30 mM $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 10 mM $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$ and 0.56 g HMTA. After the first step hydrothermal treatment at 80 °C for 14 hours, NiMn LDH/rGO composite was obtained. Subsequently, the NiMn LDH/rGO composite was re-dispersed in 20 mL DI water followed by adding 50 mM thioacetamide. After the second

step hydrothermal treatment at 160 °C for 8 hours, the black product was washed and freeze dried, obtaining the final NMGS composite. The amount of GO was also varied to optimize the electrochemical performance of NMGS, NMGS with GO feeding concentration of 0.5, 1.0 and 2.0 mg/mL are labeled as NMGS1, NMGS2 and NMGS4. Similarly, pure GO was also selected as the starting material, and the final product is denoted as rGO after the two step hydrothermal reactions.

2.2 Materials Characterization

The X-ray diffraction (XRD) (Shimadzu powder diffractometer; Cu K α -radiation ($\lambda = 1.5406 \text{ \AA}$)) technique was applied to investigate the crystal structure of the samples. Scanning electron microscopy (SEM, JEOL 7600F) and Transmission electron microscope (TEM, JEOL 2010 UHR) were applied to reveal the structure and morphology of the samples. Raman spectroscopy was employed to characterize the chemical states of the samples with a monochromatic laser with a wavelength of 633 nm. X-ray photoelectron spectroscopy (XPS) analysis was performed using the VG ESCA Lab XPS system equipped with monochromatic Al K α X-ray source ($h\nu = 1486.7 \text{ eV}$), to investigate the chemical bonds of samples. N₂ adsorption/desorption experiments were implemented applying the Tristar II 3020 analyzer, the specific surface area and total pore volume of the samples were calculated using the Brunauer-Emmett-Teller (BET) method. Thermal gravimetric analysis (TGA, TA Instruments 2950) was also applied to estimate the carbon content in the samples, with a heating rate of 10 °C/min from room temperature to 700 °C in air atmosphere.

2.3 Electrochemical Testing and Analysis

The electrochemical tests were conducted in a CR2032 half-cell configuration, with the Na plate as both reference and counter electrode. The working electrode was prepared based on slurry. Firstly, the active materials, carbon black and polyvinylidene fluoride (PVDF) (weight ratio of

8:1:1) were mixed in NMP. Then the slurry was loaded onto a copper foil and dried at 70 °C in vacuum overnight. The mass loading of the active materials was 1.0 ~1.5 mg. The assembly of the half-cell was conducted in the Argon filled glove box with O₂ and H₂O level < 0.1 ppm, and the assembled cells were aged overnight to allow electrolyte penetration as well as cell stabilization. The electrolyte employed is 1M NaClO₄ in EC (ethylene carbonate): DMC (dimethyl carbonate) (v/v 1:1), with 5wt % FEC if not specified. Ether-based electrolyte 1 M NaCF₃SO₃ in diethylene glycol dimethyl ether (DEGDME) was also applied to extend the cycling stability, with narrowed voltage window of 0.5~ 3.0 V. Cyclic voltammetry (CV) measurements were conducted by Autolab with a scan rate of 0.1 mV/s between 0.01 ~ 3.0 V versus Na/Na⁺. Electrochemical impedance spectroscopy (EIS) was also measured by Autolab with AC voltage of 10 mV amplitude in a frequency range of 0.01~100 KHz at open circuit potential. The galvanostatic charge/discharge (GCD) and cycling tests were conducted by the Neware battery-testing instrument, to reveal the rate performance and cycling stability of the electrode materials. Galvanostatic intermittence titration techniques (GITT) were applied and measured by Autolab based on the following equation[42]:

$$D = \frac{4L^2}{\pi\tau} \left(\frac{\Delta E_s}{\Delta E t} \right)^2$$

in which t is the current pulse duration (s), τ is the relaxation time (s), and ΔE_s is the steady-state potential change by the current pulse. $\Delta E t$ is the potential change resulted from the constant current pulse with eliminated IR drop. L is sodium ion diffusion length (cm); for compact electrode, it is equal to the thickness of electrode. In our case, constant current pulse of 100 mA/g was applied with duration of 1200s while the relaxation time is 1800s.

3. Results and discussion

Figure 1. (a) X-ray diffraction patterns of NS, NMS and NMGS; SEM images of (b) NS; (c) NMS; and (d) NMGS.

In order to characterize the crystal structure and composition of the samples, X-ray diffraction (XRD) measurements were carried out and the XRD analyses are shown in [Figure 1a](#). It can be seen that for NS, it is composed of multiphase Ni sulfides, including NiS (# 00-002-1280 hexagonal), NiS_2 (# 04-002-2589 cubic) and Ni_3S_4 (# 04-003-2272, cubic), with diffraction peaks corresponding to different crystal planes of Ni sulfides. The XRD pattern and SEM image of the NiMn LDH precursor were collected as shown in [Fig. S1](#), validating the successful preparation of NiMn LDH with micro-flower morphology. With the introduction of Mn and graphene oxide (GO) into the sulfidation reaction, the final composition of the products NMS and NMGS are similar to that of NS, which are also composed of NiS (# 00-002-1280 hexagonal), NiS_2 (# 04-002-2589

cubic) and Ni_3S_4 (# 04-003-2272, cubic). However, the 2-theta value of (200) crystal plane of NiS_2 for NS and NMS is slightly different, as can be seen from Fig. S2a. Compared with NS, the 2-theta value of NMS is smaller, indicating a slightly larger lattice parameter, which can be resulted from the Mn-doping in multiphase Ni sulfides.[25] The presence of Mn in NMS is also confirmed by SEM EDX, as can be seen in Figure S2(c-d). The low magnification SEM image of the composite has been provided as in Fig. S2b. It can be seen that the composite resembles the morphology of crumpled reduced graphene oxide. The morphology of the samples were revealed by SEM under the same magnification as seen in Figure 1(b-d). It is noticed that both NS and NMS consist of nanoparticles, while the NMS nanoparticles size is slightly larger than that of NS. The morphology of NMGS can be seen from Figure 1d, the crumpled large sheets indicate the presence of rGO, and the nanoparticles were found randomly distributed on the rGO surface, demonstrating successful introduction of rGO and the well attachment of the NMS nanoparticles on the rGO surface.

Figure 2. (a) TEM images of NMGS at high magnification, (b) High resolution TEM image of NMGS; (c) N₂-isotherms of NS, NMS and NMGS, inset is the table summarizing the surface area and pore volume; (d) pore size distribution of NS, NMS and NMGS.

The fine nanostructures of NMGS were further revealed by TEM. As seen in **Figure 2a**, large and thin rGO sheets with high transparency is clearly observed with nanoparticles randomly distributed on the surface, consistent with the SEM observations. The size of the nanoparticles is around tens of nanometers. The lattice fringes of the nanoparticles can be distinguished under high resolution conditions. As shown in Figure 2b, lattice fringes of the nanoparticles can be clearly distinguished with measured d-spacing of 0.54 nm, which is in consistence of the (111) crystal plan of Ni₃S₄ (cubic). The surface area and pore size distribution of the samples were revealed by Brunauer-Emmett-Teller (BET) measurements. The N₂ adsorption-desorption isotherms of the three samples can be seen in Figure 2c. The isotherm shape of NS and NMS are quite similar, indicating similar amount of surface areas and pore volumes. For the NMGS, the isotherm shape is a typical IV type curves, indicating mesoporous structure and larger surface area.[41] The pore size distribution for the three samples are plotted in Figure 2d. It is noticed that for NS and NMS, no obvious pores can be extracted. On the contrary, the pores present in NMGS have a distributed size of less than 100 nm, creating more surface area. The surface area and pore volume of NS, NMS and NMGS are summarized in the inset table in Figure 2c for comparison. With the incorporation of rGO, NMGS exhibits larger surface area and higher pore volume, which is conducive to electrolyte uptake and beneficial to the electrochemical performance.[22, 43]

Figure 3. (a) Raman spectrum of NMGS; XPS spectra of NMGS (b) C 1s spectra; and (c) Ni 2p spectra; (d) S 2p spectra.

The Raman spectrum of NMGS was obtained as shown in **Figure 3a**. Two peaks with wavenumbers of 1350 and 1581 cm^{-1} are observed, corresponding to the D (disorder) band and G (graphitic) band of graphitic structured carbon materials, which can be ascribed to the A_{1g} breathing vibration and the E_{2g} in-plane vibrational mode of sp^2 -bonded carbon respectively.[44, 45] The high intensity ratio between D band to G band is indicative of plenty defects, which can also be extracted from the XPS C 1s spectra in Figure 3b. The Raman spectra of GO and rGO were also collected as shown in **Fig. S3a**, the characteristic D band and G band are clearly observed for both GO and rGO. The intensity ratio of D band to G band I_D/I_G for rGO (~ 0.99) is higher than GO (~ 0.89), indicative of the increased size of sp^2 carbon domains and increased amount of defects.[46] It is also noticed that the wavenumber of G band for rGO is blue shifted to 1579.6 cm^{-1} .

¹ compared to $\sim 1587.1 \text{ cm}^{-1}$ of GO, which is caused by the “self-healing” effects that recover the hexagonal carbon networks.[47, 48] The characteristic 2D band of graphene is also restored for the rGO sample, confirming the reduction of GO to rGO.[22, 47, 48] From the XRD patterns of GO and rGO as in Figure S3b, it can be seen that rGO exhibits a broadened peak located at 2θ of 24.6° compared to 2θ of 10.8° for GO, indicating reduced interlayer distance of 0.36 nm for rGO compared to 0.82 nm of GO, due to the reduction of GO and the rGO restacking.[46] The SEM energy dispersive X-ray mapping and spectrum of rGO can be found in Figure S3(c-d). Presence of O and S elements in rGO are also verified from the XPS results of the C-O and C-S bonds derived from Figure 3b. It can be seen that the dominating XPS peak located at 284.6 eV corresponds C=C sp^2 hybridized bonds, while there are still some C-C and C-O bonds present, in association with the presence of defects.[48, 49] The peak located at 287.9 eV can be assigned to C-S bond, indicating the S doping into the graphitic structure.[48, 50] The Ni 2p and S 2p spectra of NMGS were also obtained as shown in Figure 3c-d. It can be seen from Figure 3c that two doublets located at 853.7 and 871.0 eV; 856.3 and 874.2 eV with two satellite peaks can be deconvoluted. The peaks located at binding energy of 853.7 and 871.0 eV suggests the Ni $2\text{p}_{3/2}$ and Ni $2\text{p}_{1/2}$ of Ni^{2+} (typical of Ni-S bonds), while the peaks located at binding energy of 856.3 and 874.2 eV are indicative of the Ni $2\text{p}_{3/2}$ and Ni $2\text{p}_{1/2}$ of Ni^{3+} , [51, 52] showing the coexistence of divalent and trivalent Ni ions. The Mn 3p spectrum of NMGS can be found in Fig. S4b. The peak located at 641.4 eV is in association of the Mn $2\text{p}_{3/2}$, typical of Mn-S bond in MnS, while the possibility of Mn-O bond in MnO or Mn_3O_4 could not be eliminated due to the similar bonding energy.[52] From a detail slow scan XRD analyses of NMGS as shown in Figure S4d, there are no MnS_x or MnO_x species that can be detected. Therefore, the XPS peak of the Mn $2\text{p}_{3/2}$ located at 641.4 eV is assigned to Mn-S bonds in NMS. As can be seen in the inset of Figure S4b, the atomic

ratio of Mn in NMS at the surface is 1.7%. The atomic ratio between S to Ni is ~ 1.96 , correlating with the major phase of NiS_2 in NMS. The S 2p spectrum can be seen in Figure 3d, the peak located at 168.7 eV can be ascribed to S-O or SO_4^{2-} species, which is probably caused by oxidation at the surface.[35] Aside from this peak, a peak located at the binding energy of 163.7 eV and a pair of spin-orbit doublets can be deconvoluted. The peaks located at 163.7 eV is indicative of C-S bond, in association with the S doping into the graphitic structure,[50] while the peaks located at 161.9 and 162.9 eV can be ascribed to the S $2p_{3/2}$ and S $2p_{1/2}$, typical of S^{2-} in sulfides.[52]

Figure 4. The first 4 Cyclic voltammograms (CV) of (a) NS; (b) NMS and (c) NMGS measured in a potential range of 0.01V $\sim$ 3.0 vs. Na/Na^+ at a scan rate of 0.1 mV/s; (d) the EIS spectrum of NS, NMS and NMGS obtained after the 4 CV scans.

In order to compare the electrochemical performance of the samples, sodium ion half cells were assembled in the glove box. Cyclic voltammogram (CV) curves of the three samples can be seen

from Figure 4a-c, obtained under scan rates of 0.1 mV/s in potential range of 0.01~3.0 V for 4 cycles. It can be seen that for NS, during the first sodiation process, two cathodic peaks were noticed at ~ 1.1 V and 0.8 V, which is possibly related to the conversion-based mechanism forming Ni metal and Na₂S, and the formation of solid electrolyte interface (SEI).[53-55] After sodiation, the peak at ~2.2V is indicative of the reversed oxidation process. However, for the NS sample, both the cathodic and anodic current densities decreased dramatically upon cycling, hardly retaining the redox peaks after 4 cycles, indicating poor performance retention. NMS samples have similar electrochemical behaviors with smaller polarization between the cathodic and anodic peaks. In addition, the current density is retained with distinguished redox peaks after the cycling, demonstrating increased retention capability of NMS compared with NS. With the addition of GO, NMGS exhibits another cathodic peak at ~ 2.0 V during the first sodiation process, which is possibly related with the reduction of doped S in the presence of rGO.[56, 57] In the subsequent cycles, the current densities of both cathodic and anodic scans are well preserved and almost overlapped with each other, representing further improved electrochemical stability compared with NMS. The electrochemical impedance spectroscopy (EIS) spectra of samples were collected as shown in Fig 4d, in which the semi-circle at the high-medium frequency region represents the charge transfer resistance (R_{ct}). It is noticed that compared with NS, with the incorporation of Mn, the R_{ct} of NMS is decreased, indicating faster electrochemical reaction kinetics. The better retention and faster charge transfer kinetics of NMS can be ascribed to its enhanced electronic conductivity and higher sodium ion diffusion coefficient than NS, as shown in Fig. S5 and Fig. S6. The sheet resistances of NS and NMS are measured by four point probe method based on pressed pellets. The measured sheet resistance values of NS and NMS based pellets are 2.868 Ω /sq and 1.049 Ω /sq, respectively. The conductivity of NS and NMS based pellets are calculated to be

67.05 and 120.67 S/cm, demonstrating the higher electronic conductivity of NMS than NS powder based pellet. With the addition of rGO, the R_{ct} of NMGS is further improved compared with NMS, indicating the further facilitated charge transfer, in agreement with the CV analysis. The content of GO was optimized based on the electrochemical performance as shown in Fig. S7 and Fig. S8. It can be seen in Fig. S7a that with various feeding concentration of GO, the crystal structures of the samples remains the same with different morphology. The electrochemical performances of NMGS with various GO feeding concentration were also evaluated as shown in Fig. S8. NMGS2 exhibits highest specific capacity at various current densities with better rate performance, while the cycling stability of NMGS2 is also superior than that of the other two samples. As a result, the feeding concentration of GO is optimized to be 1.0 mg/mL. The weight content of rGO in NMGS after the sulfidation process was also estimated using thermal gravimetric analysis (TGA). As shown in Fig. S9, in the temperature range up to 700 °C, NMS can retain a weight percentage of 78.9 % after the decomposition, while NMGS can only retain a weight percentage of 59.8 % due to the extra contribution from rGO, thus the rGO content is estimated to be ~ 24 wt.%.

Figure 5. (a) the GCD curves of NMGS at various current densities; (b) the specific capacity of NS, NMS and NMGS under different current densities, solid symbol is for discharge capacities while the hollow symbol is for the charge capacities; (c) the specific capacity of NS, NMS and NMGS upon 150 cycles at current density of 500 mA/g and (d) the high resolution TEM images of NMGS discharged to 0.01V, inset is the selected area electron diffraction (SAED) pattern.

The galvanostatic charge discharge (GCD) curves of NS, NMS and NMGS were measured at 50 mA/g between voltage range of 0.01~3.0V, as plotted in [Fig. S10](#). It can be seen that both samples deliver a pair of plateaus in subsequent GCD cycles, corresponding to the redox peaks in CV curves shown in Figure 4. Compared with the decreasing capacity of NS, the discharge/charge capacities of NMS are well retained in the subsequent GCD cycles, showing good capacity retention. In contrast, for NMGS the GCD curves in the subsequent cycles are almost overlapped, with higher capacity values than NS and NMS. NMGS exhibits a very high first discharge capacity of 1141.2 mAh/g, indicating a low first cycle coulombic efficiency (CE), which is in association with electrolyte decomposition, SEI formation and the larger surface area of NMGS.[54, 58] The GCD curves of rGO itself is also presented as shown in [Fig. S11a](#). It can be seen that the initial CE of rGO is very limited, leading to the low initial CE of NMGS. The TEM image of NMGS discharged to 0.01V was also captured as shown in [Fig. S12\(a-b\)](#). It can be seen that compared with the original NMGS, the size of the nanoparticles was obviously reduced after being fully discharged, in association with the nanoparticles breakage caused by volume change upon sodiation, leading to the discharge capacity fade after the first cycle. Thus the higher capacity decay of NMGS in the first cycle than NS and NMS can be ascribed to the higher contribution of electrolyte decomposition to the overall capacity, due to the presence of rGO and the higher surface area of NMGS.[59] The contribution of reduced graphene oxide towards sodium capacity is to enhance surface area/porosity to create more active sites. Inclusion of rGO provides the conductive

pathways for fast electron transfer and also acts as a stable scaffolds that buffers stress that was caused by metal sulfides volume change during testing, leading to improved capacity, rate capability and cycling stability of the electrode materials. In the meantime, the conductivity/porosity of composites can be controlled by varying the experimental conditions.[60, 61] This issue of low initial CE of NMGS is tackled by replacing the electrolyte, which is discussed later. The GCD curves of NMGS at different current densities were also shown as in Figure 5a. It can be seen that with increased current densities, the specific capacity was reduced, however the shape of the GCD curves were well retained with a pair of oxidation/reduction plateaus, showing good capacity retention. Obvious voltage hysteresis of NMGS can be observed from the GCD curves upon increasing current density, due to the limited kinetics of the electrode materials which is in association with electrode polarization and the electronic/ionic conductivity.[62] This phenomenon is commonly observed in conversion-based sulfide materials. The specific capacities of the samples under different current densities were plotted as shown in Figure 5b. NS exhibits high specific capacities approaching 400 mAh/g at low current density of 50 mA/g, which decreases to 8 mAh/g at increased current density of 5000 mA/g. In comparison, NMS delivers better capacity retention capabilities than NS with higher specific capacities at increased current densities. The increased rate performance of NMS over NS can be attributed to the reduced R_{ct} , increased electronic conductivity, and also the slightly increased sodium diffusion coefficient derived by galvanostatic intermittent titration technique (GITT) measurements. With the formation of rGO, NMGS exhibits improved discharge capacity of 460.9 mAh/g at 50 mA/g. Upon increasing current densities, NMGS delivers notably higher capacities than NMS, still retaining discharge capacity of 169.4 mAh/g as the current density is increased 100 times (to 5000 mA/g), which is much higher than that of NS and NMS. When the current density is decreased

back to 50 mA/g, the specific capacity of NMGS can be restored to 395 mAh/g, showing excellent rate performance. The cycling stability of the samples were also evaluated, which were cycled at current density of 500 mA/g for 150 times. It is seen from Figure 5c that for NS, it suffers from a sharp capacity decay in the first tens of cycles and exhibits capacity of only ~ 30 mAh/g afterwards. NMS delivers improved capacity retention properties in the first tens of cycles, but the capacity is also gradually decreased upon further cycling. On the other hand, NMGS exhibits much higher capacity retention, retaining capacity of 240.6 mAh/g after 150 cycles, demonstrating good cycling stability of ~ 70%.

The electrochemical reaction of NMGS upon discharging was investigated using TEM. As can be seen in Figure 5d, in the high resolution TEM image of NMGS that was subjected to discharge at 0.01V, three sets of lattice fringes are observed with d-spacings measured to be $d_1=0.255$ nm, $d_2=0.380$ nm and $d_3=0.176$ nm, corresponding to the remnant NiS_2 (210), the discharge products Na_2S (111) and pure Ni metal (200). The SAED pattern in the inset also confirms the presence of the products after discharge, namely Na_2S and pure Ni, proving the effect of conversion-based mechanism; in agreement with the earlier works on FeS_2 and Ni_3S_2 [63, 64]

Figure 6. (a) The specific capacity of NMGS at different current densities and (b) the cycling stability of NMGS in different electrolyte systems. Solid symbol is for discharge capacities while the hollow symbol is for the charge capacities.

Electrolyte plays a very important role in determining the electrochemical performance of electrode materials. It is reported that for conversion-based anode materials, the cycling stability can be extended to thousands of cycles by applying ether-based electrolyte, which is due to the smaller apparent activation energy, reduced voltage polarization and the suppressed reaction between electrolyte and poly-sulfides.[65-67] In order to extend the cycling performance of NMGS, ether-based electrolyte (1 M NaCF₃SO₃ in diethylene glycol dimethyl ether (DEGDME)) was also employed in our work. The voltage window is narrowed to 0.5~3.0 V to avoid deep discharge with enhanced cycling stability.[65, 67] As seen in Figure 6a, the first cycle CE of NMGS in ether-based electrolyte is much improved compared to that in the carbonate-based electrolyte. At low current density, the specific capacity of NMGS in ether-based electrolyte is 388.4 mAh/g (loading mass of ~ 0.75 mg, excluding the mass of binder and carbon black), lower than that in ether-based electrolyte due to the smaller voltage window applied that suppresses the solid electrolyte interface formation and polysulfide-electrolyte interactions.[66, 67] However, the capacity retention of NMGS is improved in ether-based electrolyte, delivering capacity of 229.2 mAh/g at 5000 mA/g. When the current density is brought back to 50 mA/g, the capacity of NMGS in ether-based electrolyte can be restored to 338.6 mAh/g. In addition, as shown in Figure 6b, the cycling stability of NMGS in ether-based electrolytes is also significantly improved, delivering specific capacity of 269.2 mAh/g after being cycled for 150 times. When the cycle number is extended to 2000 cycles, specific capacity of 206.1 mAh/g can still be retained, showing superior cycling stability than that of NMGS in carbonate-based electrolyte. The TEM image of NMGS after the 2000 electrochemical cycles is also captured, as shown in Fig. S12c. It can be seen that even after 2000 cycles, the morphology of nanoparticles dispersed on the surface of rGO are still maintained, explaining the good cycling stability of NMGS in ether-based electrolyte.

The electrochemical reaction mechanism of NMGS in ether-based electrolyte is also studied as shown in Figure S13. As can be seen from the EDX mapping and spectrum in Fig. S13a, after being discharged to 0.5 V, Na is detected and uniformly dispersed in the discharge product. From the high magnification SEM image in Figure S13b, small nanoparticles are observed with some agglomeration noticed. Similarly, small nanoparticles with size of less than 10 nm are also observed from Figure S13(c-d), which is probably caused by nanoparticle breakage associated with Na⁺ insertion. From the SAED pattern in the inset of Figure S13d, 5 sets of diffraction rings are observed, the d-spacings are calculated to be $d_1 = 0.393$ nm; $d_2 = 0.291$ nm; $d_3 = 0.203$ nm; $d_4 = 0.183$ nm; $d_5 = 0.169$ nm. D-spacings of $d_1 = 0.393$ and $d_3 = 0.203$ nm can be ascribed to (111) crystal planes of Na₂S and (111) crystal planes of Ni, respectively. The other d-spacing values of $d_2 = 0.291$ nm and $d_4 = 0.183$ nm, $d_5 = 0.169$ nm are related with the NiS₂ ($d_{(200)} = 0.283$ nm) and Ni₃S₄ ($d_{(511)} = 0.182$ nm; $d_{(440)} = 0.167$ nm) respectively. The slightly larger d-spacing values in the discharge product than the standard NiS₂ and Ni₃S₄ can be ascribed to Na⁺ intercalation, leading to expanded crystal structures. Based on the above discussions, it is concluded that in ether-based electrolyte, it is intercalation reaction for NMGS while conversion reaction also takes place.

The electrochemical performance of NMGS is also compared with other conversion-based sulfide materials as sodium ion battery anode, as shown in Table S1. It can be seen that conversion-based sulfide materials with various composition and morphology has been prepared and applied as anode materials in SIB. With the introduction of heteroatom Mn-doping, our multiphase Mn-doped Ni sulfides have expanded crystal structures, higher sodium diffusion coefficient and smaller charge transfer resistance, leading to enhanced rate performance. In addition, the formation of rGO helps to anchor the NMS nanoparticles, providing high surface area and electron conduction highways. As a result, compared to other Ni sulfide based materials reported in literatures,[4, 53-

55, 68-70] our NMGS exhibits competitive specific capacity (388.4 mAh/g at 50 mA/g) and excellent rate performance. NMGS is able to retain ~ 60 % specific capacity even when the current density is increased for 100 times from 50 mA/g to 5000 mA/g, as shown in Fig. S14. On the other hand, when compared with other conversion-based sulfide materials,[64, 71-75] NMGS delivers excellent rate performance with retained specific capacity of 229.2 mAh/g at high current density of 5000 mA/g. Although NMGS does not exhibit the highest capacity, the specific capacity of NMGS can reach 606.4 mAh/g [460.9/(1-24%)] in carbonate-based electrolyte excluding the weight of rGO, which is also quite competitive. In addition, in ether-based electrolyte system NMGS exhibits superior cycling stability, with capacity retention of 70.2% after 1100 cycles and 63.5% even after 2000 cycles, while other conversion-based sulfide materials hardly go beyond 1000 cycles with limited capacity retention. Therefore, our NMGS can be regarded as a promising SIB anode materials with excellent electrochemical performance. From TEM and SAED analyses, we also revealed that the electrochemical discharge of the NMGS electrode in carbonate-based electrolyte is based on electrochemical conversion mechanism that correlates with the high specific capacity of NMGS in carbonate-based electrolytes.

4. Conclusion

In summary, using NiMn layered double hydroxide/graphene oxide as the precursor, multiphase Mn-doped Ni sulfides nanoparticles anchored on the surface of rGO (NMGS) can be obtained. Smaller charge transfer resistance, higher electronic conductivity and higher sodium ion diffusion coefficient are resulted from Mn-doping, together with enhanced surface area and further reduced charge transfer resistance upon formation of rGO that enables NMGS to deliver a specific capacity of 460.9 mAh/g at 50 mA/g while maintaining capacity of 169.4 mAh/g at 5000 mA/g, showing good rate performance. In addition, NMGS can maintain capacity of 240.6 mAh/g after being cycled at 500 mA/g 150 times. By employing ether-based electrolyte, NMGS delivers further improved rate performance and cycling stability, retaining capacity of 229.2 mAh/g at 5000 mA/g with improved capacity of 269.2 after 150 cycles. Furthermore, capacity of 206.1 mAh/g can still be maintained even after 2000 cycles at 500 mA/g, showing excellent cycling stability. The high capacity, high rate performance and outstanding cycling stability of NMGS emphasizes the potential of metal sulfide as SIB anode materials, paving the way for future studies and applications of metal sulfide based materials for sodium ion battery.

Acknowledgement

This work was financially supported by the National Research Foundation Investigatorship, Award No. NRF-NRFI2016-05 and the Campus for Research Excellence and Technological Enterprise (CREATE), under the National Research Foundation, Prime Minister's Office, Singapore.

References

- [1] D. Kundu, E. Talaie, V. Duffort, L.F. Nazar, *Angew. Chem.* 54 (2015) 3431-3448.
- [2] M.D. Slater, D. Kim, E. Lee, C.S. Johnson, *Adv. Funct. Mater.* 23 (2013) 947-958.
- [3] V. Palomares, P. Serras, I. Villaluenga, K.B. Hueso, J. Carretero-González, T. Rojo, *Energy Environ. Sci.* 5 (2012) 5884.
- [4] W. Qin, T. Chen, T. Lu, D.H.C. Chua, L. Pan, *J. Power Sources* 302 (2016) 202-209.
- [5] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, *Chem. Rev.* 114 (2014) 11636-11682.
- [6] M.H. Han, E. Gonzalo, G. Singh, T. Rojo, *Energy Environ. Sci.* 8 (2015) 81-102.
- [7] Z. Jian, L. Zhao, H. Pan, Y.-S. Hu, H. Li, W. Chen, L. Chen, *Electrochem. Commun.* 14 (2012) 86-89.
- [8] J. Kang, S. Baek, V. Mathew, J. Gim, J. Song, H. Park, E. Chae, A.K. Rai, J. Kim, *J. Mater. Chem.* 22 (2012) 20857.
- [9] S.Y. Lim, H. Kim, R.A. Shakoor, Y. Jung, J.W. Choi, *J. Electrochem. Soc.* 159 (2012) A1393-A1397.
- [10] H. Lee, Y.I. Kim, J.K. Park, J.W. Choi, *Chem. Commun.* 48 (2012) 8416-8418.
- [11] Y. Liu, Y. Qiao, W. Zhang, Z. Li, X. Ji, L. Miao, L. Yuan, X. Hu, Y. Huang, *Nano Energy* 12 (2015) 386-393.
- [12] Z. Jian, W. Luo, X. Ji, *J. Am. Chem. Soc.* 137 (2015) 11566-11569.
- [13] J. Ni, S. Fu, C. Wu, J. Maier, Y. Yu, L. Li, *Adv. Mater.* 28 (2016) 2259-2265.
- [14] B. Jache, P. Adelhelm, *Angew. Chem.* 53 (2014) 10169-10173.
- [15] H. Kim, J. Hong, G. Yoon, H. Kim, K.-Y. Park, M.-S. Park, W.-S. Yoon, K. Kang, *Energy Environ. Sci.* 8 (2015) 2963-2969.
- [16] M. Krengel, P. Adelhelm, F. Klein, W. Bensch, *Chem. Commun.* 51 (2015) 13500-13503.
- [17] Y. Wen, K. He, Y. Zhu, F. Han, Y. Xu, I. Matsuda, Y. Ishii, J. Cumings, C. Wang, *Nat. Commun.* 5 (2014) : ncomms5033.
- [18] S. Komaba, W. Murata, T. Ishikawa, N. Yabuuchi, T. Ozeki, T. Nakayama, A. Ogata, K. Gotoh, K. Fujiwara, *Adv. Funct. Mater.* 21 (2011) 3859-3867.
- [19] X.-Y. Yu, L. Yu, X.W.D. Lou, *Adv. Energy Mater.* 6 (2016) 1501333.
- [20] Y. Zhang, Q. Zhou, J. Zhu, Q. Yan, S.X. Dou, W. Sun, *Adv. Funct. Mater.* 27 (2017) 1702317.
- [21] S.H. Choi, Y.N. Ko, J.-K. Lee, Y.C. Kang, *Adv. Funct. Mater.* 25 (2015) 1780-1788.
- [22] J. Chen, S. Li, V. Kumar, P.S. Lee, *Adv. Energy Mater.* 7 (2017) 1700180.
- [23] C. Zhu, P. Kopold, W. Li, P.A. van Aken, J. Maier, Y. Yu, *J. Mater. Chem. A* 3 (2015) 20487-20493.
- [24] Y. Xu, M. Zhou, Y. Lei, *Adv. Energy Mater.* 6 (2016) 1502514.
- [25] Q. Chen, F. Lu, Y. Xia, H. Wang, X. Kuang, *J. Mater. Chem. A* 5 (2017) 4075-4083.
- [26] T. Wang, P. Hu, C. Zhang, H. Du, Z. Zhang, X. Wang, S. Chen, J. Xiong, G. Cui, *ACS Appl. Mater. Interfaces*, 8 (2016) 7811-7817.
- [27] D. Zhang, W. Sun, Y. Zhang, Y. Dou, Y. Jiang, S.X. Dou, *Adv. Funct. Mater.* 26 (2016) 7479-7485.
- [28] J. Cui, S. Yao, J.-K. Kim, *Energy Storage Mater.* 7 (2017) 64-114.
- [29] J. Chen, Y. Zhang, G. Zou, Z. Huang, S. Li, H. Liao, J. Wang, H. Hou, X. Ji, *Small*, 12 (2016) 5554-5563.
- [30] W. Duan, Z. Zhu, H. Li, Z. Hu, K. Zhang, F. Cheng, J. Chen, *J. Mater. Chem. A* 2 (2014) 8668.

- [31] L. Fan, X. Li, B. Yan, J. Feng, D. Xiong, D. Li, L. Gu, Y. Wen, S. Lawes, X. Sun, *Adv. Energy Mater.* 6 (2016) 1502057.
- [32] Y.T. Weng, T.Y. Huang, C.H. Lim, P.S. Shao, S. Hy, C.Y. Kuo, J.H. Cheng, B.J. Hwang, J.F. Lee, N.L. Wu, *Nanoscale* 7 (2015) 20075-20081.
- [33] L. Wu, X. Hu, J. Qian, F. Pei, F. Wu, R. Mao, X. Ai, H. Yang, Y. Cao, *Energy Environ. Sci.*, 7 (2014) 323-328.
- [34] Z. Shadike, M.-H. Cao, F. Ding, L. Sang, Z.-W. Fu, *Chem. Commun.* 51 (2015) 10486-10489.
- [35] S.Y. Lee, Y.C. Kang, *Chem-Eur J.* 22 (2016) 2769-2774.
- [36] S. Peng, X. Han, L. Li, Z. Zhu, F. Cheng, M. Srinivansan, S. Adams, S. Ramakrishna, *Small*, 12 (2016) 1359-1368.
- [37] Y.L. Ding, P. Kopold, K. Hahn, P.A. van Aken, J. Maier, Y. Yu, *Adv. Mater.* 28 (2016) 7774-7782.
- [38] X.Y. Yu, X.W. Lou, *Adv. Energy Mater.* (2017) 1701592.
- [39] Y. Zhao, A. Manthiram, *Chem. Mater.* 27 (2015) 6139-6145.
- [40] Q. Wang, D. O'Hare, *Chem. Rev.* 112 (2012) 4124-4155.
- [41] J. Zhao, J. Chen, S. Xu, M. Shao, Q. Zhang, F. Wei, J. Ma, M. Wei, D.G. Evans, X. Duan, *Adv. Funct. Mater.* 24 (2014) 2938-2946.
- [42] D.T. Ngo, H.T. Le, C. Kim, J.-Y. Lee, J.G. Fisher, I.-D. Kim, C.-J. Park, *Energy Environ. Sci.* 8 (2015) 3577-3588.
- [43] X. Rui, W. Sun, C. Wu, Y. Yu, Q. Yan, *Adv. Mater.* 27 (2015) 6670-6676.
- [44] L. Shen, J. Wang, G. Xu, H. Li, H. Dou, X. Zhang, *Adv. Energy Mater.* 5 (2015) 1400977.
- [45] C.Y. Foo, A. Sumboja, D.J.H. Tan, J. Wang, P.S. Lee, *Adv. Energy Mater.* 4 (2014) 1400236.
- [46] J. Xu, S. Gai, F. He, N. Niu, P. Gao, Y. Chen, P. Yang, *Dalton Trans.* 43 (2014) 11667-11675.
- [47] G.T. How, A. Pandikumar, H.N. Ming, L.H. Ngee, *Sci. Rep.* 4 (2014) 5044.
- [48] W.S.V. Lee, M. Leng, M. Li, X.L. Huang, J.M. Xue, *Nano Energy* 12 (2015) 250-257.
- [49] D.R. Dreyer, S. Park, C.W. Bielawski, R.S. Ruoff, *Chem. Soc. Rev.* 39 (2010) 228-240.
- [50] J. Chen, X. Wang, J. Wang, P.S. Lee, *Adv. Energy Mater.* 6 (2016) 1501745.
- [51] J. Xiao, L. Wan, S. Yang, F. Xiao, S. Wang, *Nano Lett.* 14 (2014) 831-838.
- [52] J.F. Moulder, J. Chastain, *Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data*, Physical Electronics Division, Perkin-Elmer Corporation. 1992.
- [53] X. Song, X. Li, Z. Bai, B. Yan, D. Li, X. Sun, *Nano Energy* 26 (2016) 533-540.
- [54] T. Wang, P. Hu, C. Zhang, H. Du, Z. Zhang, X. Wang, S. Chen, J. Xiong, G. Cui, *ACS Appl. Mater. Interfaces*, 8 (2016) 7811-7817.
- [55] D. Zhang, W. Sun, Y. Zhang, Y. Dou, Y. Jiang, S.X. Dou, *Adv. Funct. Mater.* 26 (2016) 7479-7485.
- [56] X. Lu, B.W. Kirby, W. Xu, G. Li, J.Y. Kim, J.P. Lemmon, V.L. Sprenkle, Z. Yang, *Energy Environ. Sci.*, 6 (2013) 299-306.
- [57] S. Xin, Y.X. Yin, Y.G. Guo, L.J. Wan, *Adv. Mater.* 26 (2014) 1261-1265.
- [58] J. Sun, H.-W. Lee, M. Pasta, H. Yuan, G. Zheng, Y. Sun, Y. Li, Y. Cui, *Nature Nanotech.* 10 (2015) 980-985.
- [59] L. David, R. Bhandavat, U. Barrera, G. Singh, *Sci. Rep.* 5 (2015) 9792.
- [60] L. David, G. Singh, *The J. Phys. Chem. C* 118 (2014) 28401-28408.
- [61] L. David, K. Shareef, M. Abass, G. Singh, *RSC Adv.* 6 (2016) 53894-53902.
- [62] S. Li, Y. Dong, L. Xu, X. Xu, L. He, L. Mai, *Adv. Mater.* 26 (2014) 3545-3553.

- [63] X. Xia, Q. Wang, Q. Zhu, J. Xie, J. Wang, D. Zhuang, S. Zhang, G. Cao, X. Zhao, *Mater. Today Energy* 5 (2017) 99-106.
- [64] Z. Liu, T. Lu, T. Song, X.-Y. Yu, X.W. Lou, U. Paik, *Energy Environ. Sci.* 10 (2017) 1576-1580.
- [65] Z. Hu, Z. Zhu, F. Cheng, K. Zhang, J. Wang, C. Chen, J. Chen, *Energy Environ. Sci.* 8 (2015) 1309-1316.
- [66] S. Peng, X. Han, L. Li, Z. Zhu, F. Cheng, M. Srinivansan, S. Adams, S. Ramakrishna, *Small*, 12 (2016) 1359-1368.
- [67] S. Zhu, Q. Li, Q. Wei, R. Sun, X. Liu, Q. An, L. Mai, *ACS appl. Mater. Interfaces*, 9 (2017) 311-316.
- [68] R. Sun, S. Liu, Q. Wei, J. Sheng, S. Zhu, Q. An, L. Mai, *Small* 13 (2017) 201701744.
- [69] Q. Pan, J. Xie, T. Zhu, G. Cao, X. Zhao, S. Zhang, *Inorg. Chem.*, 53 (2014) 3511-3518.
- [70] X. Xia, J. Xie, S. Zhang, B. Pan, G. Cao, X. Zhao, *J. Mater. Sci. Tech.* 33 (2017) 775-780.
- [71] Q. Wang, W. Zhang, C. Guo, Y. Liu, C. Wang, Z. Guo, *Adv. Funct. Mater.* (2017) 1703390.
- [72] Y.X. Wang, J. Yang, S.L. Chou, H.K. Liu, W.X. Zhang, D. Zhao, S.X. Dou, *Nat. Commun.* 6 (2015) 8689.
- [73] L. David, R. Bhandavat, G. Singh, *ACS Nano*, 8 (2014) 1759-1770.
- [74] Y.X. Wang, S.L. Chou, D. Wexler, H.K. Liu, S.X. Dou, *Chem-Eur J.* 20 (2014) 9607-9612.
- [75] X. Geng, Y. Jiao, Y. Han, A. Mukhopadhyay, L. Yang, H. Zhu, *Adv. Funct. Mater.* (2017) 1702998.