# To Promote the Catalytic Conversion of Polysulfides Using Ni–B Alloy Nanoparticles on Carbon Nanotube Microspheres under High Sulfur Loading and a Lean Electrolyte

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ABSTRACT: Despit	e their high theoretical	energy density, the	Sprov drving	a Sulfur loading	<b>b</b>

application of lithium–sulfur batteries is seriously hindered by the polysulfide shuttle and sluggish kinetics, especially with high sulfur loading and under low electrolyte usage. Herein, to facilitate the conversion of lithium polysulfides, nickel–boron (Ni–B) alloy nanoparticles, dispersed uniformly on carbon nanotube microspheres (CNTMs), are used as sulfur hosts for lithium–sulfur batteries. It is demonstrated that Ni–B alloy nanoparticles can not only anchor polysulfides through Ni–S and B–S interactions but also exhibit high electrocatalytic capability toward the conversion of intermediate polysulfide species. In addition, the intertwined CNT microspheres provide an additional conductive scaffold in response to the fast electrochemical redox. The enhanced redox kinetics is beneficial to



improve the specific capacity and cycling stability of the sulfur cathode, based on the fast conversion of lithium polysulfides and effective deposition of the final sulfide products. Conclusively, the S/Ni–B/CNTM composite delivers a high specific capacity (1112.7 mAh  $g_s^{-1}$ ) along with good cycle performance under both high sulfur loading (8.3 mg cm<sup>-2</sup>) and a lean electrolyte (3  $\mu$ L mg<sub>s</sub><sup>-1</sup>). Consequently, this study opens up a path to design new sulfur hosts toward lithium–sulfur batteries.

KEYWORDS: nickel-boron alloy, catalytic conversion, deposition, sulfur electrode, lithium-sulfur batteries

# 1. INTRODUCTION

Lithium-sulfur (Li-S) batteries are considered as one of the most promising new secondary batteries. Their theoretical energy density (2600 Wh kg<sup>-1</sup>) is several times higher than that of state-of-the-art lithium-ion batteries with intercalation compounds as cathodes and anodes.<sup>1-4</sup> Furthermore, the additional features of sulfur, including high elemental abundance and environmental friendliness, are also attractive as active materials in the high-energy battery system. Nevertheless, several challenges make the commercialization of Li-S batteries uncertain, in particular, the sluggish kinetics due to the low intrinsic electrical/ionic conductivity of both sulfur and discharged products (Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S) and the wellknown shuttle effect resulting from the soluble intermediate lithium polysulfides (LiPS) in ether-based electrolytes.<sup>5-9</sup> These issues adversely affect the electrochemical performance of Li-S batteries, leading to poor utilization of sulfur, low Coulombic efficiency, and unsatisfactory cycling stability of the sulfur cathode.

Tremendous efforts are being made to suppress the polysulfide shuttling and boost the electrochemical redox of sulfur cathodes, including optimization of the sulfur host and binder and employment of interlayers and redox mediators.<sup>11,12</sup> In addition, using electrolyte additives and fabricating

artificial layers to protect the Li/electrolyte interface can affect the lithium deposition and thus also improve the electrochemical properties of Li-S batteries.<sup>13,14</sup> In terms of the design of sulfur cathodes, carbon nanomaterials are demonstrated to be effective, such as hollow carbon spheres, threedimensional (3D) carbon nanotube (CNT)-graphene frameworks, and hierarchical porous structures.<sup>15-18</sup> Usually, versatile carbon nanomaterials offer good frameworks for electron transfer and ion migration and buffer the volume fluctuation of the sulfur cathode in the discharge and charge processes, which are vital for the improvement of sulfur utilization and cycling stability. However, the hydrophobic feature of carbon nanomaterials means that soluble polysulfide species cannot be trapped sufficiently based on powerless physical adsorption, and the intermediate LiPS would dissolve into the electrolyte inevitably during the long-term cycle.

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Recently, transition-metal compounds (MX, X = S, O, and N) with polar surfaces and electrocatalytic activities were introduced into Li–S batteries to chemically adsorb LiPS and increase the redox kinetics.<sup>19–24</sup> However, the chemical bonding between polar compounds and LiPS is usually based on the Lewis acid-base interaction, where M-S bonding coexists with X-Li bonding. Herein, the strong X-Li bonding would hinder the diffusion of Li ions. Meanwhile, despite the high electrochemical activity for the catalytic conversion of LiPS, such transition-metal compounds as sulfur hosts often have inferior electrical conductivity, inevitably leading to the accumulation of insulating reduzates (Li2S2/Li2S) and generation of "dead sulfur" on the interface of hosts in charge-discharge processes. Subsequently, the catalytic transition-metal compounds would be passivated, and the capacity of the sulfur cathode decreases quickly.<sup>25,26</sup> With the development of catalytic science, single-atom catalysts and metal nanocluster catalysts are also employed in Li-S batteries to expedite the redox reaction kinetics of LiPS or regulate the deposition of Li<sub>2</sub>S, while the complex synthetic pathways restrict the application.<sup>10,27</sup> To truly realize the high energy density of batteries, it is essential to increase the S loading in the electrode and operate in the lean electrolyte mode.<sup>2</sup> Herein, an electrolyte is essential to drive the dissolution and deposition processes of elemental sulfur via transformation of soluble polysulfide species. Therefore, the design strategy of the sulfur host must have a synergistic combination of strong adsorption, high electrocatalytic activity, and good electron conduction to yield Li-S batteries with excellent reaction kinetics under high S loading and low electrolyte usage.

Recently, various metal nanoparticles (NPs) were used as sulfur hosts in batteries, such as Pt, Ni, and Co, which serve as electroactive sites to enhance the electrochemical reaction kinetics owing to the powerful chemical interaction with polysulfides.<sup>29,31,32</sup> Importantly, the high intrinsic conductivity avoids additional resistance and decreases electrochemical polarization in the sulfur cathode. Usually, alloys exhibit better catalytic activity as compared with individual metals, which are extensively researched in the field of electrocatalysis, such as electrochemical water splitting and metal–air batteries.<sup>33,34</sup> In view of the similar chemical properties of sulfur and oxygen, it is important to systematically understand the catalytic performance of alloys toward the conversion of LiPS in Li–S batteries.<sup>35</sup>

Metal-boron (M-B) alloys, in which the elemental boron possesses an empty orbital, can chemically adsorb LiPS via M-S and B-S synergetic interactions.<sup>36,37</sup> Different from polar transition-metal compounds, M-B alloys can bond with LiPS selectively rather than Li ions, thus not only increasing the chemical anchoring and electrocatalytic sites but also accelerating the diffusion of Li ions. In this work, nickelboron (Ni-B) alloy nanoparticles are loaded uniformly on carbon nanotube microspheres (Ni-B/CNTMs) to serve as sulfur hosts in Li-S batteries. On the one hand, Ni-B alloy nanoparticles can boost electrochemical kinetics for the conversion of LiPS and accelerate the diffusion of Li ions on the interface of the electrode simultaneously. On the other hand, the microspheres built by intertwined CNTs can not only guarantee good electron conduction for the electrochemical reaction but also buffer the volume fluctuation during the charge and discharge processes to ensure the structural stability of the sulfur cathode. Thanks to the accelerated masstransfer and redox kinetics, a "two-stage Li2S deposition

behavior" on the Ni–B/CNTM matrix is proposed for the first time, which is significant for enhancing the capacity and achieving the stable cycling of Li–S batteries.

#### 2. EXPERIMENTAL SECTION

2.1. Preparation of CNTM, Ni-B, and Ni-B/CNTM. Multiwalled carbon nanotubes (CNTs, 0.2 g) and  $\rm NiCl_2.6H_2O~(0.3~g)$  were dispersed in deionized water (40 mL) under magnetic stirring. To realize a homogeneous suspension, the resulting mixed solution was further subjected to ultrasonic processing for 2 h, denoted suspension A. NaOH (0.192 g) and NaBH<sub>4</sub> (0.214 g) were completely dissolved in deionized water (20 mL) to fabricate solution B. Subsequently, solution B was added to suspension A drop by drop at a speed of 600  $\mu$ L min<sup>-1</sup> and continuously stirred for 2 h at 0 °C. Then, the obtained mixture was collected by centrifugation, washed to neutral, and then re-dispersed in deionized water (60 mL). Ni-B/CNTM was obtained using a spray-dryer, and the inlet temperature was 125 °C. A CNTM was prepared by dispersing CNTs in deionized water (60 mL) and then collected by the spray-drying process. To get pure Ni-B, solution B was dropped slowly into a NiCl<sub>2</sub> solution at 0 °C. The resulting product was obtained by centrifugation, washing, and vacuum drying for 12 h at a suitable temperature (70 °C).

**2.2. Preparation of the Sulfur-Based Composites.** The S/Ni– B/CNTM composite was prepared with the liquid-phase impregnation method. Typically, sulfur powder (0.75 g) was completely dissolved into a mixed solution with carbon disulfide (CS<sub>2</sub>) and *N*methyl-2-pyrrolidone (NMP) (v/v, 1.5:1). Then, under magnetic stirring at 60 °C, Ni–B/CNTM (0.25 g) was added gradually to the sulfur-containing solution until the solvent was removed completely. After cooling down to ambient temperature, the S/Ni–B/CNTM composite was obtained. The S/CNTM composite was prepared in the same way.

2.3. Material Characterization. The surface morphology and microstructure were measured with a scanning electron microscope (SEM, JSM-7800F) and a transmission electron microscope (TEM, JEM-2800). The crystallographic structure was studied by X-ray diffraction (XRD, Rigaku Mini Flex II) with Cu K $\alpha$  radiation, and the scan rate was 2° min<sup>-1</sup>. The Brunauer-Emmett-Teller (BET) method was performed to measure the specific surface area on the JW-BK112 system, and the infrared (IR) spectrum was recorded on a Bruker-TENSOR 27 spectrometer. The LiPS adsorption tests were carried out using a UV-visible absorption spectrophotometer (Varian Cary 100 Conc), and the chemical interaction on the surface was studied by the X-ray photoelectron spectra (XPS, PHI5000 Versa Probe-ESCALAB 250xi). A thermogravimetric analyzer (TG, METTLER TOLEDO, TGA/DSC1) was used to confirm the Ni-B loading in Ni-B/CNTM and the sulfur content in sulfur-based composites. The Ni-B content was calculated as follows

$$m_1 + m_2 = 100 \text{ wt \%}$$
 (1)

$$m_1 + X \cdot m_2 = Y \tag{2}$$

where  $m_1$  and  $m_2$  represent the contents of CNTs and Ni–B in Ni– B/CNTM, respectively. *X* and *Y* are the weight changes of the pure Ni–B alloy and Ni–B/CNTM obtained by TG tests, respectively.

**2.4. Electrochemical Measurements.** The S/Ni–B/CNTM and S/CNTM cathodes were prepared by dispersing sulfur-based composites, a conductive agent (super P), and poly(vinyldifluoride) (PVdF) in NMP with a weight ratio of 8:1:1. The slurry was coated on an aluminum foil with a carbon coating and dried overnight in an oven at 60 °C. Then, it was punched into disks, and the diameter of the sulfur cathode was 10 mm. The typical S-loading density was 1.0–1.5 mg cm<sup>-2</sup>. The slurry was coated on a carbon cloth with the same method to fabricate sulfur cathodes with a high S loading of 5.7–8.3 mg cm<sup>-2</sup>, and the thickness of the used carbon cloth was about 300  $\mu$ m (Cetech, WOS1009). The electrolyte was obtained by dissolving lithium bis(trifluoromethanesulfony)imide (LiTFSI, 1.0 M) and lithium nitrate (0.2 M) in 1,3-dioxolane (DOL) and dimethyl ether (DME) with a ratio of 1:1 (volume ratio). The sulfur-based cathode



Capacity

Figure 1. Schematic of the preparation process for S/Ni-B/CNTM and acceleration of the transformation of Li<sup>+</sup> on the Ni-B/CNTM matrix.



Figure 2. (a) SEM image of Ni-B/CNTM. (b, c) TEM images of Ni-B/CNTM. Inset: Selected area electron diffraction pattern. (d) High-resolution TEM (HRTEM) image of Ni-B/CNTM. (e) XRD patterns of the as-prepared CNTM and Ni-B/CNTM. (f–i) STEM image of Ni-B/CNTM and corresponding EDS elemental mappings.

was assembled into a CR2032 coin cell with a lithium foil (14 mm for diameter) and a Celgard 2300 separator (16 mm for diameter) in an Ar glovebox. The electrolyte/sulfur ratio (E/S) was set to 10  $\mu$ L mg<sup>-1</sup> for normal electrochemical experiments. The charge–discharge tests were performed between 1.6 and 2.6 V (vs Li/Li<sup>+</sup>) at various C rates (1C = 1672 mA g<sub>s</sub><sup>-1</sup>) with LAND-CT2001A instruments. The CHI 600A electrochemical workstation was used to construct cyclic voltammetry (CV) curves, and the Zahner IM6ex electrochemical workstation was used to record electrochemical impedance spectra (EIS), in which the amplitude was 5 mV and the frequency range was 100 kHz to 10 mHz.

For the LiPS adsorption experiment, a 1 M Li<sub>2</sub>S<sub>6</sub> solution was obtained by dissolving stoichiometric S and Li<sub>2</sub>S in the DME/DOL mixed solution with a ratio of 1:1 (volume ratio) at 60 °C in an Ar glovebox and magnetic stirring for 48 h. The Li<sub>2</sub>S<sub>6</sub> solution was diluted with DME to 2 mM before use. Host materials (10 mg) were added in a diluted Li<sub>2</sub>S<sub>6</sub> solution and settled for 3 h.

**2.5.** Nucleation Tests of Polysulfides. The working electrode was an Al foil coated with the mixture of Ni–B/CNTM (or CNTM), a conductive agent (super P), and PVdF in NMP with the mass ratio of 8:1:1. The Li<sub>2</sub>S<sub>8</sub> (1 M) catholyte was obtained by dissolving stoichiometric S and Li<sub>2</sub>S, LiTFSI (1 M), and lithium nitrate (0.2 M) in tetraglyme and stirred at 60 °C for 48 h. When the CR2032 coin cell was assembled, a normal electrolyte (5  $\mu$ L) and the Li<sub>2</sub>S<sub>8</sub> catholyte (20  $\mu$ L) were added to the anode and cathode sites, respectively. The chronoamperometry test was performed with the VERTEX.C.EIS electrochemical workstation. Cells were first discharged to 2.09 V under a constant current of 0.257 mA and then kept at a constant voltage of 2.05 V for 20 000 s. Cells were disassembled at various stages for further characterization.

## 3. RESULTS AND DISCUSSION

3.1. Preparation and Characterization of Ni–B/CNTM and S/Ni–B/CNTM Composites. The schematic illustration



Figure 3. (a) XRD pattern of the S/Ni-B/CNTM composite. (b-e) STEM image of S/Ni-B/CNTM and (b-d) corresponding EDS mappings of B, Ni, and C elements, respectively.



**Figure 4.** (a) Discharge/charge curves of S/Ni–B/CNTM and S/CNTM composites in the first cycle. (b) Cycling curves and Coulombic efficiency of low S-loading batteries at a 0.2C rate with a normal E/S ratio  $(10 \,\mu L \text{ mg}^{-1})$ . (c, d) Cycling performances of high S-loading electrodes under the lean electrolyte condition. (e) Rate performance of the S/CNTM and S/Ni–B/CNTM composites. (f) Long-term cycling performance at a 1C rate.

for the preparation process of S/Ni-B/CNTM is shown in Figure 1. First, the decoration of Ni-B alloy nanoparticles on the CNT surface is achieved by the reduction reaction of Ni<sup>2+</sup> with NaBH<sub>4</sub> at 0 °C. The slow reaction at a low temperature is beneficial for the uniform deposition of Ni-B alloy nanoparticles on the CNT surface. Then, the Ni-B/CNTM composite is prepared via spray-drying. The densely intertwined CNTs can offer favorable electrical conduction frameworks for achieving the high utilization of active sulfur, while the spherical morphology can increase the tap density of the S-based composite for delivering a high volumetric capacity.<sup>25,39,40</sup> Importantly, as catalysts, Ni–B alloy nanoparticles could accelerate the conversion of intermediate LiPS in the process of redox reaction. Finally, the sulfur-based composite is obtained with a liquid-phase impregnation method, in which elemental sulfur is in situ redeposited on the Ni-B/CNTM matrix after the mixed solution of CS<sub>2</sub> and NMP is removed completely. The use of NMP can increase the wetting of CS<sub>2</sub> on the carbon surface, resulting in better sulfur encapsulation.

SEM and TEM images are employed to analyze the surface morphology and microstructure of the as-obtained materials. The Ni-B/CNTM composite presents a rough and nearspherical morphology with an inhomogeneous size of several micrometers (Figure 2a,b), and Ni-B nanocrystallites with a narrow size distribution of 3-5 nm are distributed densely and homogeneously on the CNT surface without aggregation (Figures 2c and S1). The good dispersion and small size of Ni-B nanoparticles are helpful to increase contact with soluble intermediate LiPS, thus offering sufficient active sites for a subsequent electrochemical reaction.<sup>42</sup> Furthermore, energydispersive X-ray spectroscopy (EDS) mappings also confirm the homogeneous distribution of C, Ni, and B in the Ni-B/ CNTM composite (Figure 2f-i). The atom ratio of B and Ni is detected as 1:3.4 in the composite by the inductively coupled plasma-mass spectrometry (ICP-MS) test, while the ratio is 1:2.3 on the surface as shown in the XPS spectrum (Figure S2) due to the segregation of elemental B onto the surface of Ni-B nanoparticles.<sup>43</sup> As indicated in the HRTEM image (Figure 2d), the lattice spacings are 0.30 and 0.20 nm,

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**Figure 5.** (a) UV–vis adsorption feature of the  $Li_2S_6$  solution after coming in contact with different absorbents. Inset: photographs of  $Li_2S_6$  solution before and after coming in contact with as-obtained samples. XPS spectra of (b) Ni 2p, (c) B 1s regions of Ni–B/CNTM before and after coming in contact with the  $Li_2S_6$  solution, and (d) S 2p region of Ni–B/CNTM/LiPS.

corresponding well to the (004) and (020) planes of Ni<sub>3</sub>B, respectively. Additionally, the corresponding selected area electron diffraction (SAED) pattern presents concentric rings (Figure 2c), suggesting that the as-prepared Ni-B alloy nanoparticles exist in a polycrystalline state. As shown in the XRD pattern in Figure 2e, the Ni-B/CNTM composite displays the typical nanocrystalline structure with a broad peak at around  $40^{\circ}$ ,  $^{43,44}$  while the strong peak at around  $25^{\circ}$  is ascribed to the (002) plane of CNTs.<sup>16</sup> TG profiles of Ni-B and Ni-B/CNTM in an O<sub>2</sub> atmosphere are shown in Figure S3. With increasing temperature up to 800 °C, CNT is gradually decomposed and Ni-B is oxidized to NiO and  $Ni_2B_3O_6$  (Figure S4) with the weight change. Thus, the Ni-B loading can be calculated to be about 20 wt % in the Ni-B/ CNTM composite. Both the XPS spectrum and IR spectra (Figures S2 and S5) clearly show that the Ni-B particles contain an oxidation series on the surface, while the surface oxide layer plays an insignificant role in the interaction between Ni-B and LiPS, which will be further explained in the following section.

A facile liquid-phase infiltration method with  $CS_2$  and NMP as solvents is employed to achieve the integration of the asobtained materials and elemental sulfur, in which the sulfur contents are 75.1 and 75.8 wt % for the S/Ni–B/CNTM and S/CNTM samples, respectively (Figure S6). The sulfur exists in a crystalline state (JCPDS #08-0247), as shown in the XRD pattern, and the characteristic peaks of the as-prepared Ni–B/ CNTM sample are nonperceptible owing to the weak peak intensity (Figure 3a). As indicated in the SEM image and EDS elemental mappings, the near-spherical morphology is maintained well and elemental sulfur is distributed homogeneously in a microsphere (Figure 3b–e). Furthermore, the elemental sulfur is distributed homogeneously among Ni–B/ CNTs, coexisting with B, Ni, and C elements as demonstrated in TEM–EDS mappings (Figure S7). The specific surface areas of the Ni–B/CNTM and CNTM samples are 776.5 and 1101.7 cm<sup>2</sup> g<sup>-1</sup>, respectively, which drop to 345.8 and 390.5 cm<sup>2</sup> g<sup>-1</sup> for sulfur-based composites, further verifying the desirable loading of elemental sulfur into the host (Figure S8).

3.2. Electrochemical Performance of the S/Ni-B/ **CNTM Composite.** The electrochemical properties of the S/ Ni-B/CNTM composite are estimated in the CR2032 coin cell. As shown in Figure 4a, the S/Ni-B/CNTM composite shows an initial specific capacity of 1203.4 mAh  $\mathrm{g_s}^{-1}$  at a 0.2C rate, obviously higher than that of the S/CNTM (1116.9 mAh  $g_s^{-1}$ ). In addition, a smaller potential dip can be detected in the discharge profile, owing to the mild sedimentary overpotential.<sup>39</sup> Importantly, the S/Ni-B/CNTM sample delivers much higher Coulombic efficiency (96.1% vs 89.6%) and capacity retention (79% vs 59%) as compared to the S/CNTM composite after 100 cycles as illustrated in Figure 4b, indicating that Ni-B/CNTM can effectively suppress the shuttle reaction in Li-S batteries for a better cycling test. For the S/CNTM composite, the interaction between hydrophobic CNTs and hydrophilic polysulfides is weak. With the accumulation of LiPS, the shuttle effect gradually increased, thus leading to a sharp decrease of Coulombic efficiency after 60 cycles. Achieving high sulfur utilization and stable cycle under lean electrolyte conditions and with high S loading is challenging, which might lead to both exacerbation of the polysulfide shuttling and passivation of the sulfur electrode. Herein, the S/Ni-B/CNTM shows large discharge capacity (1163.0 mAh  $g_s^{-1}$ ), high Coulombic efficiency (98.1%), and good capacity retention (72.3%) after 160 cycles under an E/S of 5  $\mu$ L mg<sup>-1</sup> and S loading of 5.7 mg cm<sup>-2</sup>. In contrast, the battery with CNTM as the sulfur host failed after 30 cycles

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Figure 6. (a, b) Cyclic voltammograms (CVs) of the as-obtained S-based composites at different scanning rates. (c, d) Linear relationships between the peak current density and the square root of the scanning rate for anodic and cathodic processes, respectively.

(Figure 4c). Under the more severe demand of  $E/S = 3 \mu L$  $mg^{-1}$  and 8.3  $mg_s$  cm<sup>-2</sup>, a high initial capacity of 1112.7 mAh gs<sup>-1</sup> and stable cycling life with a good capacity retention of 76% can still be achieved at a 0.05C rate (Figure 4d). At a low rate (0.1C), the S/Ni-B/CNTM composite still presents a high specific capacity of 910.4 mAh  $g_s^{-1}$  and good cycling stability (Figure S9). As compared with previous publications under low electrolyte usage or high S loading (Table S1), the S/Ni-B/CNTM composite exhibits excellent electrochemical properties. Especially, this performance is achieved under both severe conditions simultaneously. This electrochemical behavior is enabled by the enhanced electrochemical kinetics with Ni-B alloy nanoparticles on CNTs. In addition, the S/Ni-B/ CNTM composite delivers high discharge capacities of 1249.5, 1196.7, 1104.9, 979.3, and 750.5 mAh  $g_{\rm s}^{-1}$  at rates of 0.1, 0.2, 0.5, 1, and 2C, respectively (Figure 4e). Especially, when the C-rate is adjusted to 0.1C, the change in capacity can be neglected. On the contrary, the low capacity of 242.5 mAh  $g_s^{-1}$ at a high rate (2C) is only obtained for the S/CNTM composite with severe capacity fading after coming back to the 0.1C rate. Furthermore, the S/Ni-B/CNTM composite also exhibits good electrochemical performance during long-term cycles at a 1C rate, in which the discharge capacity is 1013.2 mAh  $g_s^{-1}$  in the first cycle with a low capacity damping of 0.07% per cycle. After 500 cycles, the Coulombic efficiency of the S/Ni-B/CNTM composite is maintained at 96.4%, which is obviously superior to that of the control group (90.6% after 340 cycles, Figure 4f). As proved in the following section, the rate-determining step of the electrochemical reaction in the Li–S battery is the diffusion process, especially at high C rates. Ni-B nanoalloys can accelerate the diffusion on the surface of the CNT matrix; thus, the S/Ni-B/CNTM composite can

achieve a more obvious improvement in capacity at the 1C rate. The enhanced diffusion, electrocatalytic ability enabled by Ni–B alloy nanoparticles, and the resulting two-stage  $Li_2S$  deposition behavior guarantee excellent electrochemical performance in the discharge/charge processes of the S/Ni–B/CNTM composite.

3.3. Electrochemical Kinetics of the Ni-B/CNTM Composite. Different from conventional transition-metal compounds, the elemental B of the Ni-B alloy possesses an empty 2p orbital. Thus, Ni-B alloy nanoparticles can anchor LiPS via Ni-S and B-S interactions, increasing the chemically absorbing sites.<sup>36,37</sup> Significantly, there are no anions in Ni-B alloy nanoparticles for bonding Li ions; Li ions can be freely diffused in the discharge/charge processes (Figure 1). As a representative intermediate species, Li<sub>2</sub>S<sub>6</sub> is widely studied for the adsorption feature on host materials. More importantly, the tolerance of its experimental preparation to the sulfur/lithium ratio is more acceptable.<sup>38</sup> Thus, Li<sub>2</sub>S<sub>6</sub> is employed to probe the adsorption behavior of Ni-B/CNTM toward LiPS. As shown in Figure 5a, after settling for 3 h, the LiPS solution with Ni-B/CNTM immersed becomes transparent and colorless, in which the characteristic absorbance of  $S_6^{2-}$  almost disappears, while the changes of solution color and absorbance are negligible for CNTM. This implies the stronger affinity of Ni-B alloy nanoparticles to LiPS. XPS measurements are used to further illustrate the interaction on Ni-B/CNTM. The Ni 3d spectra of the Ni-B/CNTM composite before and after contact with the Li<sub>2</sub>S<sub>6</sub> solution are shown in Figure 5b. The main characteristic peak at 853.0 eV is related to the binding energy of the metallic Ni in the Ni-B alloy, and the peaks at 855.5 and 859.2 eV can be assigned to a trace of oxidative species on the surface of Ni.43 After adsorbing Li<sub>2</sub>S<sub>6</sub>, the



**Figure 7.** (a, b) EIS plots of the S/Ni–B/CNTM and S/CNTM electrodes at different temperatures. (c) Relationships between logarithmic values of the reciprocal of  $R_{ct}$  and the reciprocal of absolute temperatures. (d, e) EIS plots of the S/CNTM and S/Ni–B/CNTM electrodes after different cycles. (f) Fitted  $R_{ct}$  values of the S/CNTM and S/Ni–B/CNTM electrodes at different cycles.

binding energy is decreased slightly to 852.5 eV for Ni-B alloy nanoparticles. Similarly, Figure 5c shows the B 1s spectra of the Ni-B/CNTM and Ni-B/CNTM/LiPS. After adsorbing  $Li_2S_{61}$  the peak position (190.5 eV) is also shifted to a lower position (189.7 eV). The variations of binding energies in Ni  $2p_{3/2}$  and B 1s spectra are attributed to the electron transfer of LiPS toward the Ni–B alloy, resulting in the strong chemical interaction between Ni–B and LiPS.<sup>25,37,45,46</sup> In the S 2p core level (Figure 5d), the two  $2p_{3/2}$  peaks at 161.7 and 163.4 eV with the peak area ratio of 1:2 correspond to the terminal S  $(S_T^{-1})$  and bridging S  $(S_B^{0})$ , respectively. The peak at around 167.7 eV is assigned to the slightly oxidized sulfur generated in the process of transferring samples. The chemical interaction between LiPS and Ni-B can be further validated by the slight increase of the S<sub>B</sub><sup>0</sup> 2p<sub>3/2</sub> binding energy in Ni-B/CNTM/ LiPS, as compared with that (163.1 eV) in pure  $\text{Li}_2\text{S}_6$ .<sup>47</sup> In addition, after coming in contact with Li<sub>2</sub>S<sub>6</sub>, the peak position in O 1s spectra shows a small change (Figure S10a), and the signal of Li 1s in the XPS spectrum is rather weak (Figure S10b). This indicates that the Ni-B alloy and the oxide layer on the surface of the Ni-B alloy show an insignificant interaction with Li ions. The exclusive anchor mechanism of Ni-B/CNTM exhibits a strong interaction with LiPS and simultaneously does not hinder the free transfer of Li ions in the redox processes.

To experimentally explore the mass-transfer kinetics on Ni– B/CNTM, the composites with low S-loading are constructed. Figure 6a,b shows the CVs of the S/CNTM and S/Ni–B/ CNTM electrodes measured with the potential range from 2.6 to 1.6 V (vs Li/Li<sup>+</sup>) at different scanning rates between 0.05 and 0.5 mV s<sup>-1</sup>, respectively. The typical features of CV curves for sulfur-based composites can be obtained: two reduction peaks in the cathodic process and one merged oxidation peak in the anodic process, matching with the multistep redox conversion from sulfur to Li<sub>2</sub>S and its reverse process.<sup>48,49</sup> The S/Ni-B/CNTM composite shows higher peak current density and smaller polarization, suggesting faster electrochemical kinetics. According to the Randles-Sevcik equation,<sup>20</sup> the anodic and cathodic peak currents of both composites are proportional to the square root of scanning rates as illustrated in Figure 6c,d, indicating that the electrochemical process is dominated mainly by diffusion. What is more, the fitted slopes of peaks A, C1, and C2 for the S/Ni-B/CNTM electrode exceed obviously that of the S/CNTM electrode, indicating faster diffusion. Electrochemical impedance spectra (EIS) at different depths of discharge (DODs) and stages of charge (SOCs) are also recorded to understand the effect of Ni-B alloy nanoparticles on the diffusion behavior.<sup>39,40</sup> As shown in Figure S11a,b, all EIS plots of the S/CNTM and S/Ni-B/ CNTM electrodes exhibit two semicircles and one sloped line, corresponding to the deposition-layer formation process, charge-transfer process, and the Warburg diffusion process, respectively. Apparently, the S/Ni-B/CNTM composite presents good diffusion behavior during all of the discharge and charge processes, as compared to the S/CNTM composite (Figures S11c,d and S12, Note S1, and Table S2).

To evaluate the electrocatalytic activity of Ni–B alloy nanoparticles, the activation energy ( $E_a$ ) and exchange current densities ( $i^0$ ) in the conversion process of LiPS are measured.<sup>30,50,51</sup> First,  $E_a$  is calculated from EIS data at various temperatures, where the logarithmic values of the reciprocal of  $R_{ct}$  exhibit a linear relationship with the inverse of temperature (Figure 7a–c). According to the Arrhenius equation, the S/Ni–B/CNTM composite shows a lower activation energy ( $35.2 \text{ kJ} \text{ mol}^{-1}$ ) for the charge-transfer process, as compared to that ( $42.8 \text{ kJ} \text{ mol}^{-1}$ ) of the S/CNTM composite (Note S2 and Table S3). Furthermore, Tafel plots and corresponding  $i^0$  derived from CV curves are shown in



**Figure 8.** Deposition kinetics and morphology changes of  $Li_2S$  on different matrixes. Chronoamperometry profiles for (a) Ni–B/CNTM and (b) CNTM. SEM images for (a1, a3) Ni–B/CNTM and (b1, b3) CNTM. Schematic of the deposition processes of LiPS ( $Li_2S$ ) at positions I and II on (a2, a4) Ni–B/CNTM and (b2, b4) CNTM.

Figure S13. The exchange current densities are 7.73 and 320  $\mu$ A cm<sup>-2</sup> for the S/Ni–B/CNTM electrode in both anodic and cathodic processes, which are obviously higher than those (1.22 and 290  $\mu$ A cm<sup>-2</sup>) for the S/CNTM electrode. Therefore, the S/Ni–B/CNTM composite shows excellent electrocatalytic activity toward the conversion of LiPS, based on the low activation energy and the high exchange current density on Ni–B alloy nanoparticles. In addition, EIS plots after various cycles are employed to further evaluate the stability of catalysts during cycling. As compared to S/CNTM, the S/Ni–B/CNTM electrode presents a moderate change in  $R_{\rm ct}$  during cycling (Figure 7d–f and Table S4), confirming the stable electrochemical activity on Ni–B alloy nanoparticles for the catalytic conversion of LiPS.

**3.4. Deposition Kinetics of Li<sub>2</sub>S on the Ni–B/CNTM Composite.** The accelerated diffusion of Li ions and improved redox kinetics of intermediate LiPS do have a great impact on the subsequent deposition of the final product Li<sub>2</sub>S. According to the Bewick, Fleischmann, and Thirsk (BFT) models and the Scharifker and Hills (SH) models, the nucleation and growth of lithiation products on the matrix could be distinguished for four classical models: twodimensional instantaneous (2DI), 2D progressive (2DP), 3D instantaneous (3DI), and 3D progressive (3DP). The growth of the nuclei is considerably affected by the mass transfer of electrodepositing species to the nuclei: surface diffusion (2D) or bulk diffusion (3D).<sup>52–55</sup>

In this section, chronoamperometry tests and SEM are performed to investigate the electrodeposition kinetics of the

final product Li<sub>2</sub>S. Li<sub>2</sub>S<sub>8</sub> is the initial species of lithium polysulfide in the discharge process; thus, the Li<sub>2</sub>S<sub>8</sub>/tetraglyme catholyte is employed for the deposition tests of polysulfides, which can reflect the nucleation and growth behaviors on the matrix more adequately and completely. As shown in Figure 8a, there are two peaks at around 744 and 3918 s for the Ni-B/CNTM matrix (denoted peak I and peak II, respectively). Coupled with the dimensionless current-time curves in Figure S14, the Li<sub>2</sub>S deposition process on the Ni-B/CNTM matrix can be divided into two stages: 3D deposition in the bulk and 2D deposition on the surface (Table S5). First, Ni-B alloy nanoparticles with more active sites induce Li<sub>2</sub>S to nucleate rapidly, and then Li<sub>2</sub>S grows following the 3DI model among microspheres, as demonstrated by a loose reticular morphology (Figure 8a1,a2). As the deposition of Li<sub>2</sub>S continues, the surface deposition is dominant following the 2DI model on Li<sub>2</sub>S present at an earlier stage, leading to the formation of a uniform and thin deposition layer, while the porous structure as ion channels is still retained (Figure 8a3,a4). This two-stage Li<sub>2</sub>S deposition behavior on the Ni-B alloy matrix not only increases the deposition capacity (235.2 mAh  $g^{-1}$ ) but also enables the transport of electrons/ions in the uniform and thin deposition layer, beneficial to the subsequent electrochemical reaction. On the contrary, for CNTM, the Li<sub>2</sub>S deposition occurs in the bulk and on the surface with the 2DP model (Figures 8b and S14b and Table S5), leading to the formation of large Li<sub>2</sub>S aggregates, poor conductivity of electrons/ions, and passivation of the cathode.

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As the desired host of sulfur, both high catalytic activity and good conductivity are indispensable to achieve high sulfur utilization and stable cycle performance of sulfur-based composites with high S loading and under lean electrolyte conditions. Herein, Ni-B alloy nanoparticles, dispersed uniformly on the CNTM matrix, exhibit the desired electrocatalytic ability for the conversion of intermediate LiPS. Meanwhile, the intertwined CNT microspheres provide an additional conductive scaffold in response to the fast electrochemical redox. In addition, the unique structure of highly dispersed Ni-B alloy nanoparticles on porous and conductive CNT microspheres enables the subsequent uniform deposition of the final product Li2S based on the "twostage deposition behavior". Therefore, the rational design of the Ni-B/CNTM composite as the catalytic host of sulfur can ensure high specific capacity and stable cycling life of Li-S batteries under the conditions of both high S loading and low electrolyte usage.

## 4. CONCLUSIONS

In this work, Ni-B alloy nanoparticles are loaded homogeneously on the CNT surface via the reduction reaction of Ni(II) with NaBH<sub>4</sub> at 0 °C. The Ni-B/CNTM composite is prepared subsequently via spray-drying, in which Ni-B alloys are calculated to be about 20 wt %. The Ni-B/CNTM composite shows a near-spherical morphology with an inhomogeneous size of several micrometers, and Ni-B nanocrystallites are distributed with a narrow size distribution of 3-5 nm. When used as the sulfur host, the Ni-B/CNTM composite presents synergy advantages of highly dispersed Ni-B alloy nanoparticles as a catalyst and intertwined CNT microspheres as a conductive network. In particular, Ni-B alloy nanoparticles not only exclusively anchor soluble polysulfide species through Ni-S and B-S bonding but also increase the conversion kinetics of intermediate polysulfide species. In addition, the unique structure of highly dispersed Ni-B alloy nanoparticles on porous and conductive CNT microspheres enables the subsequent uniform and thin deposition of the final product Li<sub>2</sub>S based on the two-stage deposition behavior, thus improving the sulfur utilization and cycle life of Li-S batteries under the conditions of both high Sloading and low electrolyte usage. Specifically, the S/Ni-B/ CNTM composite delivers a high reversible capacity (1112.7 mAh  $g_s^{-1}$ ) along with good cycle life under both high S-loading (8.3 mg cm<sup>-2</sup>) and lean electrolyte (3  $\mu$ L mg<sup>-1</sup>) conditions. This result provides a promising approach to design new sulfur-based composites for high-energy Li-S batteries.

# ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c03791.

TEM images; XPS and IR spectra; TG profiles; XRD pattern; N<sub>2</sub> adsorption–desorption curves; EIS plots and the relationships between Z' and  $\omega^{-1/2}$ ; CV curves and Tafel curves; calculation methods for the diffusion coefficient of Li ions and the activation energy; peak fitting of the nucleation and growth models for Li<sub>2</sub>S; and fitting data for EIS tests (PDF).

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#### Notes

The authors declare no competing financial interest.

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