

# Highly Stable Lithium–Sulfur Batteries Promised by Siloxene: An Effective Cathode Material to Regulate the Adsorption and Conversion of Polysulfides

Yang Wang, Liping Zhou, Jingyun Huang,\* Xinyang Wang, Xinling Xu, Jianguo Lu,\* Yang Tian, Zhizhen Ye,\* Haichao Tang, Shuit-Tong Lee, and Yingying Lu\*

Designing an appropriate cathode is still a challenge for lithium-sulfur batteries (LSBs) to overcome the polysulfides shuttling and sluggish redox reactions. Herein, 2D siloxene nanosheets are developed by a rational wet-chemistry exfoliation approach, from which S@siloxene@graphene (Si/G) hybrids are constructed as cathodes in Li-S cells. The siloxene possesses corrugated 2D Si backbone with abundant O grafted in Si<sub>6</sub> rings and hydroxyl-functionalized surface, which can effectively intercept polysulfides via synergistic effects of chemical trapping capability and kinetically enhanced polysulfides conversion. Theoretical analysis further reveals that siloxene can significantly elevate the adsorption energies and lower energy barrier for Li<sup>+</sup> diffusion. The LSBs assembled with 2D Si/G hybrid cathodes exhibit greatly enhanced rate performance (919, 759, and 646 mAh  $g^{-1}$ at 4 C with sulfur loading of 1, 2.9, and 4.2 mg  $cm^{-2}$ , respectively) and superb durability (demonstrated by 1000 cycles with an initial capacity of 951 mAh g<sup>-1</sup> and negligible 0.032% decay rate at 1 C with sulfur loading of 4.2 mg cm<sup>-2</sup>). It is expected that the study presented here may open up a new vision toward developing high-performance LSBs with siloxene for practical applications.

Y. Wang, L. P. Zhou, Prof. J. Y. Huang, X. L. Xu, Prof. J. G. Lu, Y. Tian, Prof. Z. Z. Ye, H. C. Tang School of Materials Science and Engineering State Key Laboratory of Silicon Materials Zhejiang University Hangzhou 310027, China E-mail: huangjy@zju.edu.cn; lujianguo@zju.edu.cn; yezz@zju.edu.cn X. Y. Wang, Prof. Y. Y. Lu State Key Laboratory of Chemical Engineering Institute of Pharmaceutical Engineering College of Chemical and Biological Engineering Zhejiang University Hangzhou 310027, China E-mail: yingyinglu@zju.edu.cn Prof. S.-T. Lee Jiangsu Key Laboratory for Carbon-Based Functional Materials and Devices Institute of Functional Nano and Soft Materials (FUNSOM) Soochow University Suzhou, Jiangsu 215123, China The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.201910331.

#### DOI: 10.1002/adfm.201910331

# 1. Introduction

To keep pace with thriving development of electric vehicles and grid level energy storage, developing advanced battery systems with sustainable high gravimetric and volumetric energy densities and prolonged cycle reliability becomes increasingly paramount. Conventional lithium-ion batteries relying on intercalation mechanism are obviously unable to meet the demands imposed on next generation energy-storage systems, either on performance or expense requirements.<sup>[1-3]</sup> Among the emerging battery technologies, lithium-sulfur batteries (LSBs) have attracted extensive attention owing to unparalleled features including high energy density, non-toxicity, and low cost.<sup>[4,5]</sup> However, the practical implementation of LSBs, close to commercial application, is plagued with several dilemmas, including insulating nature of sulfur and its final discharge products, highly soluble polysulfides and large volume fluctuation

upon lithiation/delithiation process.<sup>[6–8]</sup> Among these intractable issues, dissolved polysulfides in organic electrolytes and their subsequent inter-electrode migration, namely, shuttling effect, are particularly detrimental to the performances of LSBs, which could lead to rapid capacity attenuation, inefficient sulfur utilization, low coulombic efficiency, and worse still, lithium dendrite issues.<sup>[9,10]</sup> Besides, the sluggish electrochemical conversion kinetics of soluble polysulfides can cause grievous polarization effect, resulting in inferior rate performance.<sup>[10]</sup>

Massive efforts have been concentrated on cathode design to address the aforementioned challenges. Due to highly conductive matrix and tunable architectures, carbonaceous materials are commonly employed as sulfur hosts, which, to some extent, mitigates the notorious shuttling effect and boosts the electrochemical kinetics of sulfur species.<sup>[11,12]</sup> Unfortunately, the nonpolar characteristic of pristine carbon host has made the diffusion of polysulfides propelled by the concentration gradient not effectively mitigated.<sup>[13]</sup> Additionally, by combining polar metal compounds (such as transitional-metal oxides,<sup>[14–16]</sup> carbides,<sup>[17]</sup> nitrides,<sup>[18,19]</sup> sulfides,<sup>[20,21]</sup> and heterostructure<sup>[22,23]</sup>) with car bonaceous materials, the resultant cathodes could effectively



immobilize polysulfides and improve the cycling stability of LSBs due to the strong adsorption ability of such metal compounds toward polysulfides.

Recently, many researches have been embarking on polar two-dimensional (2D) sulfur host materials. By contrast, nanostructured 2D materials possess many advantages over bulk structure. Owing to strong covalent bonds in plane and weak van der Waals' forces between interlayers, 2D materials are more prone to layer peeling than breaking, thus they can form complete well-aligned structure to provide both physical shield and chemisorption to polysulfides.<sup>[24]</sup> Besides, many 2D materials have been demonstrated to have unique sulfur species catalytic property, thus ameliorating the sluggish kinetics. Common polar 2D materials employed as sulfur host are molybdenum compounds  $(MoS_2)^{[25,26]} Sn_{0.063}MoO_3^{[27]}$ , MXenes<sup>[28]</sup> and their ramification,<sup>[29]</sup> phosphorene,<sup>[1]</sup> borophene,<sup>[30]</sup> graphitic carbon nitride  $(C_3N_4, C_4N_4)$ ,<sup>[31,32]</sup> etc. Although these 2D materials are considered as ideal candidates for Li-S cathodes, there are still some defects needed to be improved. For instance, i) the heavy transition metal atoms in 2D materials are not beneficial to the cost control of LSBs and the development LSBs with high gravimetric energy density; ii) rigorous and complicated preparation processes are not in line with the demands of large-scale manufacturing.

Siloxene is a novel Si-based 2D material with three planar structure types: Weiss-type structure (Si-H and Si-OH bonds alternating on the surface of Si6 rings), Kautsky structure (Si<sub>6</sub> rings interconnecting with abundant O (Si-O-Si) and hydroxyl-functionalized group on the surface), and chain-like siloxene.<sup>[33]</sup> The common method to prepare siloxene is the deintercalation of Ca atom by different oxidant (metal chlorides, I<sub>2</sub>, aqueous HCl, etc.)<sup>[34,35]</sup> from CaSi<sub>2</sub>, which is a hexagonal layered structure consisting of alternating Ca layers and corrugated Si (111) planes.<sup>[36]</sup> In the fields of solar-electric energy conversion<sup>[37]</sup> and lithium storage,<sup>[38,39]</sup> siloxene has been demonstrated as an efficient metal-free semiconductor for photocatalytic water-splitting, and an excellent anode material for Li-ion batteries. Nevertheless, as a unique 2D material, the exploration of siloxene's potential application in electrochemical energy storage is still very much in its infancy. To our knowledge, the utilization of siloxene to demonstrate the development of high-performance LSBs has not been reported yet. Herein, ultrathin siloxene nanosheets have been synthesized via a simple and scalable wet-chemistry exfoliation approach and selected as the sulfur host. The detailed synthetic strategy is outlined in Scheme 1. Concretely, by treating CaSi<sub>2</sub> with concentrated aqueous HCl, Ca atom can be easily extracted from the layered CaSi2. With the generation of water and hydrogen, the retained silicene (2D silicon layer) is oxidized into siloxene in the oxygenated environment due to strong reducibility of silicene. The asprepared siloxene nanosheets maintain the corrugated 2D silicene backbone with abundant O doped in the Si<sub>6</sub> rings and hydroxyl on the surface. When used as sulfur host, the siloxene nanosheets show excellent polysulfides regulation capability. The cells with S@siloxene@graphene (Si/G) composite cathode display superior electrochemical performance, including highly reversible capacity, outstanding rate capability (delivering a reversible capacities of 919, 759, and 646 mAh  $g^{-1}$  at 4 C with areal sulfur loading of 1.0, 2.9, and 4.2 mg cm<sup>-2</sup>, respectively)





**Scheme 1.** Preparation process illustration of siloxene nanosheets, the structure of as-prepared siloxene nanosheets, and Li-S cell configuration employing the siloxene nanosheets.

and superb cycle stability (only 0.032% capacity decay rate per cycle over 1000 cycles at 1 C with a high areal sulfur loading of 4.2 mg cm<sup>-2</sup>). Computational studies based on first principle calculation indicate that the improvement is related to the effective polysulfides immobilization capability and low energy barrier for Li-ion diffusion, thus lowering the polarization and improving the utilization of sulfur. Moreover, electrochemical experiments reveal that siloxene could also facilitate the conversion kinetics of polysulfides, which shortens the existence time of polysulfides and therefore reduces the probability of their shuttling. Combing with simple and easily scalable preparation process as well as low-cost precursor material (CaSi<sub>2</sub> can be synthesized by directly heating a mixture of high-purity Ca and Si via a solid-state reaction method,[37] and the Ca and Si are abundant in earth), we strongly believe that siloxene is a promising candidate cathode material for high-performance LSBs.

# 2. Results and Discussion

The morphology and microstructure of the as-prepared siloxene nanosheets were confirmed by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). As exhibited in Figure 1a, the low-resolution TEM image of siloxene, dropped on a carbon nanotube (CNT) grid, shows the smooth and uniform 2D structure with several microns lateral dimension. Besides, the scanning transmission electron microscope (STEM, presented in Figure 1d), shows the high transparency of the sheet-like siloxene, thus indicating their ultrathin nature. Layer stacking characteristic is also found in our resulting siloxene samples, shown in Figure 1b,e, which means that, like other 2D materials, the agglomeration due to interlayer interaction forces is inevitable. However, the stacked nanosheets still show homogeneous transparent morphology, indicating that the agglomeration is not very serious. Corresponding energy dispersive X-ray spectroscopy (EDS) analysis is depicted in Figure S1,







**Figure 1.** Surface morphology characterization of siloxene nanosheets. a,b) Transmission electron microscopy (TEM) of resulting siloxene nanosheets. c) The high-resolution TEM (HR-TEM) image of siloxene nanosheets and relevant selected area electron diffraction (SAED) pattern (inset). d,e) The scanning transmission electron microscope (STEM) image of siloxene nanosheets. f) Atomic force microscopy (AFM) to measure the thickness of siloxene nanosheets.

Supporting Information, which reveals the presence of Si and O atoms throughout the siloxene nanosheets. The introduction of O atoms into planar Si begins in the process of the Si layer being stripped from CaSi2, owing to that newly formed layered Si nanosheets (silicene) are highly reactive and thus can be rapidly oxidized.<sup>[39]</sup> SEM images (Figure S2, Supporting Information) display the graphene-like structure of siloxene nanosheets with crumpled morphology, which is in contrast to the bulk CaSi<sub>2</sub> with clearly compact stepped stacking structure (Figure S3, Supporting Information), revealing the effective exfoliation of siloxene nanosheets from CaSi2. In the high-resolution TEM (HRTEM) image (Figure 1c), it is clear that the atomic arrangement of such siloxene nanosheets have amorphous characteristics, which is consistent with the selected area electron diffraction (SAED) pattern (inset in Figure 1c). The thickness of the resultant siloxene nanosheets was measured in the range of 5-6 nm by AFM (Figure 1f), corresponding to about ten individual siloxene layers.<sup>[35]</sup> Figure S4a, Supporting Information, shows the N2 adsorption-desorption isotherms of obtained siloxene nanosheets and the measured surface area via Brunauer-Emmett-Teller (BET) method is 95.59 m<sup>2</sup> g<sup>-1</sup>, which could promote uniform deposition of active sulfur and provide effective adsorption and catalytic sites for immobilizing polysulfides. Subsequent pore size distribution (Figure S4b, Supporting Information) calculated via Barrett-Joyner-Halenda (BJH) method depicts single peak at about 11 nm that indicates the presence of mesopores, and the total pore volume of siloxene is  $0.1 \text{ cm}^3 \text{ g}^{-1}$ .

The chemical states of siloxene nanosheets were evaluated by X-ray photoelectron spectroscopy (XPS). Based on the widerange spectrum analysis (Figure S5a, Supporting Information), the O/Si atomic ratio of as-prepared siloxene nanosheets was calculated to be 1.42. The calculated O/Si atomic ratio is <2, which indicates that the atomic ratio in the 2D siloxene does not conform to the stoichiometric ratio of bulk silica, and also reveals the uniqueness of 2D structure. Figure 2a exhibits the core-level spectrum of Si 2p states of the siloxene nanosheets. In order to confirm the oxidation states of siloxene nanosheets, the Si 2p spectrum can be fitted into five peaks with binding energy between 99.3 and 103.5 eV, attributed to Si<sup>0</sup>, Si<sup>1+</sup>, Si<sup>2+</sup>, Si<sup>3+</sup>, and Si<sup>4+</sup>.<sup>[39,40]</sup> The results of XPS fitting also indicate that the chemical states of Si in the resultant siloxene distinguish from the one in bulk SiO<sub>2</sub> (Si<sup>4+</sup>). Figure S5b, Supporting Information, presents a broad O 1s spectrum that relates to the Si-O-Si bridges in the Si6 rings and hydroxyl on the surface of siloxene.<sup>[33,34]</sup> To determine the detailed phase of the siloxene nanosheets and identify the structural transformation before the wet-chemistry exfoliation, X-ray diffraction (XRD) was carried out. Figure S6, Supporting Information, displays the XRD patterns of resulting siloxene and CaSi2 precursor. In the XRD of the CaSi2 precursor, the peaks of CaSi2 mainly match with the JCPDS No: 75-2192, indicating that the precursor mainly exists in hexagonal CaSi<sub>2</sub> phase, and the tetragonal CaSi<sub>2</sub> phase (JCPDS No: 75-2193) is also observed. Besides, in the XRD of the CaSi<sub>2</sub> precursor, some impurity peaks can be attributed to FeSi<sub>2</sub> (JCPDS No: 35-0822 Tetragonal, P4/mmm), which is due to the reaction of iron impurity remaining in the preparation of CaSi<sub>2</sub> with silicon. While in the XRD pattern of siloxene nanosheets, all characteristic diffraction peaks of CaSi2 and impurity FeSi2 disappear and a new diffraction peak located at around 24.3° (2 $\theta$ ) is found. The newly presented diffraction peak in the siloxene nanosheets attributes to the diffraction pattern of (001) stacking layer of siloxene<sup>[35]</sup> and the calculated layer spacing parameter is 3.65 Å based on Bragg's formula.

Fourier transform infrared (FTIR) and Raman spectra were conducted to further reveal the chemical composition of resultant siloxene nanosheets. Figure 2b displays the FTIR spectrum with characteristic bands at 452, 869, 1050, and 2137 cm<sup>-1</sup>,







**Figure 2.** Chemical characterization of the siloxene sheets. a) The core-level spectrum of Si 2p XPS of siloxene nanosheets. b) Fourier transform infrared and c) Raman spectrum of siloxene nanosheets. The Raman peak position maps of d) Si–Si (bending vibration), e) Si–O, and f) Si-Si (stretching vibration) mode, respectively.

attributing to the stretching vibrations of Si-Si, Si-H, Si-O-Si, and OSi<sub>2</sub>≡Si-H modes, respectively.<sup>[39,41]</sup> The FTIR spectrum bands at 3400 cm<sup>-1</sup> originate from vibrations of -OH, revealing the oxidation and hydroxylation during the exfoliation process of silicene from CaSi<sub>2</sub>. Combing the presence of OSi<sub>2</sub>≡Si–H rather than  $Si_3 \equiv Si - H$  mode in the siloxene, the structure type of the as-prepared siloxene should be defined as Kautsky-type siloxene structure that possesses Si-O-Si bridge grafted in Si<sub>6</sub> rings and hydroxyl-functionalized group on the surface. As noted, the Si-H mode in siloxene highlights that the edge or other surface of Si<sub>6</sub> rings is saturated by H atoms. Raman spectrum of the siloxene nanosheets (Figure 2c) clearly depicts the Si-Si (386 and 518 cm<sup>-1</sup>, corresponding to bending and stretching vibration, respectively), Si-O (492 cm<sup>-1</sup>) and Si-H (637 and 738 cm<sup>-1</sup>, corresponding to bending and stretching vibration, respectively) vibration, which demonstrates the existence of Si-Si, Si-O, and Si-H mode in the siloxene nanosheet.<sup>[37]</sup> The Raman result is consistent with the abovementioned FTIR analysis. Raman maps of Si-O and Si-Si were also conducted to understand the vibrational characteristics in more detail. Figure 2d-f exhibits the peak position maps of Si-Si (bending vibration), Si-O, and Si-Si (stretching vibration) modes, respectively. It is clear that both the peak positions of Si-O and Si-Si vary within the detected area, which can be intuitively judged from the color change in maps. The peak intensity maps (Figure S7, Supporting Information) also suggest the variations of relevant peak of Si-Si and Si-O. Additionally, Figure S8, Supporting Information, shows the IR maps of Si-O-Si and -OH modes, which clearly reveals that the vibration intensity of Si-O-Si and -OH vary within the detected area. The results shown in the Raman and IR maps reveal the heterogeneous distribution of the chemical structure in siloxene nanosheets, due to Raman and IR, peak shift and intensity of chemical structure are closely related to the chemical environment.

To demonstrate the electrochemical application of the asprepared siloxene nanosheets, S@siloxene@graphene hybrid

electrodes (denoted as Si/G electrodes, with sulfur contents of 60 wt%, which was confirmed by thermogravimetric analysis; as presented in Figure S9, Supporting Information) are synthesized by conventional melt-diffusion method (the detailed preparation process is described in Experimental Section), in which graphene is used to improve the electrical conductivity of electrodes. Figure S10a-c, Supporting Information, shows the SEM and TEM images of Si/G composite after impregnation of electroactive S constituent. It is obvious that, after sulfur impregnation, the obtained Si/G encapsulated sulfur composites still maintain the 2D morphology. Besides, the different sharp contrast can be observed inside the Si/G, indicating the encapsulation of sulfur. Combined with the energy dispersive spectroscopy (EDS) for elemental distribution of C, Si, O, and S atoms (Figure S10d-g, Supporting Information), it can be conclude that siloxene, graphene, and sulfur are highly dispersed. The electrochemical performances of Si/G electrodes are evaluated by galvanostatic charge/discharge tests. As demonstrated in Figure 3a, the Si/G-1 electrode (Si/G electrode with areal sulfur loading of 1.0 mg cm<sup>-2</sup>) obtains a high initial discharge capacity of 1289 mAh  $g^{-1}$  at 0.1 C (1 C = 1675 mA  $g^{-1}$ ) activation. Subsequently, the rate capability of the Si/G-1 electrode is measured, which displays the average reversible specific capacities of 1204, 1122, 1049, 966, and 919 mAh  $g^{-1}$  at the current densities set for 0.2, 0.5, 1, 2, and 4 C, respectively. For the control, the S@graphene hybrid electrodes (prepared by the same method, denoted as pure-G electrodes) are also tested under identical conditions. By contrast, the pure-G electrode exhibits an inferior rate capability with lower initial discharge capacity of 1073 mAh g<sup>-1</sup> at 0.1 C and average reversible specific capacities of 859, 760, 602, 507, and 417 mAh  $g^{-1}$  at the current densities of 0.2, 0.5, 1, 2, and 4 C, respectively. Remarkably, when the current density switches back to 0.1 C, the average discharge capacity of Si/G-1 cathode recovers to 1218 mAh g<sup>-1</sup>, which is close to the initial value (1289 mAh g<sup>-1</sup>) and exceeds that of the pure-G electrode (811 mAh g<sup>-1</sup>), revealing good reversibility.

www.advancedsciencenews.com

IDVANCED

SCIENCE NEWS



**Figure 3.** The galvanostatic charge/discharge tests of cells with Si/G and pure-G electrodes. a) The rate performance of Si/G-1, Si/G-2.9, and Si/G-4.2 representing the Si/G electrodes with areal sulfur loadings of 1, 2.9, and 4.2 mg cm<sup>-2</sup>, respectively; pure-G with areal sulfur loading of 1 mg cm<sup>-2</sup>. b) The galvanostatic charge/discharge profiles at 4 C. c) The comparison of cycling performance under 0.5 C with areal sulfur loading of 2.9 mg cm<sup>-2</sup>. d) The long-term cycling stability test of Si/G electrode under high sulfur loading of 4.2 mg cm<sup>-2</sup> at 1 C during 1000 cycles.

Since the high mass loading of sulfur is essential for the high energy density of LSBs, the Si/G electrodes with areal sulfur loading of 2.9 and 4.2 mg cm<sup>-2</sup> (denoted as Si/G-2.9 and Si/G-4.2, respectively) are further evaluated. It is noted that the Si/G-2.9 and Si/G-4.2 electrodes still achieve outstanding rate capability comparing with pure-G electrode. Even at high current density of 4 C, the Si/G-2.9 and Si/G-4.2 electrodes remain high reversible capacities of 759 and 646 mAh  $g^{-1}$ , respectively, indicating lower polarization and better reaction kinetics of Si/G electrode than pure-G electrode. The galvanostatic charge/discharge profiles of the Li-S batteries with Si/G and pure-G electrode at 4 C are presented in Figure 3b. Obviously, there are two well-defined plateaus in the discharge profile, which depicts the typical multistep conversion of S. The initial discharge plateau at around 2.3 V represents the dissolution of sulfur to high-order soluble (Li<sub>2</sub>S<sub>x</sub>,  $4 \le x \le 8$ ), and another plateau at around 2.1 V corresponds to the formation of Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S.<sup>[41]</sup> For the charge profile, the plateau implies the reverse transformation from Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S to Li<sub>2</sub>S<sub>8</sub>/S<sub>8</sub>. It is evident that the discharge capacity of Si/G-1 electrode obtained at the low discharge plateau is much higher than that of the pure G electrode, which indicates that the polysulfides dissolution in organic electrolyte is significantly alleviated, thus enlarging the



utilization of active sulfur.<sup>[42]</sup> In addition, the Si/G-1 electrode possesses much lower overpotential than that of the pure G electrode (Figure 3b), and this situation is consistent even with increasing the areal sulfur loading of Si/G to 4.2 mg cm<sup>-2</sup>. As known, the overpotential is closely linked to electrochemical reaction kinetics, which is particularly prominent under high sulfur loading conditions.<sup>[43]</sup> This observation suggests that the presence of siloxene nanosheets in the electrode of LSBs is capable of accelerating polysulfides redox conversion.

Cycling performances of Si/G and pure-G electrode evaluated at 0.5 C with areal sulfur loading of 2.9 mg  $\rm cm^{-2}$  are depicted in Figure 3c. The cell-employed Si/G electrode delivers higher initial discharge capacity of 1011 mAh g<sup>-1</sup> than that of pure-G electrode (687 mAh  $g^{-1}$ ), which reveals that the activation and utilization of sulfur in pure-G electrode are much lower due to sluggish sulfur species redox kinetics. After 500 cycles, the specific discharge capacity of Si/G electrode decreases to 783 mAh g<sup>-1</sup> with a capacity retention of 77.4%, superior to the pure-G electrode (maintained 203 mAh g<sup>-1</sup> after 500 cycles at 0.5 C, corresponding to 29.5% capacity retention). The stable cycling performance is attributed to the efficient anchoring effect of siloxene nanosheets for polysulfides.<sup>[44]</sup> The results further highlight the merits of siloxene nanosheets in mitigating the shuttling effect of polysulfides. Figure S11, Supporting Information, shows the digital images of Li2S6 in DOL/DME

solution before and after addition of the as-prepared siloxene nanosheets and graphene powders, which preliminarily confirms the immobilization capability of siloxene to polysulfides via the visible decoloration of the Li<sub>2</sub>S<sub>6</sub> solution. The superior polysulfides regulation capability can be further confirmed by the morphology evolutions of lithium metal anode surfaces at the current density of 0.5 C after 100 cycles (Figure S12, Supporting Information). As depicted in Figure S12, Supporting Information, the surface of lithium anode cycled with pure-G cathode exhibits much higher roughness with prominent gullies and cracks than that of Si/G cathode, which indicates that chemical reactions between Li metal and diffused polysulfides from cathode side are more serious in cell with pure-G cathode. Besides, severe diffusion of polysulfides to the Li anode can also be verified in the EDX analysis of Li metal (Figure S12a,c, Supporting Information). The anode matched with Si/G cathode has very low sulfur content in the surface of Li metal, suggesting stronger polysulfides trapping capability of Si/G cathode. Such phenomenon is well in accord with the results of electrochemical cycling tests, demonstrating that siloxene can serve as a good sulfur host for LSBs. Since high-S loadings are accompanied by serious polysulfides dissolution loss, it is very necessary to verify the long-term cycling stability of LSBs



electrodes under high sulfur loading conditions. Therefore, in order to further verify the superiority of the siloxene nanosheets in LSBs electrode, the high areal sulfur loading of Si/G electrode is tested. As depicted in Figure 3d, remarkably, the cell employed Si/G electrode with a high areal sulfur loading of 4.2 mg cm<sup>-2</sup> at 1 C still delivers a high initial discharge capacity of 851 mAh g<sup>-1</sup> and possesses an ultralow capacity fading rate of 0.032% per cycle over 1000 cycles, suggesting the excellent long-term stability for practical application. These electrochemical results strongly demonstrate that siloxene nanosheets play a very important role in improving the electrochemical performance of LSBs.

In order to further unravel the superiority of siloxene nanosheets in cathodes of LSBs at the atomic level, first-principle calculations based on density functional theory (DFT) were applied to further investigate the chemical interactions between soluble polysulfides and siloxene nanosheets. The Li<sub>2</sub>S<sub>6</sub> was chosen as the representative polysulfides prototype molecule to check the chemical binding. Figure S13a, Supporting Information, presents the optimized configuration of Kautsky-type siloxene structure with Si-O-Si bridge grafted in Si6 rings and hydroxyl-functionalized group on the corrugated surface, which is consistent with the abovementioned structure characterization. Since such siloxene was obtained by oxidation during the process of peeling off the silicene (2D silicon layer) from CaSi2, it is necessary to select silicene (the optimized model of silicene is exhibited in Figure S13b, Supporting Information) as a control object to reveal the effect of structural transformation brought about by oxidation on polysulfides trapping. Figure 4a,b shows the optimized adsorption geometry with the Li<sub>2</sub>S<sub>6</sub> molecule on the surface of siloxene and silicene, respectively. The calculated binding energy of Li<sub>2</sub>S<sub>6</sub> on

siloxene surface is -3.44 eV, which is much higher than that on carbon hexatomic ring matrix,[5,45,46] indicating that the siloxene nanosheets possess strong chemical anchoring capability for polysulfides. Notably, the binding energy of Li<sub>2</sub>S<sub>6</sub> on silicene is decreased to -1.26 eV, revealing that the silicene has lower affinity to the  $Li_2S_6$  molecule than siloxene. To further understand the strong electrostatic interactions, different charge density (DCD) and Bader charge analysis were observed. As a result, the DCD of siloxene adsorbed Li<sub>2</sub>S<sub>6</sub> showed more distinct phenomenon of electrostatic interaction than that of silicene. In detail, based on Bader charge analysis, we found that the charge transfer from siloxene to Li<sub>2</sub>S<sub>6</sub> is much higher (2.46 e) while the charge transfer from silicene is about 0.1 e. In order to investigate the huge difference in the charge transfer of siloxene and silicene, we analyzed the S atoms. It was found that the S atoms can get more electrons (0.69 e per S atom) on the surface of siloxene than silicene (0.27 e per S atom), which induce a higher adsorption energy. In addition, the results of DCD and Bader charge analysis are consistence with the adsorption energy of Li<sub>2</sub>S<sub>6</sub> on the surface of siloxene and silicene, respectively. The PDOS (projected density of states) of Si and S atoms before and after adsorption was calculated via DFT to further investigate the detailed explanation on the interaction between siloxene and Li<sub>2</sub>S<sub>6</sub>. PDOS plots of Si atom (Figure S14, Supporting Information) present that partial electrons of Si in siloxene have obviously transferred to Li2S6 molecule, and this phenomenon is more pronounced than that in silicene judging by the obvious positive shift of Si PDOS in siloxene.<sup>[21,47]</sup> PDOS plots of S (Figure S15, Supporting Information) reveal that S atoms could obtain more electrons after adsorbed on siloxene than on silicene. These results indicate that the siloxene has a higher affinity for polysulfides than



**Figure 4.** Density functional theory (DFT) calculations. Adsorption energies of  $Li_2S_6$  molecule on a) siloxene and b) silicene surfaces. Top view schematic illustrations of corresponding diffusion pathway for Li<sup>+</sup> on c) siloxene and d) silicene surfaces, and the corresponding diffusion energy barriers of Li<sup>+</sup> on e) siloxene and f) silicene. The purple, green, yellow, pink, and red balls represent the Si, Li, S, H, and O atoms, respectively.





silicene, which enhances the capability to inhibit polysulfides shuttling. Owing to that Li ion diffusion on host materials is closely related to the further conversion of Li<sub>2</sub>S<sub>n</sub><sup>[48]</sup> the diffusion barriers for Li ion on siloxene and silicene are simulated. shown in Figure 4c-f. The diffusion energy barrier of Li ion on the surface of siloxene is 0.13 eV, which is much lower than that on the surface of silicene (0.68 eV), indicating that Si<sub>6</sub> matrix promotes the diffusion of Li ion after oxidation. The lower Li ion diffusion energy on siloxene than that on silicene originates from the existence of abundant electronegative heteroatom O doped in the Si6 rings and hydroxyl on the surface, which substantially improves the wettability of Si6 matrix and modifies the surface chemistry toward accelerating Li ion diffusion.<sup>[49,50]</sup> The lower Li ion diffusion energy barrier suggests that siloxene nanosheets can promote the reaction between lithium and polysulfides, thus reducing the electrochemical polarization and improving polysulfides conversion efficiency.

Besides chemical trapping ability, improving polysulfides redox conversion reactions is also very important to suppressing the shuttling effect. Figure 5a displays the cyclic voltammetry (CV) profiles comparison between Si/G and pure-G cathodes at a scan rate of 0.1 mV s<sup>-1</sup>. Two reversible cathodic peaks attribute to the solid-to-liquid phase transformation (from elemental sulfur to soluble polysulfides) and following conversion from soluble polysulfides to solid-state Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S, and one anodic peak is related to the reconversion of Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub> to sulfur,<sup>[6,51]</sup> which is in harmony with the analysis of galvanostatic charge/discharge profiles. All peaks of Si/G cathode are sharper and possess stronger peak current density in contrast to those of pure-G cathode, suggesting better redox reactivity and higher utilization of active S species.<sup>[52]</sup> Meanwhile, comparing the peak potentials (Figure 5b), the Si/G cathode shows significantly higher cathodic reaction potentials and lower anodic reaction potential, which reveals that the introduced siloxene nanosheets can efficiently suppress the electrochemical polarization via accelerated redox kinetics of polysulfides transformation.<sup>[10,53]</sup> Moreover, the cathodic peaks of Si/G cathode show higher onset potentials (Figure 5c) comparing with those of pure-G cathode, further verifying the better kinetics of polysulfides. As demonstrated in Figure S16, Supporting Information, it is evident that the CV profiles of Si/G cathode are more stable than the pure-G counterpart, indicating enhanced cycling reversibility of electrochemical reaction and continuous suppression of electrochemical polarization.<sup>[54]</sup> Electrochemical impedance spectra (EIS) were also tested to reveal the chargetransfer capability across the electrode-electrolyte interface.



**Figure 5.** Analysis of electrochemical redox reaction kinetics. a) The CV profiles of Li-S cells with Si/G and pure-G cathodes at a scan rate of 0.1 mV s<sup>-1</sup>, the corresponding b) peak potentials and c) onset potentials comparisons. Tafal plots for Si/G and pure-G cathodes: d,e) are in correspondence with the cathodic and anodic peaks marked with A and C peaks in the CV profile, respectively. CV profiles of the f) Si/G and g) pure-G cathodes recorded at scan rates of 0.1–0.5 mV s<sup>-1</sup>, and the relevant *b* value calculated from plot of log *i* versus log  $\nu$  for h) Si/G and i) pure-G cathodes.



As shown in Figure S17, Supporting Information, the Si/G cathode exhibits lower charge-transfer resistance (27.5  $\Omega$ ) than that of pure-G cathode (49.3  $\Omega$ ), and after 500 cycles, the charge-transfer resistance of Si/G cathode is still relatively low, demonstrating the positive role of siloxene nanosheets in enhancing electrochemical reaction kinetics. Figure 5d,e presents the cathodic and anodic Tafel plot comparisons of Li-S cells with Si/G and pure-G cathodes. The calculated Tafel slopes of cathodic and anodic peaks (corresponding to the peaks marked with A and C in the CV profile) for Si/G cathode are 56.7 and 86.9 mV dec<sup>-1</sup>, respectively. While on the pure-G cathode, the relevant Tafel slopes are increased into 66.4 and 341.9 mV dec<sup>-1</sup>, respectively. The lower Tafel slopes demonstrate that the existence of siloxene could significantly enhance the kinetics in polysulfides conversion reactions.<sup>[55]</sup>

Additionally, CV tests of Li-S cells with Si/G and pure-G cathodes measured under different sweep rates were also carried out to reveal the electrochemical reaction kinetic behavior of different cathodes. Figure 5f,g shows the CV profiles of the Si/G and pure-G cathodes at different scanning rates ranging from 0.1 to 0.5 mV s<sup>-1</sup>, respectively. The logarithm of cathodic and anodic peaks current density (A, B, and C peaks) of both the Si/G and pure-G cathodes has a linear relationship with the logarithm of relevant scanning rates (demonstrated in Figure 5h,i), according to the formula:  $i = av^{b}$ , where i represents the peak current density, v represents the scanning rates of CV tests, and b value is positively correlated with the lithium ion diffusion coefficient.<sup>[56]</sup> Since the electrode kinetics are closely related to the lithium ion diffusion coefficient, [57,58] the *b* value can be used to assess the ease of the polysulfides conversion reactions in the electrode. Obviously, all the A, B, and C peaks of Si/G cathode are higher than those of pure-G cathode, which confirms rapid lithium ion diffusivity arising from the fast conversion of polysulfides. As noticed, for pure-G cathode, the *b* value of B peak is lower than the value of A peak, suggesting that the solid-to-liquid reaction of S<sub>8</sub> to long-chain polysulfides is faster than the liquid-to-solid reaction of longchain polysulfides to Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S.<sup>[56]</sup> However, for Si/G cathode, in addition to the increase in the values of A and B peaks, the value of B peak is greater than the value of A peak, which indicates that the conversion reaction of long-chain polysulfides to solid-state Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S is significantly improved, hence reducing the existence time of long-chain polysulfides and inhibiting the shuttling effect. Therefore, these kinetic results give clear evidence that the presence of siloxene nanosheets is capable of kinetically enhancing polysulfides redox conversion, which is critical in improving the performance of LSBs, including rate capability and cycling stability.

# 3. Conclusions

In summary, the 2D siloxene nanosheets prepared by chemical exfoliation of  $CaSi_2$  in aqueous HCl are proposed for the first time to employ as sulfur hosts in LSBs. It is proven that the 2D siloxene nanosheets are capable of serving as not only a resultful shuttle-suppressing shield for polysulfides via dual lithiophilic–sulfiphilic chemisorption sites but also a promoter in accelerating polysulfides redox reactions kinetics, lowering electrochemical polarization, decreasing the energy barrier for Li<sup>+</sup> diffusion, and improving sulfur utilization. Consequently, benefiting from these synergistic effects, the siloxene nanosheets enable high-loading LSBs with enhanced capacity, excellent rate performance, and superior long-term cyclability. The cell employed Si/G electrode delivers a high capacity of 919, 759, and 646 mA h g<sup>-1</sup> at 4 C with areal sulfur loading of 1, 2.9, and 4.2 mg cm<sup>-2</sup>, respectively, and simultaneously achieves a low capacity decay of 0.032% during 1000 cycles at 1 C with a high areal sulfur loading of 4.2 mg cm<sup>-2</sup>. We demonstrate the potential application value of the siloxene nanosheets for energy storage and this result brings a new insight to develop high-performance LSBs.

### 4. Experimental Section

Preparation of Siloxene Nanosheets: The 2D siloxene nanosheets were prepared by chemical exfoliation of CaSi<sub>2</sub> (Shanghai urchem Ltd.) in aqueous HCl. Specifically, CaSi<sub>2</sub> powder (1 g) was gradually added in the aqueous HCl (6 mol L<sup>-1</sup>, 400 mL), which was magnetically stirred for 4 days. After the reaction was completed, the solution was ultrasonically treated to precipitate the suspended particles that are not sufficiently reacted. The upper solution was then centrifuged and the obtained centrifugal product was added to HCl solution to continue sonication to further remove the bottom precipitate and retain the upper solution. Repeat the ultrasound and centrifugation steps several times, and collect the final centrifugal product then dry it at 60 °C for 24 h to obtain 2D siloxene nanosheets.

Preparation of Si/G and Pure-G Cathodes: Typically, 0.4 g as-prepared siloxene nanosheets, 0.4 g graphene (Graphene was purchased directly from XFNANO nanotechnology co., LTD., The grade of graphene was about 5  $\mu$ m in diameter and 1–5 nm in thickness), and 1.2 g sulfur powder were completely mixed together then sealed under Ar atmosphere in an autoclave and heated at 155 °C for 12 h to make sulfur fully infiltrate the host materials to obtain S@siloxene@graphene (Si/G) composite. The working electrode was prepared by blending the Si/G composite and polyvinylidene fluoride (PVDF) under the weight ratio of 9:1 in *N*-methylpyrrolidone (NMP) solvent. The obtained homogeneous slurry was casted on the Al foil current collector via traditional doctor blade method and dried at 60 °C overnight to get Si/G cathode. The areal sulfur loading of Si/G cathode is 1.0, 2.9, and 4.2 mg cm<sup>-2</sup>. The pure-G cathode was prepared according to the same process by using 0.8 g graphene to replace 0.4 g siloxene nanosheets and 0.4 g graphene.

Electrochemical Measurements: Electrochemical experiments of the Si/G and pure-G cathodes were carried out with CR2016 coin cells, fabricated in an Ar-filled glovebox, and using Li foil as the counter electrode. The electrolyte used in this study was composed of a mixture of 1 m bis (trifluoromethylsulfonyl) imide in 1,3-dioxolane/1,2dimethoxy-ethane (DOL/DME; 1:1 v/v) with 1 wt% LiNO3 additive. The amount of electrolyte in each cell was 15  $\mu$ L mg<sup>-1</sup> for areal sulfur loading of 1.0 mg cm^-2, 10  $\mu L$  mg^-1 for areal sulfur loading of 2.9 and 4.2 mg cm<sup>-2</sup>. The galvanostatic charge-discharge tests (including rate performance and cycling stability) were measured by Neware BTS-4000 battery equipment with a voltage window of 1.8-2.8 V versus Li<sup>+</sup>/Li and all the Li-S cells were tested at 25 °C in a thermostat. Cyclic voltammetry (CV) (performed at scan rates of 0.1-0.5 mV s<sup>-1</sup>) and electrochemical impedance spectroscopy (EIS) measurements (obtained in the frequency range of 1 MHz to 0.1 Hz) were conducted on CHI760E multichannel electrochemical workstation. The  ${\rm Li}_2 S_6$  electrolyte used in adsorption test was prepared by dissolving stoichiometric amounts of Li2S and sulfur in a mixture solvent of 1,3-dioxolane/1,2-dimethoxy-ethane (DOL/ DME) with a volume ratio of 1:1.

*Material Characterization*: The morphology characterizations of siloxene nanosheets were investigated by SEM (SU8010, HITACHI), 120 kV low-resolution TEM (HT-7700, HITACHI) and 200 kV



high-resolution TEM (JEM-2100, JEOL). STEM images were collected on a Philips-FEI Tecnai G2 F30 S-Twin system. XRD measurements were carried out on Empyrean 200 895 XRD system (Cu Ka radiation,  $\lambda = 0.1540598$  nm, PANalytical B.V.). The elements' chemical states were analyzed by XPS (Escalab 250Xi, Thermo Fisher Scientific). AFM (AFM, Bruker Vecco and Oxford Cypher S) analysis was used to determine the thickness of siloxene nanosheets. Chemical composition of resultant siloxene nanosheets was studied by Raman spectra (LabRAM, HR Evolution) and FTIR (Nicolet5700, Thermo Fisher Scientific). The IR maps of siloxene were conducted on nanoIR2-fs (Anasys Instruments). The specific surface area Pore size distribution were calculated from the adsorption–desorption data obtained by AUTOSORB-IQ2-MP equipment (Quantachrome).

Computational Method: Density functional theory (DFT) calculation was carried out via the Vienna Ab-Initio Simulation Package.<sup>[59]</sup> Projector augmented-wave (PAW) pseudopotentials with a cutoff energy of 400 eV for the wave functions expansion was employed to describe the electron-ion interaction. The Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation (GGA) exchance-correlation was applied as the exchange and correlation functionals.<sup>[60,61]</sup> The supercell of silicene and siloxene with 15 Å vacuum layer were used to simulate the adsorption of  $Li_2S_6$  on the surface of silene and siloxene, respectively. In the brillouin zone integration on the grid with  $3 \times 3 \times 1$  for geometry optimization and  $5 \times 5 \times 1$  k-grid mesh for calculation of density of states during the DFT calculations. In addition, the climbing image nudged elastic band (CI-NEB) method<sup>[62]</sup> was used to simulate the diffusion of Li on the surface of silicene and siloxene. Five images were inserted between the initial and final configurations in the transition state search began with an NEB calculation. And the corrected adsorption energy of  $Li_2S_6$  ( $\Delta E_{ads}$ ) was defined as:

$$\Delta E_{ads} = E_{total} - E_{host} - E_{guest} \tag{1}$$

where  $E_{\text{total}}$  is the total energy of silene and siloxene surface adsorbed with the Li<sub>2</sub>S<sub>6</sub>,  $E_{\text{host}}$  is the total energy of silene and siloxene, and  $E_{\text{guest}}$  is the total energy of Li<sub>2</sub>S<sub>6</sub>.

# **Supporting Information**

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

## Acknowledgements

This work was financially supported by Zhejiang Provincial Public Technology Research (LGG18E020001) and the National Natural Science Foundation of China (Grant 91833301). The authors thank the senior visiting Chair Prof. S. T. Lee from Soochow University for the inspiration and guide.

# **Conflict of Interest**

The authors declare no conflict of interest.

# **Keywords**

conversion kinetics, lithium-sulfur batteries, polysulfides, siloxene nanosheets, two-dimensional materials

Received: December 12, 2019 Revised: January 10, 2020

Published online:

#### www.afm-journal.de

- L. Li, L. Chen, S. Mukherjee, J. Gao, H. Sun, Z. Liu, X. Ma, T. Gupta, C. V. Singh, W. Ren, H.-M. Cheng, N. Koratkar, *Adv. Mater.* 2017, *29*, 1602734.
- [2] J. Song, X. Guo, J. Zhang, Y. Chen, C. Zhang, L. Luo, F. Wang, G. Wang, J. Mater. Chem. A 2019, 7, 6507.
- [3] Y. Yuan, Y. Lu, B.-E. Jia, H. Tang, L. Chen, Y.-J. Zeng, Y. Hou, Q. Zhang, Q. He, L. Jiao, J. Leng, Z. Ye, J. Lu, *Nano-Micro Lett.* 2019, 11, 42.
- [4] Y. Chen, W. Zhang, D. Zhou, H. Tian, D. Su, C. Wang, D. Stockdale, F. Kang, B. Li, G. Wang, ACS Nano 2019, 13, 4731.
- [5] S. Shen, X. Xia, Y. Zhong, S. Deng, D. Xie, B. Liu, Y. Zhang, G. Pan, X. Wang, J. Tu, *Adv. Mater.* **2019**, *31*, 1900009.
- [6] Q. Wu, X. Zhou, J. Xu, F. Cao, C. Li, ACS Nano 2019, 13, 9520.
- [7] K. E. Hendrickson, L. Ma, G. Cohn, Y. Lu, L. A. Archer, Adv. Sci. 2015, 2, 1500068.
- [8] Z. Xiao, Z. Yang, Z. Li, P. Li, R. Wang, ACS Nano 2019, 13, 3404.
- Z. Wang, J. Shen, J. Liu, X. Xu, Z. Liu, R. Hu, L. Yang, Y. Feng, Z. Shi, L. Ouyang, Y. Yu, M. Zhu, Adv. Mater. 2019, 31, 1902228.
- [10] X. Gao, X. Yang, M. Li, Q. Sun, J. Liang, J. Luo, J. Wang, W. Li, J. Liang, Y. Liu, S. Wang, Y. Hu, Q. Xiao, R. Li, T.-K. Sham, X. Sun, *Adv. Funct. Mater.* **2019**, *29*, 1806724.
- [11] R. Ummethala, M. Fritzsche, T. Jaumann, J. Balach, S. Oswald, R. Nowak, N. Sobczak, I. Kaban, M. H. Ruemmeli, L. Giebeler, *Energy Storage Mater.* **2018**, *10*, 206.
- [12] D. Gueon, J. T. Hwang, S. B. Yang, E. Cho, K. Sohn, D.-K. Yang, J. H. Moon, ACS Nano 2018, 12, 226.
- [13] J. Wu, X. Li, H. Zeng, Y. Xue, F. Chen, Z. Xue, Y. Ye, X. Xie, J. Mater. Chem. A 2019, 7, 7897.
- [14] S. B. Patil, H. J. Kim, H.-K. Lim, S. M. Oh, J. Kim, J. Shin, H. Kim, J. W. Choi, S.-J. Hwang, ACS Energy Lett. 2018, 3, 412.
- [15] Y. Chen, S. Choi, D. Su, X. Gao, G. Wang, Nano Energy 2018, 47, 331.
- [16] H.-E. Wang, K. Yin, N. Qin, X. Zhao, F.-J. Xia, Z.-Y. Hu, G. Guo, G. Cao, W. Zhang, J. Mater. Chem. A 2019, 7, 10346.
- [17] H. Li, S. Ma, H. Cai, H. Zhou, Z. Huang, Z. Hou, J. Wu, W. Yang, H. Yi, C. Fu, Y. Kuang, *Energy Storage Mater.* **2019**, *18*, 338.
- [18] Z. H. Li, Q. He, X. Xu, Y. Zhao, X. W. Liu, C. Zhou, D. Ai, L. X. Xia, L. Q. Mai, Adv. Mater. 2018, 30, 1804089.
- [19] C. Ye, Y. Jiao, H. Jin, A. D. Slattery, K. Davey, H. Wang, S.-Z. Qiao, Angew. Chem., Int. Ed. 2018, 57, 16703.
- [20] B. Liu, S. Huang, D. Kong, J. Hu, H. Y. Yang, J. Mater. Chem. A 2019, 7, 7604.
- [21] H. Zhang, M. Zou, W. Zhao, Y. Wang, Y. Chen, Y. Wu, L. Dai, A. Cao, ACS Nano 2019, 13, 3982.
- [22] X. Li, G. Guo, N. Qin, Z. Deng, Z. Lu, D. Shen, X. Zhao, Y. Li, B.-L. Su, H.-E. Wang, *Nanoscale* **2018**, *10*, 15505.
- [23] H.-E. Wang, K. Yin, X. Zhao, N. Qin, Y. Li, Z. Deng, L. Zheng, B.-L. Su, Z. Lu, *Chem. Commun.* **2018**, *54*, 12250.
- [24] B. Li, H. Xu, Y. Ma, S. Yang, Nanoscale Horiz. 2019, 4, 77.
- [25] J. Wu, H. Zeng, X. Li, X. Xiang, Y. Liao, Z. Xue, Y. Ye, X. Xie, Adv. Energy Mater. 2018, 8, 1802430.
- [26] H.-E. Wang, X. Li, N. Qin, X. Zhao, H. Cheng, G. Cao, W. Zhang, J. Mater. Chem. A 2019, 7, 12068.
- [27] W. Yang, J. Xiao, Y. Ma, S. Cui, P. Zhang, P. Zhai, L. Meng, X. Wang, Y. Wei, Z. Du, B. Li, Z. Sun, S. Yang, Q. Zhang, Y. Gong, *Adv. Energy Mater.* **2019**, *9*, 1803137.
- [28] D. Guo, F. Ming, H. Su, Y. Wu, W. Wahyudi, M. Li, M. N. Hedhili, G. Sheng, L.-J. Li, H. N. Alshareef, Y. Li, Z. Lai, *Nano Energy* **2019**, *61*, 478.
- [29] X. Huang, J. Tang, B. Luo, R. Knibbe, T. Lin, H. Hu, M. Rana, Y. Hu, X. Zhu, Q. Gu, D. Wang, L. Wang, *Adv. Energy Mater.* **2019**, *9*, 1901872.
- [30] D. Rao, X. Liu, H. Yang, L. Zhang, G. Qiao, X. Shen, X. Yan, G. Wang, R. Lu, J. Mater. Chem. A 2019, 7, 7092.

#### **ADVANCED** SCIENCE NEWS

www.advancedsciencenews.com

- [31] T. Li, C. He, W. Zhang, J. Mater. Chem. A 2019, 7, 4134.
- [32] Y. Qie, J. Liu, S. Wang, S. Gong, Q. Sun, Carbon 2018, 129, 38-44.
- [33] K. Krishnamoorthy, P. Pazhamalai, S.-J. Kim, *Energy Environ. Sci.* 2018, 11, 1595.
- [34] H. Imagawa, N. Takahashi, T. Nonaka, Y. Kato, K. Nishikawa, H. Itahara, J. Mater. Chem. A 2015, 3, 9411.
- [35] J. Liu, Y. Yang, P. Lyu, P. Nachtigall, Y. Xu, Adv. Mater. 2018, 30, 1800838.
- [36] H. Nakano, T. Mitsuoka, M. Harada, K. Horibuchi, H. Nozaki, N. Takahashi, T. Nonaka, Y. Seno, H. Nakamura, *Angew. Chem., Int.* Ed. 2006, 45, 6303.
- [37] S. Li, H. Wang, D. Li, X. Zhang, Y. Wang, J. Xie, J. Wang, Y. Tian, W. Ni, Y. Xie, J. Mater. Chem. A 2016, 4, 15841.
- [38] S.-Y. Oh, H. Imagawa, H. Itahara, J. Mater. Chem. A 2014, 2, 12501.
- [39] K. Xu, L. Ben, H. Li, X. Huang, Nano Res. 2015, 8, 2654.
- [40] R. Fu, K. Zhang, R. P. Zaccaria, H. Huang, Y. Xia, Z. Liu, Nano Energy 2017, 39, 546.
- [41] J. Wu, N. You, X. Li, H. Zeng, S. Li, Z. Xue, Y. Ye, X. Xie, J. Mater. Chem. A 2019, 7, 7644.
- [42] T.-Z. Zhuang, J.-Q. Huang, H.-J. Peng, L.-Y. He, X.-B. Cheng, C.-M. Chen, Q. Zhang, Small 2016, 12, 381.
- [43] L.-P. Lv, C.-F. Guo, W. Sun, Y. Wang, Small 2019, 15, 1804338.
- [44] L. Fan, H. L. Zhuang, K. Zhang, V. R. Cooper, Q. Li, Y. Lu, Adv. Sci. 2016, 3, 1600175.
- [45] G. Zhou, E. Paek, G. S. Hwang, A. Manthiram, Nat. Commun. 2015, 6, 7760.
- [46] Z. Sun, J. Zhang, L. Yin, G. Hu, R. Fang, H.-M. Cheng, F. Li, Nat. Commun. 2017, 8, 14627.
- [47] S.-Q. Yang, C.-B. Li, J. Du, Y.-J. Zhao, Appl. Surf. Sci. 2019, 491, 187.

- [48] D. Wang, F. Li, R. Lian, J. Xu, D. Kan, Y. Liu, G. Chen, Y. Gogotsi, Y. Wei, ACS Nano 2019, 13, 11078.
- [49] C. Wang, K. Su, W. Wan, H. Guo, H. Zhou, J. Chen, X. Zhang, Y. Huang, J. Mater. Chem. A 2014, 2, 5018.
- [50] F. Sun, J. Wang, H. Chen, W. Li, W. Qiao, D. Long, L. Ling, ACS Appl. Mater. Interfaces 2013, 5, 5630.
- [51] Y. Wang, J. Huang, X. Chen, L. Wang, Z. Ye, Carbon 2018, 137, 368–378.
- [52] C. Zheng, S. Niu, W. Lv, G. Zhou, J. Li, S. Fan, Y. Deng, Z. Pan, B. Li, F. Kang, Q.-H. Yang, *Nano Energy* **2017**, *33*, 306.
- [53] N. Wang, B. Chen, K. Qin, E. Liu, C. Shi, C. He, N. Zhao, Nano Energy 2019, 60, 332.
- [54] S. Luo, C. Zheng, W. Sun, Y. Wang, J. Ke, Q. Guo, S. Liu, X. Hong, Y. Li, W. Xie, *Electrochim. Acta* **2018**, 289, 94.
- [55] J. Xie, B.-Q. Li, H.-J. Peng, Y.-W. Song, M. Zhao, X. Chen, Q. Zhang, J.-Q. Huang, *Adv. Mater.* **2019**, *31*, 1903813.
- [56] Y. Tao, Y. Wei, Y. Liu, J. Wang, W. Qiao, L. Ling, D. Long, *Energy Environ. Sci.* 2016, 9, 3230.
- [57] G. Zhou, H. Tian, Y. Jin, X. Tao, B. Liu, R. Zhang, Z. W. Seh, D. Zhuo, Y. Liu, J. Sun, J. Zhao, C. Zu, D. S. Wu, Q. Zhang, Y. Cui, *Proc. Natl. Acad. Sci. USA* **2017**, *114*, 840.
- [58] X. Tao, J. Wang, C. Liu, H. Wang, H. Yao, G. Zheng, Z. W. Seh, Q. Cai, W. Li, G. Zhou, C. Zu, Y. Cui, *Nat. Commun.* **2016**, *7*, 11203.
- [59] G. Kresse, D. Joubert, Phys. Rev. B 1999, 59, 1758.
- [60] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865.
- [61] P. E. Blöchl, Phys. Rev. B 1994, 50, 17953.
- [62] G. Henkelman, B. P. Uberuaga, H. Jónsson, J. Chem. Phys. 2000, 113, 9901.

