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Self-Assembly-Induced Alternately Stacked Single-Layer MoS₂ and N-doped Graphene: a Novel van der Waals Heterostructure for Lithium-Ion Batteries

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ABSTRACT: In this article, a simple self-assembly strategy for fabricating van der Waals heterostructures from isolated two-dimensional atomic crystals is presented. Specifically, dopamine (DOPA), an excellent self-assembly agent and carbon precursor, was adsorbed on exfoliated MoS₂ monolayers through electrostatic interaction, and the surface-modified monolayers self-assembled spontaneously into DOPA-intercalated MoS₂. The subsequent *in-situ* conversion of DOPA to highly conductive nitrogen-doped graphene (NDG) in the interlayer space of MoS₂ led to the formation of a novel NDG/MoS₂ nanocomposite with well-defined alternating structure. The NDG/MoS₂ was then studied as an anode for lithium-ion batteries (LIBs). The results show that alternating arrangement of NDG and MoS₂ triggers synergistic effect between the two components. The kinetics and cycle life of the anode are greatly improved due to the enhanced electron and Li⁺ transport as well as the effective immobilization of soluble polysulfide by NDG. A reversible capacity of more than 460 mAh/g could be delivered even at 5 A/g. Moreover, the abundant voids created at the MoS₂-NDG interface also accommodate the volume change during cycling and provide additional active sites for Li⁺ storage. These endow the NDG/MoS₂ heterostructure with low charge-transfer resistance, high sulfur reservation and structural robustness, rendering it an advanced anode material for LIBs.

KEYWORDS: *molybdenum disulfide (MoS₂), dopamine, self-assembly, lithium-ion batteries, heterostructure*

INTRODUCTION

In recent years, the growing demands for portable electronic devices and electrical vehicles have stimulated significant research efforts to develop advanced lithium-ion battery (LIB) electrode materials, especially those with higher energy density, faster rate capability and longer cycle life. Currently, the performances of traditional LIB electrodes based on the insertion storage of Li^+ are limited by their intrinsic low theoretical capacities. By contrast, the electrode materials based on both conversion and interfacial storage of Li^+ show great promise as alternatives in virtue of their predominant merits in capacity.¹⁻³ Among such dual-mechanism systems, molybdenum disulfide (MoS_2) has attracted great attention owing to its tunable structures and Li^+ storage behavior.⁴⁻⁸

As a typical transition metal dichalcogenide, MoS_2 has two-dimensional (2D) layered structure, analogous to that of graphite. The covalent bonded S-Mo-S three atom layers are stacked together through van der Waals forces with an interlayer distance of 0.62 nm. Such structural features facilitate the insertion and extraction of foreign species,⁹ making MoS_2 an attractive host material for energy storage.¹⁰⁻¹³ In addition to insertion, MoS_2 can be converted to Mo and Li_2S when further discharged, leading to a substantial gain in capacity resulting from the conversion and interfacial storage of Li^+ .¹⁴⁻¹⁶ Nevertheless, MoS_2 suffers from sluggish kinetics due to its limited electron and Li^+ conductivity, especially along the c-direction. Furthermore, the shuttle effect caused by the soluble polysulfide intermediates results in a loss of active material and continuous capacity decay.¹⁷ Reducing the number of layers¹⁸⁻²⁰ or expanding the interlayer spacing²¹⁻²³ of MoS_2 can somewhat meliorate the electron and Li^+ transport. Another popular approach to improve the performance of the MoS_2 -based electrodes is to integrate MoS_2 with carbonaceous materials²⁴⁻³⁰ or conductive

polymers³¹⁻³² to fabricate nanocomposites with specially designed architectures. For example, Maier et al. prepared one-dimensional (1D) carbon nanofibers embedded with ultrasmall MoS₂ nanoplates via electrospinning, which exhibited outstanding lithium and sodium storage due to the blurred storage mechanisms.³³ Yu et al. decorated carbon nanowires with MoS₂ sheets and found a new electrochemical process for the Li⁺ storage of MoS₂ due to the synergistic effect between the two components.³⁴ A MoS₂-carbon interoverlapped superstructure was fabricated by Li et al. via hydrothermal synthesis of MoS₂ in the presence of oleic acid (OA), amidation of OA with dopamine (DOPA), followed by self-polymerization of DOPA and subsequent carbonization, which exhibited superior electrochemical performance due to the ideal interface contact.³⁵

Heterostructures made by stacking of different atomic layers (van der Waals heterostructure) are a class of materials with fascinating properties.³⁶ The structural similarity of MoS₂ and graphene provides a high possibility to fabricate MoS₂/graphene heterostructures. It is believed that the intimate face-to-face contact between MoS₂ and graphene may trigger synergistic effects and maximize the Li⁺ storage potential of both components. Self-assembly of monolayers of two different types of 2D materials is a facile strategy for fabrication of van der Waals nanocomposites with well-defined alternating structure. However, although both exfoliated MoS₂^{19, 37-38} and graphene oxide (GO) can be suspended in aqueous solutions, owing to their negatively charged surfaces, direct assembly of MoS₂ monolayers and GO into alternately stacked MoS₂/GO heterostructure is hampered by the electrostatic repulsion between the two components; simply mixing the two components would lead to restacked MoS₂ dispersed in GO. Besides, the mismatch in lateral dimensions of MoS₂ and GO also makes the preparation of stable MoS₂/GO heterostructure

difficult. Previous work has shown that polydopamine (PDOPA), a biomimetic adhesive polymer,³⁹⁻⁴⁰ can be easily coated on various material surfaces by covalent polymerization of DOPA as well as non-covalent self-assembly.⁴¹⁻⁴² The carbonized thin PDOPA coatings have similar structure and electrical conductivity to those of multilayered graphene doped with heteroatoms.⁴³ Inspired by the self-assembly potential of DOPA and intercalation chemistry of MoS₂,⁴⁴⁻⁴⁵ in this work, for the first time a nitrogen-doped graphene (NDG)/MoS₂ van der Waals heterostructure with well-defined alternating NDG/MoS₂ layers was fabricated via a facile electrostatic attraction-induced self-assembly approach. Bulk MoS₂ was first exfoliated to monolayers through intercalation with Li⁺. Positively charged DOPA monomers were then attached and adsorbed on the negatively charged MoS₂ surfaces through electrostatic interaction, triggering spontaneous self-assembly of the DOPA-modified MoS₂ monolayers to form a new intercalated compound, (DOPA)_xMoS₂. Without the need of DOPA polymerization, the intercalated DOPA can be directly *in-situ* converted to NDG in the confined 2D space by carbonization, giving rise to the NDG/MoS₂ van der Waals heterostructure. The unique feature of the NDG/MoS₂ heterostructure lies in its alternately stacked structure with largely expanded interlayer space. It not only well addresses the issue of poor electron and Li⁺ conductivity of MoS₂-based anodes, but also provides additional Li⁺ storage sites at the MoS₂-NDG interface, effectively protects the active materials and accommodates the volume change during cycling. These endow the NDG/MoS₂ heterostructure with low charge-transfer resistance, high sulfur reservation and structural robustness, rendering it an advanced LIB anode material with excellent cycling stability and high rate capability.

EXPERIMENTAL SECTION

Materials. Dopamine hydrochloride (DOPA-HCl), MoS₂ powder and n-butyllithium solution (1.6 M in hexane) were purchased from Sigma-Aldrich (USA) and used as received. Electrolyte (1M LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) at a 1:1 volume ratio) and lithium foil were purchased from Charslton Technologies Pte Ltd (Singapore).

Fabrication of the NDG/MoS₂ Heterostructure. Firstly, the lithium intercalated MoS₂ was synthesized by immersing 1.5g MoS₂ powder in 8 ml 1.6 M butyllithium solution for 3 days. The Li_xMoS₂ obtained was collected by centrifugation and washed with hexane for 3 times. After the exfoliation of Li_xMoS₂ in water (1 mg/ml) under ultrasonication, the mixture was centrifuged at 2000 rpm for 5 min to remove any unexfoliated material. The pH of the suspension was about 11.4. An excess amount of DOPA-HCl aqueous solution was then added into the suspension under stirring. The black flake-like floccules were formed within several minutes. They were isolated by centrifugation and washed with water for 3 times. The black solid was freeze dried and annealed at 600 °C for 2 h (the argon flow is about 10 sccm and the system pressure is about 0.1 mbar).

As a control experiment, the pH of the aqueous solution was adjusted to 11.4 by NaOH in the absence of MoS₂, and then DOPA-HCl was added (0.5 mg/ml). After 10 minutes, the solution was centrifuged at 11000 rpm for 10 minutes. No precipitation was found at the bottom of the tube.

Structural and Morphological Characterization. The morphologies of the samples were studied using a field-emission scanning electron microscope (FESEM, JEOL JSM 7600) at an accelerating voltage of 5 kV and a transmission electron microscope (TEM, JEOL 2100) at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Kratos

Analytical AXIS His spectrometer with a monochromatized Al Ka X-ray source (1486.6 eV photons). X-ray diffraction (XRD) patterns were recorded on a Bruker GADDS X-ray diffractometer. Fourier transform infrared spectroscopic (FTIR) measurements were performed using a Shimadzu FTIR IR Prestige-21 with KBr pellets. Raman spectra were obtained using a Renishaw Invia Raman microscope with an excitation wavelength of 488 nm. The compositions of the samples were determined by thermogravimetric analysis (TGA, TA Q500) at a heating rate of 10 °C/min in air.

Electrochemical Measurements. Electrochemical tests of the NDG/MoS₂ anodes were conducted using standard CR2032 coin cells with Celgard® 2600 membrane as the separator. The working electrodes were composed of 70 wt% NDG/MoS₂, 20 wt% carbon black, and 10 wt% polyvinylidene fluoride. The capacities are calculated based on the mass of NDG/MoS₂. The cells were cycled between 0.005~3.0 V vs Li⁺/Li under different current density. The cyclic voltammetry (CV) was studied on a PGSTAT302N Autolab electrochemical workstation between 0.005~3.0 V with a scan rate of 0.1 mV/s. The electrochemical impedance spectroscopy (EIS) was measured between 10⁻² to 10⁶ Hz with an amplitude of 5 mV.

RESULTS AND DISCUSSION

Fabrication of the NDG/MoS₂ van der Waals Heterostructure. The fabrication process for the NDG/MoS₂ heterostructure is illustrated in Figure 1. Bulk MoS₂ was firstly intercalated by Li⁺ due to the weak interlayer interaction, forming the Li_xMoS₂ intermediate (Figure 1a). Upon contact with water, the Li⁺ ions were hydrated, causing an expansion of the interlayer space, while water was reduced to H₂ and OH⁻ by the negatively charged MoS₂.⁴⁶ The microbubbles formed further separated the expanded MoS₂ layers, yielding a stable colloidal suspension of

MoS₂ monolayers (Figure 1b). The negative charges on the MoS₂ surface hindered restacking of the MoS₂ monolayers, which was confirmed by the zeta potential test result (> -25 mV). When the DOPA-HCl aqueous solution was added, the positively charged ammonium groups ($-\text{NH}_3^+$) of DOPA was attracted and adsorbed onto the surfaces of the MoS₂ monolayers due to electrostatic interaction. This “neutralization” of surface charges destabilized the colloidal particles and caused flocculation of the suspension immediately, during which the DOPA monomers were sandwiched by MoS₂ monolayers and self-assembled into an intercalated intermediate (DOPA)_xMoS₂ (Figure 1c). It is noted that, the composition of the (DOPA)_xMoS₂ changed only slightly when varying the feed ratio of DOPA to MoS₂, implying the electrostatic attraction-induced self-assembly dominated in this process. When annealed, DOPA molecules were polymerized in the confined MoS₂ interlayer space and *in-situ* carbonized to NDG, while the MoS₂ preserved its monolayer morphology due to the separation by NDG, forming a novel NDG/MoS₂ nanocomposite with well-defined alternating structure.

Structural Verification. The extent of intercalation and carbonization could be monitored by the interlayer distance of MoS₂ derived from the position of its (002) XRD peak (Figure 2a). The XRD pattern of original MoS₂ matches well with hexagonal 2H-MoS₂ (JCPDS: 65-1951), which shows a strong diffraction peak at 14.4° with an interlayer distance of 0.62 nm. This distance increases slightly to 0.64 nm (13.9°) after the Li⁺ intercalation, accompanied by a phase transition from 2H to 1T MoS₂.⁴⁷ After the intercalation of DOPA, the (002) peak moves significantly to a lower angle (7.0°), indicating a further expansion of 0.65 nm along the *c*-axis and the formation of a new intercalated compound, (DOPA)_xMoS₂. The increased interlayer spacing is smaller than the length of a DOPA molecule (0.75-8.0 nm). It thus can be speculated

that with the -NH_3^+ group interacting with the MoS_2 monolayer, the benzenediol tail of DOPA may adopt a tilted arrangement to increase the structural stability of $(\text{DOPA})_x\text{MoS}_2$.⁴⁸⁻⁴⁹ It is reported that DOPA can self-polymerize under mild basic condition and this process usually takes hours.⁴⁰ Due to the existence of hydrolyzed LiOH , the pH of the exfoliated MoS_2 suspension is around 11.4, which may induce oxidative polymerization of DOPA. To confirm this, FTIR measurement was conducted and the spectra are shown in Figure 2b. The characteristic bands of DOPA can be found at $1603/1488\text{ cm}^{-1}$, 1270 cm^{-1} and 1192 cm^{-1} , corresponding to the in-plane skeletal vibration of aromatic ring, C-N and O-H stretching vibration, respectively. The small shoulder peak at 1717 cm^{-1} can be assigned to the stretching vibration of C=O derived from the oxidation of DOPA.⁴² The absence of indole structure indicates that DOPA polymerization did not take place.⁵⁰ Furthermore, no precipitation was found in the control experiment (Experimental Section). Therefore, DOPA exists in both original and oxidized forms between MoS_2 monolayers probably due to the anchoring of its -NH_3^+ groups and the very fast “neutralization” between DOPA and MoS_2 (within minutes). All the aforementioned FTIR bands almost could not be observed after annealing. Meanwhile, the (002) diffraction peak shifts to 8.9° , indicating that the expansion in *c*-axis direction shrinks to 0.37 nm (Figure 2a). This increment is close to the interlayer distance of graphite (0.34 nm), implying the *in situ* conversion of DOPA to NDG lying parallel to the MoS_2 monolayers.^{35, 50} In addition, after annealing, a high order (00*l*) peak is also observed at 17.6° with an interlayer distance of 0.50 nm, which is exactly half of the MoS_2 interlayer spacing. This can be attributed to the distance between NDG and MoS_2 monolayers and confirms the successful fabrication of the NDG/ MoS_2 heterostructure. The average thickness of the heterostructure is calculated to be $\sim 7.9\text{ nm}$ based on

the full width at half maximum (FWHM) of the (002) diffraction peak, corresponding to 8 pairs of alternately stacked MoS₂ and NDG.

The conversion from (DOPA)_xMoS₂ to the NDG/MoS₂ is further studied by Raman. As shown in Figure 2c, the (DOPA)_xMoS₂ shows two peaks at 378 and 401 cm⁻¹, corresponding to the in-plane (E_{2g}¹) and out of plane (A_{1g}) vibration of MoS₂. These two peaks are well retained after carbonization, indicating that the restacking of MoS₂ does not occur,⁵¹ while two characteristic peaks of carbon, the D and G bands, emerge at 1386 and 1576 cm⁻¹, respectively, with an intensity ratio of 0.9, indicating the defect-rich nature of NDG.

XPS analysis was conducted to probe the chemical states of Mo, N and C. As shown in Figure 2d, the C 1s spectrum can be deconvoluted into 3 components at 284.6, 285.3 and 286.2 eV, corresponding to the sp² C and sp³ C in C-O and C-N, respectively.⁵² The C-N configuration accounts for 21% of all carbon, indicating the N-rich nature of NDG. Figure 2e shows the Mo 3d region at high resolution. The peaks at 232.9 and 229.8 eV could be assigned to the 3d_{3/2} and 3d_{5/2} of Mo⁴⁺ in MoS₂, while the lower energy peak at 227.0 eV could be assigned to the 2s of S²⁻. No oxidation and reduction of Mo⁴⁺ is observed, indicating that the MoS₂ is stoichiometric. Due to the strong overlapping of Mo 2p_{3/2} and shielding effect of MoS₂, only weak N 1s signal is detected.⁵³ Three types of N, i.e., pyridinic, pyrrolic and graphitic N, are found at 397.1, 398.8 and 400.7 eV, respectively (Figure 2f). The XPS survey spectrum of the NDG/MoS₂ heterostructure and the detailed bonding information of S 2p are shown in Figure S1.

Figure S2 shows the composition of the NDG/MoS₂ nanocomposites determined by TGA. The contents of NDG and MoS₂ are 16 wt% and 84 wt%, respectively, assuming all the NDG is combusted in air while the MoS₂ is converted to MoO₃.

Morphology of the NDG/MoS₂ Heterostructure. The morphology of the NDG/MoS₂ nanocomposite was characterized by SEM and TEM. As shown in Figure 3a, the NDG/MoS₂ exhibits porous, distorted plate-like morphology. Each “plate” is comprised of numerous crumpled nanosheets with a thickness of less than 20 nm (Figure 3b). The morphology of NDG/MoS₂ is almost the same as that of (DOPA)_xMoS₂ (Figure S3), indicating a good reservation of the layered structure during annealing. The absence of charging (without coating) during electron microscopy indicates good electrical conductivity of the heterostructure. The TEM images of the NDG/MoS₂ are shown in Figure 3c-d and Figure S4. The NDG/MoS₂ nanosheets are randomly scrolled and entangled with each other, showing typical morphology of 2D nanomaterials. The corrugation increases the thermodynamic stability of the heterostructure and also allows the observation of the alternately stacked structure. Figure 3d shows a HRTEM image of a nanoflake with its basal plane in edge region parallel to the beam direction. It can be seen that dark and gray lines are alternately arranged at the edge of the nanoflake, which can be identified as MoS₂ and NDG, respectively, due to their difference in atomic number. This clearly verifies the well-defined alternating structure fabricated by this electrostatic attraction-induced self-assembly approach. The distance between adjacent MoS₂ monolayers is measured to be 0.98 nm, indicating the single-layered nature of MoS₂ with enlarged interlayer distance, consistent with the above XRD results. The NDG is almost parallel to the neighboring MoS₂, indicating that the formation of NDG is confined in the 2D inter-layer space of MoS₂ monolayers with the latter acting as the template, therefore replicating the shape of MoS₂. To further confirm the formation of NDG from DOPA in the annealing process, the morphology of the NDG is investigated by dissolving NDG/MoS₂ in aqua regia. The successful removal of MoS₂ is confirmed by EDX (Figure S5), which shows negligible S and Mo contents after the aqua regia

treatment. The morphology of the NDG is shown in Figure 3e-f. Though partially merged together due to the strong oxidation of aqua regia, the NDG still exhibits irregular sheet-like morphology with smooth surface, similar to that of graphene. Figure 3f shows a typical TEM image of a few partially overlapped flat NDG nanosheets with distinguishable edges, demonstrating their ultrathin nature.

Electrochemical Performances of the NDG/MoS₂ Heterostructure. The NDG/MoS₂ heterostructure was evaluated as an anode material for LIBs. Its lithiation/delithiation behaviors were firstly investigated via CV. As shown in Figure 4a, three reduction peaks are observed in the first cathodic scan. The peak at 1.0 V is indicative of the formation of Li_xMoS₂, which decomposes into Mo nanoparticles embedded Li₂S matrix when further discharged, giving a cathodic peak at about 0.55 V. The slope starting from 0.8 V could be assigned to the insertion of extra Li⁺ into the expanded interlayer space or the defects of MoS₂.^{16, 54} The formation of a solid electrolyte interphase (SEI) on the NDG is observed at 0.55 V, similar to that formed on reduced GO,⁵⁵⁻⁵⁶ indicating their structural similarity. The capacity below 0.5 V is mainly attributed to the binding of Li⁺ on the basal plane of the NDG nanosheets. During the anodic scanning, Li⁺ stored on the surfaces of NDG are first released, giving a broad peak at about 1.2 V. The weak peak at 1.7 V is attributed to the partial oxidation of Mo to MoS₂.³¹ The pronounced peak at 2.3 V is associated with the oxidation of Li₂S to sulfur. Therefore, majority of the MoS₂ is converted to sulfur and Mo after the first cycle. In the following scan, the newly emerged cathodic peak at 1.9 V is indicative of the lithiation of S to Li₂S, while the anodic peak at 2.3 V remains, indicating the Li₂S/S couple dominates the redox process.

Figure S6 shows the galvanostatic discharge/charge curves of the NDG/MoS₂ anode for the 1st, 2nd, 5th, 10th and 50th cycles. The evolution of the plateaus matches well with the CV plot, indicating the redox reaction between Li⁺ and S instead of MoS₂. The initial charge and discharge capacities are 750 and 1000 mAh/g, respectively, with a Coulombic efficiency of 75%, which is much higher than those of other reported MoS₂-based anodes with similar carbon content.^{33, 50} The capacity loss is mainly caused by the formation of SEI film and the irreversible conversion from MoS₂ to Mo/Li₂S. After the first cycle, the reversible (charge) capacity quickly increases to 1040 mAh/g with Coulombic efficiency of above 97%. This quick stabilization can be attributed to the ultrathin nature of the NDG/MoS₂ heterostructure, which shortens the electron and Li⁺ pathway and ensures complete lithiation/delithiation.

The pristine bulk MoS₂ exhibits rather poor cycling stability (Figure S7). The initial capacity is only 580 m Ah/g and the reversible capacity decreases quickly to 280 mAh/g after 50 cycles, with a capacity retention of only 48%. The lower conductivity and dissolution of polysulfide intermediates are believed to account for the lower activity and fast capacity decay, similar to that of the Li-S battery. Instead, excellent cycling stability is achieved for the NDG/MoS₂ anode, as shown in Figure 4c. A slightly increase in the reversible capacity is observed from the second cycle onward. This “activation” process is observed for all the samples tested and may be attributed to the cycling-induced penetration of electrolyte and expansion of defect sites and vacancies.^{16, 22, 50, 53} Clearly, the NDG/MoS₂ heterostructure can effectively alleviate the diffusion of soluble polysulfide, which could be ascribed to the physical protection and chemical adsorption functions of the NDG nanosheets. The MoS₂ monolayers are sandwiched between the neighboring NDG nanosheets. This face-to face intimate contact helps to confine the as-formed polysulfide within the framework. Moreover, doping of carbon with heteroatoms, nitrogen for

example, could improve its interactions with the sulfur-containing species at the electron-modified interface.⁵⁷⁻⁵⁸ Thus, the nitrogen atoms in NDG may immobilize the polysulfide anions and hinder their diffusion, leading to higher sulfur utilization and cycling stability.

The rate capabilities of the NDG/MoS₂ anode are shown in Figure 4c. The reversible capacities at 0.1, 0.2, 0.5 1.0, 2.0, and 5.0 A/g are 1050, 970, 810, 700, 630, and 460 mAh/g, respectively, demonstrating superior rate performance. The reversible capacity fully rebounds (830 mAh/g) when the current density is reset to 1 A/g, indicating the robustness of the van der Waals heterostructure. The NDG/MoS₂ anode shows excellent high rate stability and its reversible capacity is still above 820 mAh/g up till the 100th cycle at 1A/g. The electrochemical performance of the NDG/MoS₂ anode is superior to those of hierarchical structured carbon@MoS₂ nanospheres²⁸ and porous carbon nanofiber hosted MoS₂,²⁹ and comparable to that of core-shell structured MoS₂@carbon nanosheets with much higher MoS₂ content.³⁰

The superior rate and cycling performance is validated by the electrochemical impedance measurement, as shown in Figure 5a. The equivalent circuit model and fitted parameters are listed in Figure S8 and Table S1. In comparison with the pristine MoS₂, the diameter of the semicircle at high/medium frequencies is greatly reduced for the NDG/MoS₂ anode before cycling, indicating its significantly lowered charge-transfer resistance (R_{ct}) at the electrode-electrolyte interface. The Warburg impedance (Z_w), which is related to the solid-state diffusion resistance of Li⁺, is also dramatically decreased as indicated by the larger slope of the oblique line at low-frequency. Therefore, a much improved electrochemical performance is expected because of the enhanced electron and Li⁺ transport. A new semicircle appears at high frequency after cycling, which corresponds to the resistance (R_f) and constant phase element (CPE_2) of the

SEI film. The total resistance, however, is almost unchanged, indicating the excellent cycling stability of the NDG/MoS₂ heterostructure.

Clearly, the excellent electrochemical performance of the NDG/MoS₂ anode could be attributed to its unique structure and the synergistic effect between the two components, as illustrated in Figure 5b. Firstly, the *in-situ* formed NDG is intimately face-to-face in contact with the neighboring MoS₂ monolayers, which not only prevents the restacking of MoS₂, but also greatly enhances the electrical conductivity of the heterostructure. The NDG serves as excellent conductive channels and transfers electrons to the MoS₂ monolayers, resulting in fast lithiation/delithiation kinetics. Moreover, the abundant MoS₂-NDG interfaces provide additional active sites for Li⁺ storage, which contributes to the high reversible capacity. Secondly, the expanded interlayer spacing reduces the diffusion resistance of Li⁺ into the interspace, thus ensuring sufficient utilization of MoS₂ with improved dynamics. Meanwhile, the voids between the NDG and MoS₂ accommodate the local volume expansion/contraction during cycling and protect the heterostructure from pulverization, increasing the long-term cycling stability of the MoS₂-NDG heterostructure even under high current densities. Thirdly, the NDG exhibits dual functions in the alleviation of shuttle effect, thus overcoming the intrinsic capacity fading of the electrode. On one hand, the NDG nanosheets sandwich the MoS₂ monolayers and hence act as physical barriers to hinder the diffusion of the soluble “products” into the electrolyte. On the other hand, owing to the improved interactions between the nitrogen atoms and sulfur containing species, the NDG can help to anchor the polysulfide anions at electron-modified interfaces by chemical adsorption. The above factors endow the unique NDG/MoS₂ van der Waals heterostructure with good conductivity, fast Li⁺ diffusion, high sulfur utilization and structural

robustness, resulting in its excellent cycling stability and rate capacities as an advanced anode for LIBs.

CONCLUSIONS

In this work, for the first time we demonstrate a facile self-assembly approach for the synthesis of a novel NDG/MoS₂ van der Waals heterostructure. The *in-situ* formed NDG/MoS₂ nanosheets with an overall thickness of only ~8 nm are composed of alternately stacked NDG and MoS₂ monolayers. Thus, it is not only an excellent Li⁺ and electron conductor, but also a good host to immobilize the soluble polysulfide anions. When studied as a LIB anode, the NDG/MoS₂ shows excellent rate capabilities and cycling stability. The reversible capacity is above 820 mAh/g at 1 A/g after high-rate charge-discharge. Moreover, this self-assembly approach may also be adopted for synthesis of other NDG-intercalated 2D materials. The corresponding van der Waals heterostructures may exhibit a variety of unique properties arising from the synergistic effect between the two components.

Supporting Information

XPS spectrum of the NDG/MoS₂, TGA curves of the (DOPA)_xMoS₂ and NDG/MoS₂, SEM images of (DOPA)_xMoS₂, TEM images of NDG/MoS₂, EDX spectrum of the NDG, charge/discharge profiles of the NDG/MoS₂ anode, cycling stability of pristine MoS₂ anode at 50 mA/g, equivalent circuit models of the Nyquist plots and fitted impedance parameters.

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Figure 1. Schematic illustration of the fabrication process of NDG/MoS₂ van der Waals heterostructure: a) intercalation of MoS₂. b) exfoliation of Li_xMoS₂ and c) self-assembly of (DOPA)_xMoS₂ followed by annealing.

Figure 2. a) XRD patterns and schematics of pristine MoS₂, Li_xMoS₂, (DOPA)_xMoS₂ and NDG/MoS₂. b) FTIR and c) Roman spectra of the (DOPA)_xMoS₂ and NDG/MoS₂. XPS d) C 1s, e) Mo 3d and f) N 1S spectra of the NDG/MoS₂.

Figure 3. a-b) SEM and c-d) TEM images of the NDG/MoS₂ heterostructure. e) SEM and f) TEM images of the NDG after the removal of MoS₂ in aqua regia.

Figure 4. Electrochemical properties of the NDG/MoS₂ anode: a) CV curve, b) cycling stability at 0.1 A/g and c) rate capabilities and high rate stability at various current densities. The capacities are calculated based on the mass of NDG/MoS₂.

Figure 5. a) Nyquist plots of the pristine MoS₂ and NDG/MoS₂ anode before and after cycling. b) An illustration of the synergistic effect between the two components in the NDG/MoS₂ van der Waals heterostructure.

Self-Assembly-Induced Alternately Stacked Single-Layer MoS₂ and N-doped Graphene: a Novel van der Waals Heterostructure for Lithium-Ion Batteries

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