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Three-Dimensionally Reinforced Freestanding Cathode for High-**Energy Room-Temperature Sodium–Sulfur Batteries**

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Supporting Information

ABSTRACT: Room-temperature sodium-sulfur (RT Na-S) battery cathodes suffer from poor conductivity, rapid dissolution of intermediate products, and potentially destructive volume change during cycling. The optimal way to minimize these problems could be a construction of a nanocomposite cathode scaffold combining different components selected for their particular functions. Here, we have combined the excellent electronic conductivity of reduced graphene oxide, polysulfide adsorption ability of the ultrafine manganese oxide nanocrystals, rapid ion/electron dissemination efficiency of nanosized sulfur, and outstanding mechanical stiffness and good electrical conductivity of Na alginate/polyaniline hybrid binder in a single electrode heterostructure. At 0.2 A g⁻¹, an RT Na-S battery containing the freestanding cathode delivers an initial specific cap acity of 631 mA h g⁻¹. By delivering a nominal discharge voltage of 1.81 V,



our Na-S batteries bestow a high specific energy of 737 W h kg⁻¹ at the 2nd cycle and 660 W h kg⁻¹ was retained after 50 cycles. The effect of the amount of electrolyte additive is also well demonstrated in this study. The electrode fabrication process provides a new approach to tailor the design and preparation of effective cathodes for the room-temperature sodium-sulfur batteries.

KEYWORDS: freestanding cathode, sodium-sulfur batteries, manganese oxide, sodium alginate, polyaniline, X-ray photoelectron spectroscopy, solid-state ⁵⁵Mn NMR spectroscopy

INTRODUCTION

Due to high-cost maintenance, the large-scale use of high temperature sodium-sulfur batteries for electric energy storage is prohibitively expensive at present. In comparison, because of their lower-cost maintenance, lightweight, and portability, Room-temperature sodium-sulfur (RT Na-S) batteries are attractive. However, problems with the sulfur cathode, including intermediate polysulfide dissolution and shuttling, low electronic conductivity, and dramatic volume change of sulfur during reversible insertion/extraction of bigger Na⁺ cation, can deteriorate the performance and reliability of the RT Na-S batteries as they conk out after a few cycles. Nevertheless, for practical applications such as submersibles, aerial drones, power packs, etc. where lightweight and low cost are more important than longevity, the RT Na-S batteries with high energy are most sought after. Numerous cathode preparation strategies have been employed to increase the energy density of RT Na-S batteries; physical infiltration of sulfur into porous conductive hosts is one successful approach.^{1–13} Sulfur composite with conductive polyacrylonitrile (PAN) has also significantly improved the performance of

RT Na-S batteries.¹⁴⁻¹⁶ Inverse vulcanization is another effective strategy, in which a sulfur-rich copolymer is prepared and used as an alternative cathode material.^{17,18} However, unfortunately, none of these classes of cathode composites possesses sufficient elasticity to resist the severe stress induced in the electrode during repeated Na^+ insertion/extraction processes. Therefore, although all of these approaches could successfully mitigate the conductivity and dissolution problems, the huge volume change of sulfur during conversion, which has been identified as one of the challenging obstacles for the Na-S batteries, still persists. Designing a single cathode scaffold that overcomes all of the aforementioned problems would improve the long-term cycling performance of RT Na-S batteries. This type of cathode may be developed through preparation of a hybrid composite, incorporating different constituent materials with specific functionalities.

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Here, we perceive this approach by preparing and illustrating a unique hybrid cathode scaffold for RT Na-S batteries made of reduced graphene oxide, sulfur nanoparticles, a mixedvalence manganese oxide (Mn_rO_v) , and a hybrid Na alginate/ polyaniline conductive, adhesive matrix. Sulfur nanoparticles could shorten the diffusion path for both Na⁺ and electron and thus facilitate the conversion reaction at room temperature. Reduced graphene oxide provides excellent electronic conductivity and physically confines the active sulfur particles. Different classes of polar compounds including metal oxides, metal sulfides, etc. have been well demonstrated to be excellent polysulfide immobilizers in lithium-sulfur batteries.¹⁹⁻²³ The stability of metal oxide in the electrolyte after binding to polysulfides should be considered while selecting an effective metal oxide for high-performance sulfur-based cathodes. Considering this fact, we have chosen the mixed-valence manganese oxide as a polysulfide immobilizer in this study, based on the fact that Guo et al. demonstrated that in comparison to MnO2 mixed-valence manganese oxide (i.e., Mn₃O₄) is more stable in a liquid-phase polysulfide environment in Li-S batteries, resulting in long-term suppression of the polysulfide shuttle.²³ Traditionally, in both lithium-sulfur and sodium-sulfur batteries, several works were devoted to the synthesis and engineering of the porous carbonaceous materials to suppress polysulfide dissolution and unfortunately less attention was paid to the use of appropriate binders. Binders always play a crucial role to enhance the performance of conversion-based electrode materials. It is therefore strongly believed that the consideration of a suitable binder could promote the performance of electrode materials, suffering from substantial volume changes during cycling. Considering the inherent mechanical stiffness with appropriate swelling property of the polysaccharides,²⁴ in this work, sodium alginate is incorporated as a binder to ensure electrode integrity during insertion and extraction of Na⁺ ions. Moreover, to obtain an excellent electronically conductive network along with required mechanical reinforcement throughout the electrode, polyaniline was doped into the sodium alginate binder to coalesce a hybrid conducting Na alginate/polyaniline matrix. The resulting Na alginate/polyaniline hybrid matrix could serve as an electronically/ionically conductive network throughout the cathode to improve the overall conductivity. A threedimensionally reinforced freestanding cathode with an average sulfur loading of 2.05 mg cm⁻² was prepared through vacuum filtration and later vacuum drying of the final composite. Delivering a nominal discharge voltage of 1.81 V, our Na-S batteries bestow a high specific energy of 737 W h kg⁻¹ (based on the active mass of sulfur and sodium) at the second cycle. A specific energy of 660 W h kg⁻¹ was retained after 50 cycles.

EXPERIMENTAL SECTION

Synthesis. Reduced graphene oxide (rGO) was prepared through hydrazine reduction of graphene oxide (GO).²⁵ Graphene oxide synthesized through Hummer's route was dispersed in 500 mL of deionized water by ultrasonication. The GO suspension was then maintained a pH of 10 by addition of KOH, and 5 mL of hydrazine hydrate was then added to the suspension. The suspension was refluxed for 24 h. The resulting rGO was collected by vacuum filtration followed by repeated wash with deionized water and drying at 80 °C for 48 h. Mixed-valence manganese oxide (Mn_xO_y) nanoparticles were prepared following the previously reported chemical precipitation approach with slight modifications.²⁶ First, 10 mmol (1.98 g) of $MnCl_2$ ·4H₂O was dissolved in 100 mL of aqueous NaOH solution containing 20 mmol (0.8 g) NaOH. To this

solution, 20 mg of cetyl trimethyl ammonium bromide was added under stirring. A brown-colored precipitate was obtained after 24 h and collected after repeated washing with deionized water. The precipitate was calcined at 550 °C for 2 h at a ramping rate of 5 °C min⁻¹. After successful synthesis of the rGO and Mn_vO_v nanoparticles, 50 mg of rGO and 20 mg of Mn_xO_y nanoparticles were well dispersed in 200 mL of deionized water. A solution of the ethylene diamine-sulfur complex (prepared by adding 400 mg of sublimed sulfur to 50 mL of ethylene diamine) was added slowly to the above dispersion of rGO and Mn_xO_y. After incorporation of the ethylenediamine-sulfur solution, whole dispersion was stirred for 12 h to get the uniform deposition of sulfur nanoparticles. The ternary composite (designated as rGO/S/Mn_xO_y) was collected by centrifugation and then vacuum dried. The rGO/S/Mn_xO_y composite was given a heat treatment at 150 °C in Ar for 2 h to obtain good physical contact among sulfur, rGO, and Mn_xO_y . Furthermore, to create an interparticle adhesion and improve overall ionic and electronic conductivity of the cathode, the rGO/S/Mn_xO_y composite was well mixed with the Na alginate/polyaniline hybrid matrix. In this process, the as-prepared rGO/S/Mn_xO_y composite was first well dispersed in deionized water, followed by the addition of 50 mg of sodium alginate and 50 μ L of aniline. The temperature of the resulting solution was maintained at 5 °C. While stirring, a precooled ammonium persulfate aqueous solution was mixed dropwise to the above solution and the final composite dispersion was stirred overnight at 5 °C. A freestanding cathode was constructed through vacuum filtration using AAO membrane, followed by drying at 60 °C in vacuum. The as-obtained freestanding cathode is designated as rGO/S/Mn_xO_y@ SA-PANI. For a control experiment, the rGO/S/Mn_xO_y composite with the PVdF binder was taken as an active material. The control cathode was fabricated by coating the suspension on aluminum foil. The control cathode is designated as rGO/S/Mn_xO_v@PVdF.

Material Characterization. X-ray diffraction (XRD) measurements were carried out on a Philips X'-pert diffractometer equipped with Cu K α radiation ($\lambda = 1.5418$ Å). The morphologies of the asprepared samples were examined with a field emission gun scanning electron microscope (FEG-SEM; JEOL-7600F) and a field emission gun transmission electron microscope (FEG-TEM, JEOL-2100F). Fourier transform infrared (FTIR) spectra were recorded on a Thermo Scientific FTIR analyzer (NICOLET 8700). Raman spectra were obtained using a micro-Raman spectrometer (Renishaw inVia, U.K.). The X-ray photoelectron spectroscopy (XPS) spectra were observed using an X-ray photoelectron spectrometer (Kratos Analytical, AXIS Supra). A thermogravimetric analyzer (TA-DTG Q600) was used to record thermal degradation responses of the samples at a ramping rate of 3 °C min⁻¹. The mechanical flexibility of the freestanding cathode was tested using a Nanoindenter instrument (TI-900, Hysitron). Six indentations were performed with 100 μ N load.

Electrochemical Measurements. The rGO/S/Mn_xO_y@SA-PANI freestanding electrode was used as a cathode for RT Na-S batteries. For the rGO/S/Mn_xO_y@PVdF composite, the cathode was fabricated following the slurry coating technique using 90 wt % rGO/ S/Mn_xO_y composite and 10 wt % PVdF binder. After, the cathodes containing 2.05 mg cm⁻² of sulfur were then coupled with sodium metal anode in an Ar-filled glovebox (Mbraun) to assemble the batteries. Celgard 2400 membrane soaked with 40 μ L of electrolyte prepared from 1 M sodium perchlorate (NaClO₄) with 0.1 M sodium nitrate (NaNO₃) additive in tetraethylene glycol dimethyl ether (TEGDME) was incorporated as the separator. The cyclic voltammetry (CV) response was recorded at 20 μ V s⁻¹ between 1.2 and 2.8 V (vs Na⁺/Na). Charge-discharge cycling performance of the RT Na-S batteries was recorded within 1.2-2.8 V at the various current rates. Impedance spectra were recorded from 0.1 Hz to 1 MHz using $\Delta V = 5$ mV. Performances of all cells were carried out at 20 °C. Specific capacity of the cathodes was estimated based on the weight percentage of sulfur present in the cathode.

 XPS^{-} and S^{-} Mn NMR Characterizations of Polysulfide-Adsorbed Mn_xO_y Sample. To examine the interaction between Mn_xO_y and intermediate compounds, solid-state S^{-} Mn NMR and XPS



Figure 1. Schematic illustration of freestanding cathode synthesis and the role of the binder. (a) Schematic illustration of the freestanding cathode preparation. (b) Schematic of the proposed role of the polysaccharide binder to counteract volume expansion of sulfur during sodium-ion insertion.

studies were conducted on a Mn_xO_y sample that had adsorbed sodium polysulfides. First, a Na_2S_6 solution was synthesized by mixing a stoichiometric ratio of elemental sulfur (S_8) and Na_2S . The deep brown color of Na_2S_6 solution turned completely colorless after Mn_xO_y was added into it. To record the ⁵⁵Mn NMR spectrum, pristine Mn_xO_y and polysulfide-adsorbed Mn_xO_y were then individually packed into 7 mm outer diameter zirconia MAS rotors. These steps were completed in an Ar-filled glovebox (Mbraun). The ⁵⁵Mn NMR spectra were recorded on a 300 MHz NMR spectrometer (VARIAN, Mercury Plus) at 3.5 kHz spinning frequency using KMnO₄ as a reference. For XPS study, pristine Mn_xO_y and polysulfide-adsorbed Mn_xO_y were pelletized individually under an inert atmosphere. The required Mn 2p and S 2p XPS spectra were recorded on an X-ray photoelectron spectrometer (Kratos Analytical, AXIS Supra).

RESULTS AND DISCUSSION

It is well understood that a three-dimensional porous electrode structure might improve the access of liquid electrolyte to the active material and thus facilitate the ion-diffusion process. To construct such a porous electrode architecture, we grab a facile bottom-up approach, illustrated in Figure 1a. In this approach, a ternary composite made of rGO, sulfur, and Mn_xO_y was first synthesized and then incorporated within a Na alginate/ polyaniline hybrid matrix. Figure 1b represents the schematic of the possible role of sodium alginate, a representative high-modulus polysaccharide binder, to counteract the severe

volume fluctuation of sulfur during Na^+ insertion and extraction cycles.

The as-synthesized reduced graphene oxide and manganese oxide were thoroughly characterized prior to preparation of their composite. The XRD pattern of rGO exhibits characteristic peaks at 23.86 and 42.88° (Figure S1). The two Raman peaks at 1342 cm⁻¹ (D band) and 1580 cm⁻¹ (G band) and their relatively high intensity ratio ($I_{\rm D}/I_{\rm G}$ = 1.51) further confirm the successful reduction of GO (Figure S2). The electrical conductivity of as-synthesized rGO is estimated to be 4.8×10^3 S m⁻¹, which might be sufficient to enhance the overall conductivity of the cathode and thus increase the extent of active material conversion. The formation of manganese oxide containing multivalent cations was confirmed through Xray diffraction and X-ray photoelectron spectroscopy. The XRD pattern of manganese oxide (Figure S3) consists of standard diffraction peaks of different manganese oxides, including Mn₃O₄ (JCPDS 24-0734) and MnO₂ (JCPDS 39-0375), confirming the presence of different valence states of manganese in Mn_xO_y . The Mn 2p XPS spectrum of Mn_xO_y consists of two characteristic peaks centered at 641.2 and 652.8 eV, respectively, corresponding to Mn $2p_{3/2}$ and Mn $2p_{1/2}$ components (Figure S4). The deconvoluted Mn 2p_{3/2} peak exhibits two major peak components at 640.6 and 642.5 eV and a weak peak component at 641.65 eV. The major peaks at 640.3 and 642.5 eV are attributed to Mn²⁺ and Mn⁴⁺ oxidation



Figure 2. Morphological characteristics of materials. (a) SEM image of reduced graphene oxide. (b) SEM image of sulfur nanoparticles. (c) SEM image of Mn_xO_y nanoparticles. (d, e) SEM images of the rGO/S/Mn_xO_y@SA-PANI cathode at low and high magnifications, respectively. (f) TEM image of reduced graphene oxide (the inset shows the SAED pattern). TEM images of (g) sulfur nanoparticles, (h) Mn_xO_y nanoparticles, and (i) rGO/S/Mn_xO_y@SA-PANI cathode. (j-m) Scanning TEM image and distribution mapping of different elements in the rGO/S/Mn_xO_y@SA-PANI cathode.

states. The weak peak at 641.5 eV, related to Mn³⁺ oxidation state, might be due to the presence of small amount of Mn_2O_3 . The as-prepared rGO/S/Mn_xO_y@SA-PANI composite cathode was characterized by the XRD technique, and the diffraction pattern was compared to the diffraction patterns of individual samples (Figure S5a). From Figure S5a, it is interesting to observe that the final composite rGO/S/ Mn_xO_v@SA-PANI exhibits an XRD pattern that is very similar to that of the SA-PANI matrix;^{27,28} no diffraction peaks were detected for rGO, sulfur, or Mn_xO_y. This suggests that the rGO/S/Mn_xO_y ternary composite was well encapsulated by the hybrid SA-PANI matrix.²⁹ The rGO/S/Mn_xO_y@ SA-PANI composite was further analyzed by the FTIR characterization technique, and the spectrum is represented in Figure S5b. The peaks observed at 458, 502, and 630 cm⁻¹ could be due to the Mn-O bond in manganese oxide. The intense peak at 1120 cm⁻¹ is ascribed to the stretching vibration of -N = quinoid = N- moiety.³⁰ The peak observed at 1300 cm⁻¹ is due to the vibration of the C-N bond, whereas the peaks observed at 1476 and 1568 cm⁻¹ are due to the C-C bond in quinoid and benzenoid rings, respectively. Peaks appeared at 2930 and 3440 cm⁻¹ could be attributed to the O-H group in sodium alginate and N-H group in polyaniline, respectively.³¹ To determine the areal loading of sulfur, thermogravimetric analysis of the rGO/S/Mn_xO_v@SA-PANI composite was carried out. The detected weight loss of 60.7% at around 450 °C could be inferred to thermal evaporation of sulfur, as well as thermal degradation of sodium alginate and polyaniline (Figure S5c). Considering the thermal

degradation behavior of each pure component, the calculation reveals the presence of 56.1 wt % sulfur in the rGO/S/ $Mn_xO_y@SA-PANI$ freestanding cathode. The nanoindentation technique was used to investigate the mechanical properties of the as-obtained freestanding electrode. The thickness of the as-obtained freestanding cathode was 35 μ m. The nanoindentation experiment was performed with 100 μ N load. A total of six indentations were recorded at six different positions far apart from each other. The reduced Young's modulus of the freestanding cathode was estimated to be 1.15 (±0.16) GPa, which indicates a better mechanical reinforcement. This indicates that the freestanding rGO/S/Mn_xO_y@ SA-PANI composite films are suitable to directly serve as self-supporting electrodes in Na-S batteries.

The microstructures and morphologies of the individual constituent materials and their final composite were characterized through scanning electron microscopy and transmission electron microscopy, as shown in Figure 2. The SEM image reveals that rGO owned a highly exfoliated wrinkled structure after hydrazine reduction of GO (Figure 2a). Figure 2b represents the microstructure of sulfur nanoparticles with an average size of 30-50 nm. The Mn_xO_y nanoparticles owned cubic morphology with a homogeneous particle size of 10-15 nm (Figure 2c). From SEM images of the freestanding cathode, it can be noticed that different components were well encapsulated and 3D interconnected to each other by the Na alginate/polyaniline (SA–PANI) hybrid nanofibers (Figures 2d,e and S6). To gain more insight into the microstructures, the samples were further analyzed through transmission



Figure 3. Cell performance of RT Na–S batteries. (a) Cyclic voltammetry curves of the rGO/S/Mn_xO_y@SA–PANI cathode at a scan rate of 20 μ V s⁻¹. (b) Charge–discharge profiles of the rGO/S/Mn_xO_y@SA–PANI cathode at 0.2 A g⁻¹. (c) Comparison between cycling performances of the rGO/S/Mn_xO_y@PVdF and rGO/S/Mn_xO_y@ SA–PANI cathodes at 0.2 A g⁻¹ in an electrolyte comprising 1 M NaClO₄ and 0.1 M NaNO₃ in TEGDME. (d) Charge–discharge profiles of the rGO/S/Mn_xO_y@SA–PANI cathode at different current rates. (e) Comparison between rate performances of the rGO/S/Mn_xO_y@PVdF and the rGO/S/Mn_xO_y@SA–PANI electrodes at different currents. (f) Cycling performance of the rGO/S/Mn_xO_y@SA–PANI cathode at 0.5 A g⁻¹ using two different electrolytes containing different amounts of the NaNO₃ additive. SEM images of (g) fresh sodium metal surface before cycling, (h) after 200 cycles using an electrolyte containing 0.1 M NaNO₃ additive, and (i) after 200 cycles using an electrolyte containing 0.2 M NaNO₃ additive.

electron microscopy. The TEM image of rGO reveals its crumpled sheetlike structure (Figure 2f), whereas the selected area diffraction pattern of rGO (Figure 2f, inset) shows strong diffraction points, which are characteristic of successfully reduced graphene oxide. The TEM images of sulfur and Mn_xO_y nanoparticles are shown in Figure 2g,h, respectively. Figure 2i displays the TEM image of the freestanding cathode, which confirms that sulfur and Mn_xO_y were embedded on the surface of rGO and hybrid SA-PANI matrix. The highresolution TEM image shows the interface between the components, suggesting the close attachment of sulfur and Mn_rO_v nanoparticles to the surface of the rGO sheets (Figure S7). The distribution of constituent materials in the cathode was visualized by scanning transmission electron microscopy (abbreviated as STEM). The STEM images of the selected area show that the constituent elements of various components were uniformly dispersed within a single particle, without aggregation or noticeable gradients in distribution (Figure 2jm).

The as-obtained rGO/S/Mn_xO_y@SA–PANI freestanding film was used as an electrode against sodium to evaluate its electrochemical behavior in Na–S batteries. Figure 3a shows the cyclic voltammetry curves of the cathode within 1.2–2.8 V vs Na⁺/Na, at the scanning potential rate of 20 μ V s⁻¹. During cathodic scan, the Na–S battery exhibited first cathodic peak at 2.28 V, corresponding to the conversion of solid-phase sulfur (S₈) to liquid-phase (electrolyte-soluble), long-chain Na polysulfides (Na₂S_n; 6 ≤ n ≤ 8), whereas the following weak peak located at 1.92 V could be attributed to further reduction of long-chain Na polysulfides (Na₂S_n; $6 \le n \le 8$) to middleorder sodium polysulfides (Na₂S_n; $3 \le n \le 4$).³² The last cathodic peak at 1.62 V is related to conversion from liquidphase, middle-order Na polysulfides (Na₂S_n; $3 \le n \le 4$) to insoluble short-chain Na polysulfides (Na₂S_n; $1 \le n \le 2$). During the subsequent anodic scan, the Na-S battery exhibited two prominent peaks at 1.85 and 2.37 V, respectively. The first oxidation peak at 1.85 V corresponds to oxidation of the short-chain Na polysulfides (Na₂S_n; $1 \le n \le 3$) to the longchain Na polysulfides (Na₂S_n; $4 \le n \le 8$), whereas the second anodic represents the further oxidation of the long-chain Na polysulfides (Na₂S_n; $4 \le n \le 8$) to elemental sulfur (S₈). The identical positions of the peaks and the almost identical area under the CV curves indicate an excellent Na⁺-ion storage reversibility of the rGO/S/Mn_xO_y@SA-PANI cathode in Na-S batteries. Figure 3b shows charge-discharge curves of the rGO/S/Mn_xO_v@SA-PANI freestanding cathode for first, second, and fifth cycles at 0.2 A g^{-1} . The discharge curves exhibit three reaction plateaus at 2.28, 1.92, and 1.62 V, which agree well with the three cathodic peaks observed during reduction of sulfur to short-chain sodium polysulfides. Figure 3c shows a comparison between the cyclic performance of the rGO/S/Mn_xO_v@SA-PANI and rGO/S/Mn_xO_v@PVdF cathodes at 0.2 A g⁻¹. An irreversible capacity contribution was observed for both the cathodes during initial discharge of the cells. The irreversible capacity contribution during the first discharge process arises from the decomposition of NaNO3 additive to generate a protective layer called solid-electrolyte interface (SEI) on the metal anode surface. The rGO/S/

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Mn_rO_v@PVdF cathode showed a reversible sodium storage capacity of 562 mA h g^{-1} at 2nd cycle and 385 mA h g^{-1} (i.e., 68.5% of the specific capacity obtained at 2nd cycle) after 50 cycles. In comparison, the rGO/S/Mn_xO_y@SA-PANI freestanding cathode showed a reversible Na⁺ storage capacity of 631 mA h g⁻¹ at 2nd cycle and retained a significantly high specific capacity of 535 mA h g^{-1} (i.e., 84.8% retention of capacity) after 50 cycles, suggesting an improvement in capacity retention. As described in the Supporting Information and Figure S8, by delivering a nominal discharge voltage of 1.81 V, our Na-S batteries bestow a high specific energy of 737 W h kg⁻¹ at second cycle and 660 W h kg⁻¹ was retained after 50 cycles. Table S1 shows that our Na-S batteries containing a prerequisite amount of the active material (sulfur loading = 2.05 mg cm^{-2}) delivered an as much as high specific energy of 688 W h kg⁻¹ after 20 cycles. The substantially improved electrochemical performance of the rGO/S/ Mn_vO_v@SA-PANI cathode can be attributed to the Na alginate/polyaniline (SA-PANI) hybrid binder, which enhanced the conductivity, as well as improved the mechanical stability of the electrode. PVdF, on the other side, has no inherent electronic conductivity and possesses low mechanical stiffness, leading to comparatively poor electrochemical performance for the rGO/S/Mn_xO_y@PVdF cathode. The charge-discharge curves of the rGO/S/Mn_vO_v@SA-PANI cathode at different currents are shown in Figure 3d. An obvious decrease in specific capacities was observed with raising the current from 0.05 to 0.5 A g^{-1} . Figure 3e compares the rate performance of the rGO/S/Mn_xO_y@SA-PANI and rGO/S/Mn_xO_v@PVdF cathodes. The rGO/S/Mn_xO_v@SA-PANI cathode exhibited average reversible specific capacities of approximately 885, 780, 610, and 425 mA h g^{-1} at the corresponding currents of 0.05, 0.1, 0.2, and 0.5 A g⁻¹. After 20 cycles, when the current rate was switched from 0.5 to 0.05 A g^{-1} , the rGO/S/Mn_xO_y@SA–PANI cathode became enable to recover ~85% of its average initial capacity. The rate performance of the rGO/S/MnxOv@SA-PANI cathode was found to be better than that of the rGO/S/Mn_xO_y@PVdF cathode. The outstanding electrochemical performance of the rGO/S/Mn_xO_v@SA-PANI freestanding cathode in terms of high specific capacity and energy density might be attributed to its three-dimensionally interlinked, mixed ionic/electronic conductive nanoarchitecture, which could create better percolation network for electrons and ions. On the contrary, due to poor conductivity of the PVdF binder, both electron and ion percolation in rGO/S/Mn_xO_y@PVdF might get impeded, causing lower specific capacity. However, to visualize the microstructural change of the rGO/S/Mn_xO_v@SA-PANI freestanding cathode at different states of charge during charge-discharge, ex situ SEM images were captured on the electrode material, stopping the Na-S cells at different potentials. For this purpose, we have used Swagelok-type cells, as they can be dismantled without any disturbance to the electrodes of our interest. The ex situ SEM images taken on the electrode materials at different states of charge are collectively shown in Figure S9. From Figure S9, it can be observed that during the progress of the discharge process, sulfur is continuously reduced to form a mixed phase of higherand middle-order polysulfides at 2.1 V. At the deep discharged state (i.e., at 1.2 V), a uniform dense phase of insoluble lowerorder polysulfides can be noticed. This observation suggests that the freestanding cathode effectively allowed complete reduction of sulfur and facilitated the uniform deposition of

insoluble lower-order polysulfides on the electrode surface. The uniform deposition of lower-order polysulfides on the electrode surface is essential to be reutilized during the redox reaction. However, on subsequent charge process, the dense phase of lower-order polysulfides was found to be gradually disappeared, although at 2.0 V (during the charge process) small amount of reduced product aggregation still can be observed. At the fully charged state (i.e., at 2.8 V), the freestanding cathode was able to restore the three-dimensionally interconnected structure. These observations indicate the superiority of our freestanding cathode in terms of reversible Na⁺-ion storage capability without any major disturbance to the microstructure.

To further investigate the robustness of the rGO/S/ Mn_xO_y@SA-PANI freestanding cathode, a long-term cycling response was recorded at 0.5 A g^{-1} current rate. At 0.5 A g^{-1} current rate, the freestanding cathode showed a reversible capacity of 424 mA h g^{-1} at 2nd cycle and 270 mA h g^{-1} (i.e., 64% capacity retention) after 200 cycles, with a gradual capacity loss (Figure 3f). To investigate the reason of gradual capacity decay during long-term cycling, the morphology of cycled sodium anode was investigated through a scanning electron microscope. In comparison to the surface of sodium metal before cycling, the cycled sodium anode exhibited a severely rough surface (Figure 3g,h). During cycling of roomtemperature Na-S batteries, the NaNO₃ additive decomposes to form a solid-electrolyte interface (SEI) on the anode surface, which prevents the parasitic reaction between dissolved polysulfides and metallic sodium. The observed rough surface of cycled sodium anode could be attributed to the fact that the electrolyte containing 0.1 M of NaNO3 additive was insufficient to form a long-lasting SEI on the anode surface. Thus, the poor passivation of the anode was unable to protect the highly reactive sodium metal surface for a longer time, causing gradual capacity decay. In Li-S batteries, it has been demonstrated that during progressive consumption of LiNO₃ on the Li anode, it is more effective to adopt sufficient amount of LiNO3 (SEI-forming agent) in the electrolyte.³³ Similarly, in this work, a remarkable enhancement in the cycling stability was observed in the electrolyte containing a comparatively higher amount (i.e., 0.2 M) of $NaNO_3$. Using the suitable amount of $NaNO_3$ in the electrolyte, the freestanding cathode delivered a reversible specific capacity of 436 mA h g⁻¹ at 2nd cycle and 345 mA h g^{-1} after 200 cycles, with an improved capacity retention of 79%. The improved capacity retention characteristic was maintained till 400 cycles (Figure 3f). The surface of the sodium metal anode after 200 charge-discharge cycles of the Na-S cell with the electrolyte containing 0.2 M NaNO₃ was investigated and found to be comparatively smooth (Figure 3i). This indicates that 0.2 M NaNO₃ might formed a stable SEI and hence the chemical reaction between sodium metal and soluble polysulfides was suppressed. The extent of chemical reaction between the sodium anode and soluble higher-order sodium polysulfides to form insoluble and resistive lower-order sodium polysulfides was investigated by measuring the impedance of the cells after cycling (Figure S10). The Na-S cell with the electrolyte containing 0.2 M NaNO₃ experienced a lower charge-transfer resistance after 200 cycles, which could probably be accounted due to the formation of a stable SEI layer on the anode surface, minimizing irreversible deposition of insulating phase of lower-order sodium polysulfides.



Figure 4. Demonstration of polysulfide adsorption ability of Mn_xO_y and its mechanism. (a) Solid-state ⁵⁵Mn NMR spectra of Mn_xO_y at different states. (b) S 2p XPS spectrum of Mn_xO_y after Na_2S_6 adsorption. (c) Mn 2p XPS spectra of Mn_xO_y before and after adsorption of Na_2S_6 . (d) Schematic of the possible surface redox reaction between Na_2S_6 and Mn_xO_y , where Mn_xO_y is reduced after interaction with Na_2S_6 and simultaneously Na_2S_6 gets oxidized to a polythionate complex; the inset shows camera images of Na_2S_6 solution without Mn_xO_y (left bottle) and with Mn_xO_y (right bottle).

To investigate the interactions between sodium polysulfides and Mn_xO_y solid-state ⁵⁵Mn NMR and XPS experiments were conducted on pristine Mn_xO_y and polysulfide-adsorbed Mn_xO_y . Figure 4a collectively shows and compares the ⁵⁵Mn spectra. The pristine Mn_xO_y exhibited two ⁵⁵Mn peaks at -740.1 and -780.2 ppm, which indicate the presence of mixed-valence metal cations. The peak at -740.1 ppm corresponds to Mn^{4+} in MnO_2 , whereas the peak at -780.2ppm could be ascribed to the Mn²⁺ oxidation state. The ⁵⁵Mn NMR spectrum of the Na_2S_6 -adsorbed Mn_xO_v sample exhibited three peaks at -740.4, -766.2, and -780.3 ppm. The slight downfield shifts of two original peaks, from -740.1to -740.4 ppm and from -780.2 to -780.3 ppm, upon exposure to Na₂S₆ solution, indicate a weak dipole-dipole interaction between two polar materials, Mn_xO_y and Na₂S₆. However, the new peak at -766.2 ppm suggests an intermediate oxidation state of manganese (Mn^{n+} ; 2 < n < 4), which could be the consequence of a redox reaction between Mn_xO_y and Na₂S₆. However, to examine the origin of the intermediate oxidation state of Mn in Mn_xO_y after adsorption of Na2S6, XPS analysis was carried out. Figure 4b describes the S 2p_{3/2} XPS spectrum of a polysulfide-adsorbed

 Mn_xO_y sample. The peaks at different binding energies in this spectrum suggest the presence of nonidentical sulfur atoms. The S $2p_{3/2}$ peak at 167.9 eV could be assigned to the central sulfur (i.e., S=O) of thiosulfate $(S_2O_3^2)$ group, which could arise from oxidation of Na2S6 by MnxOy. The oxidation of Na₂S₆ to thiosulfate is associated with a decrease in manganese oxidation state from Mn⁴⁺ to an intermediate oxidation state (i.e., Mn^{n+} , 2 < n < 4), as evident from the appearance of new peak in the ⁵⁵Mn NMR spectrum. To identify this distinct intermediate oxidation state of manganese, Mn 2p XPS characterization was further carried out for Mn_xO_y, before and after adsorption of Na₂S₆. Due to spin-orbit coupling, the high-resolution Mn 2p XPS exhibited a doublet consisting of two energy states Mn $2p_{3/2}$ and Mn $2p_{1/2}$ with different binding energies at 641.2 and 652.8 eV, respectively (Figure 4c). After deconvolution, the Mn $2p_{3/2}$ peak shows two major components at 640.6 and 642.5 eV, attributable to Mn²⁺ and Mn^{4+} oxidation states, respectively, in the Mn_xO_y nanomatrix. The weak peak component appearing at 641.5 eV could be ascribed to the Mn³⁺ oxidation state, owing to the presence of a minute amount of MnOOH on the surface of Mn_xO_y nanoparticles.³⁴ The calculation of relative area under the

corresponding peaks reveals that after adsorption of Na_2S_6 the relative abundance of Mn^{3+} in Mn_xO_y was found to be enhanced significantly from 7.3% (before adsorption of polysulfide) to 34.7%, whereas the relative abundance of Mn^{4+} decreased from 62.5% (before adsorption of polysulfide) to 38.8% (Table 1). It is interesting to observe that Mn_xO_y did

Table 1. Relative Ratio of Different Oxidation States of Manganese in Mixed Manganese Oxide at Different States (i.e., before and after Interaction with Na_2S_6) as Calculated from the Area under Corresponding Peak Components

| compounds | Mn ⁴⁺ (%) | Mn ³⁺ (%) | Mn ²⁺ (%) |
|---|----------------------|----------------------|----------------------|
| pristine Mn _x O _y | 62.5 | 7.3 | 30.2 |
| Na ₂ S ₆ -adsorbed Mn _x O _y | 38.8 | 34.7 | 26.5 |

not involve in the redox reaction with sodium as it did not exhibit any redox peak within 1.2-2.8 V vs Na⁺/Na (Figure S11). This confirms that the reduction of Mn^{4+} to Mn^{3+} in Mn_xO_y occurs only during interaction with sodium polysulfides, which act as a reducing agent. A schematic of the possible surface redox reaction between Mn_xO_y metal oxide and Na_2S_6 is represented in Figure 4d. The schematic shows that Mn_xO_y gets reduced during interaction with Na_2S_{6y} and simultaneously Na₂S₆ is oxidized to sodium polythionates. To visualize the strong affinity of Mn_xO_y metal oxide toward Na_2S_6 , an adsorption experiment was performed using chemically synthesized Na2S6 catholyte as a representative polysulfide. The dark brown color of Na₂S₆ solution turned colorless after incorporation of Mn_vO_v nanoparticles, owing to the polysulfide adsorption ability of Mn_xO_y , as shown in the inset of Figure 4d.

CONCLUSIONS

In conclusion, we have synthesized a freestanding cathode, consisting of reduced graphene oxide, sulfur nanoparticles, manganese oxide, and Na alginate/polyaniline hybrid binder, thorough a bottom-up approach. Each of these components provides a particular function in the resulting cathode, allowing a RT Na-S battery incorporating this cathode to realize a high gravimetric specific energy of 737 W h kg⁻¹ along with excellent cyclability and rate capability. Both solid-state ⁵⁵Mn NMR analysis and XPS survey reveal that during interaction with Mn_rO_v some of the sodium polysulfide molecules oxidize to polythionate complexes. The polythionate complexes could serve as internal mediators to anchor higher-order polysulfides and thus restrict their dissolution. This work also demonstrates the beneficial effect of using a suitable amount of SEI-forming additive in the liquid electrolyte. Finally, considering the intriguing features of the freestanding cathode, it is expected that the synthesis strategy will encourage further efforts toward effective cathodes for sodium-sulfur batteries.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b00203.

Synthesis methods; calculation of average cell potential; XRD patterns of rGO and Mn_xO_y ; Raman spectra of GO and rGO; deconvoluted Mn 2p XPS spectrum of Mn_xO_y ; FTIR spectrum of final cathode; and TGA plot of sulfur, polyaniline, sodium alginate, and the final cathode (PDF)

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Notes

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