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3D printing of hybrid MoS$_2$-graphene aerogels as highly porous electrode materials for sodium ion battery anodes

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**HIGHLIGHTS**

- MoS$_2$-reduced graphene oxide aerogels have been firstly printed with a three-dimensional freeze printing method.
- The hybrid structure consists of small MoS$_2$ patches attached on larger two-dimensional rGO flakes in a macroporous framework.
- The hybrid aerogels are utilized for sodium ion battery anodes.

**ABSTRACT**

This study reports a 3D freeze-printing method that integrates inkjet printing and freeze casting to control both the microstructure and macroporosity via formation of ice microcrystals during printing. A viscous aqueous ink consisting of a molecular MoS$_2$ precursor (ammonium thiomolybdate) mixed with graphene oxide (GO) nanosheets is used in the printing process. Post-treatments by freeze-drying and reductive thermal annealing convert the printed intermediate mixture into a hybrid structure consisting of MoS$_2$ nanoparticles anchored on the surface of 2D rGO nanosheets in a macroporous framework, which is fully characterized with FESEM, TEM, XRD, Raman spectroscopy and TGA. The resulting hybrid MoS$_2$-rGO aerogels are studied as anodes for sodium ion batteries. They present a high initial specific capacity over 429 mAh/g at C/3.3 rate in the potential range of 2.5–0.10 V (vs Na$^+$/Na). The process involves both reversible 2 Na$^+$ insertion and slow irreversible conversion of MoS$_2$ to metallic Mo. At higher rates, the conversion reaction is suppressed and the electrode is dominated by fast Na$^+$ intercalation with good stability. This demonstrates that the 3D printing technology can be used as a processing technique to control the materials properties for energy storage.

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**Keywords:**
- 3D printing
- Hybrid MoS$_2$/graphene aerogel
- Freeze-casting
- Sodium ion battery
- Porous electrode materials

**GRAPHICAL ABSTRACT**

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**1. Introduction**

3D printing, a technique for rapid prototyping of materials, architecture, and systems, has recently been applied for the fabrication of Li-ion battery (LIB) electrodes in interdigitated microarchitectures with a
printed feature size around 100 μm [1,2]. While these studies demonstrate the potential of 3D printing for future personal design of energy storage devices, they have mainly focused on a proof-of-concept using well-established electrode materials such as the lithium iron phosphate (LFP) and lithium titanium oxide (LTO). The theoretical specific capacity of these materials is relatively low, being 170 mAh/g for LFP and 174 mAh/g for LTO. Thus, it was not challenging to maintain the integrity of the 3D printed structures during charge-discharge cycles due to the relatively small volume changes (<5%). Other studies have explored the 3D printing process for rapid prototyping of freestanding disk electrodes for LIB coin cells [3] or improving Li+ ion transport in electrodes by printing LiMn1−xFexPO4 nanocrystal inks into parallel lines [4].

Another direction in 3D printing research is to utilize the layer-by-layer additive technology as a materials processing tool to control the internal micro-/nano- structures of the printed materials in desired macrostructures. A recent study by Rocha et al. [5] demonstrated the successful printing of woodpile and interdigitated structures using chemically modified graphene (CMG) ink interfaced with the current collectors printed with a copper colloid ink. The printed precursors were subject to freeze-drying and thermal treatment to form reduced CMG flakes. The materials not only retained the original 3D printed macro-architecture but also formed a highly porous internal structure with interconnected pores on the order of ~5 μm. Moreover, the high electrical conductivity and large surface area of the reduced CMG flakes led to relatively high-powered electrochemical supercapacitors [5]. In principle, this method can be applied on fabricating advanced secondary batteries by incorporating proper energy storage materials. In this work, we use a further improved 3D freeze-printing (3DFP) method as a novel materials processing technique to prepare highly porous MoS2/graphene hybrid aerogels as the anode for more challenging future sodium ion batteries (SIBs). Such interconnected porous structures are critical in mitigating the stress induced by the larger volume changes during charge-discharge cycles than that in the previous LIB studies due to the combination of higher specific capacity (over 300 mAh/g) and larger ion size (0.102 nm for Na+ vs 0.076 nm for Li) [6,7].

Graphene and molybdenum disulfide (MoS2) belong to a broad family of two-dimensional (2D) layered materials which have been widely investigated due to their exceptional properties [8]. For instance, MoS2 forms a layered structure containing three-atom layers (S-Mo-S) stacked together through van der Waals interactions, which facilitates...
intercalation of ions. However, it suffers from fast structure deteriora-
tion and low electrical conductivity [9,10]. On the other side, graphene
is the most promising 2D single atom thick material, especially as a con-
ductive backbone due to its high electrical conductivity, superior flexi-
bility, and excellent chemical resistance [10]. Therefore, hybrid 2D
materials, like MoS$_2$/graphene, have attracted broad attention in order
to combine the advantages from both components for applications
such as LIBs [9–11], SIBs [12], electromagnetic wave absorber [10],
chemical sensor [13], etc. Graphene oxide (GO) is a form of heavily ox-
idized graphene which can be better dispersed in aqueous solutions
making the materials processing much more flexible. For this reason,
GO has been included in 3D printing inks to improve the electrical

![Figure 3](image1.png)

**Fig. 3.** Low a) and high b) magnification SEM images of MoS$_2$-rGO printed on a Ni foam. EDS layered elemental mapping of c) all elements, d) sulfur (red), e) molybdenum (purple), f) carbon (green) and g) oxygen (blue).

![Figure 4](image2.png)

**Fig. 4.** An EDS spectrum of the MoS$_2$-rGO aerogel on the nickel foam.
conductivity of the printed electrodes [2,5]. More importantly, GO can be converted into reduced graphene oxide (rGO) through a postdeposition thermal annealing process to remove the oxygenated functional groups and reorganize GO into higher quality graphene [5]. Thus, the electrical conductivity is increased by several orders of magnitude which is essential for high-power energy storage applications. In this work, we print 3D MoS$_2$/graphene hybrid aerogel, shown in Fig. 1, as anodes for SIBs using the 3DFP technique developed in our previous study on 3D printing of graphene aerogels [14–17]. The key innovation is employing a cold substrate plate at −30 °C (Fig. 1a) so that the aqueous ink droplets can be rapidly frozen as ice during printing. An aqueous GO-based ink consisting of adjustable concentration of GO nanoflakes and ammonium thiomybdate (ATM) as the MoS$_2$ precursor is used in the printing process. The post-printing freeze-drying followed by thermal treatment in Ar gas containing 3% H$_2$ preserves the porous structure created by ice crystals during 3D printing while converting ATM into MoS$_2$ by thermal decomposition and thermally reducing GO into rGO. Such printed hybrid aerogels form a continuous highly conductive rGO backbone with the nanoscale MoS$_2$ sheets attached to the graphene surface serving as the Na$^+$ intercalation host. The half-cell SIB tests demonstrate that such 3D printed MoS$_2$/graphene aerogels can achieve a specific capacity close to the theoretical values at low charge-discharge rates and good stability at higher rates. This study demonstrates an innovative method to fabricate hybrid aerogel-based 3D architectures for broad electrical energy storage devices.

2. Results and discussion

The 3D hybrid MoS$_2$/rGO aerogels were printed by the 3DFP technique, which combines inkjet printing with freeze casting. The schematic of the 3DFP setup is shown in Fig. 1a–c. ATM and GO nanoflakes (300–800 nm in average size) were dispersed in deionized (DI) water and utilized as the precursor ink. To ensure a good interface with the printed material for battery tests, a Ni foam with interconnected ~300 μm diameter pores (Fig. 2a and b) is used as the current collector, which was firmly pressed onto a cold plate set at −30 °C. The ATM-GO droplets rapidly froze into ice crystals, as illustrated in Fig. 1d. During this process, the ATM-GO precursors were squeezed between ice crystals to form a continuous matrix. The 3D printed patterns were placed in a freezer set at −70 °C for 24 h to achieve further ice crystal growth and then transferred to a freezer dryer to remove the ice template and form an ATM-GO precursor aerogel, as shown in Fig. 1e. The 3D macro architecture can be controlled in any pattern down to 100 μm resolution via the preset 3D printing models. An example is shown in Fig. 1f. In this study, a simple continuous film is used. The precursor aerogel was then thermally annealed in 3% hydrogen (97% argon) for 2 h at 600 °C to produce the MoS$_2$/rGO hybrid aerogel represented by the characteristic color change from red-brown (Fig. 1f) to black-grey (Fig. 1g). The printed architectures were clearly retained after going through all these processes. To the best of our knowledge, it is the first time to achieve 3D printing of MoS$_2$/rGO hybrid aerogels.

The microstructures of printed hybrid MoS$_2$/rGO aerogel were characterized in details. The low-magnification SEM image in Fig. 3a reveals the rather uniform morphology of the MoS$_2$/rGO aerogel, which comprises of an interconnected network of micron-sized flakes. The high-magnification SEM image in Fig. 3b reveals the presence of 5–10 μm pores among wrinkled rGO flakes (5–10 μm in size) stacked into 100–200 nm thick framework. From the cross-sectional SEM image in Fig. 2c, the thickness of the printed MoS$_2$/rGO aerogel film is estimated to be ~700 μm, which is partially embedded in the 650 μm thick pressed nickel foam. Such Ni foam with interconnected pores of 200–300 μm is commonly used as the 3D current collector in LIBs. It also plays an important role in this study to regulate the freeze-printing process. It’s worth noting that the morphology of the obtained MoS$_2$/rGO aerogel (Figs. 2d, 3a and b) is quite different from that obtained by traditional 3D printed/freeze-dried materials on planar substrates which consisted of columnar or wall-like structures separated by large voids of ~100–300 μm in size generated by ice crystals [14,18]. The open 3D Ni foam framework apparently changed the temperature gradient and eliminated the formation of large columnar ice crystals from surface of the cold plate. The large temperature gradient along a particular direction is known to be the driving force for the freeze casting in previous studies [14,16]. The EDS mapping in Fig. 3c–g shows a homogeneous mixture of carbon, oxygen, molybdenum and sulfur throughout the aerogel (with a representative EDS spectrum in Fig. 4 showing the signal from all four elements).

The microstructure was further characterized by high-resolution TEM. The bright-field TEM image in Fig. 5a shows that the hybrid structure consists of small darker MoS$_2$ patches attached on larger thin rGO flakes. Further study by high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) images in Fig. 5b–d show that MoS$_2$ forms a dense layer consisting of 10 to 50 nm nanoparticles on the surface of much larger rGO flakes. The high-resolution images (Figs. 5e and f) and SAED patterns (insets in Fig. 5e and f) indicate that the MoS$_2$ nanoparticles are polycrystals and most of them have the hexagonal lattices aligned in the rGO surface plane (as reflected in the dominating six-fold SAED patterns). In contrast, the morphology of the materials produced by 3D printed ATM alone show very different morphologies and random crystal orientations (see Fig. 6). The hybrid structure of MoS$_2$/rGO consisting of small MoS$_2$ patches on larger rGO flakes is further illustrated with more TEM images and EDS mapping in Fig. 7.
The structure and materials properties of the 3D printed MoS2-rGO aerogels are further characterized with XRD, Raman spectroscopy and thermal gravimetric analyses (TGA). The XRD spectrum in Fig. 8a matches well with the pattern of JCPDS: 37-1492 database. The signature diffraction peak (002) at the \(2\theta\) of 14.22° corresponds to a d-spacing of 0.62 nm which is consistent with the HRTEM images of bare MoS2 in Fig. 6c. The relatively large spacing and weak interlayer interactions are advantageous to the intercalation of sodium ions. It’s worth noting that there is no (002) diffraction from rGO layers, suggesting that the commonly encountered issue of rGO restacking was avoided likely due to the high MoS2 content on rGO surface [19,20].

The Raman spectra in Fig. 8b show the signature peaks of MoS2 at 379 and 403 cm\(^{-1}\) corresponding to the first-order Raman active modes \(E_{12g}\) and \(A_{1g}\), respectively. These bands originate from the opposite vibration of two S atoms with respect to the Mo atom and the out-plane vibration of S atoms, respectively [21,22]. A smaller peak at 458 cm\(^{-1}\) is associated with 2 \(LA(M)\) which originates from the second-order zone-edge phonon [23–25]. The two peaks at the Raman shift of 1353.0 and 1600.0 cm\(^{-1}\) are associated with the D and G bands of rGO originating from the vibrational modes from sp\(^3\)-bonded carbon atoms in amorphous carbon or defect sites and the in-plane vibration of sp\(^2\)-bonded carbon atoms, respectively. The ratio of peak intensity of D and G bands is close to 1.0, indicating the relatively large average size of sp\(^2\) domains in the final rGO [26]. In addition, two weak peaks corresponding to 2D and S3 bands are observed at 2676 and 2940 cm\(^{-1}\), respectively. The large intensity ratio of \(I_{2D}/I_{2D} = -2.0\) in inset of Fig. 8b.

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Fig. 6. a) and b) Low-magnification TEM images and c) HRTEM image of bare MoS2 materials produced with reductive thermal treatment of the 3D printed structure using the ATM precursor alone. A lattice spacing of 0.63 nm corresponding to the interlayer spacing of MoS2 can be seen in the TEM image in panel c.

Fig. 7. HAADF-STEM images at a) low and b) high magnifications of a MoS2-rGO particle. EDS elemental mapping of the STEM image with c) molybdenum (purple), d) sulfur (blue), e) oxygen (green) and f) carbon (red). HRTEM images (g and h) of MoS2-rGO showing the lattice of MoS2 and rGO, respectively, with SAED patterns from the red-boxed area shown in the insets.
indicates the presence of a relatively high concentration of defects in the rGO lattice, which may be necessary to obtain a strong interaction between rGO template and the MoS2 nanoparticles. Based on all above characterizations, we can conclude that the 3D printed materials form a highly porous MoS2-rGO aerogel after thermal treatment, with small MoS2 nanoparticles strongly anchored on the framework of thin stack of rGO sheets as illustrated in Fig. 8c.

Thermogravimetric analysis (TGA) was carried out to determine the mass composition of the MoS2-rGO aerogels. The mass loss was measured from room temperature to 650 °C in air. As shown in Fig. 8d, bare rGO (blue) remained stable below 350 °C and then slowly lost 10% of the mass up to ~480 °C. The mass rapidly dropped above 480 °C and reach a steady level of 12% after 550 °C, likely in form of residual graphitized carbon. Bare MoS2 (red) was oxidized to MoO3 as illustrated by the 7% mass drop after 500 °C. The MoS2-rGO aerogel (black) behaved as a combination of the above two components. The mass percentage of MoS2 was measured to be 78% at the temperature above 600 °C. Based on these TGA data, the total weight percentage of the MoS2-rGO aerogel at 650 °C in air can be expressed as:

\[
\text{Total Weight} \% = \left( \left( \text{Weight}\%_{\text{MoS2}} \times 93\% \right) + \left( \text{Weight}\%_{\text{rGO}} \times 12\% \right) \right) \tag{1}
\]

\[
78\% = \left( \left( \text{Weight}\%_{\text{MoS2}} \times 93\% \right) + \left( 1 - \text{Weight}\%_{\text{MoS2}} \right) \times 12\% \right) \tag{2}
\]

Thus, the mass percentage of MoS2 in the MoS2-rGO aerogels can be calculated to be 81.5%. This value is used in calculating the specific capacity of Na+ storage in later sections.

SIBs have been at the forefront of recent energy storage research since the high cost of lithium precursors makes LIBs unsustainable for large-scale applications such as grid-storage backup [27,28]. SIBs can replace Li+ ions with more abundant Na+ ions which have very similar chemical properties. But this encounters a challenge since few materials can serve as stable intercalation host for the large Na+ ions (with an ionic radius of 0.102 nm vs 0.076 nm for Li) [6,7]. Recently MoS2 has been recognized as an attractive electrode material for SIBs owing to its suitable layered structure for Na+ intercalation [29–34]. However, the low intrinsic electrical conductivity hinders its ability as a standalone electrode material. Numerous efforts have been made to combine carbon based materials with MoS2 to form composites for better performance [12,19,20,35–42]. We envision that the highly porous 3D printed MoS2-rGO hybrid structure may be an effective way to fully use the Na+ ion storage capability of MoS2 and 3D printing for fabrication of complex-structures, which may find broad applications in energy storage devices.

The Na+ storage properties of the 3D printed MoS2-rGO aerogels on nickel foam in the half-cell configuration using CR2032 coin cells are shown in Fig. 9. The insertion and extraction specific capacities from the sequential galvanostatic charge-discharge tests at five constant current densities ranging from 100 to 1000 mA/g are shown in Fig. 9a. Ten complete charge-discharge cycles have been applied at each current rate. In the initial 10 cycles at 100 mA/g current density, the insertion capacity rapidly drops from about 800 mAh/g (in the 1st cycle) to 429 mAh/g (in the 10th cycle). Such initial instability is commonly observed in SIB materials [12,38]. This value drops to 334, 284, 236 and 189 mA/h as the current density is raised to 250, 500, 750 and 1000 mA/g at the 1st, 250, 750 and 1000 mA/g at the 2nd, 750 and 1000 mA/g at the 3rd, and 500, 750 and 1000 mA/g at the 4th cycles, respectively. The cell becomes more stable in later high-current cycles. At the 51st cycle, the previous charge-discharge sequence is repeated. While the specific capacity slightly drops in the 2nd sequence, to 277 mAh/g (at 100 mA/g in the 51st cycle), 193 mAh/g (at 250 mA/g in the 61st cycle), 169 mAh/g (at 500 mA/g in the 71st cycle), 139 mAh/g (at 750 mA/g in the 81st cycle) and 122 mAh/g (at 1000 mA/g in the 91st cycle), respectively, it is noteworthy that the capacity values remain almost constant at high charge-discharge rates from the 71st to 100th cycles.

The corresponding specific capacity during extraction is somewhat lower than the insertion processes. The difference is substantial in the initial 10 cycles at the lowest current density of 100 mA/g but quickly decreases in later cycles, particularly at higher current densities. In the second-rate sequence from the 51st to 100th cycles, the difference
between the insertion and extraction cycles becomes negligible except at the lowest current density of 100 mA/g. Another way to view this is by the columbic efficiency which is calculated as the percentage ratio of the Na⁺ extraction capacity to the Na⁺ insertion capacity of the prior step, as shown in the right axis of Fig. 9a. After conditioning the cell in the first 50 cycles at varied current densities, the cell attains ≥97% columbic efficiency in later cycles when the current density was above 250 mA/g. Even at the lowest current density of 100 mA/g, the columbic efficiency is above 91%.

The representative charge-discharge curves at the last cycles of each current density in the first-rate performance sequence (cycles 1–50) are shown in Fig. 9b in comparison with those in the 1st cycles. The potential decreases as Na⁺ ions are inserted in the MoS₂-rGO aerogel electrode and increases as Na⁺ ions are extracted. The low columbic efficiency (~52%) in the first cycle is mainly attributed to the long slope at the potential below 0.5 V (vs Na/Na⁺). In stabilized cycles, the potential rises quickly in both charge and discharge processes, giving the steep curves with small bendings at ~1.7 V (for extraction) and ~0.7 V (for insertion). At higher current densities, it becomes closer to smooth tilt lines. These features, particularly the first Na⁺ insertion curve, are quite different from the long horizontal plateaus observed in charge-discharge curves with exfoliated bulk MoS₂ materials [12,38]. Such smooth tilt curves are more like the behavior of pseudocapacitors rather than typical batteries. Consistent with the charge-discharge curves, the cyclic voltammograms (CV) in Fig. 9c are dominated by the smooth pseudocapacitor features with only a pair of broad, weak redox waves superimposed on the high capacitive baseline current. A main factor for such pseudocapacitor behavior could be the formation of small (10–50 nm) MoS₂ nanoparticles anchored on the rGO framework. This induces a high magnitude of surface reaction exceeding the bulk intercalation, which is known to generate pseudocapacitive features. Since the surface reaction are much faster, the electrodes tended to be more stable at higher charge-discharge rates and were able to present rather high capacity (~189 mAh/g) at the highest current rate of 1000 mA/g in 41–50th cycles. The highly conductive rGO framework provides the fast electron transport to facilitate such fast surface reactions of the MoS₂ nanoparticles.

It has been well established that the Na⁺ insertion mechanism in MoS₂ involves a two-step process, i.e. reversible Na⁺ intercalation to form NaₓMoS₂ (up to x = 2) followed by an irreversible conversion reaction to form Mo metal and sodium sulfide, as illustrated in Eqs. (3) and (4) [38]:

\[
\text{MoS}_2 + x\text{Na}^+ + xe^- \rightarrow \text{Na}_x\text{MoS}_2 \quad (\text{with } x \leq 2) \tag{3}
\]

\[
\text{Na}_x\text{MoS}_2 + (4 - x)\text{Na}^+ + (4 - x)e^- \rightarrow 2\text{Na}_2\text{S} + \text{Mo} \quad (\text{with } 2 \leq x \leq 4) \tag{4}
\]

The theoretical capacity following Eq. (3) is 334 mAh/g which can be expanded up to 667 mAh/g if reaction (4) is involved. To avoid the irreversible degradation, the low potential limit in our battery tests (as shown in Fig. 9) was set at 0.10 V (vs Na/Na⁺) even though substantially higher specific capacity can be obtained with lower potential setting, such as 0.01 or 0.005 V (vs Na/Na⁺) in literature [12,38,39]. Referring to the theoretical capacity of 334 mAh/g, the C-rates in the rate-

Fig. 9. Electrochemical characterization of the MoS₂-rGO aerogel. a) Rate performance at 5 different current density values (100, 250, 500, 750, and 1000 mA/g), each for 10 charge-discharge cycles in the potential range of 2.5–0.1 V (vs Na/Na⁺). b) The galvanostatic charge-discharge curves of the first cycle at 100 mA/g in comparison with those in the 10th cycle at the current density values (100, 250, 500, 750, and 1000 mA/g) in the rate-performance test shown in (a); c) Cyclic voltammetry curves at the scan rate of 0.1, 0.5 and 1.0 mV/s in the potential range of 2.5–0.1 V (vs Na/Na⁺).

Fig. 10. Comparison of the galvanostatic charge-discharge rate performance of a bare nickel foam with the MoS₂-rGO aerogel in a Ni foam at current rates of 100, 250, 500, 750 and 1000 mA/g.

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an increased $R_e$ at lower potential due to formation of thicker solid electrolyte interphase (SEI) on the MoS$_2$ surface. The 3D printed MoS$_2$-rGO aerogel electrode was able to reduce the SEI formation. Reversible charge-discharge profiles and good electrode stability can be obtained by implementing C/1.3 or higher C-rates. It is noteworthy that the specific capacity of 193 mAh/g and columbic efficiency of 97% at 250 mA/g (i.e. C/1.3) after the electrode was stabilized in cycles 61–70 are promising metrics for future SIBs. Higher C-rates (>1.5 C) yielded even better columbic efficiency over 99%.

More control experiments have been carried out to support of the advantages of the 3D printed porous MoS$_2$-rGO aerogel structure. Fig. 12 illustrates that direct printing MoS$_2$-rGO aerogel on a planar copper foil can improve the stability and columbic efficiency at the lowest current density (100 mA/g). But the capacity quickly faded as the C-rate is increased, which is mainly due to the poor adhesion and high resistance at the interface of MoS$_2$-rGO aerogel and Cu surface. Fig. 13 shows that the conventional thin-film electrode made by the composite consisting of MoS$_2$ powder mixed with carbon black and polyvinylidene fluoride binder (at 70:20:10 weight ratio) also show better stability and columbic efficiency at the lowest current density (100 mA/g). However, the specific capacity is below 200 mAh/g, significantly lower than that of the 3D printed MoS$_2$-rGO aerogel in Ni foam (~429 to 800 mAh/g). Particularly, the 3D printed MoS$_2$-rGO aerogel in Ni foam is far better than the conventional electrodes at the current density above 250 mA/g. Interestingly, even though the MoS$_2$ nanoparticle size is larger (~200 nm) in the composite electrode, it is still behaved as pseudocapacitors. Clear battery-like redox waves were only observed by CV in the first two cycles. The Na$^+$ intercalation may have quickly disrupt the MoS$_2$ crystal structure and break it into smaller nanoparticles in these cycles.

3. Conclusion

The MoS$_2$-rGO aerogel has been successfully printed by a 3D freeze-printing method, which integrates inkjet printing and freeze casting to provide the capability to control microstructure of hybrid materials in addition to the macroscopic architectures. A MoS$_2$ precursor (ammonium thiomolybdate) mixed with single layer graphene oxide sheets is used as the ink. The post-treatments by freeze-drying and thermal annealing are able to convert the MoS$_2$ precursor and GO into a hybrid structure consisting of MoS$_2$ nanoparticles anchored on the surface of a highly porous rGO framework. The interconnected graphene network in such 3D aerogels has been found to effectively enhance the electrical conductivity and mechanical strength while the large pores (~3–5 μm) facilitate the fast ion transport. The electrical energy storage capability of this porous MoS$_2$-rGO aerogel has been demonstrated as an anode for sodium ion batteries. In the initial 10 cycles, it shows a high specific
capacity changing from ~800 to 429 mAh/g at 100 mA/g (~C/3.3 rate), which involves both reversible 2 Na⁺ insertion and irreversible conversion of MoS₂ into metallic Mo. At higher rates in later cycles, the conversion reaction is substantially reduced, showing significantly improved stability that is dominated by fast pseudocapacitive surface reactions of Na⁺ ion with MoS₂ nanoparticles. This study demonstrates the potential to use 3D printing technology to fabricate the macroporous electrode materials that can sustain high-capacity intercalation of large Na⁺ ions, which opens a new direction of 3D printing for energy storage applications.

4. Experiment

Ammonium thiomolybdate (ATM) and graphene oxide (GO) were purchased from Sigma Aldrich (St. Louis, MO, USA) and Cheap Tubes (Cambridgeport, VT, USA), respectively. In typical experiments, 72 mg ATM and 20 mg GO were dispersed into 2 mL water to form a viscous precursor ink for 3D drop-on-demand (DOD) inkjet printing. ATM-GO ink droplets were deposited onto a 0.65 mm thick (1.6 mm unpressed) stainless steel coin cell (CR2032, MTI Corporation, Richmond, CA). A 0.65 mm thick glass substrate (8979 eV). Raman spectra were obtained using a Renishaw inVia confocal Raman microscope (Gloucestershire, UK) at a laser wavelength of 532 nm. Thermal gravimetric analyses were carried out with a TA Instrument Q50 (New Castle, DE) from room temperature to 650 °C.

To evaluate electrochemical performance, the MoS₂-rGO electrode was assembled against a 16-mm dia. sodium disk anode in a stainless steel coin cell (CR2032, MTI Corporation, Richmond, CA). A 0.65 mm thick glass fiber disk (El-Cell, Hamburg, Germany) was used as the separator. The cell was assembled in an argon filled M-Braun LabStar50 stainless steel glovebox (Garching, Germany) with <1 ppm of O₂ and H₂O contents. The electrolyte consisted of 1.0 M sodium perchlorate (NaClO₄) in propylene carbonate (PC). Galvanostatic charge-discharge cycles were performed using a 8-channel battery analyzer (MTI Corporation, Richmond, CA). All gravimetric capacities were calculated relative to the mass of MoS₂. Cyclic voltammetry (CV) measurements and electrochemical impedance spectroscopy (EIS) were performed using a CHI760D potentiostat (CH Instruments, Austin, TX).

CRediT authorship contribution statement

Emery Brown: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing - original draft, Writing - review & editing. Pengli Yan: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing - original draft, Writing - review & editing. Halil Tekik: Formal
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