In Situ Growth and Wrapping of Aminoanthraquinone Nanowires in 3D Graphene Framework as Foldable Organic Cathode for Lithium-Ion Batteries

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Small conjugated carbonyl compounds are intriguing candidates for organic electrode materials because of their abundance, high theoretical capacity, and adjustable molecular structure. However, their dissolution in aprotic electrolytes and poor conductivity eclipse them in terms of practical capacity, cycle life, and rate capability. Herein, we report a foldable and binder-free nanocomposite electrode consisting of 2-aminoanthraquinone (AAQ) nanowires wrapped within the 3D graphene framework, which is prepared through antisolvent crystallization followed by a facile chemical reduction and self-assembly process. The nanocomposite exhibited a very high capacity of 265 mAh g⁻¹ at 0.1 C for AAQ, realizing 100% utilization of active material. Furthermore, the nanocomposite shows superior cycling stability (82% capacity retention after 200 cycles at 0.2 C and 76% capacity retention after 1000 cycles at 0.4 C) and excellent rate performance (153 mA h⁻¹ at 5 C). Particularly, the nanocomposite can deliver the highest capacity of 165 mA h⁻¹ among all reported anthraquinone- and anthraquinone-analogues-based electrodes per mass of the whole electrode, which is essential for practical application. Such outstanding electrochemical performance could be largely attributed to the wrapping structure of the flexible composite, which provides both conductivity and structural integrity.

Introduction

In the last decade, organic electrode materials have attracted growing attention owing to the bottleneck of inorganic ones, which suffer from limited availability, low capacity of cathode materials, and safety. In contrast, organic compounds have advantages of abundance, low cost, high theoretical capacity, and environmental benignity. Among them, quinone and its derivatives represent the most promising candidates to develop next-generation batteries with renewable materials and desirable properties because they could be extracted from biomass and exhibit high carbonyl utilization. Particularly, anthraquinone (AQ) has a high theoretical capacity of 257 mAh g⁻¹ and a charge/discharge voltage of 2.2–2.3 V, which implies the potential of realizing a high energy density over 578 Wh kg⁻¹. In this respect, much effort has been devoted to investigating the performance of AQ and its analogues as cathodes for Li-ion batteries during the last few years. However, as AQ has low conductivity and is easy to crystallize and grow into microrods, it is hard to control its morphology and ensure close contact with conductive additives, resulting in low capacity and poor rate performance. Furthermore, it suffers from dissolution in aprotic electrolyte and thus shows very short cycle life. To overcome these challenges, some efforts focused on filling active materials into the pores of mesoporous carbon or carbon nanotubes (CNTs), which provide a nanoconfinement effect and conductive host whereas others worked on designing favorable molecular structures to attain better morphology and properties. The former restrains active materials into the nanochannels of carbon frameworks, but the open porous structure has limited capability of suppressing the dissolution of organic compounds, which generally requires additional optimization of separators or electrolytes. The latter is a promising strategy to discover favorable molecular structures. However, it is arduous and expensive because it is hard to predict the electrochemical performance of a certain compound and obtain pure target products. As an advantageous structure for energy storage, nanowires can provide short ion-diffusion length and continuous electron-conductive pathways. Nevertheless, it is a challenge to suppress structure degradation of nanowires during lithiation/delithiation processes. On the other hand, graphene has advantageous properties of high conductivity, large surface area, excellent flexibility, and chemical stability. Therefore, it is attractive to prepare AQ analogues with nanowire structure and integrate them with graphene efficiently to obtain a flexible and high-performance organic cathode material for lithium-ion batteries, which has not been realized yet.

Herein, we synthesized 2-aminoanthraquinone (AAQ) nanowires with an average diameter of 100 nm at room tempera-
ture through antisolvent crystallization and attached them to graphene oxide (GO) nanosheets simultaneously. Followed by chemical reduction and self-assembly process, we obtained a flexible self-supported 3D AAQ/graphene nanocomposite (AAQ@G) with AAQ nanowires wrapped by reduced GO (RGO) sheets. We chose AAQ as the active material based on the consideration that it has an almost unchanged theoretical capacity of 240 mAh g\(^{-1}\) compared to AQ and the amino group makes interaction between the AQ and the amino group. In addition, AAQ nanowires could be assembled onto GO nanosheets more effectively owing to the combined electrostatic and π–π stacking interactions between them. The free-standing AAQ@G nanocomposite can serve as electrode directly without any other conductive carbon or binder. It delivers a very high discharge capacity of 265 mAh g\(^{-1}\) at a current density of 24 mA g\(^{-1}\) (0.1 C) for the AAQ, which realizes 100% utilization of AAQ. In addition, it shows long cycle life with 76% capacity retention after a long term of 1000 cycles at 0.4 C and superior rate performance with a high capacity of 153 mAh g\(^{-1}\) at 5 C, which has rarely been achieved before. If normalized to the mass of the whole electrode for evaluation of its practical application, the AAQ@G nanocomposite can deliver a capacity of 165 mAh g\(^{-1}\) at 0.1 C, which is the highest value reported so far. To the best of our knowledge, the AAQ@G nanocomposite with such superior comprehensive performance represents one of the best cathode materials among AQ and its analogues.

**Results and Discussion**

**Nanowires encapsulation**

To obtain a nanocomposite with uniform microstructure, antisolvent crystallization was adopted, as illustrated in Figure 1 a. First, GO was dispersed in water and AAQ was dissolved in DMSO and protonated by adding equal molar ratio of hydrochloric acid. After dropwise addition of AAQH\(^+\)Cl/DMSO solution into GO aqueous solution under stirring, AAQH\(^+\)Cl\(-\) nanowires grew in situ on the surface of GO. AAQH\(^+\)Cl\(-\) started to crystallize owing to the poor solubility in DMSO/H\(_2\)O mixture solvent and self-assembled into nanowires possibly owing to π–π interaction between the AAQH\(^+\)Cl\(-\) molecules.\(^{[27]}\) Because AAQH\(^+\)Cl\(-\) was positively charged, the nanowires were easily absorbed/assembled on the negatively charged GO sheets by electrostatic interaction in addition to the π–π stacking interaction, evidenced by significant fluorescence quenching of AAQH\(^+\)Cl\(-\) in the fluorescence spectra (Figure S1 a). Then, the mixture was redispersed in water and reduced by sodium ascorbate (VcNa) under heating, during which the GO sheets self-assembled into 3D graphene network with AAQ nanowires wrapped by the graphene sheets simultaneously (Figure 1 b).

Finally, the 3D AAQ@G aerogel was obtained after freeze-drying (Figure 1 c) and used as flexible electrode directly upon mechanical pressing (Figure 1 d). In a control experiment, the pristine AAQ electrode was prepared by mixing AAQ, super P, and poly(vinyl difluoride) (PVDF) in N-methylpyrrolidinone (NMP) with a weight ratio of 6:3:1 and pasting the slurry on aluminum foil.

The formation of AAQ nanowires on RGO was confirmed by X-ray diffraction (XRD), FTIR spectroscopy, and Raman spectroscopy. In the XRD pattern of AAQ@G (Figure S1 b), two peaks at 2θ = 11° and 14.3° are the same as those of AAQ but the peak at 14.3° becomes less intense. The same situation occurs in the multiple peaks located at 20–30°, which may be owed to different preferred orientation after antisolvent recrystallization in water.\(^{[28,29]}\) The peak of AAQ@G located at 24–30° results from the combination of a broad peak of RGO at 18–30° and several small peaks of AAQ in this range. Notably, this peak is narrower and has higher 2θ than that of RGO, indicating that the presence of AAQ could promote the reduction of GO probably thanks to the electrostatic interaction and π–π interaction. In the FTIR spectra (Figure S1 c–d), both AAQ and AAQ@G have a peak at 1339 cm\(^{-1}\), which is assigned to the stretching vibration of the C–N bond. The absorption peaks at 1677 and 1588 cm\(^{-1}\) are ascribed to the stretching vibrations of the C–O and C=C bonds, respectively.\(^{[30]}\) Raman analysis also provides complementary information for the integration of AAQ and RGO (Figure S1 e–f). It should be noted that there is a little bit redshift in the FTIR and Raman spectra of AAQ@G compared to that of pristine GO.
to AAQ, probably owed to the \(\pi-\pi\) interaction between AAQ and graphene. Together with the fluorescence spectra, these results indicate that the molecule structure of AAQ is intact in the nanocomposite and a strong coupling exists between AAQ and graphene. The mass percentage of AAQ was determined to be about 50% by thermogravimetric analysis (TGA, Figure S2).

The morphology of the \(\text{AAQH}^+\text{Cl}^-@\text{GO}\) precursor and AAQ@G aerogel were characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM), respectively. As shown in Figure 2a, b, AAQH\(^+\)Cl\(^-\) nanowires are wrapped by GO sheets, indicating that antisolvent crystallization could induce the formation of nanowires and the nanowires can absorb onto the GO sheets. The inset image of Figure 2b shows the corresponding electron diffraction patterns of AAQH\(^+\)Cl\(^-\) in a selected area. The diffraction spots of the AAQH\(^+\)Cl\(^-\) nanowire are well resolved and consistent with the XRD data (Figures S3 and S1 b), suggesting a high crystallinity of the active material. In addition, the diffraction rings assigned to GO are also observed, which indicates the successful combination of AAQH\(^+\)Cl\(^-\) and GO\(^{[31–34]}\). After chemical reduction, the AAQ@G aerogel with 3D porous structure was obtained. As displayed in Figure 2c, the pore sizes range from several micrometers to tens of micrometers, which is beneficial for electrolyte penetration and ion transportation. From the high magnification of SEM images of the skeleton of the AAQ@G aerogel (Figure 2d), it can be seen that AAQ nanowires with diameters of 50–150 nm and length of 1–2 \(\mu\)m are wrapped by graphene uniformly. In contrast, the pristine AAQ in the control electrode prepared by mixing AAQ with conductive carbon and binder also showed a wire morphology but much longer (more than ten micrometers) and thicker (several hundreds of nanometers) and most of them were exposed in the electrode (Figure S4). The homogenous growth of AAQ nanowires within the RGO framework is mainly attributed to the \(\pi-\pi\) interaction between graphene and AAQ containing conjugated aromatic rings\(^{[35]}\). It is worthy to note that the 1D highly crystalline structure of AAQ can shorten the pathway of ion diffusion and promote charge transport\(^{[36]}\) whereas the 3D conductive network of graphene with wrapping function can improve the electronic conductivity and increase the utilization of the active material as well as mitigate the dissolution of AAQ molecules\(^{[37]}\). The nitrogen adsorption–desorption isothersms and the pore-size distributions of the as-prepared AAQ@RGO composite and 3D RGO are shown in Figure S10. 

\(\text{N}_2\)-sorption analysis (Figure S10a) demonstrated that the

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**Figure 2.** a, b) Low- and high-magnification TEM images of AAQH\(^+\)Cl\(^-\)@GO precursor with inset showing selected-area electron diffraction pattern of AAQH\(^+\)Cl\(^-\)@GO. c, d) Low- and high-magnification SEM images of 3D AAQ@G nanocomposite with inset showing AAQ nanowires wrapped by graphene. e, f) Cross-section SEM image of the pressed AAQ@G film. g) Photographs of the flexible AAQ@G composite film at its initial, folded and recovered states. h) \(I-V\) curves of AAQ@G composite film at its initial, folded and recovered states.
Brunauer–Emmett–Teller (BET) surface area of AAQ@RGO is 155.0 m$^2$ g$^{-1}$, which is lower than that of 3D RGO (251.4 m$^2$ g$^{-1}$). This indicates that the presence of AAQ could promote the reduction of GO, resulting in closer stacking of the RGO sheets and compact wrapping of AAQ nanowires, which is in agreement with the XRD pattern.

With the highly porous structure and excellent mechanical stability, the as-prepared AAQ@G aerogel with a thickness of about 5 mm could be greatly compressed to form $\approx$ 50 μm-thick flexible AAQ@G film with a packing density of approximately 0.7 g cm$^{-3}$ (Figure 2e), in which the 3D continuous porous network was well maintained and the AAQ nanowires were encapsulated within the graphene sheets owing to the robust interlock of graphene sheets (Figure 2f). Furthermore, after folding the AAQ@G film and unfolding it, there was no obvious change in the appearance and electrical conductivity, indicating a superior mechanical flexibility for the AAQ@G film (Figure 2g,h). With a high electrical conductivity of 5.4 S cm$^{-1}$, the AAQ@G film was used directly as cathode material without adding any other additives to assemble the cells.

Electrochemical performance

The electrochemical performance of AAQ@G and pristine AAQ was evaluated by cyclic voltammetry (CV) and galvanostatic charge/discharge tests of CR2016-type coin cells. The CV curve of pristine AAQ shows two pairs of redox peaks (Figure 3a), demonstrating a two-step reaction with Li ions, as shown in Figure 1e. During the cathodic scan from 3.0 to 1.5 V, two reduction peaks are located at 2.10 and 2.22 V, reflecting the insertion of Li ions, whereas an oxidation peak at 2.24 V with a small shoulder at 2.28 V can be observed during the anodic scan, corresponding to the deinsertion of Li ions. In contrast, the CV curve of AAQ@G exhibits a similar peak location but with different peak shape. It has a reduction peak at 2.1 V with a small shoulder at 2.21 V and an oxidation peak at 2.28 V with a small shoulder at 2.23 V, indicating faster lithiation/delithiation kinetics of AAQ@G than pristine AAQ, which could be ascribed to the highly crystalline nanowire structure of AAQ and increased electronic conductivity in the presence of graphene.$^{38,39}$ In addition, AAQ@G has a sharper peak shape and

![Figure 3. a) CV curves of RGO, pristine AAQ electrode, and AAQ@G electrode at the second scan cycle. b) Charge and discharge profiles of RGO, pristine AAQ electrode, and AAQ@G electrode at 0.1 C. The specific capacity is based on the mass of the whole electrode. c) Rate performance of pristine AAQ electrode and AAQ@G electrode. The specific capacity is based on the mass of AAQ. d) EIS spectra of pristine AAQ electrode and AAQ@G electrode before cycle. e) Cycle performance of pristine AAQ electrode and AAQ@G electrode at 0.2 C. The specific capacity is based on the mass of AAQ. f) EIS spectra of pristine AAQ electrode and AAQ@G electrode after 200 cycles.](https://www.chemsuschem.org/content/10/15/3419.full.html)
higher peak current, which indicates the nanocomposite has more electrochemical active species and higher capacity. Note that the peak at 1.58 V of pristine AAQ and the peak at 1.68 V of AAQ@G are attributed to the irreversibly decomposition of electrolyte, which disappears in the following scans. The CV curve of RGO in potential range of 1.5–3.0 V is also provided in Figure 3a and shows no obvious redox peaks, implying that RGO has a small contribution to the capacity of the composite.

The galvanostatic charge/discharge tests were performed after 10 cycles of activation at 100 mA g\(^{-1}\) and the initial Coulombic efficiency of AAQ@G was 85.83% (Figure S5). According to the charge and discharge profiles of AAQ@G and pristine AAQ at a current density of 0.1 C (24 mA g\(^{-1}\)) (Figure S5b), the electrochemical activity of AAQ was remarkably improved by anchoring its nanowires within the graphene network. The discharge capacity based on the mass of the whole electrode increased from 58.5 mAh g\(^{-1}\) for pristine AAQ (60% AAQ) to 165 mAh g\(^{-1}\) for AAQ@G (50% AAQ). After deducting the capacity contribution of RGO (for calculation method, see the Supporting Information, Figure S6), it can be calculated that the specific capacity of AAQ@G was 265 mAh g\(^{-1}\), whereas the specific capacity of pristine AAQ was merely 98 mAh g\(^{-1}\) based on the mass of active material. Interestingly, the initial capacity of AAQ@G exceeds its theoretical value (240 mAh g\(^{-1}\)), which may be owed to the synergistic effect of AAQ and RGO. The higher specific capacity of AAQ nanowires results from its smaller size and larger surface area, which enables more AAQ to contact with the graphene network and react with Li ions, resulting in full utilization of the active material. In good accordance with the CV curves, AAQ@G shows average discharge and charge plateaus at 2.18 and 2.24 V, respectively. The voltage difference between the charge and discharge curves of AAQ@G is smaller than that of pristine AAQ, indicating that the composite electrode has weaker polarization.

In addition to higher capacity, the AAQ@G electrode also exhibited superiority in rate performance and cycling stability. Figure 3c compares the rate performance of pristine AAQ and AAQ@G from 0.1 C to 5 C. It can be seen that the discharge capacity of AAQ@G is always higher than that of pristine AAQ. At 0.1 C, pristine AAQ and AAQ@G show discharge capacities of 98 and 265 mAh g\(^{-1}\), respectively. Even at a high rate of 5 C, AAQ@G still delivers a capacity of 153 mAh g\(^{-1}\), which is superior to most AAQ analogues reported (Table S1). In contrast, the discharge capacity of pristine AAQ retains only 13 mAh g\(^{-1}\) at 5 C. When the current density is reduced to 0.1 C, AAQ@G recovers a capacity of 230 mAh g\(^{-1}\) whereas AAQ reaches only 65 mAh g\(^{-1}\), suggesting that AAQ@G has better reversibility. It should be noted that the electrode preparation in previous reports involved using a large amount of conductive carbon and polymer binder. Therefore, normalizing the capacity to the entire electrode is essential for practical applications. In this respect, AAQ@G can deliver a capacity of 165 mAh g\(^{-1}\) at 0.1 C (Figure S6a), which is the highest value reported so far to the best of our knowledge (Table S1). The excellent rate performance of AAQ@G can be related to its unique structure and morphology. AAQ nanowires wrapped by RGO provide continuous pathway for electron flow and short distance for ion transport. Additionally, the 3D RGO framework with interconnected pores facilitates rapid charge transfer and Li\(^+\) diffusion throughout the whole electrode. To further explain the outstanding rate performance of AAQ@G, electrochemical impedance spectroscopy (EIS) was performed. Figure 3d shows the Nyquist plots of AAQ and AAQ@G, which consist of two parts. The semicircle in the high-to-middle frequency region corresponds to the charge-transfer resistance (R\(ct\)) between the electrode and electrolyte whereas the sloping line at 45\(^\circ\) at the low-frequency region represents the Warburg impedance (Z\(_W\)) associated with lithium-ion diffusion in the electrode. The EIS results were simulated by using an equivalent circuit and the fitted parameters are shown in Figure S7. Compared to pristine AAQ electrode, the AAQ@G electrode shows a smaller semicircle diameter and a shorter 45\(^\circ\) curvature, indicating that AAQ@G exhibits faster charge-transfer kinetics and more efficient Li\(^+\) diffusion than pristine AAQ.

As for the cycle performance displayed in Figure 3e, pristine AAQ delivers an initial capacity of 90 mAh g\(^{-1}\) at 0.2 C and undergoes rapid capacity decay after 200 cycles, with only 26% of the initial capacity retained. The poor cycle performance may be owed to the low electronic conductivity and dissolution of active material. In contrast, the AAQ@G still remains a high capacity of 206 mAh g\(^{-1}\) after 200 cycles, corresponding to a capacity retention of 82%. The Nyquist plot of AAQ@G after 200 cycles (Figure 3f) shows similar impedance to the EIS before cycling but with two semicircles in the high-to-middle frequency region. The additional semicircle corresponds to the formation of the solid-electrolyte interface (SEI). In comparison, the EIS of pristine AAQ after 200 cycles exhibits much larger impedance than that before cycling, which further verifies superior structural stability of AAQ@G.

More importantly, after a long term of 1000 cycles at 0.4 C, the discharge capacity of AAQ@G still reaches 183 mAh g\(^{-1}\) (Figure 4a), which corresponds to 76% of the initial capacity (241 mAh g\(^{-1}\)). In contrast, the capacity of pristine AAQ after 1000 cycles (Figure S8) retained merely 13 mAh g\(^{-1}\), corresponding to 16% of the initial capacity. A comparison of the cycling performance of AAQ@G and other AQ analogues for lithium-ion batteries reported previously is given in Table S1. Our AAQ@G shows the longest cycle life among these small organic molecules. The excellent cycling stability of the AAQ@G composite could be attributed to the wrapping structure of RGO, which improves the electronic conductivity and suppresses the dissolution of AAQ to a great extent. This can be evidenced on the photos of the disassembled cells (Figure 4b,c). The color of the separator in the pristine AAQ cell is much deeper than that of AAQ@G, implying stronger dissolution of AAQ in the pristine AAQ cell. TEM images and energy-dispersive spectroscopy (EDS) mapping reveal that AAQ were still uniformly distributed on the surface of graphene after 1000 cycles (Figure 4d–h). This indicates that the 3D graphene framework can effectively protect AAQ from detaching from the electrode and dissolving into the electrolyte. In contrast, the SEM images and EDS mapping of pristine AAQ are displayed in Figure S9. It can be seen that AAQ has diminished in
the electrode with N element almost undetectable in the EDS mapping of the pristine AAQ electrode. To study the dissolution of AAQ in the electrolyte, SEM images of the AAQ@G electrode after 5 cycles are shown in Figure S11. We can see that the re-precipitate AAQ exhibits nanowires or particle morphology so the advantages of the initial nanowire–RGO composite morphology still play a role. In addition, the initial nanowire–RGO composite morphology ensures the uniform distribution of AAQ throughout the conductive graphene framework, leading to effective adsorption of the active material onto graphene sheets in the following cycles. This is important for the stable cycling performance of AAQ@G electrode. Furthermore, a UV/Vis study on the electrolyte after different cycles is shown in Figure S12. The absorption spectrum of AAQ features two clear peaks at 245 and 292 nm and a weak peak at 450 nm. As for the AAQ@G electrode, the electrolytes of the cycled cells show weak absorbance on the whole. Specifically, the absorption intensity decreased first and then increased with the cycle number. There is little difference between the electrolytes after 50 and after 250 cycles, which indicates that the dissolution of AAQ in the electrolyte tended to an equilibrium situation after tens of cycles. In contrast, the electrolytes of cycled pristine AAQ cells exhibit stronger absorption in the UV region and visible region. The peak intensity reached a high value in the initial cycles and increased with the cycle number. In comparison, AAQ@G could adsorb AAQ effectively whereas the pristine AAQ electrode suffers from serious dissolution.

Figure 4. a) Long-term cycle performance of AAQ@G electrode at 0.4 C. The specific capacity is based on the mass of AAQ. Photographs of the disassembled cells of b) pristine AAQ and c) AAQ@G. d) TEM image of the AAQ@G after 1000 cycles. e–h) EDS mapping of AAQ@G after 1000 cycles: f) carbon, g) oxygen, and h) nitrogen distribution in the selected area (e).

Conclusions

We developed a novel organic graphene nanocomposite as a high-performance flexible cathode for lithium-ion batteries. The self-supported composite with 2-aminanthraquinone (AAQ) nanowires anchored within the 3D graphene network was synthesized through antisolvent crystallization followed by self-assembly. The small size of AAQ nanowires and its uniform distribution in the reduced graphene oxide (RGO) framework promoted the reaction kinetics and made full use of the active material, resulting in higher reversible capacity (265 mAh g\(^{-1}\)) at 0.1 C than pristine AAQ and other anthraquinone analogues reported. Particularly, the free-standing AAQ@G nanocomposite can show the highest capacity (165 mAh g\(^{-1}\)) normalized by the mass of the whole electrode. The nanocomposite also exhibited very long cycle life and superior rate performance with 76% capacity retention after a long term of 1000 cycles at 0.4 C and 58% capacity retention at 5 C, which have rarely been demonstrated in previous work. Such outstanding electrochemical performance makes our AAQ@G promising for practical application and could be ascribed to its unique hierarchical structure. The 1D nanostructure of AAQ promotes electron flow and shortens the distance of ion diffusion whereas the introduction of the 3D graphene network with wrapping function greatly improves the electronic conductivity of the electrode and protects AAQ from dissolution. This study provides an exciting pathway to promote the electrochemical performance and practical application of organic electrodes by elaborate control of microstructure and integration with advanced carbon materials.

Experimental Section

Synthesis of AAQ@GO

GO was prepared from graphite flakes by a modified Hummers method.\(^{[46]}\) AAQ (Fluorochem) underwent a simple purification before use. AAQ (1 g) was dissolved in ethanol (300 mL) and the solution was filtrated to remove insoluble particles. After removing the solvent by reduced pressure distillation, AAQ powder was obtained. The AAQ@GO was synthesized by the antisolvent crystallization method. Typically, of AAQ (10 mg) was dissolved in DMSO (5 mL, dimethylsulfoxide). Then 45 μL 1 M HCl solution was added. The mixed solution was ultrasonicated for 5 min. Subsequently, the protonated AAQ/DMSO solution was dropwise added into 0.4 mg mL\(^{-1}\) GO aqueous solution (25 mL) under stirring. After stirring for another 20 min, the mixture was centrifuged to remove the solvent. The resulting solid was dispersed in water by stirring for 30 min to get AAQ@GO aqueous dispersion (2 mg mL\(^{-1}\)).

Synthesis of AAQ@G

AAQ@G was synthesized according to the following procedure: 1 mM sodium ascorbate aqueous solution (30 μL) was added into 2 mg mL\(^{-1}\) AAQHCl@GO aqueous dispersion (3 mL) and then the homogeneous mixture was heated at 100°C for 2 h without stirring. The as-prepared AAQ@G hydrogel was taken out of the vial with a tweezer and washed with DI water 3 times. After freeze-
drying, the targeted AAQ@G aerogel with 3D framework was obtained.

Characterizations

FTIR spectral measurements were performed using a Nicolet 6700 instrument. XRD analysis was conducted on a Rigaku D/Max 2500 X-ray diffractometer with CuKα radiation (λ = 1.54 Å) at a generator voltage of 40 kV and a generator current of 20 mA with a scanning speed of 5° min⁻¹ from 8 to 50°. Raman spectra were recorded with an Xplora Laser Raman spectrometer at 332 nm. Fluorescence spectra were recorded on a RF-5301 fluorescence spectrophotometer (Shimadzu, Japan) equipped with 1.0 cm quartz cells at 288 K. We set the excitation wavelength at 370 nm. The excitation and emission slit widths were 5.0 nm. Mettler Toledo A39 TGA1 (Switzerland) was used to operate the TG analysis of AAQ, RGO, and AAQ@RGO in the range of 100 to 800° at a rate of 10° min⁻¹ in N₂. SEM images were observed on a Zeiss Ultra-55 field emission SEM. TEM studies were conducted on a FEI Tecnai G2 20 Twin electron microscope at an operating voltage of 200 kV. The electrical conductivity of the sample films was calculated on a four-probe meter (Shanghai Qianfeng Electronic Instrument co. Limited, SB120/2) using the four probe method. The BET test was tested under an Autosorb IQ Gas Sorption System at 77 K. UV/Vis spectra were recorded using a Lambda 750 UV/Visible Spectrophotometer (PerkinElmer, America).

Electrochemical measurements

Electrochemical experiments were performed in coin-type cells (CR2016) with lithium foil as the counter electrode. The AAQ@G aerogel was pressed and directly served as the working electrodes with an area mass loading of ~3.5 mg cm⁻². The pristine AAQ electrode was fabricated by mixing 60 wt% AAQ, 30 wt% carbon black (Super P) and 10 wt% PVDF and pasting on pure Al foil (99.6%). The mass loading of pristine AAQ electrode was ~2 mg cm⁻². The cathode was separated from the lithium anode by a polypropylene membrane (Celgard 2400). The electrolyte was 1.0 M LiNO₃ in 1,2-dimethoxyethane (DME)/1,3-dioxolane (DOL) (1:1 volume ratio). The cells were assembled in an argon-filled glove box with the concentrations of moisture and oxygen below 0.1 ppm. CV tests was performed at a scan rate of 0.1 mV s⁻¹ over a range of 1.5–3.0 V and EIS was conducted over the frequency range from 100 kHz to 0.01 Hz under open circuit potential on a CHI 660E electrochemical workstation (CH Instruments Inc.). The galvanostatic charge/discharge measurements were tested at different current rates in the voltage range of 1.5–3.0 V on a LAND cell test system (Land CT2001A). The charge/discharge test was operated at 25°C.

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Conflict of interest

The authors declare no conflict of interest.

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