Dispersion—Assembly Approach to Synthesize Three-Dimensional Graphene/Polymer Composite Aerogel as a Powerful Organic Cathode for Rechargeable Li and Na Batteries

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Abstract: Polymer cathode materials are promising alternatives to inorganic counterparts for both lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs) due to their high theoretical capacity, adjustable molecular structure, and strong adaptability to different counterions in batteries, etc. However, they suffer from poor practical capacity and low rate capability because of their intrinsically poor conductivity. Herein, we report the synthesis of self-assembled graphene/poly(anthraquinonyl sulﬁde) (PAQS) composite aerogel (GPA) with efﬁcient integration of a three-dimensional (3D) graphene framework with electroactive PAQS particles via a novel dispersion—assembly strategy which can be used as a free-standing ﬂexible cathode upon mechanical pressing. The entire GPA cathode can deliver the highest capacity of 156 mAh g\(^{-1}\) at 0.1 C (1 C = 225 mAh g\(^{-1}\)) with an ultrahigh utilization (94.9%) of PAQS and exhibits an excellent rate performance with 102 mAh g\(^{-1}\) at 20 C in LIBs. Furthermore, the ﬂexible GPA ﬁlm was also tested as cathode for SIBs and demonstrated a high-rate capability with 72 mAh g\(^{-1}\) at 5 C and an ultralong cycling stability (71.4% capacity retention after 1000 cycles at 0.5 C) which has rarely been achieved before. Such excellent electrochemical performance of GPA as cathode for both LIBs and SIBs could be ascribed to the fast redox kinetics and electron transportation within GPA, resulting from the interconnected conductive framework of graphene and the intimate interaction between graphene and PAQS through an efﬁcient wrapping structure. This approach opens a universal way to develop cathode materials for powerful batteries with different metal-based counter electrodes.

Keywords: three-dimensional graphene, PAQS composite, organic cathode, lithium-ion batteries, sodium ion-batteries

1. INTRODUCTION

The application of rechargeable batteries is now recognized as an effective way to reduce our consumption of fossil fuels and decrease CO\(_2\) emission, thereby alleviating the greenhouse effect.\(^1\)–\(^3\) Lithium-ion batteries (LIBs) have become the dominant energy storage device for powerful portable electronic devices as well as electrical vehicles over the past nearly two decades.\(^4\)–\(^6\) However, commercial LIBs met their ceiling of specific capacity, which is heavily restricted by the limited choices of inorganic cathode materials in addition to suffering from environmental issues brought by the use of transition metals\(^7\)–\(^9\). Meanwhile, development of sodium-ion batteries (SIBs) would be the most attractive alternative for portable rechargeable systems due to their abundance of sodium resources and excellent capacity (1166 Ah kg\(^{-1}\)) of Na\(^+\)/Na for the redox reactions. However, this is also restricted by the limited cathode materials, and it is not easy to migrate the excellent Li\(^+\) intercalation compounds to SIB electrodes because of the size restriction caused by the large different crystal structures.\(^10\)–\(^16\) In this respect, new cathode materials going beyond traditional materials which are mainly based on transition-metal oxides are being studied. As alternatives, organic cathode materials have drawn much attention in recent years because they are not restricted by counterions and are capable of providing high theoretical capacity owing to the multielectron reactions. Further, their structures can be functionalized so that their operate voltages, solubility, and ionic conductivity can be tuned.\(^9\)–\(^10\)–\(^16\) In addition, a polymer with highly electroactive functional groups and a stable skeleton can potentially be a powerful cathode candidate because its redox kinetics are intrinsically faster than that of inorganic intercalation cathodes and can avoid the unwanted dissolution in aprotic electrolyte, which is always suffered by small organic molecules.\(^21\),\(^22\)

Among various organic polymers, conjugated carbonyl polymers have received intense attention in the past few years due to their higher theoretical capacity.\(^8\),\(^17\)–\(^20\),\(^23\) For example,
poly(anthraquinonyl sulfide) (PAQS) shows an excellent theoretical capability of 225 mAh g\(^{-1}\) and potentially has better stability compared with other organic cathode materials because the polymers based on the thiether bond are completely insoluble in any solvent.\(^{21,22}\) However, the low mass density and intrinsically poor electronic conductivity of the polymers result in low utilization and poor rate performance.\(^{8,17,24}\) To surmount the electrical insulation of polymers, a considerable amount of conductive additives which are electrochemically inactive are usually introduced to create electrodes, leading to significantly compromised electrochemical performance of the whole electrode and greatly impeding the practical use of organic active materials.\(^{16,21,22,24,25}\) To address these issues, it has been demonstrated that combining graphene, carbon nanotubes, or other nanocarbon materials which have high conductivity and large surface area with the polymer is an effective approach for achieving advanced organic cathodes.\(^{26−29}\) As a result, some polymer/nanocomposites with improved performances were prepared by method of ball milling and in situ polymerization.\(^{30−35}\) Despite these achievements, many of them still show unsatisfactory capacities for the entire electrode. Briefly, the method of ball milling limits improvement of the conductivity of the electrode and influences the performance of active polymer because binders are typically electronic insulators as well as electrochemically inactive and cannot provide an effective interaction between conductive agent and active polymer because of the limited contact area. The method of in situ polymerization is a promising strategy to develop favorable structures with strong coupling between conductive agent and in situ grown active materials as well as high mass loading. However, the application range of this method is limited because it is unavoidable that serious side reactions may occur in many reaction systems during the process of in situ polymerization, which may obtain unwanted structures of polymer and conductive agent in the final product, resulting in poor performance when used in batteries. Therefore, it remains a significant challenge to develop an effective and universal method to construct advanced polymer cathodes with high active material content and excellent electrochemical performance for both LIBs and SIBs, which are essential for real-world applications.

Herein, we report a universal dispersion—assembly method that is a combination of sonication and reduction processes to prepare self-assembled graphene/PAQS composite aerogel (GPA) which can be mechanically pressed into a highly conductive and flexible film and used directly as a free-standing cathode. The dispersion—assembly method can make PAQS dispersed uniformly on the graphene surface and effectively wrapped by graphene sheets. Remarkably, due to the intrinsic structural advantages of the three-dimensional (3D) graphene framework and high mass loading of PAQS as well as intimate interaction between them which enables rapid charge transfer, GPA was directly used as a binder-free cathode in LIB, delivering a very high discharge capacity of 156 mAh g\(^{-1}\) at 0.1 C with an ultrahigh utilization of PAQS (94.9%) and an impressive rate performance of 102 mAh g\(^{-1}\) at a high current density of 20 C. Moreover, GPA demonstrated an outstanding cycle stability with 84.1% capacity retention after a long term of 1000 cycles at 0.5 C. The electrochemical performance of the GPA cathode is superior to those of most organic cathodes that have been reported before. Furthermore, GPA can also be used as a cathode for SIB, gaining a high initial capacity of 157 mAh g\(^{-1}\) with a utilization ratio (91.1%) of PAQS, nearly equal to that in LIB, and a superior rate capability with 72 mAh g\(^{-1}\) at 5 C, which is among the highest value that has been achieved for sodium–organic batteries when normalized by the whole electrode mass. It also exhibits an excellent cycling stability with 71.4% capacity retention after 1000 cycles at 0.5 C. Such outstanding electrochemical performances achieved by a single polymer cathode for both LIB and SIB simultaneously have rarely been demonstrated in previous studies.

2. EXPERIMENTAL SECTION

2.1. Synthesis of PAQS. The PAQS was synthesized using the method reported by Song and his co-workers in 2009.\(^{21}\) Briefly, 1,5-dichloroanthraquinone (0.554 g, 2 mmol) dissolved in 5 mL of 1-methyl-2-pyrroldinon (NMP) was added into the mixture, and the reaction proceeded under refluxing and stirring overnight. The product was centrifuged after cooling to room temperature, washed several times with deionized water and acetone, and then dried at 120 °C for 12 h.

2.2. Synthesis of GPA Composites. Graphene oxide (GO) was synthesized using a modified Hummers method.\(^{36}\) We synthesized three different GPA composites with different weight ratios. First, we added 24, 14, and 9 mg PAQS into 5 mL of 2 mg/mL GO/NMP solution, respectively. The mixtures of PAQS and GO suspension in NMP were sonicated for 2 h followed by addition of 150 µL of 1 M sodium ascorbate aqueous solution to reduce the GO into 3D graphene at 95 °C for 1.5 h without stirring and obtain the composites simultaneously. The as-prepared samples were dipped into DI water and washed three times. Finally, the composites were frozen for 2 h and dried under vacuum for 12 h to obtain GPA composites with mass ratios of 2:8, 3:7, and 4:6 between graphene and PAQS, respectively.

2.3. Characterizations. Scanning electron microscopy (SEM) measurements were performed on a Zeiss Ultra-55 field emission scanning electron microscope. Transmission electron microscopy (TEM) studies were conducted on a FEI Tecnai G2 20TWIN electron microscope at an operating voltage of 200 kV. Fourier transform infrared (FTIR) spectral measurements were performed using a PerkinElmer Paragon 1000. Raman measurements were recorded on an Invia/Reflex Lasser Micro-Raman spectrocope (Horiba Jobin Yvon, Franch) with excitation laser beam wavelength of 532 nm. X-ray diffraction (XRD) analysis was performed on a Rigaku D/Max 2500 X-ray diffractometer with Cu K\(_{\alpha}\) radiation (\(k = 1.54 Å\)) at a generator voltage of 40 kV and a generator current of 20 mA with a scanning speed of 5° min\(^{-1}\) from 10 to 50°.

2.4. Electrochemical Measurements. Electrochemical experiments were carried out in CR2016 coin-type cells. The GPA composites were directly pressed and cut into pieces as the working electrodes for LIB and SIBs with an areal mass loading of ~2.3 mg/cm\(^2\), and the GPA film samples were cut into rectangles for the conductivity measurement by the four-probe system (Keithley 6221 and 6514). The pristine PAQS electrode was prepared by mixing pure PAQS, carbon black (Super-P), and poly(vinylidene fluoride) (PVDF) at a weight ratio of 60:30:10 and pasted on a glass slide for conductivity measurements or pure Al foil (99.6%) with an areal mass loading of ~2 mg/cm\(^2\) for SIB and LIB tests. For LIB fabrication, metallic lithium foil was used as the counter electrode. The electrolyte was 1 M LiTFSI in 1,2-dimethoxyethane (DME)/1,3-dioxolane (DOL) (1/1 by volume ratio). The polypropylene (PP) film (Cellgard 2400) was used as the separator. For SIB fabrication, the metallic sodium foil was used as the counter electrode. The electrolyte was 0.1 M NaPF\(_6\) in DME/DOL (1/1 by volume ratio). The glass fiber was used as the separator. The cells were assembled in an argon-filled glovebox with the concentrations of moisture and oxygen below 0.1 ppm. Cyclic voltammetry (CV) was performed at a scan rate of 1 mV/s on a CH 660D electrochemical workstation (CH Instruments). The galvanostatic charge–discharge experiments were tested using an LANHE instruments testing system in the potential range from 1.5 to 3.5 V for LIBs and 1.2−2.8 V for SIBs at different current rates.
3. RESULTS AND DISCUSSION

The typical synthesis process of GPA composite is shown in Figure 1a. We synthesized PAQS first and mixed it with GO in N-methylpyrrolidone (NMP) to form a homogeneous dispersion upon sonication. Then, it formed a gel after the system was heated at 95 °C for 1.5 h without stirring using sodium ascorbate as the reducing agent. Meanwhile, the solution became clear, indicating the brown PAQS particles were effectively encapsulated into the graphene sheets (Figure 1b). Finally, GPA composite was obtained after a freeze-drying process (Figure 1c). The mass percentage of PAQS in typical GPA was determined to be about 70% by thermogravimetric analysis (TGA, Figure S1a).

Figure 1. (a) Schematic of the synthesis process of GPA. (b) Homogenous mixture of GO and PAQS in NMP and reduction and self-assembly of GO to form 3D graphene framework with encapsulated PAQS particles. (c) Freeze-dried aerogel of graphene/PAQS composite. (d) Preparation of a flexible binder-free GPA film electrode by mechanical pressing. (e) Synthetic route to PAQS. (f) Reversible redox mechanisms of PAQS in LIBs and SIBs.

Figure 2. (a) FTIR of SGA, PAQS, and GPA. (b) XRD patterns of PAQS, GPA, and SGA. (c) Raman of SGA, PAQS, and GPA.

Figure 3. (a) SEM image of pristine PAQS. (b and c) TEM images of GPA with different magnifications. (d) Low- and (e) high-magnification SEM images of GPA. (f–i) Elemental mapping images of GPA (by SEM): carbon (g), oxygen (h), and sulfur (i) distribution in the selected area.
The self-assembled graphene aerogel (SGA) was also prepared by the same method without adding PAQS. The formation of PAQS and GPA were confirmed through FTIR (Figure 2a). The appearance of 1129 and 1413 cm\(^{-1}\) bands in the FTIR spectra, which can be assigned to the ring-sulfur stretching and ring stretching of the sulfur disubstituted aromatic ring, respectively, is evidence of the successful synthesis of PAQS.\(^{35}\) For the GPA composite, the C═C vibration from unsaturated sp2 C═C bonds (1619 cm\(^{-1}\)) is significantly downshifted, indicating a charge transfer between the PAQS and graphene due to the intimate interaction between them. The XRD pattern of the GPA composite (Figure 2b) shows two peaks at 2\(\theta\) = 23.2 and 24.8\(^{\circ}\), the same as that of pure PAQS, indicating the particles of PAQS were successfully wrapped by the graphene sheets in the 3D graphene framework. Raman spectra of the PAQS and GPA composite also demonstrate that PAQS particles were effectively embedded during the process of synthesizing the composites (Figure 2c). The Raman peaks at 1667 and 1585 cm\(^{-1}\) correspond to the C═O of anthraquinonyl group in PAQS, and the peaks at 1335 and 1597 cm\(^{-1}\) are D and G bonds from graphene. Compared to that of the pure graphene aerogel, a small red shift can be found in the Raman spectra of GPA, also supporting the charge transfer between the three-dimensional graphene framework and PAQS.\(^{38}\) Furthermore, we also tested the Raman spectra of samples with different mass ratio of PAQS (Figure S1b). It is easy to find that, with more PAQS added in the precursor mixture, the peaks of PAQS in the final product become more obvious in the spectra, indicating that this method allows plenty of PAQS to be impregnated into the graphene.\(^{39,40}\)

The morphology and microstructure of pristine PAQS and as-prepared GPA composites were characterized by field emission scanning electron microscopy (FESEM) and TEM, respectively. The particles of pristine PAQS with sizes ranging from hundreds of nanometers to several micrometers were highly stacked (Figure 3a). TEM images of GPA (Figures 3b and c) show that polymer particles (100–200 nm) were uniformly dispersed on the graphene surface and wrapped by graphene sheets, indicating that ultrasonication can effectively disperse PAQS particles in NMP solution and decrease the particle size to some extent, and these particles can be effectively encapsulated within graphene sheets via the \(\pi-\pi\) stacking interaction during the 3D self-assembly of graphene. The FESEM images of GPA (Figures 3d and e) show an interconnected 3D graphene framework with pore sizes ranging from several micrometers to submicrometers, which is beneficial for electrolyte penetration and enables fast ion transportation. Both SEM and TEM images revealed that most PAQS particles are uniformly wrapped between the graphene walls, indicating the efficient integration of the 3D graphene framework with active PAQS particles. Furthermore, the elemental mappings of the GPA composite for C, O, and S distribution also demonstrate that the PAQS particles were homogeneously distributed in the composite (Figures 3f–i), which were consistent with FESEM and TEM results.

The as-prepared GPA with a thickness of \(~4\) mm could be greatly compressed to form \(~30\) μm-thick GPA film (Figure 4a) with a packing density of 0.75 g/cm\(^3\) calculated by dividing the areal mass loading (2.3 mg/cm\(^2\)) by thickness and a conductivity of 3.6 S/cm. The 3D continuous porous network was well-maintained in the GPA film, and the PAQS particles were still wrapped by the graphene sheets (Figures 4b and c), which indicated the intrinsically excellent mechanical stability of GPA. Furthermore, after the GPA film was folded and unfolded, there was no obvious change in the electrical conductivity, indicating a superior mechanical flexibility for the GPA film (Figure 4d).

Together, these structure characterizations confirm the intimate interaction between the unique 3D porous graphene and small PAQS particles, which can afford rapid charge transfer from the graphene substrate to PAQS. The mechanically strong and electrically conductive GPA film was directly used as cathode material for the electrochemical test in coin-type cells with lithium foil as the counter electrode (Figure 5). For comparison, the pristine PAQS electrode was fabricated by mixing 60% active material, 30% super P, and 10% PTFE (denoted as C-PAQS) in which the particle sizes of PAQS are about 1 μm and relatively larger than those in GPA (Figure S2a). CV was conducted to compare the lithium-ion intercalation/deintercalation behaviors of C-PAQS and GPA between 1.2 and 3.2 V at a scan rate of 1 mV/s (Figure 6a). For C-PAQS, the reduction phase was observed at around 2.07 V, corresponding to the insertion of Li ions, while the oxidation phase was around 2.52 V, reflecting the deinsertion of Li ions and consistent with the charge–discharge profiles of C-PAQS (Figure S2b). For GPA, the reduction and oxidation phase are around 2.11 and 2.39 V,
The high-to-medium frequency region of the semicircle was assigned to the charge-transfer resistance (\(R_{ct}\)). Electrochemical impedance spectroscopy (EIS) was further performed (Figure S3). Meanwhile, the capacity and discharge plateau of GPA gradually decreased with the increase in current density because of the unavoidable electrochemical polarization. Electrochemical impedance spectroscopy (EIS) was further performed (Figure S3). The high-to-medium frequency region of the semicircle was assigned to the charge-transfer resistance (\(R_{ct}\)) between electrode and electrolyte and an inclined line in the low frequency part corresponding to Warburg impedance (\(Z_w\)) associated with lithium-ion diffusion in the electrode. \(^1\)

It can be found that GPA exhibited a lower \(R_{ct}\) which can be ascribed to the increased conductivity mainly caused by the structure advantages of the 3D graphene network (Table S1).

When considering the performance of a whole electrode, the proportion between active material and conductive additives can seriously influence the performance. In general, with the increased mass loading of active materials and reduced the proportion of conductive agent, the conductivity of the whole electrode will be decreased, leading to a poor electrochemical performance. However, although electrical conductivity of electrodes and the utilization ratio of active materials can be obviously improved by adding a large amount of conductive additive, the electrochemical performance of the electrode may still be unsatisfactory because the capacity was compromised by the typically electrochemical inactive conductive additive. Therefore, to explore the best ratio between graphene and active material for the optimum performance, we further synthesized another two GPA composites with different weight ratios of PAQS, which were noted as GPA-H (80 wt % PAQS) and GPA-L (60 wt % PAQS) and whose mass loadings were characterized by TGA (Figure S1b).

CV curves of GPA-H and GPA-L are displayed in Figure 6a. It is important to note that the polarization of GPA becomes weaker and the rate of electron transfer is improved significantly with the increasing content of graphene, evidenced by smaller separation between the redox peaks. The EIS of GPA-H and GPA-L were also tested and indicated that \(R_{ct}\) became lower with the increased amount of graphene (Figure S3 and Table S1). The rate performances of all kinds of electrodes were tested and shown in Figure 6c. C-PAQS delivered a discharge capacity of 108 mAh g\(^{-1}\) at 0.1 C, corresponding to a PAQS utilization ratio of 80% considering that the theoretical capacity of PAQS is 225 mAh g\(^{-1}\) based on a two-redox process (Figure 1f; for detailed calculation method, see Supporting Information). In contrast, the GPA exhibited a much higher capacity of 156 mAh g\(^{-1}\) at 0.1 C based on the total mass of the entire electrode. Under the same testing condition, three-dimensional graphene aerogel itself showed a low capacity of only about 22 mAh g\(^{-1}\) and thus made a negligible contribution (\(-6.6\) mAh g\(^{-1}\)) to the capacity based on its weight percentage of 30 wt % in the composite (Figure S4). Therefore, the utilization ratio of PAQS in the GPA was determined to be 94.9%, much higher than that of C-PAQS. The discharge capacity of GPA at an ultrahigh current density of 20 C still remained 65.4% of that at 0.1 C, delivering 102 mAh g\(^{-1}\), whereas C-PAQS showed nearly no electrochemical activity at 20 C. The GPA demonstrates much better rate capability than that of C-PAQS at each current density, which may be largely attributed to fast electrode reaction of PAQS by its efficient integration with the 3D graphene framework. Correspondingly, GPA shows conductivity much higher than that of C-PAQS (1.1 S/cm). The prominent performance of our GPA was higher than any other PAQS electrode and most other polymer electrodes in LIBs (Table S2).

The high-rate performances of GPA-H and GPA-L were studied under the same test conditions. As shown in Figure 6c, the capacities of GPA-H and GPA-L at 0.1 C are 171 and 139 mAh g\(^{-1}\), corresponding to the utilization ratios of 92.6 and 96.4%, respectively. As expected, with the graphene content increasing, the utilization ratio of PAQS tends to be higher because more graphene in the GPA composites means more ions and electron transport pathways to achieve full usage of PAQS. The discharge capacity of GPA-L at an exceptionally high current density of 30 C still remained 60% of that at 0.1 C, delivering 83.1 mAh g\(^{-1}\), which is slightly higher than that of GPA, indicating that rate performance can be improved obviously with the help of
the increased content of graphene. Meanwhile, GPA-H showed much lower electrochemical activity at the same current density. These results demonstrate that it is the highly interconnected 3D graphene framework with the wrapping function that ensures excellent conductivity and efficient ion transport to enable rapid and adequate electrochemical reaction of PAQS. When considering the capacity performance of the whole electrode, it is obvious that the performance of GPA is better than that of GPA-H at almost all current densities, while GPA-L is just slightly better than GPA until the current density achieves 30 C, indicating that the capacity performance cannot be improved obviously by continuing to decrease the proportion of PAQS when its weight mass has reached 70 wt % in the composite. Correspondingly, GPA-L showed conductivity (3.9 S/cm) slightly higher than of GPA (3.6 S/cm), which is much higher than that of GPA-H (2.6 S/cm). Therefore, the proportion of PAQS in GPA is optimum among these three different composites in the aspect of comprehensive electrochemical performance.

The sustainable cycling performance of the GPA composite was further highlighted by the outstanding galvanostatic discharge/charge performance after 1000 cycles at 0.5 C. As shown in Figure 6d, the initial reversible capacity of the GPA cathode was 138 and reached 157 mAh g⁻¹ after several cycles of activation. After 500 cycles, the capacity of GPA still remained at 142 mAh g⁻¹, corresponding to 90% of the highest capacity. Furthermore, after a long term of 1000 deep cycles, the capacity still reached as high as 132 mAh g⁻¹ with a decay rate of 0.015 mAh g⁻¹ cycle⁻¹, and thus, the capacity remains 84.1% at the 1000th cycle. Such excellent cycling stability has rarely been demonstrated in previous work and indicates that the wrapping structure of PAQS particles by the 3D graphene framework can accommodate the volume change and promote the structural integrity of PAQS during the charge/discharge process.

To explain the outstanding electrochemical performance of GPA, ESI was performed, and the morphology and microstructure of the GPA after 1000 cycles in LIBs were characterized by SEM and TEM (Figure 7). From Figure 7a and Table S1, it can be found that the increase in the Rct of GPA was not obvious after 1000 cycles (Figure 7a). SEM and TEM images revealed that most PAQS particles in GPA were still uniformly distributed and intact in 3D graphene frameworks after 1000 cycles (Figures 7b and c), illustrating the ideal protection of the PAQS polymer by the 3D graphene framework. These results can be attributed to two main reasons. First, ultrasonic methods can promote the polymer particles to be dispersed uniformly and prevent accumulation among the particles to effectively reduce the resistance as well as facilitate the charge transfer in the electrode. Meanwhile, the polymer particles can be tightly wrapped by the graphene sheets via π–π stacking interaction during the 3D self-assembly process of graphene so that the graphene can protect the polymer particles and improve the conductivity of them effectively. Second, the mechanically strong 3D graphene with hierarchical porous structure can not only offer a continuous network of open channels for efficient ion transport but also provide a multidimensional electron transport pathway to achieve rapid and exhaustive electrochemical reaction of active polymers.

As mentioned before, organic compounds show little sensitivity to the counterion theoretically due to their “soft” molecular structure. Therefore, we also evaluated the electrochemical performance of GPA as the SIB cathode and expected desirable performance. As demonstrated in Figure 8a, the CV curve of pristine PAQS clearly exhibits two pairs of redox peaks at 1.53/1.71 and 1.85/2.19 V respectively, which are associated with the reduction of the first and second carbonyl groups to the anions and are consistent with the charge–discharge profiles of C-PAQS (Figure 5Sa). Similarly, GPA shows two redox peaks at 1.58/1.79 and 1.92/2.18 V at a scan rate of 1 mV/s, and the curves are quite consistent with the charge–discharge profiles (Figure 8b) in which there are two slope voltage curves of about 1.75 and 2.16 V in the charge profile and two slope voltage curves of about 1.54 and 1.82 V in the discharge profile. It indicates that the uniquely designed GPA electrode also exhibits obviously faster electrochemical kinetics for sodium-ion transportation. In contrast to the CV curves in LIBs, the two pairs of redox peaks from GPA and C-PAQS are well-separated in SIBs, probably due to a larger steric and/or Coulombic repulsion for the second step Na⁺ association when the first Na⁺ ion is associated with the anthraquinonyl group of the polymer.

The GPA electrode delivered a very high reversible specific capacity of 157 mAh g⁻¹ at 0.1 C based on the mass of entire electrode and achieved a high PAQS utilization ratio of 91.1%, which is comparable to that in LIBs (Figure 8c). SGA itself achieved a discharge capacity of only 45 mAh g⁻¹ at the same current density (Figure 5Sb) and also made a negligible contribution about 13.5 mAh g⁻¹ to the reversible capacity of GPA. By contrast, the reversible capacity of the C-PAQS electrode reached only 93 mAh g⁻¹ at 0.1 C based on the whole mass of the electrode, corresponding to a much lower PAQS utilization ratio of 68.9%. At a high current density of 5 C, GPA can still achieve a high specific capacity of 72 mAh g⁻¹, which is higher than almost all organic cathodes when normalized by the mass of the whole electrode (Table S3). Furthermore, the GPA electrode exhibited an excellent cycling performance (Figure 8d). It delivered an initial discharge capacity of 138.3 mAh g⁻¹ and retained a capacity of 98.7 mAh g⁻¹ (71.4% of its initial capacity) after 1000 cycles with a Coulombic efficiency near 100%. Such outstanding cycling stability is much better than those of most reported sodium-organic batteries and potentially satisfies the demand of practical use. Similar to that in LIB, the increase in Rct of GPA was not significant after 1000 deep cycles in SIB (Figure S6 and Table S4). The similarly prominent electrochemical
performance of GPA for SIBs indicates that with our method it is simple to transplant promising organic LIB cathodes to SIBs despite the large ionic radius difference between Na\(^+\) and Li\(^+\), which is highly desirable for the metal-organic batteries.

As mentioned above, in situ polymerization is a promising strategy to produce high-performance composite materials; however, it suffers from unavoidable side reactions in many reaction systems. We also tried to synthesize a graphene/PAQS composite using in situ polymerization and performed the same electrochemical characterizations (Figure S7). We found that it was difficult to obtain a well-defined structure of PAQS as well as a 3D graphene network, which leads to a performance much worse than that of the GPA composite, which could be ascribed to the serious side reactions between GO and Na\(_2\)S during the reaction process.

4. CONCLUSION

In conclusion, we developed a simple dispersion–assembly method to prepare GPA composites as a highly flexible high-performance cathode for both LIB and SIB. This methodology can create a unique porous structure with the PAQS particles uniformly dispersed within the skeleton of 3D graphene framework and tightly encapsulated by graphene sheets to ensure rapid charge transfer between graphene and PAQS and fast charge transport throughout the whole composite. The flexible and binder-free GPA can be directly used as a LIB cathode and delivers a capacity of 102 mAh g\(^{-1}\) at a high current density of 20 C and excellent cycle stability with 84.1% retention after 1000 cycles at 0.5 C. Furthermore, GPA composites also show superior rate capability with 72 mAh g\(^{-1}\) at 5 C and excellent cycling stability with 71.4% retention after 1000 cycles at 0.5 C when used as SIB cathodes, which have rarely been reported in previous work. We believe this universal dispersion–assembly strategy can be extended to synthesize a wide range of 3D graphene/polymer composites with controlled microstructures as high-performance electrodes for LIBs and SIBs as well as other promising battery systems such as Al-ion, K-ion, and Mg-ion batteries.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b03687.

Further details of the in situ polymerization, EIS measurements, electrochemical performance, and FTIR and Raman spectroscopy measurements (PDF)

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**Notes**

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