High-Quality Graphene Microflower Design for High-Performance Li–S and Al-Ion Batteries

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Poor quality and insufficient productivity are two main obstacles for the practical application of graphene in electrochemical energy storage. Here, high-quality crumpled graphene microflower (GmF) for high-performance electrodes is designed. The GmF possesses four advantages simultaneously: highly crystallized defect-free graphene layers, low stacking degree, sub-millimeter continuous surface, and large productivity with low cost. When utilized as carbon host for sulfur cathode, the GmF-sulfur hybrid delivers decent areal capacities of 5.2 mAh cm \(^{-2}\) at 0.1 C and 3.8 mAh cm \(^{-2}\) at 0.5 C. When utilized as cathode of Al-ion battery, the GmF affords a high capacity of 100 mAh g \(^{-1}\) with 100% capacity retention after 5000 cycles and excellent rate capability from 0.1 to 20 A g \(^{-1}\). This facile and large-scale producible GmF represents a meaningful high-quality graphene powder for practical energy storage technology. Meanwhile, this unique high-quality graphene design provides an effective route to improve electrochemical properties of graphene-based electrodes.

1. Introduction

Graphene has greatly prompted the development of electrochemical energy storage (EES) technologies since its first isolation in 2004. Recent years have witnessed many breakthroughs in multiple EES systems using graphene materials, such as sulfur cathode and lithium anode of lithium–sulfur (Li–S) battery, silicon anode and metal oxide cathode of lithium-ion battery, cathode of lithium–oxygen battery, sodium-ion battery, and aluminum-ion (Al-ion) battery. These advances can be attributed to the key graphene characteristics that exactly meet the demands of EES applications and outperform those of other materials. Specifically, perfect \(\pi-\pi\) conjugated network leads to an ultrahigh charge carrier mobility of \(2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\), which facilitates the transportation of electrons and improves electric conductivity of graphene-based composite. Highly continuous graphene nanosheets provide an incessant highway for electron transportation, further reducing the electrochemical polarization. The large theoretical specific surface area \(2630 \text{ m}^2 \text{ g}^{-1}\) and unstuck graphene surface contribute to better loading and distribution of nanosized active materials. In addition, the remarkable mechanical properties of graphene can preserve the integrity of electrode in the volume expansion/shrink process during battery operation. Nevertheless, it is worth mentioning that these supreme properties are only achieved in the highest quality graphene: a single-layer, defect-free graphene sheet as large as possible. Hence, improving the quality of graphene, especially three major parameters of defect concentration, stacking degree, and lateral size of graphene sheets, is of crucial importance.

Actually, the large-scale production of high-quality graphene has been generally regarded as the most ambitious challenge to address before practical application of graphene materials. In this respect, chemical exfoliation of graphite especially oxidation into graphene oxide (GO), has been commercialized, and large size single-layer GO can be produced in ton-level scale with relatively low cost. GO is generally reduced into chemically converted graphene (CCG) for further applications in electrodes. However, CCG still contains abundant defects, greatly limiting the vital electric conductivity and other properties. Hence, reducing the defect concentration is the basic concern for real applications of GO and CCG in EES technologies. Even though methods such as heteroatom doping, chemical vapor deposition, and deliberate design of microsized morphology, whereas their productivity, precise controllability, high reproducibility, and compatibility with the industrial cast-coating technology (particularly for those monolithic graphene bulks) are challenges hard to be resolved. Therefore, it is urgent to find a new production method of graphene, especially powder-formed graphene material that accords with requirements in both quality and quantity to satisfy the demands from EES applications.

Here, we propose a new facile and highly controllable strategy to produce high-quality graphene powder, that is, crumpled graphene microflower (GmF), in large scale. Through our design, three parameters of high-quality graphene are simultaneously achieved in GmF: (i) raw materials of ultralarge...
graphene oxide (ulGO) sheets supply the sub-millimeter continuous graphene surface;[24] (ii) shrinkage and compression of ulGO sheets during spray-drying lead to a crumpled flower-shaped morphology, preventing graphene sheets from being highly stacked;[25] (iii) high-temperature annealing restores all the defect content to gain perfect π–π conjugated network in graphene.[26] Benefiting from these merits, the electrochemical properties of GmF-based electrodes are greatly improved: the areal capacity of GmF-sulfur cathode reaches 5.2 mAh cm$^{-2}$, specific capacity of GmF cathode of Al-ion battery attains 100 mAh g$^{-1}$ with 100% capacity after 5000 cycles, and ultra-high-rate capability of fast charging/discharging in 18 s.

2. Results and Discussion

2.1. Preparation of High-Quality GmF

Figure 1a schematically illustrates the fabrication process of GmFs. A barrel of ulGO solution (Figure 1b) was connected with a spray-drier to continuously prepare brown graphene oxide flower (GOF) powder with a productivity of kilogram per day (Figure 1c). The GOF was first chemically reduced into black colored reduced graphene flower (rGF) by hydrazine, and further reduced by thermal annealing at 2000 °C to gain defect-free GmF2000. Subsequently, a given amount of sulfur was infiltrated into the rGF and GmF through a melt-diffusion process, affording carbon–sulfur cathode material (rGF-S, GmF2000-S, and GmF3000-S, Table S1, Supporting Information).

During the spray-drying process, rapid evaporation of droplets leads to shrinkage and compression of ulGO sheets,[25] affording a flower-like corrugated and fluffy morphology with diameters of 1–6 μm as revealed in typical scanning electron microscopy (SEM) images (Figure 1d) and transmission electron microscopy (TEM) images (Figure S1, Supporting Information).[27,28] After reduction and high-temperature annealing treatment, such morphology was well maintained (Figure 2a,b) with numerous nanosized channels observed in the fold sites (Figure 2c,d), preventing graphene from being stacked together. In comparison, the plain graphene surface leads to a high stacking degree in reduced graphene aerogel (rGA, Figure S2, Supporting Information), which was prepared by freeze-drying of concentrated ulGO solution.[29] In respect of atomic structure, rGF contained sp$^3$ carbon, vacancy holes, and totally disordered carbon network observed by high-resolution transmission electron microscopy (HRTEM, Figure 2e). Even though preliminary annealing reduction at 2000 °C enabled most defect configurations to be restored into the sp$^2$ carbon hexagonal 2D lattice, random patches of polygons and atomic vacancy holes still remained in GmF2000’s 2D lattice. These polygons and vacancy holes are direct visual sites of defects in π–π conjugated network, impeding the formation of long-range crystalline order along the graphene 2D lattice (Figure 2f). Annealing reduction at 3000 °C totally healed the defect configurations to achieve graphene planar honeycomb crystal lattice that is entirely composed of sp$^2$-bonded carbon hexagons, displaying long-range crystalline honeycomb domains (Figure 2h). Inverse fast Fourier transform (IFFT) was conducted on the fast Fourier transform (FFT) results (of the region outlined by the square, inset in Figure 2h) to obtain an atomic-resolved lattice image, exhibiting the graphene planar honeycomb crystal lattice more clearly. These perfect 2D lattices in both HRTEM images and IFFT images are direct

![Figure 1. a) Schematic illustration of the fabrication of GmF3000-S and the corresponding local structure. b) SEM image of ulGO. c) Photograph of 100 g GOF and rGF. d) SEM image of rGF. e) Cartoon of a folded edge and channel of three graphene layers. Scale bars: (b) 100 μm and (d) 1 μm.](image)
evidences to support the perfect crystallinity and absence of topical defects in GmF3000.

Raman spectroscopy was applied to probe the defect concentration of graphene microflowers (Figure 2k). After chemical and thermal reduction, a decreased intensity ratio ($I_D/I_G$) of D band (at $\approx 1350$ cm$^{-1}$, resulted from the disordered defect-induced double-resonant Raman process$^{[32]}$) to G band (at $\approx 1598$ cm$^{-1}$, for in-plane vibration of highly symmetrical sp$^2$ carbon hexagonal) is presented: from 1.68 for rGF (abundant defects and oxygen-containing groups) to 0.0521 for GmF2000 (few defects remain), then to 0.0276 for GmF3000 (defect-free). Notably, the $I_D/I_G$ value of GmF3000 is even much lower than those of graphene grown by chemical vapor deposition,$^{[33]}$ mechanical exfoliated graphene,$^{[34]}$ highly defective GO,$^{[16]}$ and even natural graphite (0.0359–0.0721). This demonstrates gradual disappearance of defects in the atomic structure owing to the perfect restoration of highly crystallized graphene during the high-temperature annealing. The 2D band is single and broad with a longer full width at half maximum (FWHM) of 70 cm$^{-1}$ which doubles that of the 2D band of single-layer graphene, and the intensity ratio of 2D band to G band is close to 1, revealing few-bilayer turbostratic graphene structures in GmFs instead of highly AB-stack graphitic structure (black line in Figure 2k) after high-temperature annealing.$^{[26,35]}$ The X-ray photoelectron spectroscopy (XPS) measurements verified that the oxygen concentration decreased from 11.82% for rGF to negligible for 3000-rGF (Figure S3c, Supporting Information), supporting the removal of defective oxygen-containing groups.

In the X-ray diffraction (XRD) pattern of GmF3000, a broad dispersive peak spanning from 15° to 35° is observed together with a moderate sharp (002) peak at $\approx 26°$, very small (100)/(110) peak at 42°–45° and a weak (004) peak at 54° (Figure 2l), suggesting only slight, disordered stacking of self-folded few-layer graphene sheets.

Based on the basic characterizations above, we can define GMF-3000 as a new kind of scalable high-quality graphene material according to the three major technical indexes aforementioned. GmF3000 was sized 2–6 µm on average in 3D as observed in SEM and TEM images (Figure S1f, Supporting Information), providing sub-millimeter continuous graphene surface for facilitating long-range electron transportation.$^{[24]}$ In the case of defect concentration, our GmF-3000 achieved a very low defect concentration confirmed by HRTEM and IFFT images, Raman spectra, and XPS results. Almost total removal of defects (especially these oxygen-containing groups) in graphene 2D lattice restored the large-area perfect π–π conjugated graphene structure and enabled our GmF3000 to gain higher electronic conductivity than the defective GmFs (Table 1).$^{[14,17,36]}$ As to the stacking degree, our GmF3000 exhibited a few-bilayer (Figure 2g) turbostratic graphene structures to utilize more graphene surface than the highly stacked graphene. Significantly, the fabrication process of our GmF3000 is based on mature industrial production technology, raw materials, and facilities. Comparing with other techniques to improve the quality of graphene such as heteroatom doping, our methodology is more feasible, scalable, repeatable, and controllable (without uncertain doping sites and amounts), which guarantees kilogram-scale productivity of precise-structured GmF3000. These merits of GmF exactly meet the requirements in both quality and quantity for large-scale production. In particular, this scalable
GmF exists in the form of powder guaranteeing its feasibility and compatibility with industrial processing technology, while it is of high quality as those graphene materials synthesized by chemical vapor deposition.

### 2.2. Electrochemical Performance of GmF-S Composites

To demonstrate the significance of high-quality graphene design in EES technologies, we first inspected GmF as carbon host in sulfur cathode of promising high energy density Li–S batteries,[37,38] whose electrochemical performances are highly dependent on the properties of carbon hosts. Typical cyclic voltammetry (CV) curves of GmF-S electrodes demonstrate the stable and reversible lithiation/delithiation behaviors of the GmF-sulfur cathode (Figure S5a, Supporting Information).[39] The cathodic peaks at 2.3 and 2.01 V can be ascribed to the reduction of sulfur to soluble polysulfides and further to insoluble low-order S$^2$-, while the anodic peaks at 2.3 and 2.4 V are assigned to the oxidation of lithium sulfides to polysulfides and further to sulfur. The long-term cycling performances of different electrodes were analyzed at different current densities to demonstrate the advantages of high-quality graphene design. Compared with the reduced graphene aerogel-sulfur (denoted as rGA-S) hybrid, the rGF-S composite exhibited higher capacity and less decay (Figure 3a), which can be attributed to the low stacking degree and crumpled morphology of rGF that enable better employment of 2D graphene sheets.[19] Specifically, the sulfur particles were supposed to be located on the surfaces of graphene especially crumpled sites (Figure 1a), rather than embedded into highly stacked graphene layers.

Even though good capacity (1020 and 1000 mAh g$^{-1}$ at constant current rates of 0.2 and 0.3 C, 1 C = 1675 mA g$^{-1}$, Figure S5b, Supporting Information) and high capacity retention over ultralong cycle life (0.047% and 0.056% decay cycle$^{-1}$ at 0.5 and 1 C over more than 900 cycles, Figure 3c) have been achieved by our rGF-S composite, there is still a critical problem to be solved. The well-known greatest advantage of Li–S battery over LIB is its higher energy density, which mainly attributes to high capacity of sulfur cathode. In this respect, as stated by Goodenough and co-workers,[40] considering the commercially available LIB cathode has reached an areal capacity of 2 mAh cm$^{-2}$ with average discharge voltage of 3.5 V, only if the areal capacity of sulfur cathode exceeds 3.3 mAh cm$^{-2}$ can Li–S batteries gain higher energy density than commercially available LIB, for the average discharge voltage of sulfur cathode only reaches 2.1 V.[40] However, when the areal loading of rGF-S composite was increased by enhancing the coating film thickness,[41] the specific capacity of rGF-S electrode decreased from 1020 mAh g$^{-1}$ (0.8 mg cm$^{-2}$ sulfur loading) to 800 mAh g$^{-1}$ (1.1 mg cm$^{-2}$ sulfur loading). This is because the electronic and ionic conductivities of rGF-S cathode decreased as the thickness increased, which limits the utilization of sulfur.[41] To solve this problem, GmF2000 and GmF3000 with fewer defects and higher electric/ionic conductivities were utilized as conducting hosts for sulfur cathode (Figure 3a). As expected, the GmF2000-S electrode (1019 mAh g$^{-1}$ at 0.2 C) and GmF3000-S electrode (1010 mAh g$^{-1}$ at 0.2 C and 813 mAh g$^{-1}$ at 1 C) did prove higher capacities and better performance than the rGF-S electrode at both low rate and high rate (Figure S6, Supporting Information).

To reveal the relationship between defect concentration, electric/ionic conductivity, and electrochemical performance, electrochemical impedance spectroscopy (EIS) analyses of the rGF-S, GmF2000-S, and GmF3000-S electrodes were performed after three cycles in the charged state (Figure S8, Supporting Information). Obviously, the GmF3000-S electrode exhibited a much lower charge-transfer resistance (25 Ω) than the GmF2000-S electrode (75 Ω) and rGF-S electrode (168 Ω), which is description of ionic conductivity.[42] Ascribed to the ohmic resistance, the intercept of the real axis at the high frequency decreased from 5.5 Ω (rGF-S) to 3 Ω (GmF2000-S), and then to 2.3 Ω (GmF3000-S). Hence, we can conclude from these results that the fewer the defects, the higher the electric/ionic conductivities and the better the electrochemical performances (Table 1). Moreover, GmF2000-S and GmF3000-S electrodes can be fabricated at an enhanced sulfur loading of 2.5 mg cm$^{-2}$ with high specific/areal capacity and decent rate capability delivered simultaneously. GmF3000-S cathode can afford specific capacities of 1089 mAh g$^{-1}$ (2.71 mAh cm$^{-2}$) and 840 mAh g$^{-1}$ (2.1 mAh cm$^{-2}$) with decay rate of 0.08% cycle$^{-1}$ at constant current rates of 0.1 and 1 C, respectively, with good capacity retention and low overpotential (Figure 3b; Figure S7, Supporting Information). Impressively at high rate of 2 C, the GmF3000-S electrode exhibited a discharge capacity of 650 mAh g$^{-1}$ (1.63 mAh cm$^{-2}$) and retained a relatively low decay rate of 0.1% cycle$^{-1}$ over 420 cycles (Figure 3d).[43] These specific capacities, rate capability, and capacity retention of GmF3000-S electrode were much better than those of GmF2000-S electrode (Figure S7, Supporting Information), due to the lower defect concentration and higher electric/ionic conductivity GmF3000 delivered than GmF2000 that enable more uniform electrochemical reactions throughout electrode (Figure S8, Supporting Information).

Significantly, the areal sulfur loading of GmF3000-S cathode can be further enhanced by increasing the coating film thickness, delivering a high areal capacity of 5.2 mAh cm$^{-2}$

#### Table 1. Summary of GmFs' defect concentration, electric conductivity, capacity, and rate capability.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Defect content $I_G/I_D$</th>
<th>Electric conductivity [S cm$^{-1}$]</th>
<th>Sulfur cathode of Li–S battery</th>
<th>Graphene cathode of Al-ion battery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Areal capacity [mAh cm$^{-2}$]</td>
<td>Rate capability [C]</td>
<td>Specific capacity [mAh g$^{-1}$]</td>
</tr>
<tr>
<td>rGF</td>
<td>1.68</td>
<td>1.72</td>
<td>1.0</td>
<td>3 C</td>
</tr>
<tr>
<td>GmF-2000</td>
<td>0.0521</td>
<td>45</td>
<td>2.7</td>
<td>1 C</td>
</tr>
<tr>
<td>GmF-3000</td>
<td>0.0276</td>
<td>212</td>
<td>5.2</td>
<td>1 C</td>
</tr>
<tr>
<td>rGA</td>
<td>1.3</td>
<td>2.48</td>
<td>0.77</td>
<td>0.1 C</td>
</tr>
</tbody>
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eventually (Figure 4a). After 100 cycles the charge/discharge curves still exhibited few polarization and almost 4 mAh cm$^{-2}$ were retained (Figure 4b), which is still higher than the technical index of 3.3 mAh cm$^{-2}$ to compete with the Li$_{1-x}$CoO$_2$ cathode\cite{40}. The Coulombic efficiency was retained above 99% proving successful restraint of shuttle effect and good electrochemical reversibility. The GmF-3000 cathode can also afford 4.7 mAh cm$^{-2}$ at 0.2 C, 3.8 mAh cm$^{-2}$ at 0.5 C and 2 mAh cm$^{-2}$ at 1 C (Figure 4c). Due to the unique high-quality graphene design (Table 1), the sulfur loading, areal capacity, and high rate performances of GmF3000-S cathode are significantly improved compared with rGA-S, rGF-S, and GmF2000-S cathodes (Table 1). This remarkable areal capacity and rate performance of our GmF3000-S can compete with those of recently published elaborately designed carbon nanomaterials and commercially available LIB cathode (Figure S9, Supporting Information), demonstrating the successful application of high-quality graphene design in Li–S battery.

To reveal the stability of GmF’s crumpled structure and effective entrapment of sulfur/dissolved lithium polysulfide intermediates, the batteries were disassembled after different cycles inside the glove box. Postmortem SEM analysis was performed, revealing the entire morphology and microstructure of the self-folded crumpled graphene flower were well preserved after 40, 100, 180, and 250 cycles (Figure 5a–d). The magnified SEM images showed that abundant sulfur nanoparticles were embedded in GmF, consistent with the size of sulfur nanoparticles observed before cycling (Figure 2j). Interestingly, these nanoparticles were mainly distributed in the corrugated area and trapped in the grooves in the crumpled sheets (Figure 5e). On the contrary, very few sulfur nanoparticles were observed to be located on the plain surface (Figure 5f). This phenomenon directly proved that this nano-sized fold structure (Figure 2d) can greatly assist entrapment of sulfur during cycling as described in Figure 1a, exhibiting the unique advantages of flower-shaped morphology and low stacking degree. Figure 5g illustrates the solutions obtained by soaking the various cycled GmF3000-S cathodes in a mixture of 1,3-dioxolane/1,2-dimethoxyethane (DOL/DME, 1:1 by vol), exhibiting no difference in color found by
Figure 4. a) Cycling stability and Coulombic efficiency of the GmF3000-S electrode at 0.1 C at a high sulfur loading of 4.5 mg cm$^{-2}$. b) Galvanostatic charge/discharge curves of the GmF3000-S electrode at different cycle, 0.1 C and sulfur loading of 4.5 mg cm$^{-2}$ within a potential window of 1.8–2.8 V. c) Specific capacity and Coulombic efficiency of the GmF3000-S electrode at different rates from 0.1 to 1 C at sulfur loading of 4.5 mg cm$^{-2}$.

Figure 5. a–d) SEM images of the GmF3000-S electrode after 40, 100, 180, and 250 cycles, scale bar: 2 µm. e,f) Magnified SEM images of GmF3000-S electrode after 250 cycles. Scale bar: (e) 800 nm and (f) 300 nm. g) Typical colors of solutions for the GmF3000-S electrodes after various cycles and h) rGA-S electrode after three cycles in sealed vials. The solutions were obtained by soaking the cycled cathodes (discharge state) in a mixture of DOL/DME (1:1 by vol). i) UV–vis absorption spectra of the solution obtained by soaking the cycled GmF3000-S cathodes in a mixture of DOL/DME (1:1 by vol).
naked eyes even after 250 cycles. By contrast, the solution of the rGA-S electrode changed to a dark gold color (Figure 5h) due to the dissolution of brown lithium polysulfide. This low polysulfide dissolution of GmF3000-S electrode during cycling can be consolidated by overlapped curves in corresponding UV-vis absorption spectra (Figure 5i), which can be attributed to effective entrapment of sulfur species by the mesoporous channels and few-stack crumpled sheets during cycling.

2.3. Electrochemical Performances of GmF Cathode for Al-Ion Battery

The application of our high-quality graphene design is also demonstrated in Al-ion battery system. In the aspect of high-power density EES system for applications such as electrical grid storage, the capacitors always dominate for its unmatched power density (>10^4 W kg^-1). Nevertheless, capacitors and supercapacitors have long been restricted by their energy densities (lower than 10 Wh kg^-1). A rechargeable Al-ion battery system was recently reported by Dai and co-workers utilizing low-cost aluminum metal as anode and graphitic foam as cathode, affording good performances: high discharge voltage (1.8 V), stable long cycle life (7500 cycles) with especially good high-rate performance (60 mAh g^-1 at 6 A g^-1), and remarkable safety.[45] This Al-ion battery can afford an energy density of 40 Wh kg^-1 and high power density of 3000 W kg^-1, exhibiting a disruptive technology in high-power density EES system.[46,47] However, the low cathode capacity (60 mAh g^-1) limits the cell energy density, and insufficient high-rate performance restricts the cell power density to be lower than supercapacitors (>10^4 W kg^-1). A monolithic 3D graphitic foam was reported by Wu et al. delivering a better high-rate performance (60 mAh g^-1 at 12 A g^-1).[48] and Yu et al. reported a plasma-etching graphene nanoribbons on highly porous 3D graphene foam as a cathode material for Al-ion batteries, which doubled the original cathode capacity.[13] Recently, our group reported a fundamental defect-free principle as a basic guideline for enhancing the electrochemical performances of graphene cathode for Al-ion battery.[10] However, all of these reported graphene materials are monolithic, which limit their compatibility with the industrial cast-coating technology. Herein, since our GmF exists in the powder form, it can be directly and easily cast-coated onto a current collector to fabricate cathode of Al-ion battery.

Figure 6a shows the long-term galvanostatic cycling of GmF3000 cathode, which delivered high Coulombic efficiency of 98 ± 2% and high specific capacity of 100 mAh g^-1 at high current density of 5 A g^-1. Surprisingly, no capacity decay can be found even after 5000 cycles with stable Coulombic efficiency. Detailed charge/discharge curves of different cycles in Figure 6b were almost overlapped after initial activation cycles. These stable capacity, Coulombic efficiency, and charge/discharge curves demonstrate the excellent electrochemical reversibility and stability of GmF3000 powder. The GmF3000 cathode can be rapidly charged (90 s by 4 A g^-1 or 45 s by 8 A g^-1) and gradually discharged (from 0.1 to 4 A g^-1, continue to use for almost 1 h), retaining similar discharge capacity (>92 mAh g^-1, Figure 6c), voltage profiles, and average discharge voltage of ~1.85 V (Figure S10d, Supporting Information). Impressively, the GmF3000 cathode can also deliver stable capacity of 100 mAh g^-1 over 1000 cycles at ultra-high charge/discharge current densities of 10 A g^-1 (totally charged/discharged in 36 s) and 20 A g^-1 (totally charged/discharged in 18 s, Figure 6d). These remarkable ultrahigh rate performances are due to the ultrafast intercalation of AlCl^4^- ions into defect-free and high electronic-conducting graphene layers as previous reports[49,50] which will greatly improve the power density of the Al-ion battery and enable its competitiveness with supercapacitors (Figure S11d, Supporting Information).

According to the exact accordance of high-quality graphene design with requirements of Al-ion battery cathode (more active sites, higher electric conductivity, better electrolyte infiltration, and ion diffusion), those defect-few or defect-abundant graphene materials should deliver lower specific capacity and rate capability than the defect-free GmF3000. To demonstrate our high-quality graphene design, we also inspected the defective GmF2000, rGF, and rGA as cathode of Al-ion battery. The defect-few GmF2000 cathode did afford a lower capacity of 63 mAh g^-1 with 90% capacity retention after 5000 cycles (Figure 6a; Figure S11, Supporting Information) and similar rate capability behaviors (stable specific capacities within current densities from 100 mA g^-1 to 4 A g^-1, Figure S11, Supporting Information). At the same time, the rGF and rGA control samples delivered no capacity. These advances in specific capacity, reduced polarization, and high-rate performances of GmF3000 than the defective control samples are mostly attributed to the defect-free principle component in our high-quality graphene design,[10] as further supported by the EIS analysis (Figure 6e). The semicircle at the high-frequency range is a good indicator of the charge transfer resistance at the graphene surface. The GmF3000 cathode showed lower charge transfer resistance of 2.1 Ω than that of GmF2000 (2.9 Ω). Ascribed to the ohmic resistance, the intercept of the real axis at the high-frequency decreased from 11.16 Ω (GmF2000) to 5 Ω (GmF3000), which also accorded with the improved electrical conductivity by high-quality graphene design (Table 1). In addition, the low stacking degree and sub-millimeter sized graphene surface, which are other aspects of high-quality graphene design, also contribute to the ion diffusion, electrolyte infiltration, and electric conductivity, respectively. These merits further improve the cathode’s performances (especially high-rate capability) than the previously reported dense graphitic cathode.[45,51] which is consistent with calculation results recently reported.[49] Significantly, GmF is the first powder-formed graphene material that is used as graphene cathode of Al-ion battery, which guarantees its compatibility with conventional slurry-coating technology. Generally, the electrochemical performances of powder-formed electrode materials cannot rival those of macroscopic electrode materials with continuous structure and higher electronic conductivity. On the contrary, the electrochemical performances of GmF3000 powder (high capacity of 100 mAh g^-1 and excellent rate performance of stable capacity within 0.1–20 A g^-1) greatly surpass most of monolithic graphitic cathode materials (Figure 6f), favoring its real application as electrode of batteries.
3. Conclusion

In summary, we present a new large-scale synthesis approach of high-quality graphene powder and demonstrate its unique advantages for multiple energy storage applications. Four advantages are simultaneously achieved in our GmF3000: defect-free and highly crystallized graphene layers, sub-millimeter continuous high electric-conducting surface, low stacking degree, and large output with remarkable cost-effectiveness, enabling it to meet the requirements of scalable production. Owing to these merits, this high-quality GmF can greatly improve the electrochemical performances of various electrodes and batteries. The GmF3000-S cathode of Li–S battery delivers high specific areal capacity of 5.2 mAh cm⁻², which have surpassed the technical index to compete with the Li₁ₓCoO₂ cathode. The GmF3000 cathode of Al-ion battery delivers a stable specific capacity of 100 mAh g⁻¹ over 5000 cycles with remarkable ultrahigh-rate performance of stable capacity from 0.1 to 20 A g⁻¹, surpassing those of defect-few GmF2000 and most defect-few graphene materials reported. We believe that this high-quality graphene design with powder-formed GmF can also be used in other energy-storage systems including Li-ion battery and supercapacitors.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.
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Al-ion batteries, defect-free, high-quality graphene microflowers, large-scale production, lithium–sulfur batteries