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Room Temperature Production of Graphene Oxide with Thermally-labile Oxygen Functional Groups for Improved Lithium Ion Batteries Fabrication and Performance

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Graphene oxide (GO) has drawn intense research interest over the past decade, contributing to remarkable progress in its relevant applications. The chemical production of GO, however, is challenged by destructive and slowly-propagating oxidation, especially for large flake graphite. Herein, we reported a simple but effective method to produce well-oxidized and less defective GO by chemically oxidizing commercially-available expandable graphite at room temperature (25 °C). Compared to natural graphite with similar flake sizes, expandable graphite afforded faster complete oxidation under the same oxidizing conditions. In addition, chemical oxidation at room temperature, relative to higher temperatures (35 and 45 °C), resulted in reduced defect concentration in GO. Furthermore, the GO derived from the oxidation of expandable graphite at room temperature exhibited superior electrical conductivity after mild thermal treatment at 150 °C. Considering the energy-saving in both the GO synthesis and reduction, the low temperature GO conversion process can be easily integrated into many other electroconductive applications. As a proof of concept, we achieved a good LiFePO₄ (without carbon-coating) cathode formulation with our GO, contributing as a 2D binder (before annealing), and obtained a conductive cathode with improved capacity and high rate performance after mild thermal annealing at 150 °C.

Introduction

Graphene and graphene-based materials are appealing to a myriad of applications, such as energy storage devices,¹ electrocatalysis,² and sensors.³ As one of the most important precursor to graphene materials, graphene oxide (GO) has been widely adopted in both lab-scale research and industrial production due to its excellent chemical processability and production scalability.^{4–6} Currently, the exfoliation of chemically oxidized graphite, produced *via* the modified Hummers method, to GO is the most popular GO synthesis method owing to its rich oxygen functional groups and quantitative yield of single-layer GO.^{7–15} However, the harsh conditions in the strong chemical oxidation will incur permanent defects, uncontrollable functionality and even fragmentation in the resultant GO.^{16–19} In addition, it is limited by the slow diffusion of oxidizing agents.²⁰ Particularly for large flake graphite, oxidants will have difficulty reaching the core region of the graphite, resulting in non-uniform oxidation and cracking in the GO sheets.¹⁸ Therefore, much effort has been put into optimizing the chemical oxidation method, mainly focusing on the starting materials and oxidation conditions.

To facilitate oxidation and exfoliation, one strategy is to pre-intercalate the graphite to form graphite intercalation compound (GIC) with increased interlayer spacing and weakened Van der Waals interaction between graphite layers.²¹ In 1999, Kovtyukhova *et al.* demonstrated a two-step oxidation method in which natural graphite was pre-intercalated in concentrated H₂SO₄, K₂S₂O₈ and P₂O₅, followed by the Hummers method.²² It was later found that the pre-treated graphite was more susceptible to oxidation and exfoliation into monolayer GO sheets and hence the protocol has been adopted in many more recent works.^{9, 23} This two-step oxidation route, however, presents challenges for the mass production of GO due to the time-consuming pre-treatment, which involves the wetting and drying of graphite. Another strategy is to employ expanded graphite, which features a worm-like structure, as the starting material to produce GO. The expanded graphite is typically achieved by the thermal expansion of graphite bisulfate, a type of graphite intercalation compounds (GIC), also known as expandable graphite. In 2009, Luo *et al.* synthesized high-quality GO sheets using microwave-expanded graphite, where the interlayer galleries were dramatically expanded, as the starting material.²⁴ Since then, several research groups have shown that expanded graphite is a more suitable graphite source for preparing large-area GO sheets than natural graphite.^{25–27} Recently, Lu *et al.* proposed a new type of chemically expandable graphite in which the expansion was initiated by the oxygen evolution from the chemical reaction of CrO₃ graphite intercalant with H₂O₂.²⁸ Though the expanded graphite was very readily oxidized even under mild agitation-

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free condition, this novel method is challenged by the complicated procedures and the introduction of toxic Cr^{6+} ions.²⁸

With regards to oxidation conditions, Eigler *et al.* kept the oxidation at temperature below 10 °C to yield highly intact GO with preserved the structural integrity.^{29, 30} However, this low-temperature method has its limitations, namely the time-consuming procedures and low GO yield. Apart from lowering the reaction temperature, it has been reported that the addition of a small amount of water to the chemical oxidation system not only promoted oxidation but also reduced the defects in GO.^{31, 32}

Typically, the reduction of GO, by which its electrical conductivity can be restored, is required for the majority of applications such as lithium ion batteries (LIBs) and supercapacitors.^{9, 33} The common reduction methods involve chemical reduction (such as hydrazine and hydroiodic acid)^{34, 35} and thermal treatment at high temperature^{19, 36}. Zhu and co-workers reduced GO dispersion in an anhydrous organic solvent, propylene carbonate, by heating at only 150 °C, but for 12 hours.³⁷ The mild thermal reduction, without the need for reducing agent or high temperature treatment, will be very useful for the incorporation of reduced GO (rGO) into a wide range of electroconductive applications. For example, it has been shown that rGO worked well as the conductive additive in lithium ion batteries (LIBs) electrodes, effectively improving charge transport due to its good conductivity, high surface area and flexible two dimensional structure.^{6, 36, 38} The low temperature thermal treatment could help to simplify the fabrication of LIBs by allowing GO to be blended with electrode materials and then reduced in situ. Due to its good dispersibility in multiple solvents, unreduced GO can be homogeneously mixed with LiFePO_4 particles. This can enable the uniform coating/wrapping of GO around the particles, minimizing the unwanted polarization in LIBs.³⁹

In this work, we report a mild GO production approach from large-sized expandable graphite (graphite bisulfate, a type of GIC) flakes *via* the modified Hummers method, resulting in more thorough oxidation than natural graphite under the same conditions. We optimized the oxidation temperature and time for this GIC-based GO synthesis and found that well-oxidized GO was obtained at an oxidation temperature of 25 °C for 8 h (denoted as $\text{GO}_{\text{GIC-25-8h}}$). This GO, synthesized at room temperature, was found to be less defective and more prone to deoxygenation during low temperature annealing (150 °C). After 150 °C thermal reduction in air, $\text{GO}_{\text{GIC-25-8h}}$ restored more sp^2 carbon atoms and was also more conductive than other GO oxidized at higher temperature, which indicates the facile removal of oxygenated functional groups. Our work also demonstrates that the $\text{GO}_{\text{GIC-25-8h}}$ was able to blend well in typical LiFePO_4 (without carbon-coating) cathode formulation and helped to deliver pronounced improvement in the capacity and high rate performance of LIBs after mild thermal annealing process.

Experimental

Materials

The expandable graphite used in the experiments was received from Asbury Graphite Mills (Grade 1721). The natural flake graphite was from Sigma-Aldrich (Product No. 332461). Both graphite sources were carefully sieved to control the flake sizes between 200 and 300 μm for the GO synthesis reactions. KMnO_4 (99.0%), concentrated H_2SO_4 (98%), H_2O_2 aqueous solution (30% w/w) and hydrochloric acid (32 wt.%) were purchased from Chem-supply. Deionized water was used in all experimental procedures, including synthesis reaction and purification.

Synthesis of graphene oxide from expandable graphite (GIC) and natural graphite (NG) under different conditions.

The GO synthesis procedures were based on a modified Hummers method as illustrated in **Figure 1**.^{14, 40} The flake graphite (1 g) was mixed with concentrated H_2SO_4 (50 mL) in a 500 mL three-neck flask which was placed in the ice bath with mechanical stirring at 120 rpm. After cooling to below 10 °C, KMnO_4 (3 g) was slowly added to the mixture and the mixture kept in the ice bath for 1 h. Then, removing the ice bath, the temperature was elevated to the designated temperature (25, 35 and 45 °C) at which point the mixture was stirred for a specified period (4, 6 and 8 h.). After this stage, the water bath was replaced by an ice bath to minimize the temperature rise in the following steps. 150 mL of chilled water was slowly dropped into the mixture via a peristaltic pump over a period of 90 min and then the reaction system was kept in the ice bath for another 30 min. At the end of reaction, H_2O_2 was added to the mixture dropwise to react away the residual KMnO_4 until the color of the resulting product no longer changed. To remove metal ions, 300 mL diluted aqueous HCl solution (1:9) was added to the product. The product was allowed to settle overnight. The resulting sediment was washed with water and centrifuged at 13000 rpm for 15 min repeatedly until the pH of supernatant stabilized at ~4. Finally, the resultant sediment was resuspended in deionized water to a total volume of 200 mL. The GO products made from expandable graphite and natural graphite are denoted as GO_{GIC} and GO_{NG} , respectively, and the oxidation temperatures and reaction time are abbreviated as, for example, $\text{GO}_{\text{GIC-25-4h}}$ (the product derived from the GIC, with a 25 °C, 4 h reaction time).

Yield Calculation

5 mL of the purified GO aqueous dispersion was cast into a dense film on a nylon membrane *via* vacuum filtration and then dried in a 60 °C oven overnight. The polymer membrane was then gently peeled off and the weight of the freestanding GO film which was used to calculate the concentration of GO (C_{GO} , mg/mL). The yield of GO was calculated by the equation $Y_{\text{GO}} = C_{\text{GO}} \times V_{\text{GO}} / m_{\text{Gr}}$ where V_{GO} is the total volume of GO solution after purification (200 mL) and m_{Gr} is the mass of starting graphite. Specially, in the case of GO_{GIC} , m_{Gr} only refers to the graphite component, excluding the intercalating compounds.

Characterizations

Figure 1. Schematic overview of the experimental design, including GO synthesis routes with different conditions, characterizations and application tests.

X-ray diffraction (XRD) patterns were measured on a Bruker D8 advance diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The chemical compositions of GO samples were analyzed by X-ray photoelectron spectroscopy (XPS, Kratos Axis ULTRA incorporating a 165 mm hemispherical electron energy analyzer). Scanning electron microscopy (SEM) was conducted on a Joel JSM-7500FA microscopy with accelerating voltage of 15.0 kV. Atomic force microscopy (AFM) images were collected from a Bruker Dimension Icon AFM using peak force tapping mode. The statistical analysis of flake thickness was based on the line profiles of ~ 80 pieces of GO sheets from AFM images. Raman spectroscopy was carried out on individual GO sheets using a Reinshaw inVia Raman microscope with a 532 nm laser. The samples were prepared by spin-coating diluted GO dispersion ($\sim 0.1 \text{ mg/mL}$) onto a conductive silicon wafer (for SEM and AFM) or thermal oxide silicon wafer (for Raman analysis). Attenuated-total-reflectance Fourier transform infrared (ATR-FTIR) spectra were acquired from a Bruker Alpha spectrometer coupled with a platinum ATR single-reflection diamond module. TGA of GO film samples was performed on a Netzsch STA 449F3 analyzer under 100% argon or 20% oxygen/80% argon. For the argon atmosphere experiment, GO samples were heated from 50 to 700 °C at the rate of 5 K/min. For the oxygen atmosphere experiment, the GO samples were rapidly heated from 50 °C to 150, 175 or 200 °C (heating rate: 30 K/min), and the samples were kept at the high temperature for 6 h. To measure the graphite content in the expandable graphite (GIC), it was heated from 50 to 1000 °C at the rate of 5 K/min under argon atmosphere. As a contrast, the same TGA

test was performed on natural graphite. The electrical conductivity measurements for the rGO films of similar weight ($\sim 100 \text{ }\mu\text{g}$) were conducted on a Jandel RM3000 four-point probe system with a linear arrayed head (probe spacing of 1 mm).

LIB testing.

To prepare the control LIB cathodes, 10 wt.% polyvinylidene difluoride (PVDF), 10 wt.% carbon black, and 80 wt.% LiFePO_4 (LFP) were mixed with N-methyl-2-pyrrolidone (NMP) by magnetic stirring for 24 h. The homogeneous slurry was cast onto the aluminium foil which was then dried in an 80 °C vacuum oven for 12 h. The assembly of coin cells (2032) was conducted in an argon-filled glove box. Lithium foil was used as an anode, and 1 M LiPF_6 dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1 served as the electrolyte. The testing voltage in constant current mode ranged from 2.5 to 3.8 V, and the cells were charged under the constant voltage mode at 3.8 V until the current reached 10% of the current rate. To show the effects of different reduced GO_{GIC} in LIBs, half of the carbon black was replaced with $\text{GO}_{\text{GIC}}-25-8\text{h}$ and $\text{GO}_{\text{GIC}}-45-4\text{h}$, respectively, in the cathode compounds. The GO samples in the aqueous dispersions were freeze-dried for the preparation of electrodes. The freeze-dried GO_{GIC} was dispersed into NMP, forming an 8 mg/mL dispersion and then LFP, carbon black and PVDF were added. Prior to battery assembly, $\text{GO}_{\text{GIC}}/\text{LFP}$ cathodes were annealed in a 150 °C oven for 5 h in air. The charge and discharge performance tests were carried out using a Neware battery tester (Shenzhen, China) with potential range between 2.5 and 3.8 V. The cyclic

voltammetry (CV) measurement was performed on a CHI 660D electrochemical workstation with a scan rate of 0.1 mV s⁻¹.

to the left (from 10.6° to 10.1°) when the oxidation time is doubled at 45 °C, which is associated with the interlayer expansion and the

Figure 2. XRD patterns for (a) GO_{NG} from different oxidation conditions, (b) GO_{GIC} oxidized at 25 °C for different times. (c) GO_{GIC} oxidized at different temperature for 4 h, and (d) Yield comparison between GO_{NG} and GO_{GIC}.

Results and discussions

The effects of graphite sources.

GO samples were prepared by oxidizing expandable graphite (GIC) and natural graphite (NG), respectively, at different temperatures (25, 35 and 45 °C) for varying time (4, 6 and 8 h) with the modified Hummers method and the products were examined via X-ray diffraction (XRD). The XRD patterns of the two starting materials (Figure S1) showed GIC had greater interlayer spacing between graphene layers (3.41 Å vs 3.36 Å) and lower crystallinity (broader graphitic peak) than NG. This suggests that GIC, with less compact structure, can provide more accessible paths for the diffusion of oxidizing agents than NG. Experimentally, this advantage of GIC can be demonstrated by the XRD results of GO_{NG} and GO_{GIC} (Figure 2a-c). Examining Figure 2a, despite subjecting to prolonged oxidation time (8 h) and sufficiently high temperature (45 °C), GO_{NG} still showed a pronounced broad graphitic peaks at about 26° (corresponding to the interlayer spacing $d \approx 3.4$ Å), which is related to unoxidized graphite.^{41, 42} In addition, for GO_{NG}-25-4h and GO_{NG}-25-8h, the position of the sharp low-angle peak, also known as GO peak, did not change and was about 10.9° ($d = 8.1$ Å). This suggests that the interlayer distance between GO sheets did not change with the oxidation time at 25 °C.⁴¹ In contrast, there was a shift in the GO peak

oxidation degree of GO.¹⁵

As evident in Figure 2b, it was easier to oxidize GIC at 25 °C. The graphitic peak was much weaker in GO_{GIC}-25-4h (relative to the product derived from NG using the same oxidation conditions), and the graphitic peak disappeared after prolonging the oxidation time to 8 h. Meanwhile, the left shift in the GO peak (from 11.1° to 10.5°) reflected the expansion in interlayer spacing (from 8.0 Å to 8.4 Å) and hence the slight increase in the degree of oxidation with reaction time at 25 °C. The GIC can also be completely transformed into GO after 4 h of oxidation at higher temperatures of 35 °C and 45 °C, evidenced by the absence of the graphitic peaks in Figure 2c. Therefore, using GIC as the starting material allows for milder reaction condition and more effective oxidation. Note that the small and broad peaks at around 21° in the XRD patterns can be attributed to the randomly packed single graphene layers.⁴³

To measure the graphite content in GIC, the material was heated to 1000 °C under the argon atmosphere in order to gasify the intercalants, water and remove any oxygen functionalities.^{24, 44} The TGA curves (Figure S2) showed 76 wt. % of material remained in GIC, attributed to the graphite component of GIC,⁴⁵ while NG did not lose any mass after heated to 1000 °C. Therefore, the yield of GO_{GIC} can be calculated with respect to the starting graphitic material and compared with that of GO_{NG}, as illustrated in Figure 2d. In general, the GO_{GIC} had higher yield than GO_{NG} under the same reaction

Figure 3. Morphological characterizations of fully oxidized GO_{GIC} samples. (a), (c) and (e): SEM images of GO_{GIC} sheets coated onto the Si wafers and the corresponding flake size distributions. (b), (d) and (f): Frequency distributions of the number of layers in the GO samples (statistics were based on more than 80 GO flakes). The insets are the AFM images of the individual GO sheets and their corresponding height profiles.

conditions and the gap became even wider at higher temperatures due to the greater extend of oxidation in GIC. In comparison to other reported room or low temperature synthesis, our yield of 190 % for $\text{GO}_{\text{GIC}}-25-8\text{h}$ is one of the highest so far.^{29, 32, 46}

Morphological characterizations of fully oxidized GO_{GIC} .

In the subsequent work, only the fully oxidized samples ($\text{GO}_{\text{GIC}}-25-8\text{h}$, $\text{GO}_{\text{GIC}}-35-4\text{h}$ and $\text{GO}_{\text{GIC}}-45-4\text{h}$) were further characterized and compared. The lateral size distributions of GO sheets were obtained statistically from SEM images (Figure 3a, c and e). For $\text{GO}_{\text{GIC}}-25-8\text{h}$, $\text{GO}_{\text{GIC}}-35-4\text{h}$ and $\text{GO}_{\text{GIC}}-45-4\text{h}$, the average sizes were 20.1 ± 17.9 ,

27.3 ± 18.6 and 24.5 ± 22.0 (mean $\pm$ standard deviation) μm , respectively. It is noteworthy that $\text{GO}_{\text{GIC}}-25-8\text{h}$ had the smallest average lateral size as well as the highest content of $< 20 \mu\text{m}$ flakes. Although the oxidation proceeded at lower temperature, $\text{GO}_{\text{GIC}}-25-8\text{h}$ was also subjected to 8h of mechanical stirring which likely led to the mechanical cleavage of the GO sheets.^{18, 47} Examining the thickness distributions of GO_{GIC} sheets from AFM images (Figure 3b, d and f), the majority of GO_{GIC} sheets were successfully exfoliated down to single layer. The single-layer sheets were between 1.0 and 1.5 nm thick, consistent with previous literature reports.^{15, 48}

Figure 4. Chemical properties of different GO_{GIC} samples. (a) Raman spectra of GO_{GIC} flakes. (b) TGA curves for heating GO in argon at a 5 K/min heating rate. (c) The corresponding first derivative of the TGA curves in the temperature range 50 ~ 300 °C. (d-f) TGA curves for thermal annealing of GO_{GIC} at 150, 175 and 200 °C under 20 % oxygen/80 % argon atmosphere.

Chemical characterizations of fully oxidized GO_{GIC} before and after thermal reduction.

To further investigate the effects of different oxidation conditions, Raman spectroscopy (Figure S3) was used to discriminate different carbon atoms, typically featuring D (~1350 cm^{-1}), G (~1585 cm^{-1}) and 2D (~2700 cm^{-1}) peaks. The D peak is attributed to the breathing modes of six-atom carbon rings in proximity to defect areas. The 2D peak is the overtone of the D peak, while the G peak is related to the motion of sp^2 carbon atoms.⁴⁹ The ratio of the defect-activated D peak to G peak is an important parameter to reveal the defect density in GO. According to Ferrari and Robertson,⁵⁰ for graphene materials, $I_{\text{D}}/I_{\text{G}}$ initially increases with defect density at low defect concentration (stage 1) and subsequently declines after reaching a certain defect concentration (stage 2). From the Raman spectra of various GO_{GIC} in Figure S3, the value of $I_{\text{D}}/I_{\text{G}}$ tended to decrease with longer oxidation time or higher temperature. Therefore, all GO_{GIC} samples were likely to be in the stage 2 state because more defects will be introduced to the honeycomb lattice in graphene layers as the proceeding chemical oxidation or the elevating temperature.^{18, 29} Comparing the fully oxidized GO_{GIC} samples (Figure 4a), the defect density increased in the following sequence: $\text{GO}_{\text{GIC}}\text{-25-8h} < \text{GO}_{\text{GIC}}\text{-35-4h} < \text{GO}_{\text{GIC}}\text{-45-4h}$.

The weight change in GO_{GIC} with increasing temperature was tracked using thermogravimetric analysis (TGA, Figure 4b), and it was found that the greatest weight loss was observed for $\text{GO}_{\text{GIC}}\text{-45-4h}$. Only 53.6% of the material remained after heating to 700 °C, which suggested it had the highest content of thermally labile oxygenated function groups. Moreover, the corresponding first derivative TGA curves (Figure 4c) were plotted to give insight into the peak decomposition temperature (T_{d}) where GO samples underwent the greatest rate of change in the weight.^{31, 32} It was obvious that $\text{GO}_{\text{GIC}}\text{-45-4h}$ had a higher T_{d} (198 °C) than $\text{GO}_{\text{GIC}}\text{-25-8h}$ (181 °C) and $\text{GO}_{\text{GIC}}\text{-35-4h}$ (175 °C). In fact, the removal of oxygenated function groups from GO basal planes always accompanies the formation of various gases, including CO_2 , CO and H_2O .⁵¹ Because the gasification process must overcome the interlayer interactions, it can be inferred that $\text{GO}_{\text{GIC}}\text{-45-4h}$ with the highest T_{d} had the greatest amount of carboxyl group with strong hydrogen bonding ability.³¹

Mild thermal annealing in ambient air is a simple and effective route to deoxygenate GO.⁵² By comparing the weight changes for GO_{GIC} annealed at different constant temperatures (Figure 4d-f), $\text{GO}_{\text{GIC}}\text{-25-8h}$ saw the most weight loss at 150 °C, relative to other conditions, while $\text{GO}_{\text{GIC}}\text{-45-4h}$ lost more weight at 175 and 200 °C, implying deoxygenation of $\text{GO}_{\text{GIC}}\text{-25-8h}$ occurred more readily at lower temperature than $\text{GO}_{\text{GIC}}\text{-45-4h}$. As shown in Table S1, the percentage of residual mass changed from 69% to 65% in $\text{GO}_{\text{GIC}}\text{-25-8h}$ as raising the annealing temperature from 150 to 200 °C. This change was much smaller than that in $\text{GO}_{\text{GIC}}\text{-35-4h}$ or $\text{GO}_{\text{GIC}}\text{-45-4h}$, also indicative of the easier deoxygenation of $\text{GO}_{\text{GIC}}\text{-25-8h}$ at 150 °C. In addition, $\text{GO}_{\text{GIC}}\text{-35-4h}$ always experienced the lowest mass reduction, regardless of the annealing temperature, suggesting that $\text{GO}_{\text{GIC}}\text{-35-4h}$ was less oxidized than $\text{GO}_{\text{GIC}}\text{-25-8h}$ and $\text{GO}_{\text{GIC}}\text{-45-4h}$. This was consistent with the XPS scan which showed $\text{GO}_{\text{GIC}}\text{-35-4h}$ had the highest C/O ratio from XPS survey scan (Figure S4). In addition, during the 150 °C thermal treatment, the residual weights of $\text{GO}_{\text{GIC}}\text{-25-8h}$ and $\text{GO}_{\text{GIC}}\text{-45-4h}$ became stable after 5 h (d), corresponding to the completion of thermal reduction.

The XPS C 1s peak (Figure 5) can be deconvoluted into five components, including the C=C/C-C in aromatic rings (284.6 eV), C-O (286.1 eV), C=O (287.5 eV), COOH (289.0 eV) and $\pi\text{-}\pi^*$ satellite (290.6 eV),⁵³ and the fractions of these components in each sample are summarized in Table S2 and Table S3. Among the GO_{GIC} samples (Figure 5a, c, e and Table S2), the highest fraction of C=C/C-C was found in $\text{GO}_{\text{GIC}}\text{-35-4h}$ (56.6%) and the lowest was in $\text{GO}_{\text{GIC}}\text{-45-4h}$

Figure 5. XPS C 1s spectra for the fully oxidized GO_{GIC} samples, and the thermally reduced GO_{GIC} samples which were annealed at 150 °C for 5 h.

(45.1%), which indicated GO_{GIC}-35-4h retained the most intact sp² graphitic carbon while GO_{GIC}-45-4h was the most oxygen-functionalized. GO_{GIC}-25-8h had the least amounts of C=O and COOH (7.33%) compared to GO_{GIC}-35-4h (7.62%) and GO_{GIC}-45-4h (9.53%). Due to the fact that carbonyl and carboxyl groups preferentially form at the edge of GO flakes or vacancy defects,^{31, 53, 54} GO_{GIC}-25-8h was the least defective among all fully oxidized GO_{GIC} samples, consistent with results from the Raman spectra (Figure 4a) and the previous reports for GO produced at room temperature.³² Hence, room-temperature oxidation can more effectively maintain the structural integrity of GO. Comparing the ATR-FTIR spectra for GO_{GIC} (Figure S5), GO_{GIC}-35-4h had a weaker peak at ~1722 cm⁻¹ which suggested a lower concentration of carbonyl group, and this is also in agreement with the XPS results.

To investigate the changes in the functionalities after thermal reduction, the three reduced GO_{GIC} samples, annealed at 150 °C for 5 h, were examined by XPS (Figure 5b, d and f). As shown in Table S3, rGO_{GIC}-25-8h had the largest increase in the content of sp² carbon with thermal treatment (from 48.18% to 72.56%). This is indicative of its considerably easier deoxygenation and restoration of sp² domains at 150 °C thermal treatment, consistent with the isothermal TGA result (Figure 4d). Comparing the sheet resistances of the ultrathin rGO_{GIC} films (all annealed at 150 °C for 5 h) measured using the four-point probe, rGO_{GIC}-25-8h ($0.81 \pm 0.34 \text{ M}\Omega/\square$, mean $\pm$ standard deviation) was more conductive than rGO_{GIC}-35-4h ($1.13 \pm 0.14 \text{ M}\Omega/\square$) and rGO_{GIC}-45-4h ($8.48 \pm 0.73 \text{ M}\Omega/\square$), which is related to the higher fraction of graphitic carbon in rGO_{GIC}-25-8h. The π - π^* satellite peak became more pronounced after thermal reduction of

Figure 6. Electrochemical performances for $\text{rGO}_{\text{GIC}}\text{-25-8h}$ and $\text{rGO}_{\text{GIC}}\text{-45-4h}$ modified LFP cathodes in LIBs. The LIB's cathode with only carbon black as conductive additive served as a control. (a) Cyclic voltammetry for GO modified LIBs and the control at a scan rate of 0.1 mV s^{-1} . (b) The voltage profiles for the second charge/discharge cycle at 0.1 C . Inset is a magnification of the $9\text{--}23 \text{ mAh g}^{-1}$ region. (c) Performance test for LIBs showing the discharge rate capacity at different rates and the cycling stability at 2 C ($1 \text{ C} = 170 \text{ mAh g}^{-1}$).

all GO_{GIC} samples, due to the formation of π conjugation in graphene.⁵⁵

Application of GO_{GIC} and mild annealing condition for LIBs

Because of its facile thermal recovery of conductivity, we employed the GO_{GIC} as a 2D binder and conductive (after thermal annealing) additive in LiFePO_4 (LFP) cathodes for LIBs. Carbon black was used as a control conductive additive. In the experimental condition, 50% of the carbon black was replaced with either $\text{GO}_{\text{GIC}}\text{-25-8h}$ or $\text{GO}_{\text{GIC}}\text{-45-4h}$. As aforementioned, the residual weights of $\text{GO}_{\text{GIC}}\text{-25-8h}$ and $\text{GO}_{\text{GIC}}\text{-45-4h}$ stabilized after 5 h of thermal treatment at 150°C , as shown in Figure 4d. As such, the blended cathode materials were annealed at 150°C in air for 5 h prior to the assembly of LIB coin-cells. SEM images (Figure S6) showed the LFP particles were homogeneously wrapped by GO sheets, which facilitated the formation of a conducting network after mild thermal annealing. As shown in Figure 6a, cyclic voltammetry (CV) for the control and the two experimental cathodes displayed a pair of redox peaks during the anodic/cathodic scan, associated with the reversible $\text{Fe}^{2+}/\text{Fe}^{3+}$

redox reaction in LFP cathodes. LFP-carbon black had greater separation between the two redox peaks than rGO modified LFP, indicating rGO assisted in reducing polarization and improving the reversibility of LFP cathodes. The charge/discharge profiles in Figure 6b exhibited a voltage plateau at $\sim 3.42 \text{ V}$ vs. Li^+/Li for all LIBs samples, also correlated with the redox reaction in LFP. Apparently, $\text{LFP-rGO}_{\text{GIC}}\text{-25-8h}$ can reach the highest discharge capacity up to 170.8 mAh g^{-1} at 0.1 C rate. This value is similar to the theoretical specific capacity of LFP (170 mAh g^{-1}) which is likely contributed by the reversible redox reaction between Li^+ of the electrolyte and rGO .³⁹ Besides, the wider gap between discharge and charge plateaus in LFP-carbon black (inset in Figure 6b) indicated its higher polarization than $\text{LFP-rGO}_{\text{GIC}}\text{-25-8h}$ or $\text{LFP-rGO}_{\text{GIC}}\text{-45-4h}$, which was in good agreement with the CV result. According to Figure 6c, all LIBs showed good reversibility in discharge capacity as the current rate returned to 5 C and 10 C . It also clearly showed the addition of GO can enhance the specific capacity at different discharge rate (except the highest rate 20 C for LIB with $\text{rGO}_{\text{GIC}}\text{-45-4h}$) relative to LIB without GO additives (carbon black only), and improve the cycle life due to

less decay in discharge capacity of LIBs with GO after 55 cycles at 2 C rate (**Table S4**). For rGO_{GIC}-25-8h modified LFP, it consistently exhibited better rate capability than LFP-rGO_{GIC}-45-4h at all discharging rates, particularly the high rates (10 and 20 C). This is attributed to the better conductivity of rGO_{GIC}-25-8h. As demonstrated by XPS, rGO_{GIC}-25-8h had more sp² carbon which can provide a more conductive pathway for electron transport to the rGO modified LFP particles, thereby facilitating the Li⁺ insertion and extraction process.⁵⁶ Furthermore, LIBs with rGO_{GIC}-25-8h had comparable or even better battery performance relative to previous works which adopted rGO modified LFP (**Table S4**). It is noteworthy that the LFP particles employed in this work do not have any carbon coating and the entire LFP cathode fabrication process does not require any high temperature treatment (typically at 700 °C under inert atmosphere).

Conclusions

In conclusion, we have presented a simple modified Hummers method to prepare well-oxidized but less defective GO using expandable graphite as the starting material. Compared to natural graphite with the similar flake size, the oxidation of expandable graphite was easier and, more importantly, can be carried out at room temperature. The GO synthesized at room temperature has lesser carbonyl and carboxylic acid groups and most of its thermally labile oxygen groups (C-O) could be removed, with restoration of conductive sp² carbon, at a mild annealing temperature of 150 °C. Finally, we directly employed the GO in our LIB cathode formulation, which contributed as a 2D binder, and followed by the mild annealing process to afford a superior graphene-wrapped LFP cathode with improved capacity as well as rate performance. The mild but effective thermal reductive deoxygenation of this type of GO opens up the possibility of a more facile, energy saving and greener approach to preparing a variety of electroconductive applications for graphene materials.

Conflicts of interest

There are no conflicts to declare.

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Room Temperature Production of Graphene Oxide with Thermally-labile Oxygen Functional Groups for Improved Lithium Ion Batteries Fabrication and Performance

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Figure S1. The XRD curves for expandable graphite and natural graphite.

Figure S2. TGA curves of expandable graphite and natural graphite heated from 50 to 1000 $^\circ\text{C}$ at the rate of 5 K/min under pure argon atmosphere.

Figure S3. The Raman spectra of GO_{GIC} (a) at the temperature of 25 °C for different time, and (b) at different temperature for 4 h.

Figure S4. XPS survey spectra for different GO_{GIC} samples. The C/O ratios for $\text{GO}_{\text{GIC-25-8h}}$, $\text{GO}_{\text{GIC-35-4h}}$ and $\text{GO}_{\text{GIC-45-4h}}$ were 2.68, 3.05 and 2.41, respectively.

Figure S5. ATR-FTIR spectra for GO_{GIC} films which indicated the presence of C=O (the peak at $\sim 1723 \text{ cm}^{-1}$), C-O (at 1400 and 1225 cm^{-1}) and -OH ($3700\text{--}2700 \text{ cm}^{-1}$) in GO samples.^{1, 2}

Figure S6. SEM images for GO_{GIC} modified LFP cathodes and unmodified LFP cathode.

Table S1. The residual weight percentage of GO_{GIC} after 6 h of thermal treatment at 150, 175 and 200 °C in 20% O₂/80% Ar atmosphere.

Annealing temperature	150 °C	175 °C	200 °C
GO _{GIC} -25-8h	69 %	66 %	65 %
GO _{GIC} -35-4h	77 %	73 %	70 %
GO _{GIC} -45-4h	72 %	65 %	61 %

Table S2. The atomic percentages of five components in the unreduced GO_{GIC} according to the fitted C1s XPS curves in [Figure 4g-i](#).

	GO _{GIC} -25-8h	GO _{GIC} -35-4h	GO _{GIC} -45-4h
C=C/C-C	48.18%	56.53%	44.79%
C-O	44.43%	35.44%	45.61%
C=O	5.04%	4.81%	6.04%
COOH	2.29%	2.81%	3.49%
π-π*	0.05%	0.41%	0.07%

Table S3. The atomic percentages of five components in the reduced GO_{GIC} after 5 h of 150 °C thermal annealing according to the fitted C1s XPS curves in [Figure 4j-l](#).

	rGO _{GIC} -25-8h (150 °C, 5h)	rGO _{GIC} -35-4h (150 °C, 5h)	rGO _{GIC} -45-4h (150 °C, 5h)
C=C/C-C	72.56%	66.44%	63.83%
C-O	15.01%	20.00%	19.37%
C=O	5.93%	6.21%	9.10%
COOH	4.34%	4.51%	4.95%
π-π*	2.16%	2.84%	1.97%

Table S4. Summary of various rGO modified LiFePO₄ cathodes. In the case of pre-reduced GO, GO was reduced first and then mixed with other active materials for the assembly of LIBs.

Surface treatment on LFP particles	Conductive additives	Specific Capacity at 0.1 C rate (mA·h·g ⁻¹)	High rate performance (mA·h·g ⁻¹)	Capacity Fading Per Cycle (%)	Ref.
No	rGO _{GIC} -25-8h	171 (at 0.1 C)	77 (at 10 C) 54 (at 20 C)	-0.11 (55 cycles at 2 C)	This work
No	rGO _{GIC} -45-4h	166 (at 0.1 C)	45 (at 10 C) 11 (at 20 C)	-0.09 (55 cycles at 2 C)	This work
No	No rGO, carbon black only	152 (at 0.1 C)	36 (at 10 C) 13 (at 20 C)	-0.18 (55 cycles at 2 C)	This work
No	Electrophoretic deposition of GO and LFP particles on carbon cloth followed by annealing at 700 °C	174.7	90 (at 10 C)	-0.0027 (400 cycles at 2 C)	[3]
No	Pre-reduced GO (reduced by hydrazine)	Not provided	87 (at 10 C) 69 (at 20 C)	Not provided	[4]
APS-modified LFP	Reduced GO (co-heated with LFP at 600 °C under Ar/H ₂)	Not provided	105 (at 10 C) 70 (at 20 C)	-0.009 (950 cycles at 10 C)	[5]
Carbon coated LFP	Pre-reduced GO (reduced by hydrazine and annealed under N ₂ /H ₂)	152	107 (at 10 C)	0.167 (100 cycles at 0.1 C)	[6]
Hydrothermal synthesized LFP/rGO hybrids	rGO (co-heated with LFP at 700 °C)	166	75 (at 10 C) 60 (at 15 C)	-0.013 (100 cycles at 0.1 C)	[7]

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