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Sulfuric Acid Intercalated Graphite Oxide for Graphene Preparation

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Graphene has shown enormous potential for innovation in various research fields. The current chemical approaches based on exfoliation of graphite via graphite oxide (GO) are potential for large-scale synthesis of graphene but suffer from high cost, great operation difficulties, and serious waste discharge. We report a facile preparation of graphene by rapid reduction and expansion exfoliation of sulfuric acid intercalated graphite oxide (SIGO) at temperature just above 100°C in ambient atmosphere, noting that SIGO is easily available as the immediate oxidation descendent of graphite in sulfuric acid. The oxygenic and hydric groups in SIGO are mainly removed through dehydration as catalyzed by the intercalated sulfuric acid (ISA). The resultant consists of mostly single layer graphene sheets with a mean diameter of 1.07 μm after dispersion in DMF. This SIGO process is reductant free, easy operation, low-energy, environmental friendly and generates graphene with low oxygen content, less defect and high conductivity. The provided synthesis route from graphite to graphene via SIGO is compact and readily scalable.

Graphene has shown numerous potential applications in fields of electronics, optoelectronics, sensors, batteries and supercapacitors[1–3]. These require affordable graphene be produced by large quantities. This two-dimensional sp^2-bonded carbon is actually resourceful and can be mechanically exfoliated from graphite[4], but as to industrial-scale production, a chemical method is preferable[1–3]. Typically, the graphite is treated with oxidizing agent in concentrated sulfuric acid to graphite oxide (GO) and followed by chemical or thermal reduction and exfoliation to graphene[5,6].

However, the current chemical processes still suffer from several limitations. First, the purification of GO away from H_2SO_4 is very difficult accompanying serious waste acid discharges[5,7–9]. During the chemical oxidation of graphite, one of the important roles of sulfuric acid is to serve as intercalated molecules for the penetrating oxidation of bulk graphite. The resulted GO has layered structure of graphene oxide sheets and combines strongly with the ISA, forming actually the SIGO as the immediate oxidation descendent of graphite. In the traditional GO routes, ISA was usually treated as impurities and should be carefully removed from the SIGO even by repeatedly washing with vast amounts of water and hydrochloric acid[5,7–9]. Second, a chemical reduction and exfoliation of GO needs both extra mechanical energy and expensive and/or toxic reductant[10,11], while a high temperature decomposition is energy intensive[9,12]; thirdly, both chemical and thermal reductions usually introduce extra defects in graphene[12–15].

Here we report a facile preparation of graphene by rapid expansion exfoliation of SIGO at temperature just above 100°C in ambient atmosphere. It should be pointed out that although as a long-existing and easily available species in the oxidation of graphite, the SIGO has rarely been noticed. If look into the structure of the graphene oxide sheet, it can be found that although a significant fraction of the original sp^2-C in graphitic sheet have been oxidized to sp^3-C bonding to the O atoms (predominantly hydroxyl and epoxy groups) and H atoms (CH and CH_2), they are still staying in the arrayed hexagonal structures[15–19]. A direct dehydration between the O and the H atoms should be desirable for a perfect restoration of the graphitic sheet. We hope the ISA in the SIGO can catalyze a rapid and complete dehydration, which would generate high-pressure steam for the simultaneous expansion exfoliation of the SIGO. In addition, the released intensive heat may decompose the carbonyl groups bonding on the sheet edge. The generated graphene is denoted as ESIGO, and such a strategy is schematically shown in Fig. 1a.

Results

We treated graphite according to Hummers method[5]. The direct slurry resultant by centrifuging contained mainly SIGO and dissociative sulfuric acid, and the latter could be easily removed by washing with small amount of water. The content of sulfuric acid in the SIGO was adjusted by further washing with water or 2 wt% HCl. After
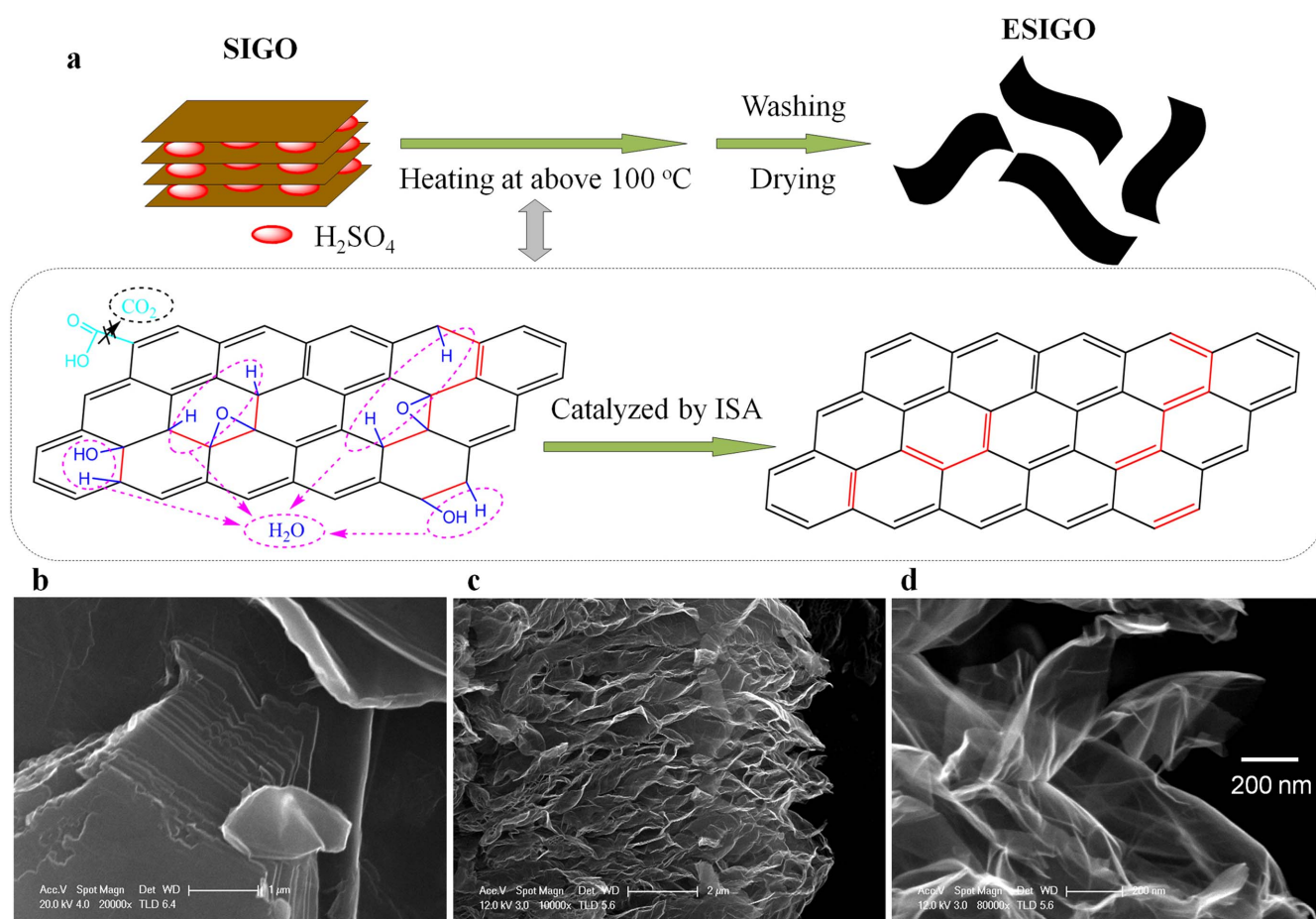
Figure 1 | The schematic of the SIGO process and the SEM observation. (a), Showing the catalytic exfoliation/reduction of sulfuric acid intercalated graphite oxide (SIGO) to graphene (ESIGO), with the interlayer sulfuric acid (ISA) serving as dehydration catalyst. (b–d), SEM images of the SIGO (b) (carbon to sulfur molar ratio $R_{C/S}$ = 35.9) and the as-exfoliated ESIGO (c, d) at 120°C in ambient atmosphere.

dried at 50°C, the carbon to sulfur atomic ratios ($R_{C/S}$) in SIGO was determined by energy dispersive X-ray (EDX) analysis as shown in Fig. S1. The sample with $R_{C/S}$ of about 14.9 looked squishy, indicating the existence of dissociative sulfuric acid. The SIGO with $R_{C/S}$ larger than 26.0 was dry and macroscopically homogeneous, suggesting the sulfuric acid was wholly immobilized in the interlayer between the graphite oxide sheets. Fig. 2a shows the X-ray diffraction (XRD) patterns of the SIGOs, indicating that the interlayer spacing of the SIGO is highly depended on the sulfuric acid content, which varies from 0.89 nm of SIGO with $R_{C/S}$ ≈ 26.0 to 0.75 nm of SIGO with $R_{C/S}$ ≈ 316 (Table S1).

The SIGO was then placed in a quartz crucible for the thermal treatment. The samples with $R_{C/S}$ between 26.0 and 40 underwent rapid expansion (within 2 minute to a expansion rate of about 550, corresponding to a density of 1.85 mg-graphene/mL after the expansion) at 110 ~ 120°C (Supplementary Video, Fig. S2). Complete exfoliation is evidenced by the total disappearance of the XRD diffraction peak of SIGO at around 10°, and the amorphous structure of expanded SIGO (ESIGO) (Fig. S3). Most of the C-H and C-O species in SIGO were removed as revealed by the Fourier transform infrared (FTIR) spectra (Fig. S4). The efficient reduction and exfoliation was also verified by the scanning electron microscopy (SEM) observation. Representative SEM images of the SIGO and ESISO are shown in Fig. 1b–d and Fig. S5. The SEM image (Fig. 1b) shows SIGO is dense in morphology. In contrast, the image (Fig. 1c) of the as-exfoliated ESIGO (without washing after the expansion) shows the fluffy morphology, and exfoliated graphene sheets can be identified in the high resolution image (Fig. 1d) of the ESIGO.

SIGO with lower sulfuric acid content has increasing difficulty in expansion (Table S1). The required temperature for rapid expansion of the SIGO with $R_{C/S}$ ≈ 55.6 increased to 150°C, and with $R_{C/S}$ ≈ 98.1 further to 250 ~ 300°C. According to the EDX analysis (Figure S1, SIGO7), SIGO washed with excess HCl solution was almost free from sulfuric acid (less than 0.5 wt%, $R_{C/S}$ ≈ 316) and other species of K and Mn involving in the Hummers method, which called as GO customarily, could only expand at temperature higher than 500°C in protection atmosphere[9]. However, this "clean" GO can become expandable at lower temperatures after reintercalated with sulfuric acid. For example, the SIGO with $R_{C/S}$ ≈ 146 could only expand at temperature above 350°C (Table S1). After immersed in 0.1 mol/L H_2SO_4 for 12 hrs, its sulfuric acid content increased to a $R_{C/S}$ of 39.7 and correspondingly the interlayer spacing increased from 0.76 to 0.83 nm (Fig. S1 and S3, Table S1). The resultant then expanded very well at ~120°C. These evidences convinced the pivotal role of the ISA in the low temperature SIGO process.

On the other hand, the sample with high sulfuric acid content which contained dissociative sulfuric acid failed to expand. However, besides a small peak at about 8°, the XRD pattern of SIGO with $R_{C/S}$ ≈ 14.9 shows also a broad XRD peak from 13° to 35° (Fig. S3), indicating graphite and/or graphene have already formed in this SIGO during drying at 50°C. The excess sulfuric acid should have catalyzed the dehydration of SIGO, but recaptured the water simultaneously owing to its strong hydroscopicity. Consequently, instead of expansion exfoliation, the reduced SIGO sintered together to graphite structure.

The ISA acted mainly as catalyst. Quantitative analysis indicated that the sulfuric acid in the SIGO remained in the ESIGO after the
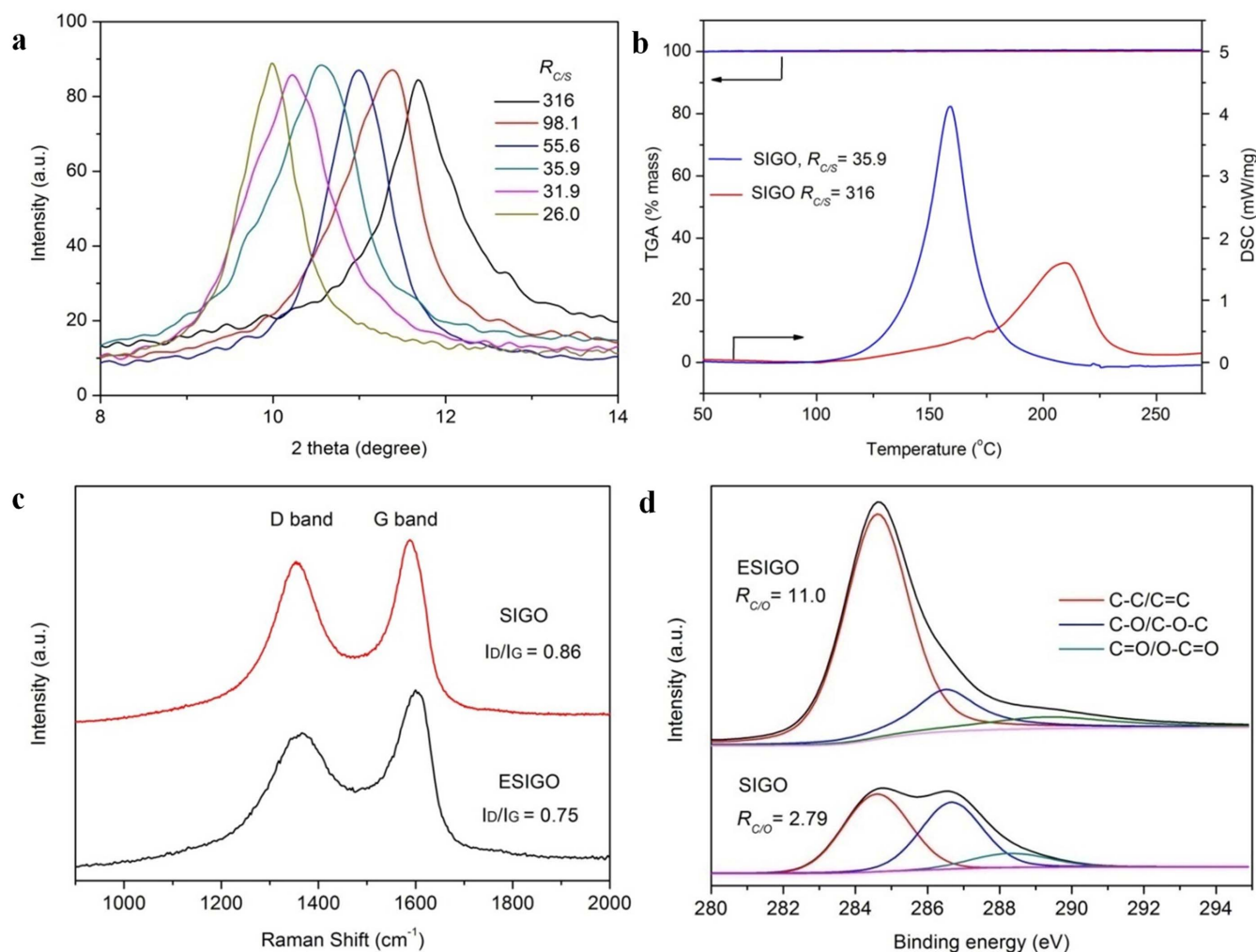
Figure 2 | Characterization of SIGO and ESIGO. (a), XRD patterns of the SIGO with different $R_{C/S}$, showing that the interlayer spacing of the GO is highly depended on the content of the ISA. (b), Normalized TGA and DSC plots for SIGO with $R_{C/S} \approx 35.9$ and $R_{C/S} \approx 316$ sealed in aluminum crucibles. (c), Raman spectra and (d) the C 1s XPS spectra of SIGO and ESIGO respectively.

expansion (Table S2). In addition, no sulfur oxide (SO_2, SO_3) was found in the gaseous product (Supplementary Discussion, Fig. S6). SIGO after neutralized by ammonia or sodium hydroxide also failed to expand at temperature below 500°C.

Differential scanning calorimetry (DSC) analysis convinced the catalysis of the ISA further. Upon heating, the SIGO sample in an open crucible would be scattered out by the vigorous gas release at temperatures above 100°C (Fig. S7). Alternatively, we performed DSC analysis by sealing the SIGO sample in an aluminum crucible (Fig. 2b). The SIGO with $R_{C/S} \approx 316$ or the "clean" GO shows a tardy and small exothermic signal peaked at 210°C[9]. In comparison, SIGO with $R_{C/S} \approx 35.9$ shows a very large and sharp DSC peak centered at about 160°C, indicating the violent reaction in the SIGO.

The significant shift of the DSC peaks in Fig. 2b may also suggest different reaction mechanisms. As the peak at 210°C of GO was attributed mainly to the decomposition of the oxygenic groups to CO_2[9,12,15], we propose that the sharp peak at 160°C of SIGO should be mainly due to the catalytic dehydration of the epoxy, hydroxyl and C-H species. Meanwhile, the carbonyl groups decomposed to CO_2 with the help of the intensive dehydration heat. However, the CO_2 should be minority (Table S2) of the gaseous product considering the carbonyl groups only occupy a small fraction of the total oxygenic groups[15–17]. Indeed, quantitative analysis indicated that the steam contributed about 88% of the gas pressure for this low temperature

expansion exfoliation of SIGO (Table S2, Fig. S2, Supplementary Discussion).

The preparation of graphene predominantly through the dehydration exfoliation makes this SIGO process significantly different from the traditional chemical or thermal GO approaches. No breakage of the relevant C-C bonds would occur, and the graphitic sheet would be best reconstructed. Such advantage has been evidenced by the Raman spectra. As shown in Fig. 2c, the I(D)/I(G) ratio decreases from about 0.86 of the SIGO to about 0.75 of the ESIGO, indicating decrease of defects. Whereas, GO reduced by various reducing chemicals usually showed significantly increase of the I(D)/I(G) ratio[16,17,20–22], which was attributed to the breakage of some sp3 C located hexatomic rings[14,15]. On the other hand, it has been well identified that the traditional thermal decomposition of GO through CO_2 evolution inevitably left behind vacancies within the graphene plane and defects at the boundaries[9,12,13].

X-ray photo emission spectroscopy (XPS) was used to evaluate the oxygen content in SIGO before and after the reduction. The XPS survey spectrum of the SIGO showed the existence of sulfate ions (~170 eV), C1s (~286 eV) and O1s (~532 eV) peaks (Fig. S8). After expansion and washed with water, the S1s peak disappeared, and the O1s peaks reduced significantly. The carbon to oxygen atomic ratio ($R_{C/O}$) was determined from the C 1s core-level spectra. As shown in Fig. 2d, the fitted peaks occurring at about 284.7, 286.7

and 289 eV are usually assigned to the unoxidized graphite carbon skeleton (C–C, C–H and C vacancies), hydroxyl or epoxide group (C–OH or C–O–C) and carboxyl group (C=O), respectively[14,18]. The calculated $R_{C/O}$ was about 2.79 : 1 of GO, which increased to about 11.1 : 1 of the ESIGO, in well agreement with the value 11.0 : 1 of ESIGO as estimated from the EDX analysis (Table S1). However, such $R_{C/O}$ of the ESIGO prepared in this work is much greater than those of chemically reduced GO ($R_{C/O} = 4.78 \sim 8.8$)[14,18,22] and comparable to that of thermally treated GO ($R_{C/O} = 9.7$) under high temperature ($\sim$1050°C) and rapid heating ($\sim$2000°C/min)[12].

The resultant graphene had a surface area of about 590 m²/g (Fig. S9). It was reported that the high temperature expanded GO with comparable surface area could be dispersed to single layer graphene in DMF[9]. To find out the thickness and size of ESIGO sheets, the as-exfoliated ESIGO was dispersed in DMF and then sampled for transmission electron microscopy (TEM) and atomic force microscopy (AFM) characterization. Typical TEM images of ESIGO are shown in Fig. 3a and b, which have sizes in the order of a few square micrometers. Fig. 3b exhibits an individual sheet, which should be a single layer graphene considering the low contrast of the high-magnification TEM image (Fig. 3c). On the other hand, the typical AFM image (Fig. 3d) displays plenty of individual sheets with the thicknesses varying from 0.8 to 1.2 nm according to the cross-sectional analysis (Fig. 3e and f), which are believed to be single layer

graphene[9]. However, compared to the high temperature treated GO, whose AFM image displayed mainly aggregated and wrinkled structure with a mean thickness of 1.75 nm[9], the monodispersity of the ESIGO has the advantage in measuring sheet thickness and diameter. Fig. 3g shows the thickness distribution of total 149 ESIGO sheets, suggesting a mean value of 1.3 nm. It can be seen that about 65% of ESIGO sheets are single layer graphene and 83% have thicknesses less than 1.5 nm. Fig. 3h shows that most of the ESIGO sheets have diameters in the range of 0.5 $\sim$ 1.5 μm with a mean of 1.07 μm, which is much greater than the high temperature treated GO[9], probably owing to the less breakage of the C-C bonds in the SIGO process as aforementioned.

The electrical conductivity of the resulted ESIGO was also measured by a four-point probe system using cylindrical sample pellets, which was higher than 1700 S/m, indicating the perfect restoration of sp^2-bonded graphitic sheet as well. The high conductivity value was also in line with the less defects and low oxygen content of the ESIGO.

Discussion

As the ISA plays important role in the oxidation of graphite to GO, this ISA catalyzed low temperature and rapid dehydration reduction of SIGO is somewhat unexpected but reasonable considering concentrated sulfuric acid traditionally a strong dehydrating agent. Such
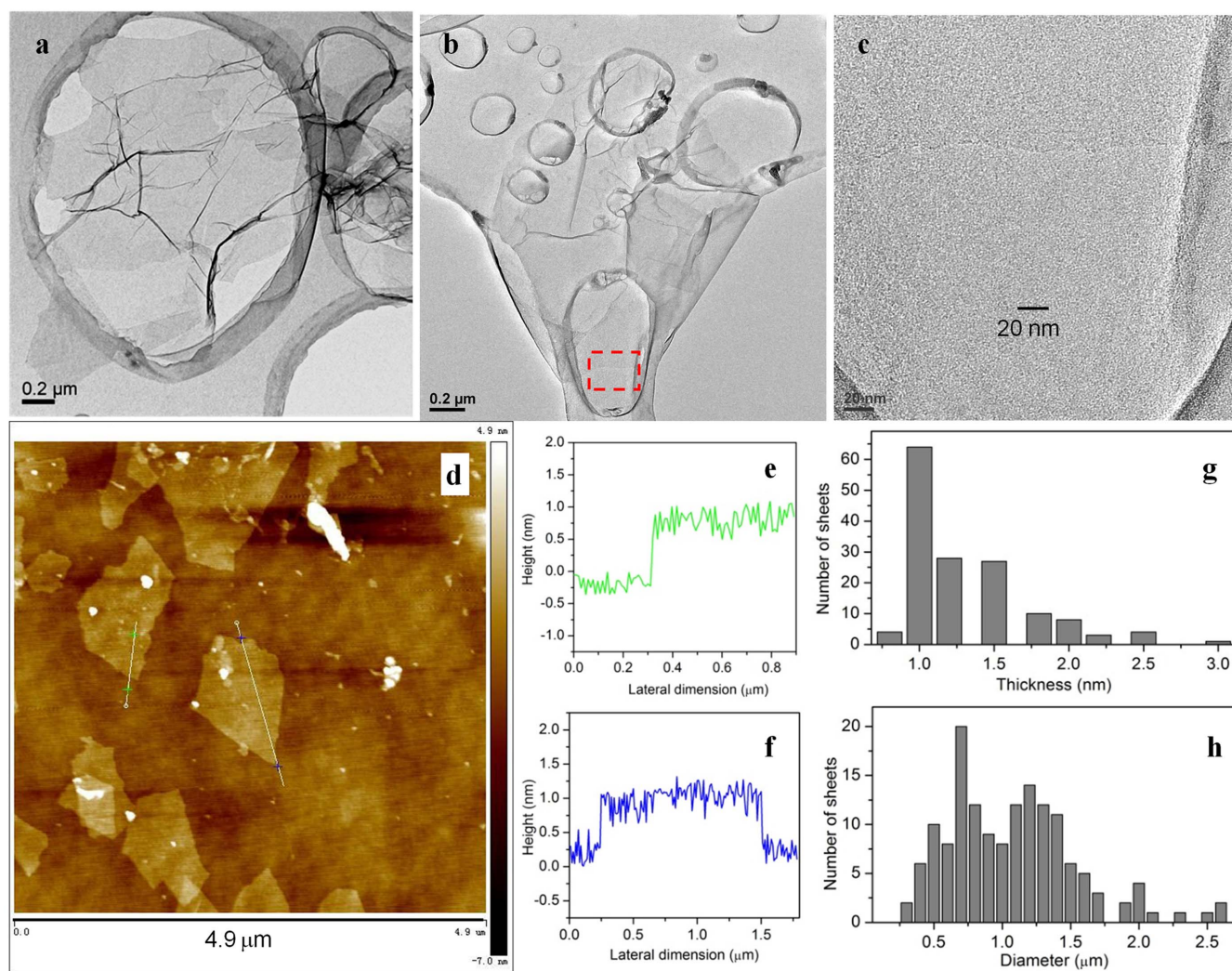

Figure 3 | The TEM and AFM characterization of ESIGO. (a–d), Representative TEM and AFM images of ESIGO on a freshly cleaned Si substrate and (c) is the high-magnification image of the red rectangle part in (b). (e) and (f), Height profiles taken along the lines in (c). (g), Histogram of sheet thicknesses from AFM images of 149 sheets. (h), Histogram of sheet diameters from the same 149 sheets.

a mechanism has led to graphene with low oxygen content, less defect and high conductivity. The great difficulties and serious waste discharge encountered in removing the sulfuric acid from SIGO in the traditional GO processes can be avoided. For example, to prepare 100 mg graphene, in the present work, at least 15 times washing with 2 wt% HCl (5 ~ 6 mL/time) were needed for the SIGO to a sulfuric content of about 0.5% (Table S1), corresponding to about 80 mL waste in a traditional GO process. While in a typical SIGO process, 4–5 times washing (~25 mL) of the SIGO can lead to a proper sulfuric acid content (4 ~ 5 wt%), and after the expansion, if necessary, the sulfuric acid can be easily removed by 2 ~ 3 times water washing due to the absence of functional groups in ESIGO, corresponding to 40 mL waste discharge in total. The data indicates about half of waste discharge can be reduced by the SIGO process in addition to the operation facilitation.

The ESIGO may find an immediate application in electrochemical capacitors[23,24]. If using sulfuric acid as electrolyte, no washing is needed to the as-exfoliated ESIGO, thus the waste discharge can be further reduced. Fig. 4a presents the cyclic voltammograms (CVs) of typical ESIGO recorded using a cast film electrode in 1 mol/L H_2SO_4. The mass load of the electrode was about 0.33 mg/cm^2, and the background current of the glassy-carbon disc was neglectable. The CVs are all fairly rectangular in shape although the applied potential scan rates were fairly fast. The electrochemical impedance of the

ESIGO electrode shows again ideal capacitor behavior (Fig. 4b). The ESIGO was also tested by galvanostatic charge–discharge cycles at different rates. The results are presented in Fig. 4c, indicating a specify capacitance of 216, 200 and 188 F/g at 2 A/g, 5 A/g and 10 A/g respectively. Particularly when the charge–discharge was cycled at the highest rate explored in this work the capacitance values remained fairly unchanged, as shown in Figure 4c and d with an impressive decrease of less than 2% after 1300 cycles, demonstrating a great stability.

According to the above discussion, this SIGO process has the advantages of reductant free, easy operation, low-energy and environmental friendly. The ESIGO shows high electrochemical performance for capacitors. The as-exfoliated ESIGO can be dispersed to single sheets in DMF. Therefore, the provided synthesis route from graphite to graphene via SIGO is compact and efficient, and should be of great significance for the preparation of graphene on ton scales[25]. Our understanding on SIGO might also open up new opportunities for the development of various graphene based devices and composite materials.

Methods

Preparation of sulfuric acid intercalated graphene oxide (SIGO). Oxidation exfoliation of graphite was carried out according to the Hummer method[5]. Typically, 10 g graphite powder was treated by $NaNO_3$ and $KMnO_4$ in 98 wt% sulfuric acid
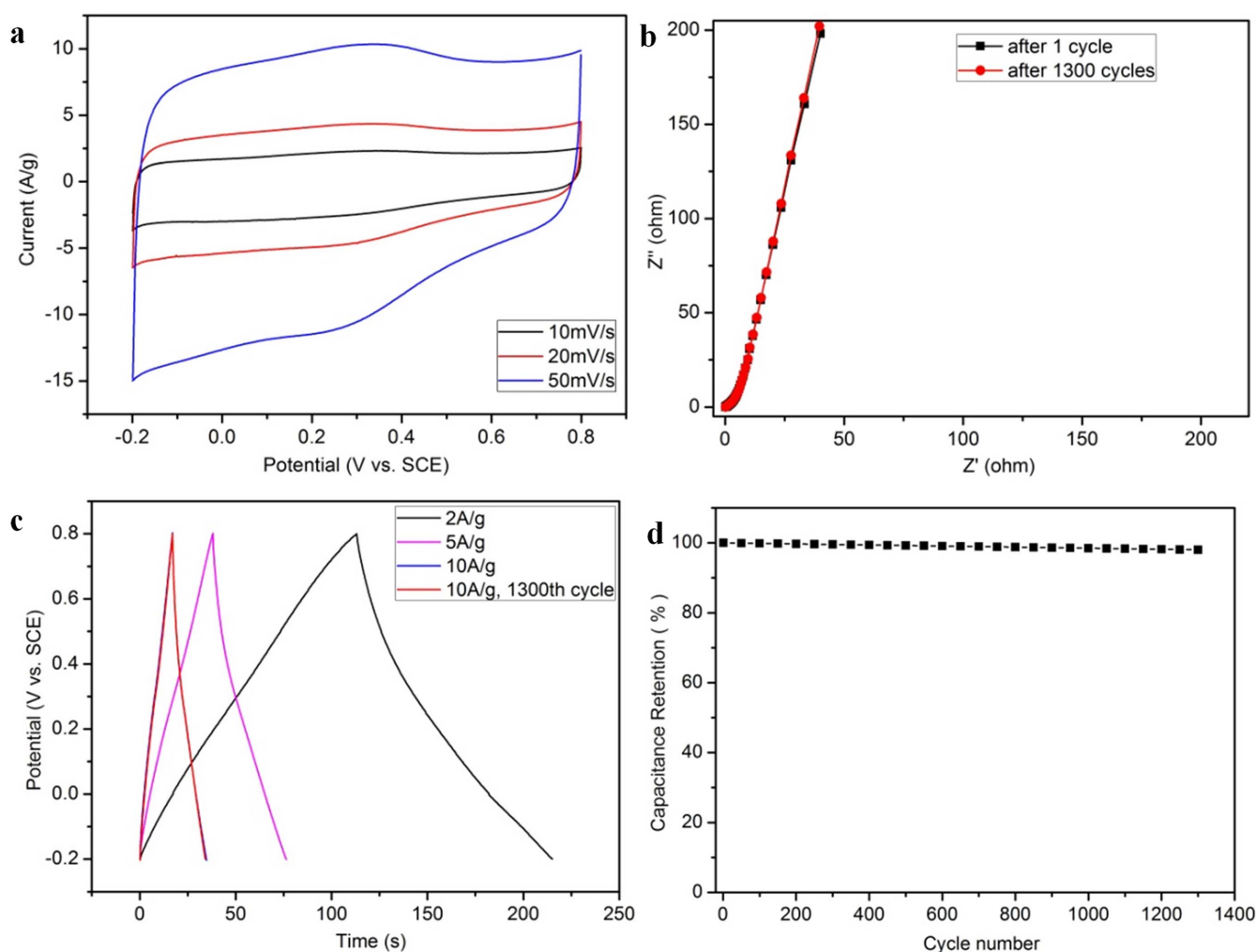

Figure 4 | The electrochemical characterization of the ESIGO. (a), Cyclic voltammetry curves of the ESIGO electrode. (b), Nyquist plots of the ESIGO electrode before and after 1300 charge/discharge cycles (sinusoidal signal of 5 mV, from 100 kHz to 0.1 Hz). (c), Charge and discharge curves at the indicated current density. (d), Cycling performance during charging/discharging at 10 A/g. The ESIGO was prepared at 120°C from SIGO with $R_{C/S} \approx 35.9$. The electrochemical tests were carried out in 1 mol/L H_2SO_4 solution at room temperature.

medium. After sedimentation, about 180 ml slurry resultant was obtained, which contained mainly SIGO and dissociative sulfuric acid, the latter can be easily removed by washing with 200 ~ 300 ml deionized water or 2 wt% HCl. The sample could be further washed by repeatedly suspending and centrifuging. For example, 5 ml the slurry was repeatedly washed with 5 ml water or 2 wt% HCl at room temperature, and the different repeated time resulted in SIGO with different sulfuric acid content or the carbon to sulfur molar ratio ($R_{C/S}$). The SIGO sample was dried in air at 50°C for use.

The SIGO with $R_{C/S} \approx 39.7$ has also been prepared by immersing the SIGO with less sulfuric content ($R_{C/S} \approx 146$) in dilute H_2SO_4 solution (0.1 mol/L) for about 12 hrs.

Expansion of SIGO. A program-controlled box furnace with a hole (38 mm in diameter) at the top was used for the heating. Quartz crucible (33 mm in diameter, 350 mm in length) with a side exhaust pipe locating at 100 mm to the open end was inserted into the furnace for about 200 mm through the hole. The SIGO samples loaded in the crucible were thermally expanded at set temperatures (Fig. S2, Supplementary Video). The resulted graphene was denoted as ESIGO, which was carefully collected, washed with water and dried for analysis.

For a quantitative analysis of the sulfuric acid in the ESIGO and the gas product, parallel experiments on the expansion of the SIGO with sulfur content of about 4.2 wt% were carried out. Firstly, the furnace temperature was controlled at 120°C for a stable temperature and gas distribution in the quartz crucible. And then a plastic bag containing no initial gas was connected to the side pipe. The SIGO sample was then fed and the top end of the crucible was sealed by a rubber stopper. Within 2 minutes, expansion of the SIGO sample occurred, resulting in inflation of the plastic bag. The robust airflow scattered the graphene to the upper end of the quartz tube or even into the bag depending on the mass of feed. Droplets of water formed on the upper inwall of the quartz crucible, where the temperature was measured to be about 30 ~ 40°C. The plastic bag with the gas showed a temperature of about 26°C (the room temperature), and the gas volume was measured and was assumed to be the volume of the generated CO_2. The weight change during the expansion process was also recorded.

After washed, the remaining sulfuric acid in the ESIGO became lower than the detection limit of energy dispersive X-ray (EDX) analysis. The condensed filtrate showed strongly acidic by the PH paper and precipitated with Ba^{2+} to $BaSO_4$. The mass of the sulfuric acid was then estimated from the mass of the precipitation. Alternatively, all the expansion generated gas (including the water) was absorbed by 2 mol/L NaOH solution with the help of long time argon flow, and then was precipitated with Ba^{2+}. EDX analysis shows that the precipitation was almost pure $BaCO_3$, and the mass of the generated CO_2 was also estimated accordingly.

Characterization and apparatus. SEM observation was conducted by FEI Sirion Field Emission Gun SEM with energy dispersive x-ray spectroscopy (EDX) for the elemental analysis. JEOL JEM-2010FEF was used for the TEM observation. Raman characterization was carried out using a RM-1000 Laser Confocal Raman Microspectroscopy (Renishaw, England) employing a 514.5 nm laser beam. Fourier transform infrared spectroscopy (FTIR) of the sample was studied at ambient temperature with a FTIR-Raman spectrometer (Nicolet, NEXUS-670). Differential scanning calorimetry (DSC) and Thermo Gravimetric analysis (TGA) were achieved on DSC Q200 and TGA Q500 (TA Instrument), as well as Setsys16 (Setaram Co.). X-ray diffraction (XRD) patterns were performed using a Shimadzu Lab XRD-6000 system with Cu Kα radiation. The X-ray photoelectron spectroscopy (XPS) was carried out with a KRATOS XSAM800 XPS. Specific surface area analysis was conducted with a Micromeritics ASAP 2020 Analyzer (Norcross, GA) in terms of the Brunauer, Emmett and Teller (BET) method using nitrogen adsorption. The Canon PC 1192 was used to take the photos and record the video. For the electrical conductivity measurement, the ESIGO sample was pressed (20 MPa) into a pellet (13 mm in diameter, 0.2 mm in thickness and 1.65 g/cm³ in density), with the help of few amount of sulfuric acid and was measured three times to obtain an average conductivity value by using a RTS-8 four-probe measurement system (4 Probes TECH).

Atomic force microscopy (AFM) measurements were performed in tapping mode on a Multimode 8 Scanning Probe Microscope (Nanoscope V, Bruker Instruments) using a silicon tip. After dispersion of the as-exfoliated ESIGO (0.05 mg/mL) by ultrasonication in DMF, samples were spin-coated onto freshly cleaned Si substrates and dried in a vacuum oven.

Electrochemical tests. The as-exfoliated ESIGO was dispersed by ultrasonication in 0.05 wt% Nafion alcohol solution to a concentration of 2.1 mg-graphene/mL, and then cast film electrode was prepared by casting 20.0 μL of the dispersion onto a prepolished glassy-carbon-disc (area, 0.1256 cm²) and dried at 85°C. The electrochemical performance of the ESIGO was characterized in 1 mol/L H_2SO_4 at room temperature. In all electrochemical measurements (Autolab), a standard one-compartment, three-electrode cell was used with a graphite counter electrode and a saturated calomel electrode (SCE) for potential reference.

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Acknowledgments

Author contributions
X.B.J. proposed the SIGO process for graphene preparation and Y.Z.H. made the initial experimental confirmation. Y.Z.H. then performed the subsequent experiments according to discussion of all authors. Z.Y.W. and Y.Z.H. analyzed the results and wrote the original draft to the paper. X.B.J. edited the original manuscript and revised it for submission. All the authors discussed the results and commented on the paper.

Additional information