



High-Quality Reduced Graphene Oxide by a Dual-Function Chemical Reduction and Healing Process

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A new chemical dual-functional reducing agent, thiophene, was used to produce high-quality reduced graphene oxide (rGO) as a result of a chemical reduction of graphene oxide (GO) and the healing of rGO. Thiophene reduced GO by donation of electrons with acceptance of oxygen while it was converted into an intermediate oxidised polymerised thiophene that was eventually transformed into polyhydrocarbon by loss of sulphur atoms. Surprisingly, the polyhydrocarbon template helped to produce good-quality rGO_C (chemically reduced) and high-quality rGO_{CT} after thermal treatment. The resulting rGO_{CT} nanosheets did not contain any nitrogen or sulphur impurities, were highly deoxygenated and showed a healing effect. Thus the electrical properties of the as-prepared rGO_{CT} were superior to those of conventional hydrazine-produced rGO that require harsh reaction conditions. Our novel dual reduction and healing method with thiophene could potentially save energy and facilitate the commercial mass production of high-quality graphene.

Graphene has attracted great interest because of its unique physical properties¹ arising from its rigid two-dimensional (2D) structure, and its potential applications in nanoelectronics², energy storage materials³, polymer composite materials⁴ and sensing⁵. Mechanical exfoliation is one of the successful approaches that have been developed for the preparation of high-quality graphene sheets suitable for fundamental studies, but large-scale production of such pure graphene sheets remains unfeasible. Instead, chemical graphitisation from graphene oxide (GO) to reduced graphene oxide (rGO) is generally used for mass production of graphene^{6–10}. Numerous reducing chemicals such as hydrazine¹¹, NaBH₄¹², hydriodic acid (HI)¹³, NaOH¹⁴, ascorbic acid¹⁵ and glucose¹⁶ have been used to convert GO to rGO. However, all of these reducing agents produce imperfect rGOs containing a high level of defects or disorders. Recently, Amarnath et al. introduced a pyrrole as a new chemical reducing agent in this process, but the C/O ratio showed that GO was not fully reduced and the resulting rGO contained high nitrogen contamination emanating from the nitrogen source¹⁷. Kaminska et al. also introduced reduction and functionalization of graphene oxide using tetrathiafulvalene¹⁸. Despite the urgent need for production of a defect-free rGO, there have not been any reports of chemical healing of the defects of heteroatom-free rGO in the reduction process of GO to rGO. In addition, the development of novel reduction methods that are environmentally friendly, mild, and cost effective ways remains a challenge for mass production of high-quality rGOs by chemical healing.

In this study, we introduce a new dual-functional reducing agent, thiophene (T) which has lower reactivity than pyrrole¹⁷ and produces high-quality, heteroatom-free rGOs by chemical healing reduction of GO. Thiophene can be used to reduce as-prepared GO by dual-functional electron donation and oxygen consumption. It is also well known that by applying a potential across a solution of thiophene, it can be polymerised, leading to its use as an oxidant of thiophene or a cross-coupling catalyst¹⁹. GO itself is also known to have oxidising capacity²⁰. Thus we hypothesized that the mild reducing agent, thiophene could be used for effective mass production of GO to rGO by becoming an oxidised polythiophene sulfoxide or sulfone through release of electrons and uptake of oxygen. Finally, a π -conjugated polyhydrocarbon could be obtained by easy removal of the sulphur dioxide (-SO₂) group of the oxidised polythiophene sulfoxide or sulfone. It is likely that the reduction and healing mechanism involves donation of electrons from thiophene monomers to reduce GO to rGO during their polymerisation into the oxidised form (i.e. thiophene sulfoxide and sulfone)^{21,22}. The resulting polyhydrocarbon intermediate can be used as a template to heal rGO, thus providing high-quality rGO (Figure 1).

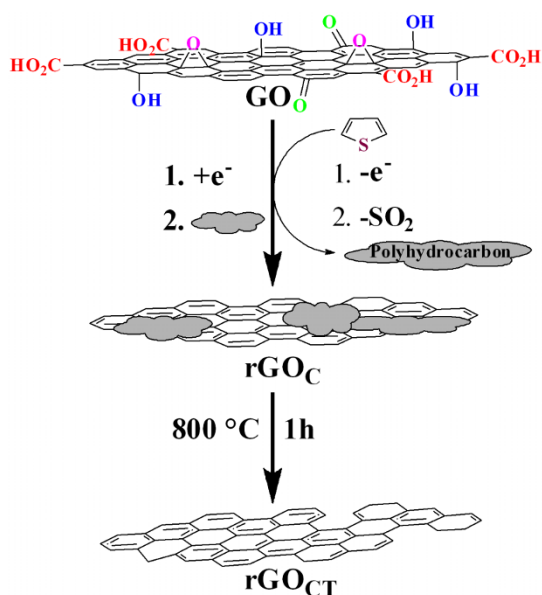


Figure 1 | Schematic diagram for the formation of rGO_C and rGO_{CT} . rGO_C was prepared by chemical reduction of as-made GO with thiophene whereas rGO_{CT} was prepared by chemical reduction followed by thermal treatment.

Results

Preparation and characterization of healed rGO. X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), Raman spectroscopy, thermogravimetric analysis (TGA), transmission electron microscopy (TEM) and atomic force microscopy (AFM) were employed for characterization of rGO. Thiophene was reacted with GO at 80 °C for 24 h to produce high-quality rGO. In the reaction mixture, GO gained electrons to produce rGO by the formation of polymerised and oxidised thiophene. The resulting polyhydrocarbons obtained from the elimination of sulphur dioxide²³ could be physically absorbed onto as-made rGO by π - π interactions¹⁷. This in-situ healing reduction process resulted in good-quality chemically reduced graphene oxide (rGO_C) without any sulphur contamination compared to normal hydrazine-produced rGO which is contaminated with nitrogen and has a reduced mass. After completion of the procedure, we could not detect any thiophene in the reaction mixture by nuclear magnetic resonance (NMR). To demonstrate that thiophene donated electrons to GO to produce rGO, we carried out a control experiment by incubating dibenzothiophene with GO. No reaction took place and GO was not reduced. NMR after 24 h revealed unchanged dibenzothiophene with both sides of the thiophene remaining blocked by benzene rings as they were before the reaction (Figure S15 and S16). Dibenzothiophene could not reduce GO to rGO. This control experiment thus strongly supported our hypothesis for the reaction mechanism. Elimination of SO_2 from the oxidised polythiophene was confirmed by detection of released SO_2 gas (see Supplementary Information, video and Figure S8 and S9)²⁴. To confirm the release of SO_2 gas and to understand the detailed reaction pathway, we used different amounts of thiophene (0.2, 1, 2 and 5 mL) with the same amount of GO solution. We found that 2 mL of thiophene was most effective to produce high-quality rGO. To further improve the quality, we carried out thermal treatment at 800 °C for 1 h. With thermal treatment, the as-prepared chemically reduced rGO_C was converted to thermally-reduced graphene oxide (rGO_{CT}) when 2 or 5 mL of thiophene had been used. We observed that after thermal treatment, the as-prepared rGO_{CT} was highly reduced and healed in comparison to $rGO_{N_2H_4}$ produced by hydrazine.

We used XPS to analyse GO and rGO produced by thiophene reduction. The high-resolution C1s XPS spectrum of the GO sheets showed a sharp peak at 284.6 eV that corresponded to C-C bonds of carbon atoms in a conjugated honey-comb lattice. Peaks at 286.7, 288.4 and 290.1 eV could be attributed to different C-O bonding configurations due to the harsh oxidation and destruction of the sp^2 atomic structure of graphite (Figure S1)²⁵. After reduction with thiophene, the intensities of all of the related oxygen peaks were sharply decreased in the rGO_C sample compared to GO, indicating that the delocalized π conjugation was restored in our rGO_C sample (Figure 2 a)¹¹. Based on the XPS analyses, the as-prepared GO had a very high oxygen atomic percentage ($C/O = 2$). In contrast, the C/O ratio of the rGO_C produced by thiophene reduction was 10.9 (Figure 2a). The C/O ratio of the as-prepared rGO_{CT} was 16.8 (Figure 2b). We concluded that the rGO from our process contained far less oxygen, confirming its high quality. The atomic composition of all samples was analysed by XPS. We did not detect any sulphur and nitrogen in GO and rGOs, confirming that despite the use of thiophene to reduce GO, the as-prepared rGOs were not contaminated by sulphur (Figure S2). We also determined the C/O ratios of rGOs produced with different amounts of thiophene (Supplementary Information, Table S1).

The interlayer distances of as-prepared GO and rGO were confirmed by XRD. The 2θ peak of graphite powder was at 26.71°, indicating that the interlayer distance was 3.34 Å (Figure S3). The as-prepared GO showed a 2θ peak at 10.27°, indicating that the graphite was fully oxidised into GO with an interlayer distance of 8.60 Å (Figure 2c). The XRD pattern of the as-prepared rGO_C showed a typical broad peak of 2θ peak with the polyhydrocarbon template at 20.1°, indicating that the interlayer distance was 4.4 Å (Figure 2c). The shift of the XRD pattern of GO (10.27°) to rGO_C powder 2θ peak (20.1°) suggested that the rGO_C was reduced well. The interlayer distance of rGO_C was 4.4 Å, which was larger than that of graphite powder (3.34 Å) and a little broader than control $rGO_{N_2H_4}$ (Figure S3). These differences were attributed to the well-ordered 2D structure of the rGO sheets within the polyhydrocarbon template. After thermal treatment followed by chemical reduction, the as-prepared rGO_{CT} powder 2θ peak shifted from 20.1° to 25.6° suggesting that rGO was fully reduced. The interlayer distance was 3.5 Å, which means that there was no polyhydrocarbon template in between the two rGO layers. The same results were obtained when 5 mL thiophene was used (Figure S4). Our XRD data for increasing amounts of thiophene (0.2, 1 and 2 mL) showed that the conversion of GO to rGO occurred gradually (Figure S5).

The quality of as-prepared rGO was assessed by TGA. TGA plots of GO (red) and rGO (blue and green) are shown in Figure 2d. In the GO sample, the major weight loss occurred between 100 and 200 °C, indicating the release of CO, CO_2 and steam from the most labile functional groups during pyrolysis²⁶. At temperatures below 800 °C, the total weight loss was about 77%. In contrast, the rGO_C (blue) sample showed higher thermal stability than GO. The major weight loss was ~26% at temperatures near 300 °C and the total weight loss was ~30% at 800 °C. This major loss of mass could be attributed to the presence of a high amount of polyhydrocarbon on the as-prepared rGO_C , whereas after thermal treatment followed by chemical reduction, total weight loss of the as-prepared rGO_{CT} (green) was only 6%. This minor mass-loss was attributed to the absence of most oxygen functional groups.

Raman spectroscopy is the most direct and non-destructive technique to characterize the structure and quality of carbon materials^{27,28}, and in particular to investigate the defects and ordered and disordered structure of graphene. Raman spectra were collected from the as-prepared samples at an excitation wavelength of 514 nm under ambient conditions by dropping DMF dispersions on a silicon (Si) substrate. For comparison, we also collected the spectra of GO and rGO obtained from reduction of GO using thiophene under the

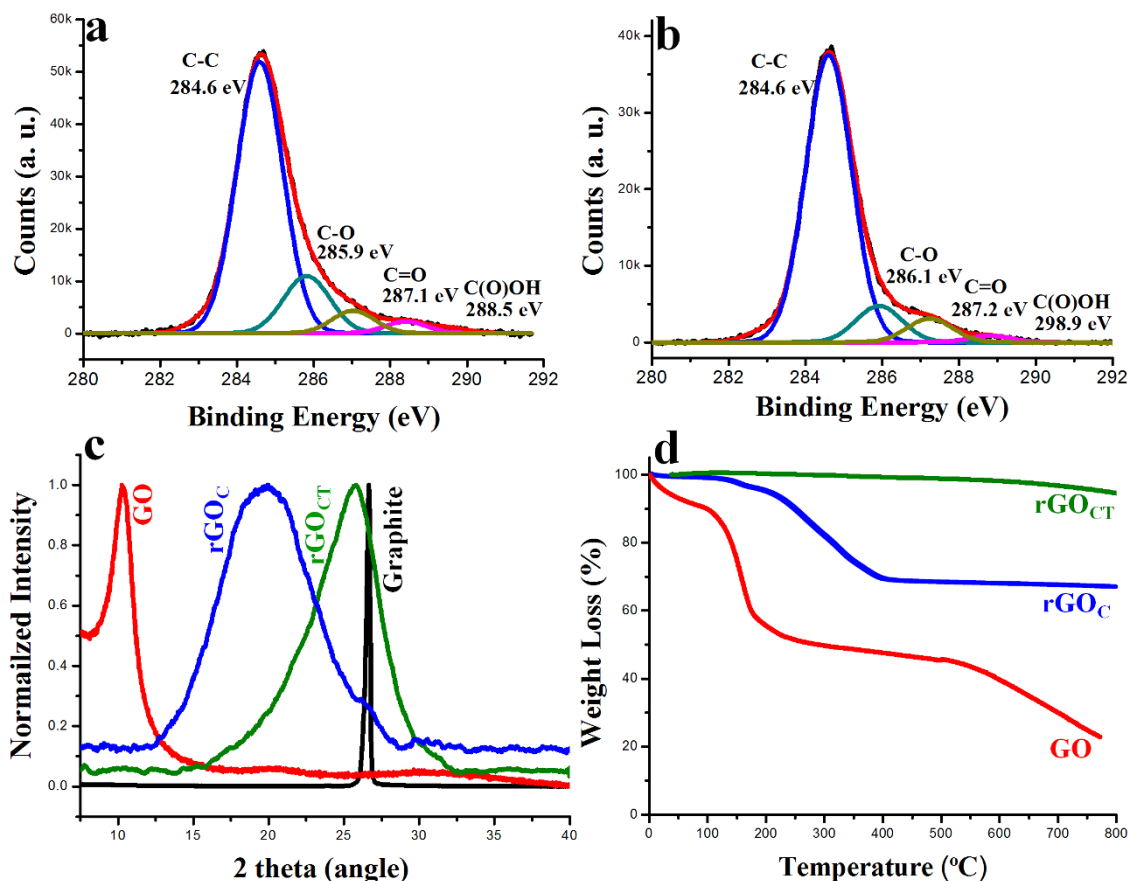


Figure 2 | Characteristic XPS, XRD and TGA data. (a) High-resolution C1s spectra of rGO_C. (b) High-resolution C1s spectra of as-prepared rGO_{CT} by thiophene. (c) Powder XRD pattern of GO (red), rGO_C (blue), rGO_{CT} (green) and graphite (black). (d) TGA plots of GO (red) and rGO_C (blue) and rGO_{CT} (green). rGO had better thermal stability than GO.

same conditions. The Raman spectra of as-prepared GO exhibited two remarkable peaks at about 1352 and 1605 cm^{-1} , corresponding to the well-defined D and G bands, respectively (Figure 3a). The G band is related to the E_{2g} -vibration mode of sp^2 carbon and domains can be used to explain the degree of graphitization, whereas the D band is associated with structural defects and partially disordered structures of the sp^2 domains²⁷. After thiophene reduction, the as-prepared rGO_C sample had a G peak at 1585 cm^{-1} and D peak at 1354 cm^{-1} . The increased I_D/I_G ratio of rGO after chemical reduction has been commonly reported in the literature¹¹. In our study, the I_D/I_G ratio of the as-prepared rGO exhibited a significant decrease in comparison to the previously reported rGO. In the case of GO, the I_D/I_G ratio was 0.91 and after thiophene reduction, the as-prepared rGO_C sample was 0.41, compared to the ratio of the control rGO_{N₂H₄} sample of 1.2 (Supplementary Information, Table S2). We concluded that production of rGO from GO by reduction with thiophene had a healing effect²⁹ in the presence of the resultant poly-hydrocarbon template in comparison to the control rGO_{N₂H₄}. When we used 0.2, 1 and 5 ml of thiophene, the corresponding I_D/I_G ratio of the as-prepared rGO_C was 0.81, 0.65 and 0.43, respectively (Figure 3a). The I_D/I_G ratio of the as-prepared rGO_C was almost the same for 2 mL and 5 mL thiophene (Figure 3a, S6 and S7). In both cases, after the thermal treatment followed by chemical reduction, the ratio increased, up to 0.85 and 0.83 respectively, indicating that the healing effect was still present after harsh thermal treatment³⁰ in comparison with the control rGO_{N₂H₄} produced by hydrazine. Furthermore, the intensity of the 2D peak at $\sim 2693 \text{ cm}^{-1}$ and S3 peak at $\sim 2938 \text{ cm}^{-1}$ increased for rGO_C and rGO_{CT}, showing better graphitisation and no charge transfer due to the absence of impurities (Figure S6)³¹. To more clearly observe this healing effect, we carried out the thiophene

treatment with partial rGO (prGO) and control rGO_{N₂H₄}. The sample produced by thiophene treatment of prGO showed a large healing effect with a sharply increased 2D peak (Figure 3b), whereas the sample produced by thiophene treatment of rGO_{N₂H₄} showed no healing effect, thus confirming our assumption. In the case of prGO, the C/O ratio was ~ 4.3 . Thus prGO could still be reduced by the donating electron of thiophene due to the presence of abundant oxygen groups, demonstrating our assumption of the healing effect of product. In contrast, rGO_{N₂H₄} had a C/O ratio of ~ 14 and it could not undergo effective further reduction by the donated electron of thiophene. Thus thiophene could not be polymerised to produce a polyhydrocarbon and a healing effect. AFM images of the as-prepared GO (Figure S12) showed that the average thickness of the layers was $\sim 1 \text{ nm}$, indicating the formation of single-layered GO¹⁶. The average thickness of as-prepared rGO_C was $\sim 2.3 \text{ nm}$, which indicated the formation of polyhydrocarbon attached to rGO layers (Figure S10), whereas the average thickness of rGO_{CT} was $\sim 1.2 \text{ nm}$ (Figure S11). High-resolution transmission electron microscopy (HRTEM) studies were also carried out for rGO sheets. HRTEM images of rGO_C showed 3–5 layers of crystalline structure due to a ring-shaped pattern consisting of many diffraction spots for each order of diffraction (Figure S13a). In contrast, the HRTEM image of the rGO_{CT} sheet (Figure S13b) was a single layer, as expected, indicating that the rGO_{CT} sheet reduced from exfoliated GO was indeed monolayer rGO_{CT} (Figure S13b). The insert of Figure S13b shows a selected area electron diffraction (SAED) pattern of rGO_{CT}, clearly demonstrating the crystalline structure of rGO. The diffraction pattern images showed that the rGOs had been restored to the hexagonal graphene framework. Furthermore, the as-prepared rGO_C and rGO_{CT} pellets (33 and 26 μm thickness, respectively) had

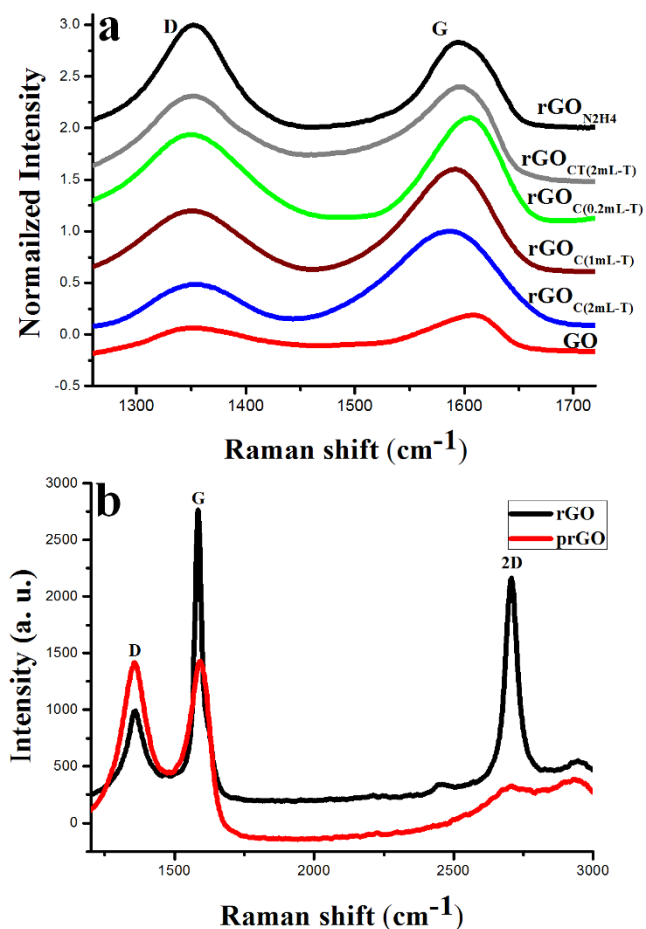


Figure 3 | Characteristic Raman data. (a) Raman spectra of GO (red), as-prepared rGO_{C(2 mL-T)} using 2 mL thiophene (T) (blue), rGO_{C(1 mL-T)} using 1 mL thiophene (T) (brown), rGO_{C(0.2 mL-T)} using 0.2 mL thiophene (T) (green), rGO_{CT(2 mL-T)} using 2 mL thiophene with chemical reduction followed by thermal treatment (grey) and rGO_{N₂H₄} by hydrazine (black). (b) Raman spectra of prGO (red) and resultant product from the treatment of prGO with thiophene (black).

a comparatively low sheet resistance (59 and 9 Ω/square, respectively), indicating their good electrical properties, whereas the control rGO_{N₂H₄} pellet (20 μm thickness) had a high sheet resistance (26 Ω/square).

Discussion

Therefore, according to our experimental result, we could conclude that the treatment of unique characteristic thiophene followed by thermal treatment produced high-quality rGOs. The as-made rGO nanosheets were well-reduced and formed a well-crystallised graphitic material without any atom impurities. The most effective part is that thiophene can produce rGO that is healed in-situ along with dual reduction with higher mass and highly graphitised rGO. This extensive reduction along with a relatively small average interlayer distance as measured by XRD is probably the main reason for the good electrical properties. This work represents an effective strategy for obtaining high-quality reduced rGO nanosheets by mass-production using a new reducing agent system, which is environmentally friendly.

In summary, the reduction of GO by thiophene was shown to be characterized by significant advantages over other reported procedures. The resulting rGO nanosheets were highly deoxygenated and formed a well crystallized graphitic material without any nitrogen or sulphur impurities. One of the biggest advantages was that the dual

functional reduction reaction with thiophene could produce in-situ healed rGO_C with a higher mass and highly graphitised rGO in comparison to the reported rGO. Thiophene reduced GO by donation of electrons with acceptance of oxygen while it was converted into an intermediate oxidised and polymerised thiophene that was eventually transformed into polyhydrocarbon by loss of sulphur atoms. Surprisingly, the polyhydrocarbon template helped to produce good-quality rGO_C (chemically reduced) and high-quality rGO_{CT} by thermal treatment. The resulting rGO_{CT} nanosheets did not contain any nitrogen and sulphur impurities, were highly deoxygenated and showed a healing effect. Thus the electrical properties of as-prepared rGO_{CT} were better than that of conventional rGO_{N₂H₄} that requires harsh reaction conditions. To the best of our knowledge, this is the first approach to prepare graphene nanosheets using thiophene as a reducing agent. Our XPS, XRD, Raman spectra, TGA, TEM and AFM experimental findings fully supported the formation of high-quality rGO. Our novel dual reduction and healing method using thiophene could potentially save energy and facilitate the commercial mass production of high-quality graphene.

Methods

Preparation of graphene oxide (GO). GO was prepared from natural graphite powder (Bay Carbon, SP-1 graphite) by the modified Hummers and Offeman's method using sulphuric acid, potassium permanganate, and sodium nitrate^{32,33}.

Reduction of GO with thiophene. GO (10 mg) was dispersed in 10 mL of DI water by stirring at room temperature, followed by the addition of 2 mL of thiophene in round bottom flask. The resultant solution was heated with condenser under N₂ atmosphere at 80°C for 24 h. The formed solid material was then collected by filtration (glass frit funnel setup with membrane filter paper 0.45 μm) and washed several times with water, ethanol, dichloromethane and acetone before drying at 60°C for 24 h in a vacuum oven to yield rGO.

SO₂ detection. The reaction setup was connected with an outlet, which was dipped into a Ca(OH)₂ water solution. The production of white solid CaSO₃ was confirmed by Energy-dispersive X-ray spectroscopy (EDX) (see Supplementary Information video).

Characterization. All X-ray photoemission spectroscopy (XPS) measurements were made with a SIGMA PROBE (ThermoVG, U.K.) with a monochromatic Al-Kα X-ray source at 100 W, using the Gaussian/Lorentzian sum function. The powder XRD pattern was acquired using a D8-Advance instrument (Germany) and Cu-Kα radiation. Raman spectroscopy measurements were performed by using a micro-Raman system (Renishaw, RM1000-In Via) with an excitation energy of 2.41 eV (λ = 514 nm). The thermal properties of rGO were characterized by TGA (Polymer Laboratories, TGA 1000 plus). AFM was performed with a SPA400 instrument containing a SPI-3800 controller (Seiko Instrument Industry Co.) at room temperature. TEM images were obtained with a JEOL JEM 3010 instrument. The EDX was observed by field emission scanning electron microscopy (SEM; JSM-6701F/INCA Energy, JEOL).

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Author contributions

S.S. and H.L. wrote the manuscript. S.S. prepared and characterised all materials. Y.K. and Y.Y. prepared graphene oxide. H.Y. measured sheet resistance. S.L. measured Raman, Y.P. measured XRD data. H.L. and S.S. supervised the work.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

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