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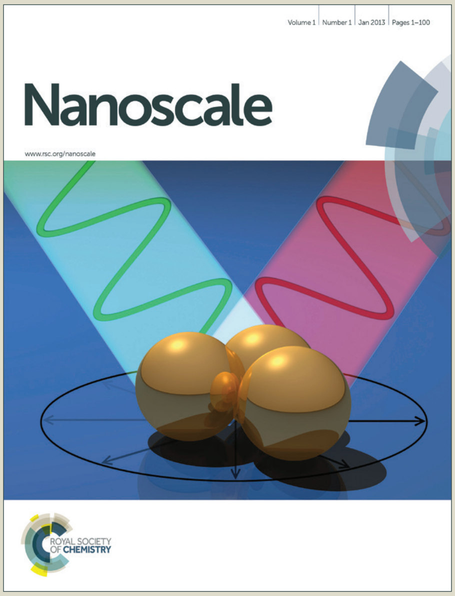

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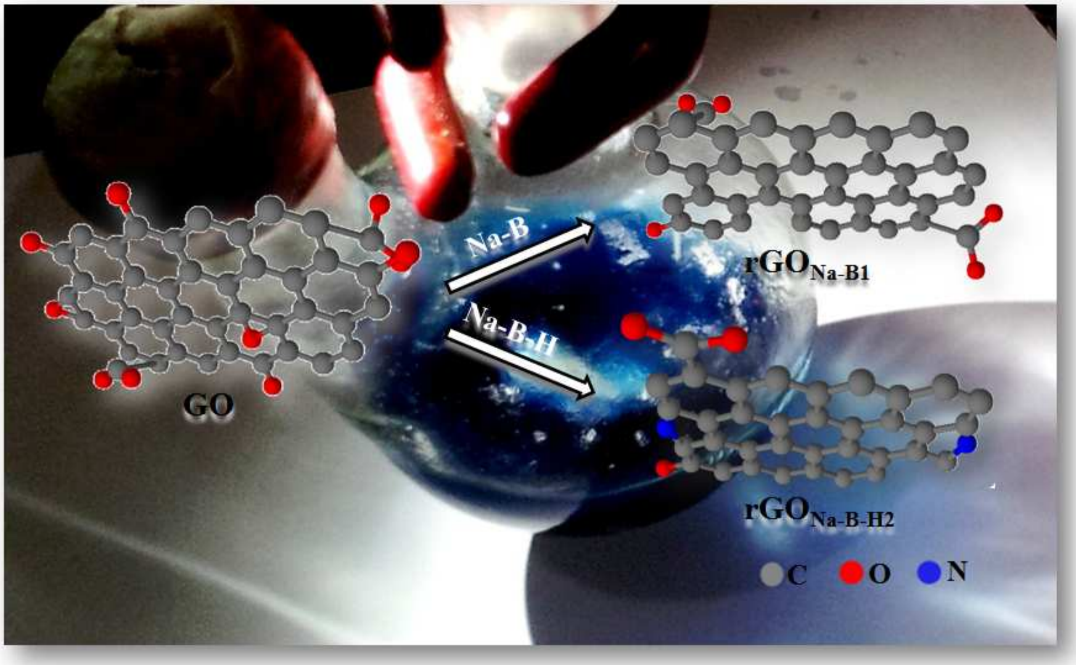
New reducing agents such as sodium-benzophenone solutions with light can generate solvated radical anions with electrons that can produce high-quality rGO or convert to the higher degree of reducded N-doped rGO with hydrazine solutions at room temperature.



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ARTICLE TYPE

Fast Synthesis of High-Quality Reduced Graphene Oxide at Room Temperature under Light Exposure†

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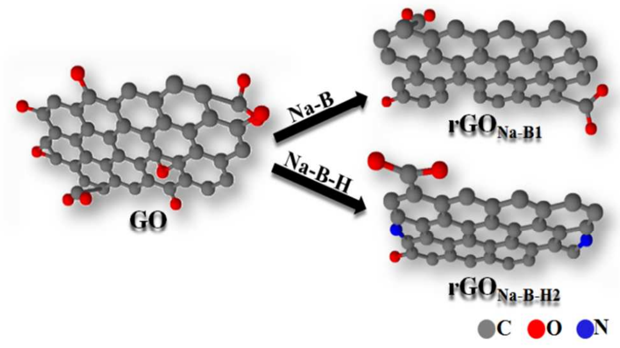
An approach is presented new reducing reagents, sodium-benzophenone (Na-B) or Na-B in the presence of the hydrazine (Na-B-H) systems under light exposure could produce rGOs with/without N-doping at room temperature in the solution phase as well as on a solid substrate. Benzophenone activated those solutions acting as a photosensitizer under light. It is assumed that the newly generated radical anions with electrons from Na-B under light can reduce GO into rGO sheets (rGO_{Na-B1}). In addition, the Na-B-H system can allow a higher degree of reduction with doping of nitrogen atoms by the introduction of hydrazine to produce radical anions and electrons with a sodium hydrazide complex, which helps to decrease the sheet resistance of the as-made $rGO_{Na-B-H2}$. The excellent properties (very low oxygen contained (C/O ~16.2), and low sheet resistance (~130 Ω per square)) of the rGOs were confirmed by XPS, XRD, IR, Raman, TGA, wettability, and sheet resistance measurements. High-quality rGO films on flexible substrates can be prepared by directly immersing the GO films in these solutions for several minutes.

Introduction

Graphene and other two-dimensional (2D) nanomaterials have attracted intense interest for a wide range of applications due to their unique 2D structures and fascinating advantages including a high electrical conductivity, optical transparency, gas barrier properties, robustness, flexibility, and environmental stability.[1,2] Graphene is typically prepared by mechanical exfoliation[3] and chemical vapour deposition (CVD)[4] for the creation of high quality and crystalline graphene sheets. However, the applicability of these well-known methods is limited by difficulties including reproduction and mass production of graphene. In order to overcome the aforementioned limits, researchers have employed chemical approaches in which chemical exfoliation of graphene oxide (GO) either by ultrasonic dispersion or rapid thermal expansion followed by chemical reduction provides a low-cost and scalable method to produce bulk quantities of graphene flakes (as-reduced GO (rGO)). These graphene flakes are broadly used in various applications including electronic devices,[5] sensors,[6,7] bio compatible materials,[8] and electrochemical energy storage and conversion devices.[9] Up to now, numerous reducing chemicals such as sodium hydride,[10] hydrogen sulphide,[11] hydrazine,[12] $NaBH_4$,[13] dimethylhydrazine,[14] hydroquinone,[15] the sequential use of $NaBH_4$ and H_2SO_4,[16] HI-AcOH,[17] vitamin C,[18] aluminium powder[19] and pyrrole[20] have been used to reduce GO to produce rGO in the solution phase. Direct reduction of GO films by well-known procedures has also been reported.[17] However, these procedures often involve highly toxic chemicals, require a long reduction time, or require high temperature treatment which is incompatible with flexible plastic substrates and produce rGO with a relatively high oxygen content. Recently, sodium combined with liquid NH_3 has been reported for the efficient conversion of GO thin films into rGO thin films,[21] requiring a very low temperature (-78°C). This makes it impossible to handle the films at room temperature and the process is not environment friendly due to the use of liquid NH_3. It is necessary to achieve fast reduction of GO into rGO at room temperature and simultaneously produce high quality rGO to allow direct patterning of GO that can produce a rGO channel. In addition, the development of novel reduction methods that are mild, cost effective remains a challenge for the use of less toxic or non-toxic chemicals. To date, there are almost no reports concerning the effortless direct convert of GO into highly reduced rGO with/without N-doping at room temperature with a very short reaction time.

Herein, for the first time, we report a new method for the fast reduction of GO to high-quality rGOs with/without N-doping by the simple exposure of light at room temperature in the solution phase as well as on a solid substrate, which can allow direct patterning of high quality rGO electrodes with/without N-doping at room temperature. We carefully designed a new reducing reagent of sodium-benzophenone (Na-B) or sodium-benzophenone in the presence of a hydrazine (Na-B-H) system that can produce rGO with/without N-doping at room temperature. It is assumed that the newly generated radical anions with electons generated from sodium-benzophenone under light can reduce GO into rGO sheets in the solution phase as well as on the solid substrate. In addition, the Na-B-H system can allow a higher degree of reduction with doping of nitrogen atoms by the introduction of hydrazine, which helps to decrease the sheet resistance. Compared to other reported routes including hydrazine reduction and sodium-ammonia or direct thermal annealing, our strategy offers significant advantages because it not only produces graphene with a very low number of remaining functional groups and a low sheet resistance with N-doping in a shorter time and at room temperature, but also provides a very environmentally friendly protocol with respect to temperature.



Scheme 1 Schematic illustration of the formation of reduced graphene oxide (rGO_{Na-B1}) by the sodium-benzopheone (Na-B) system and N-doped reduced graphene oxide ($rGO_{Na-B-H2}$) by the sodium-benzopheone-hydrazine (Na-B-H) system at room temperature.

Experimental

Materials and methods

Sodium, benzophenone, and hydrazine in a THF solution were obtained from commercial sources and used as received.

Preparation of graphene oxide (GO): GO was prepared from natural graphite powder (Bay Carbon, SP-1 graphite) by the modified Hummers and Offenman's method using sulfuric acid, potassium permanganate, and sodium nitrate.[17,26]

Preparation of reduced graphene oxide (rGO_{Na-B1}) by sodium and benzophenone: A 50 mL, two-necked, round-bottomed flask was removed from a hot oven and flushed with nitrogen. A sample of benzophenone (100 mg) together with 15 mL of freshly distilled and deoxygenated tetrahydrofuran (THF) and a stirring bar was placed in the flask. A small lump of sodium metal (350 mg) was cut into smaller pieces and placed directly into the flask against an emergent stream of nitrogen. The second neck of the flask was closed with a water condencer. The mixture was stirred for 30 min under nitrogen until a blue colour was produced in presence of a UV lamp (254 nm) or normal sodium light or by heating at 40°C in an oil bath. Then, 20 mg of dry GO dispersed in 5 mL of dry THF was added to the solution and stirring continued under the same conditions for another 40 min. Finally, a black coloured rGO_{Na-B1} solution was obtained. The rGO_{Na-B1} was collected by simple filtration and washing with ethanol and water.

Preparation of N-doped reduced graphene oxide ($rGO_{Na-B-H2}$) by sodium, benzophenone, and hydrazine: First, a blue coloured solution was prepared in the presence of a UV lamp, as described previously. 20 mg of dry GO was dispersed in 5 mL of hydrazine in a THF solution. Then, the GO solution was added to the solution of Na-B, 15 min after it was mixed, and stirring continued under the same conditions for another 30 min. Finally, a black coloured $rGO_{Na-B-H2}$ solution appeared. The $rGO_{Na-B-H2}$ was collected by simple filtration and washing with ethanol and water.

Preparation of reduced graphene oxide (rGO_{Na-H}) by the sodium hydrazide complex: First, a small lump of sodium metal (100 mg) was cut into smaller pieces and placed directly into the two-necked, round-bottomed flask against an emergent stream of nitrogen. Then, hydazine in 5 mL of a THF solution was added into the flask and heated at 50°C by an oil bath for 1 h. A white complex was produced followed by the addition of 10 mg of dry GO dispersed in a THF solution (5 mL) and stirring continued for another 1 h under the same conditions. Finally, rGO_{Na-H3} was produced. In addition, dry GO was dispersed in a hydrazine-THF solution followed by addition to only sodium and heating at 50°C where stirring continued for 1 h. Finally, rGO_{Na-H4} was obtained.

Preparation of the GO and RGO films: The GO film was prepared and then carefully transferred onto a PET film following a previously reported procedure.[21] The GO/PET film was dipped into a Na-B or Na-B-H solution for several minutes. Subsequently, the rGO/PET film was rinsed with saturated sodium bicarbonate, water, and ethanol followed by drying at room temperature. The colour of the rGO/PET film changed from pale brown to black.

rGO_{Na-B1} and $rGO_{Na-B-H2}$ films: First, a GO film was prepared on PET. Simultaneously, Na-B and Na-B-H solutions were also prepared. GO films were dipped into Na-B and Na-B-H solutions in the presence of a UV lamp. Finally, GO films were converted to rGO_{Na-B1} and $rGO_{Na-B-H2}$.

Characterization

All X-ray photoemission spectroscopy (XPS) measurements were obtained by a SIGMA PROBE (ThermoVG, U.K.) with a monochromatic Al-Kα X-ray source at 100 W. The powder XRD pattern was acquired using a D8-Adcance instrument (Germany) and Cu-Kα radiation. Raman spectroscopy measurements were taken using a micro-Raman system (Renishaw, RM1000-In Via) with excitation energy of 2.41 eV (514 nm). The thermal properties of rGO were characterized by TGA (Polymer Laboratories, TGA 1000 plus). FT-IR spectra was collected using a Thermo Nicolet AVATAR 320 instrument. The microstructures were observed by field emission scanning electron microscopy (FE-SEM; JSM-6701F/INCA Energy, JEOL). Atomic force microscopy (AFM) analysis was performed using a SPA400 instrument with a SPI-3800 controller (Seiko Instrument Industry Co.) at room temperature. The contact angles were measured using a SEO Phoenix 300 microscope at five different points. All the electrical transport measurements were made by Keithley 4200 semiconductor characterization system unit.

Results and Discussion

Our novel concept to identify a new reducing agent proceeded as follows. Metallic sodium can react with benzophenone to create a deeply coloured solution with a strong affinity to react with oxygen groups due to the generation of the solvated radical anion 'diphenylketyl' with electron.[22] Reaction of sodium metal with benzophenone results in ionization of the metal to form a sodium cation and a solvated radical anion with electron (Scheme 1, Supporting Information, Fig. S1). The deep colour of sodium metal in the solution is due to the presence of solvated radical anions with electrons. Normally, these solvated radical anions and electrons are generated by heating at ~40°C.[22] Instead of apply heating at a high temperature for a long time, we introduced only UV light to activate the solution system at room temperature since benzophenone is well known as a photosensitizer in photochemistry applications.[23] The role of benzophenone is to transfer the required energy from UV light to the solution system to generate solvated radical anions and electrons with the reaction of sodium metal. We also used conventional heating (~40°C) to generate solvated radical anions with electrons and normal sodium light, resulting in a temperature higher than room temperature. To make our solution system more competitive as a reducing agent with N-doping capability, we added anhydrous hydrazine in the solution of sodium and benzophenone. According to the literature, anhydrous hydrazine reacts with sodium metal and yields a sodium hydrazide complex, NaN_2H_3 (Supporting Information, Fig. S2).[24] Based on our hypotheses, the resulting solution produced two things at the time, solvated radical anions with electrons as well as a sodium hydrazide complex, confirmed with a blue colour solution. In fact, benzophenone acted as a photosensitizer is easily activated under light exposure to give the blue colour solution. Also, we hypothesized that these two solution systems will effectively remove oxygen functionalities due to the strong affinity of base to proton and restore the planar geometry of the GO sheets.

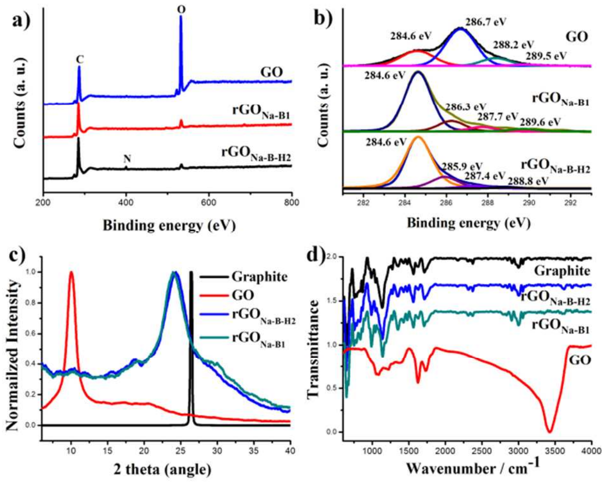


Fig. 1 a) XPS spectra of graphene oxide, reduced graphene oxide (rGO$_{Na-B1}$), and N-doped reduced graphene oxide (rGO$_{Na-B-H2}$). b) C1s XPS spectra of graphene oxide, reduced graphene oxide (rGO$_{Na-B1}$), and N-doped reduced graphene oxide (rGO$_{Na-B-H2}$). c) Powder XRD patterns of GO (red), N-doped reduced graphene oxide (rGO$_{Na-B-H2}$) (blue), reduced graphene oxide (rGO$_{Na-B1}$) (green), and graphite (black). (d) FT-IR spectra of GO (green), reduced graphene oxide (rGO$_{Na-B1}$) (blue), N-doped reduced graphene oxide (rGO$_{Na-B-H2}$) (red), and graphite (black).

We prepared two solution systems, Na-B and Na-B-H. Dry GO powder was first dispersed in the anhydrous hydrazine-THF solution and stirred for 20 min to create a stable dispersion of GO. Several lumps of sodium metal were then added to benzophenone in a THF solution followed by the addition of GO in a hydrazine solution at room temperature in the presence of UV light. After the reduction of GO with the solvated radical anions with electrons and the complex in the resulting solution, a black N-doped rGO (rGO$_{Na-B-H2}$) solution was obtained. However, in the case of only the Na-B system, dry GO was dispersed in THF and then added to the Na-B solution to produce rGO (rGO$_{Na-B1}$). A possible reduction mechanism is proposed in Figs. S1, S2 in the supporting information.[21,22,24-26] As a control experiment, we prepared only a NaN_2H_3 complex by the reaction of sodium metal with an anhydrous hydrazine-THF solution at ~50°C followed by addition of dispersed GO in THF, which resulted in the production of a rGO$_{Na-H3}$ sheet. Also, we dispersed dry GO in anhydrous hydrazine-THF followed by stirring for 20 min to create a stable dispersion of GO followed by addition to only sodium at ~50°C, which allowed the production of a rGO$_{Na-H4}$ sheet. According to the experimental analysis, rGO$_{Na-H4}$ is more reduced than rGO$_{Na-H3}$ due to the reduction with the concentrated form of the complex. This is also the first example of the use of a NaN_2H_3 complex as a reducing agent to prepare rGO sheets. In the case of UV light and normal light at room temperature, benzophene acts as a photo-sensitizer to form the complex with sodium, which is very effective in reacting with the oxygen functional groups of GO.

Characterization of the rGOs

X-ray photoemission spectroscopy (XPS) was used to investigate the chemical structure and composition of the as-prepared rGO$_{Na-B1}$ and rGO$_{Na-B-H2}$ powder samples. Based on the XPS analyses, the as-prepared GO had a very high oxygen atomic percentage (C/O ratio of 2.01, Fig. 1a). Fig. 1b shows the C1s spectra of the GO, rGO$_{Na-B1}$, and rGO$_{Na-B-H2}$ powder samples. In general, GO showed two separated peaks because the oxidation process generated a high percentage of oxygen functionalities, as shown in Fig. 1b. After reduction with the Na-B and Na-B-H systems, the intensities of all of the related oxygen peaks were sharply decreased in the rGO$_{Na-B1}$ and rGO$_{Na-B-H2}$ samples compared to GO, indicating that the C=C bonds dominate, as demonstrated by one single peak around 284.5 eV with small tails at the higher binding energy region, confirming good restoration of the C=C bonds in rGO$_{Na-B1}$ and rGO$_{Na-B-H2}$ (Fig. 1b).[17] The C1$_S$ of rGO$_{Na-B-H2}$ contained the peaks at 285.9 eV (C-O and C-N combined), 287.4 eV (C=O), 288.8 (C(O)OH); whereas C$_1$S of rGO$_{Na-B1}$ contain the peaks at 286.3 eV (C-O), 287.7 eV (C=O), 289.6 (C(O)OH).[8] We concluded that the rGOs made by our process contained far less oxygen, which is very similar to graphite, confirming its high quality (Supporting Information, Fig. S3). In contrast, the C/O ratios of the as-prepared rGO$_{Na-B1}$ and rGO$_{Na-B-H2}$ produced by reduction of the Na-B and Na-B-H systems were 13.9 and 16.2, respectively (Fig. 1b). We observed ~3.8% nitrogen in the as-made rGO (rGO$_{Na-B-H2}$) due to the presence of a nitrogen source (hydrazine) in the Na-B-H system (Fig. 1a). The corresponding N1s XPS spectrum of rGO$_{Na-B-H2}$ was obtained (Supporting Information, Fig. S5).[27] We also determined the atomic compositions of rGO$_{Na-H3}$ and rGO$_{Na-H4}$ using XPS. Significantly, our rGO$_{Na-H3}$ and rGO$_{Na-H4}$ samples showed relatively lower oxygen percentages with C/O ratios of 10.9 and 12.6, respectively (Supporting Information, Fig. S4, Table S1). The rGO$_{Na-H4}$ sample is more reduced than the rGO$_{Na-H3}$ sample. Our as-made products are quite distinct from rGO obtained by only the hydrazine reduction product (C/O ratio of 12.9, nitrogen ~3.78%) (Supporting Information, Table S1).

X-ray diffraction (XRD) is an efficient and convenient method to verify the degree of reduction of rGO. Powder XRD analysis was further used to characterize the bulk structure of the prepared rGO$_{Na-B1}$ and rGO$_{Na-B-H2}$ (Fig. 1c). The 2θ peak of graphite powder appeared at 26.71°, corresponding to an interlayer distance of 3.34 A° (Fig. 1c).[17] On the other hand, the as-prepared GO showed that 2θ peak at 10.27°, indicating that the graphite was fully oxidised into GO with an interlayer distance of 8.60 A°, demonstrating that the interlayer space increased during oxidation (Fig. 1c).[17] The XRD pattern of the as-prepared rGO$_{Na-B1}$ showed a typical sharp 2θ peak at 23.7°, indicating that the interlayer distance of rGO$_{Na-B1}$ was ~3.75 A° (Fig. 1c). The shift of that 2θ peak of GO (10.27°) to rGO$_{Na-B1}$ powder (23.7°) suggests that rGO$_{Na-B1}$ very well ordered into a two-dimensional plane by the removal of surface functional oxygen groups during reduction.

rGO$_{\text{Na-B-H2}}$ also showed a typical sharp 2θ peak at 24.6°, corresponding to an interlayer distance of rGO$_{\text{Na-B-H2}}$ was ~3.61 A°, demonstrating a higher degree of reduction than the rGO$_{\text{Na-B1}}$ powder (Fig. 1c). The interlayer distances of the as-made rGOs are 3.75 and 3.61 A°, which are very close to that of graphite powder (3.34 A°).[17] The XRD patterns of the as-prepared rGO$_{\text{Na-H3}}$ and rGO$_{\text{Na-H4}}$ are also provided in Fig. S6 in the supporting information. We also treated the only GO solution with UV lamp for 24 h as a control experiment, but did not observe any significant changes in the XRD data before and after treatment (Supporting Information, Fig. S7)

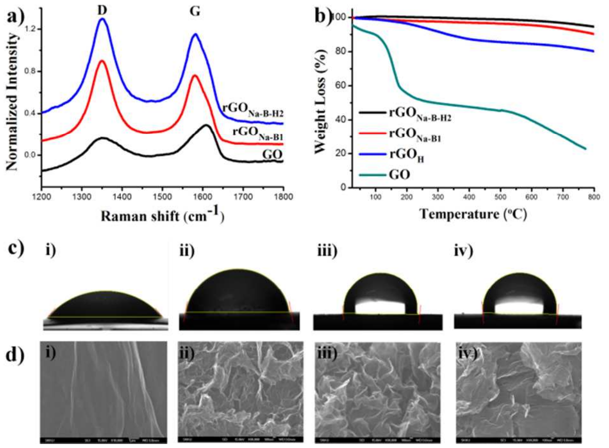


Fig. 2 (a) Raman spectra of GO (black), reduced graphene oxide (rGO$_{\text{Na-B1}}$) (red), and N-doped reduced graphene oxide (rGO$_{\text{Na-B-H2}}$) (blue). (b) TGA plots of GO (green), reduced graphene oxide (rGO$_{\text{Na-B1}}$) (red), N-doped reduced graphene oxide (rGO$_{\text{Na-B-H2}}$) (black), and the reduced graphene oxide control sample produced by hydrazine (rGO$_{\text{H}}$) (blue). (c) Water contact angles of (i) GO, (ii) rGO$_{\text{H}}$, (iii) rGO$_{\text{Na-B1}}$, and (iv) rGO$_{\text{Na-B-H2}}$. (d) SEM images of the surfaces of (i) GO, (ii) rGO$_{\text{Na-B1}}$, (iii) rGO$_{\text{Na-B-H2}}$, and (iv) rGO$_{\text{H}}$.

We utilized Fourier transform infrared spectroscopy (FTIR) to study the changes of the functional groups in GO after the reduction process.[17,21] Importantly, the FTIR spectra clearly show the progressive removal of oxygen groups by the new systems (Fig. 1d). As the GO films are reduced by the system, the peaks of all of the oxygen functional groups are significantly or entirely reduced. Actually, the oxygen-containing groups can readily react with as-made solvated radical anions with electrons to cleave the carbon-oxygen bond on the plane of GO (Supporting Information, Fig. S1). The FTIR results of the as-made rGOs are quite similar to those of normal graphite, which confirms that they contained far less oxygen and are of high quality (Fig. 1d). The FTIR spectra of rGO$_{\text{Na-H3}}$ and rGO$_{\text{Na-H4}}$ are also given in Fig. S8 in the supporting information. As previously reported, the solvated electrons and partially delocalized π-conjugation in the GO plane can stabilize the carbon radicals to facilitate the formation of π-bonds and the restoration of the π-conjugation in graphene, resulting in a high quality rGO sheet.[21,28]

Raman spectroscopy is the most direct and non-destructive technique to characterize the structure and quality of carbon materials, particularly to determine defects as well as the ordered and disordered structures of graphene.[29] Fig. 2a presents the micro-Raman spectra of the graphitic layers in the powder samples. The peak for GO (1609 cm^{-1}) at the G-band was up-shifted compared with that of graphite (1580 cm^{-1}), which was attributed to the presence of isolated double bonds that resonate at frequencies higher than that of the G-band of graphite.[17] The G-bands of rGO$_{\text{Na-B1}}$ and rGO$_{\text{Na-B-H2}}$ occurred at 1581 and 1583 cm^{-1}, respectively, which correspond to the recovery of the hexagonal network of carbon atoms with defects (Fig. 2a). The I_D/I_G ratio of rGO$_{\text{Na-B-H2}}$ did increase compared to GO and notably, rGO$_{\text{Na-B1}}$, indicating that the reduction process altered the structure of GO[17] with a high quantity of structural defects. The higher ratios of the Raman intensities (I_D/I_G) of rGO$_{\text{Na-B1}}$ and rGO$_{\text{Na-B-H2}}$ than GO indicates an increase of the number of smaller sp^2 domains.[29] The as-prepared rGO$_{\text{Na-H3}}$, rGO$_{\text{Na-H4}}$, and rGO$_{\text{H}}$ (rGO produced by hydrazine) control sample also showed similar patterns in their Raman spectra (Supporting Information, Fig. S9).

Thermogravimetric analysis (TGA) was used to further assess the level of reduction of the GO powder by evaluating the weight losses of the samples. Fig. 2b displays the TGA thermograms showing the weight losses of the GO, rGO$_{\text{Na-B1}}$, rGO$_{\text{Na-B-H2}}$, and rGO$_{\text{H}}$ control samples as a function of temperature obtained at a heating rate of 1°C min^{-1} under a nitrogen atmosphere. The GO sample showed significant weight loss with an onset temperature above 100°C, which was attributed to the elimination of interlamellar water, followed by loss of oxygen from the GO platelets themselves (such as by the evolution of CO and CO_2 from the sample) at slightly higher temperatures.[17] rGO$_{\text{Na-B1}}$ and rGO$_{\text{Na-B-H2}}$ showed much higher thermal stabilities with weight losses of ~10 and ~7 wt% for rGO$_{\text{Na-B1}}$ and rGO$_{\text{Na-B-H2}}$, respectively, which are higher than the values for GO and the rGO$_{\text{H}}$ control sample. This improvement was achieved because of the better graphitization and deoxygenation of the as-made rGO sheet due to enhanced van der Waals forces between layers.[17,21] The TGA data of rGO$_{\text{Na-H3}}$ and rGO$_{\text{Na-H4}}$ are also given in Fig. S10 in the supporting information.

The degrees of reduction of the rGO$_{\text{Na-B1}}$ and rGO$_{\text{Na-B-H2}}$ films were further assessed by their hydrophobicities. Fig. 2c shows the wettability of the GO, rGO$_{\text{H}}$, rGO$_{\text{Na-B1}}$, and rGO$_{\text{Na-B-H2}}$ samples. The water contact angles of the GO, rGO$_{\text{H}}$, rGO$_{\text{Na-B1}}$, and rGO$_{\text{Na-B-H2}}$ thin films were 48.3°, 80.9°, 95.6°, and 98.9°, respectively (Fig. 2c). Clearly, the rGO$_{\text{Na-B1}}$ and rGO$_{\text{Na-B-H2}}$ surfaces had higher hydrophobicities, indicating a high degree of reduction and more complete removal of the oxygen content.[17,21] The as-made product was systematically characterized to confirm the production of a single or few layers of rGO sheets. Atomic force microscopy (AFM) was used to characterize the average thickness of the layers of as-made rGO$_{\text{Na-B1}}$ and rGO$_{\text{Na-B-H2}}$ sheets on a mica substrate (Supporting Information, Fig. S11). A line scan of the height profile shows average thickness are ~1.04 and ~0.94 nm, which is consistent with the typical height reported for single layer graphene.[17,21] A scanning electron microscope (SEM) was further used to investigate the morphology of the as-made rGO sheets. Representative SEM images of the GO and as-produced rGO$_{\text{Na-B1}}$, rGO$_{\text{Na-B-H2}}$, and rGO$_{\text{H}}$ samples are shown in Fig. 2d. SEM images of rGO$_{\text{Na-H3}}$, rGO$_{\text{Na-H4}}$, and graphite were also obtained (Supporting Information, Fig. S12).

Fabrication of with/without N-doped rGOs

Normally, rGO films are achieved on a membrane filter by vacuum filtration of as-reduced rGO dispersions.[30] However, the dispersion of rGO sheets in solution is usually much more complicated than that of GO. Recently, researchers have demonstrated the preparation of GO paper by using a similar filtration strategy.[30] To make the resulting GO film conducting, an additional reduction step is needed involving either exposure to hydrazine vapour or HI-AcOH vapour and/or annealing under inert conditions. However, the hydrazine and HI-AcOH vapour alone is not sufficient to achieve optimum reduction[17,19] and annealing alone requires relatively high temperatures. More recently, Feng *et al.* reported that GO films can be readily converted into uniform rGO films by using Na-NH$_3$ as the reduction agent, which requires a very low temperature (-78°C). This procedure is effective, but it is not environmentally friendly due to the low temperature requirement (-78°C) and the difficulty of handling NH$_3$.[21] Importantly, with Na-B and the Na-B-H system used as the reducing agents in our approach, a GO film can be readily converted into a uniform rGO film within just several minutes at room temperature (Supporting Information, Fig. S13). Here, the solvated radical anions with electrons and complexes allow highly efficient reduction and the rapid de-oxygenation at mild conditions to obtain the best recovery of the graphene-conjugated structure. This room temperature solution reduction process is especially important for graphene-based flexible transparent conductive electrodes and also, different kinds of patterns can be easily possible at room temperature. To achieve this, a GO thin film or paper was first prepared by vacuum filtration of a GO dispersion through a nitrocellulose membrane. Next, the GO film was transferred on polyethylene terephthalate (PET) and directly dipped into the deep blue as-made solutions. The brownish GO film quickly turned to black within a few minutes in these solutions. The black rGO film was taken out, washed with de-ionized water, and dried at room temperature (Supporting Information, Fig. S13). By the application of both solution systems (Na-B-H and Na-B), we obtained with/without N-doped rGO sheets. By controlling the Na-B and Na-B-H solution systems, rGOs with a tunable resistivity can be generated. The sheet resistance of the rGOs measured with fore probe station system is another important parameter to evaluate how the π-conjugated system is restored in the rGO film.[31] The obtained average sheet resistances of the rGOs are 200 ± 5 and 130 ± 5 Ω per square for the Na-B and Na-B-H solution systems, respectively. Significantly, low sheet resistances of ~130 and ~200 Ω per square were achieved in thin films (thickness ~4 μm) of N-doped rGO and rGO, respectively, which represents the lowest sheet resistance achieved in solution-processed rGO films (Supporting Information, Table S2 and Table S3). The sheet resistances of pellets of as-made rGO$_{\text{Na-B1}}$ and rGO$_{\text{Na-B-H2}}$ are ~9 and ~5 Ω per square, respectively, with a thickness of ~11 μm (Supporting Information, Table S2). The low sheet resistances observed in the as-made rGO$_{\text{Na-B1}}$ and rGO$_{\text{Na-B-H2}}$ thin films are consistent with the highest degree of de-oxygenation and graphitization. We demonstrated that rGO$_{\text{Na-B1}}$ and rGO$_{\text{Na-B-H2}}$ thin films can be readily formed by the controlled chemical conversion of GO films in Na-B and Na-B-H solutions, which is a very clean, safe, ultrafast, and convenient method. The resulting paper could be used in many fields including membranes, anisotropic conductors, supercapacitors, and electrocatalytic oxygen reduction reactions (ORRs). The successful formation of graphene and N-doped graphene films from GO films and GO coating by directly dipping in Na-B and Na-B-H solutions holds great potential in many applications, such as sensors and neuroprosthetic devices, and can lead to the development of a new generation of antistatic coatings that possess a low sheet resistance, excellent thermal and chemical stabilities, water resistance, and low production cost.

Conclusions

In conclusion, by applying treatment with systems comprised of Na-B and Na-B-H solutions with active solvated radical anions with electrons and mixed with a complex as highly reductive agents, we devised a simple and effective method to produce graphene and N-doped graphene structures with the lowest oxygen contents (C/O ratios of 13.9 and 16.2, respectively) of all solution-reduction processes in a short time. Furthermore, we can control the degree of reduction with nitrogen doping in the rGO sheet at room temperature. We demonstrated that this approach can be used to directly reduce preformed GO thin films into rGO and N-doped rGO films with combined low sheet resistances of ~200 and 130 Ω per square with a film thickness ~4 μm, respectively. On the other hand, the sheet resistances of pellets of as-made rGO$_{\text{Na-B1}}$ and rGO$_{\text{Na-B-H2}}$ are ~9 and ~5 Ω per square, respectively, with a thickness of ~11 μm. We demonstrated the alternative *in situ* rGO and N-doped rGO fabrication, which is a very unique and easy procedure. Furthermore, the simplicity and room temperature process of this method demonstrates the possibility of the rGO and N-doped rGO thin films on PET substrates. Na-B and Na-B-H solution systems used as an ink can be employed directly to solid GO templates to produce high quality *in situ* multifunctional rGO-based composite architectures with/without N-doping. Thus, our approach offers a great deal of flexibility in the creation of graphene films with/without N-doping in addition to novel graphene-based materials and devices. This cheap and simple procedure is of great significance for large-scale applications such as flexible electronics, antistatic coatings, electrochemical devices, and conductive nanocomposites.

Notes and references

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