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Chemical reduction of an aqueous suspension of graphene oxide by nascent hydrogen

Viet Hung Pham, Hai Dinh Pham, Thanh Truong Dang, Seung Hyun Hur, Eui Jung Kim, Byung Seon Kong, Sunwook Kim and Jin Suk Chung

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One of the challenges in the chemical reduction of graphene oxide is increasing the C/O atomic ratio of the chemically-converted graphene. In this paper, we report a simple and effective method to reduce aqueous suspensions of graphene oxide using nascent hydrogen generated in situ by the reaction between Al foil and HCl, Al foil and NaOH and Zn powder and NaOH. The nascent hydrogen-reduced graphene oxides (nHRGOs) were characterized by elemental analysis, UV-vis spectra, Raman spectra, X-ray photoelectron spectroscopy, thermogravimetric analysis and electrical conductive measurements. The reduction efficiency of graphene oxide strongly depended on the reaction medium and the rate of nascent hydrogen generation. The best nHRGO achieved a C/O atomic ratio greater than 21 and a bulk electrical conductivity as high as 12,500 S/m, corresponding to the nascent hydrogen generated from the reaction between Al foil and HCl. Since nascent hydrogen could be produced on a metal surface upon oxidation in solution, other metals with low standard reduction potentials, such as Mg, Mn, and Fe, can be applied to reduce graphene oxide.

1. Introduction

Graphene and graphene-based materials have attracted research interest due to their excellent mechanical, electrical, thermal and optical properties, as well as their high specific surface areas. The most promising route for the bulk production of graphene is the chemical reduction of graphene oxide due to its simplicity, reliability, suitability for large-scale production, relatively low material cost, and versatility in terms of being well-suited to chemical functionalization. Graphene oxide is usually synthesized by exfoliation of graphite oxide, which is obtained by oxidizing graphite using strong acid and oxidants. To date, the chemical reduction of graphene oxide has been performed with various reducing agents such as hydrazine and its derivatives, NaBH₄, hydroquinone, hydroiodic acid (HI), sulfur-containing compounds, metal powders, vitamin C, and hydroxylamine. Among them, metal powders are the most powerful reducing agent producing a C/O atomic ratio of reduced graphene oxide (RGO) up to 33.5, the highest ever reported at low temperature. In addition, the reduction of graphene oxide by metal powders is usually very fast, ranging from a few to tens of minutes.

Nascent hydrogen is hydrogen at its “moment of birth” and is considered to be especially reactive. Nascent hydrogen, denoted as H* or H (atomic hydrogen), is naturally produced on a metal surface upon oxidation in solution or may be electrolytically generated by the reduction of hydrogen ions on certain cathode materials. A common method to produce nascent hydrogen is the reaction of metals, such as Mg, Al, Fe or Zn with an acid, and amphoteric metals (Al, Zn) and their alloys (Devarda or Raney nickel) with alkali solution. Although nascent hydrogen exists transiently, its lifetime is long enough to affect chemical reactions. Being monoatomic, nascent hydrogen is a powerful reducing agent, which is widely used to reduce arsenic or nitrobenzene, chalcopyrite, carbonyl compounds or to decolorize azo dyes.

Herein, we describe a new approach for the reduction of graphene oxide using nascent hydrogen in both acidic and alkaline media. The nascent hydrogen is generated in situ in a graphene oxide dispersion via reactions of Al foil or Zn powder with HCl or NaOH. The nascent hydrogen-reduced graphene oxide (nHRGO) achieves a C/O atomic ratio greater than 21 and a bulk electrical conductivity as high as 12,500 S/m.

2. Experimental

2.1 Materials

Expandable graphite (Grade 1721) was kindly provided by Asbury Carbon. Concentrated sulfuric acid (H₂SO₄), potassium permanganate (KMnO₄), hydrochloric acid (HCl), and hydrogen peroxide (H₂O₂) were purchased from Samchun Chemicals. The aluminium (Al) was household aluminum foil, and the zinc (Zn) powder (particle size < 45 µm) was purchased from Merck Chemicals. All chemicals were used as received without further purification.

2.2 Nascent hydrogen reduction of graphene oxide

The as-synthesized graphene oxide was prepared by the
modified Hummers method from expanded graphite, which was prepared by the microwave-assisted thermal expansion of expandable graphite\textsuperscript{10} (see details in the Supporting Information). The as-synthesized graphene oxide (10 mg/mL) was diluted with deionized water to 1.0 mg/mL and sonicated in an ultrasonic bath (JeioTech UC-10, 200 W) for 10 min to create a homogeneous graphene oxide dispersion. The concentrated HCl acid (35%) or NaOH powder was added to the graphene oxide dispersions to 1 mol/L. Upon adding HCl or NaOH, aggregated graphene oxide particles appeared due to a high concentration of acid or base. The aggregated graphene oxide particles in acidic solution were easily redispersed by sonication for an additional 10 min while the aggregated graphene oxide particles in the basic solution could not be redispersed, even under sonication for 1 h. Subsequently, 1.2 g of Al foil or Zn powder was added to 400 mL of graphene oxide dispersion (1 mg/mL) with mixing. The reduction was performed until all the metal dissolved. The RGOs obtained from the reduction of graphene oxide by nascent hydrogen generated \textit{in situ} from the reaction of Al foil with HCl, Al foil with NaOH and Zn powder with NaOH were denoted as nHRGO\textsubscript{Al/HCl}, nHRGO\textsubscript{Al/NaOH} and nHRGO\textsubscript{Zn/NaOH}, respectively. The nHRGOs were filtered and washed with diluted HCl acid (0.1 M) three times, and then washed with copious amounts of deionized water and dried at 100°C for 24 h.

2.3 Characterizations

The morphology of the nHRGOs was characterized by scanning electron microscopy (SEM, JEOL JSM-6500 FE). The elemental compositions of the nHRGOs were analyzed using an elemental analyzer (Flash 2000, Thermo Scientific). The UV-vis absorption spectra of graphene oxide and the nHRGOs spray-coated on a quartz substrate were recorded using a double-beam UV-Vis spectrophotometer (Analytik Jena, Specord 210 Plus). X-ray photoelectron spectroscopy (XPS) analysis was performed on a K-alpha spectrometer (Thermal Scientific) with monochromatic Al Ka radiation (hv = 1486.6 eV). Raman spectra were measured using a confocal Raman microscope (Thermo Scientific) with 532-nm wavelength incident laser light. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate of 10°C/min (Q50, TA Instruments). To measure the electrical conductivity, nHRGO powders were compressed into a 0.2-mm-thick pellet under a pressure of 4000 psi. The thicknesses of the nHRGO pellets were measured using a calliper with 0.01 mm accuracy (Absolute Digimatic, Mitutoyo). The electrical resistances of the nHRGO pellets were measured by the four-point probe method (CMT-10 MP, Advanced Instruments Technology).

3. Results and discussion

3.1 Nascent hydrogen reduction of graphene oxide

\textbf{Fig. 1.} Photographs of the graphene oxide reduction processes using nascent hydrogen
processes in this study (Fig. 1 and Fig. S1). The fact that the particles gradually appeared, indicating the graphene oxide was formation of a negative charge on the surface of these metals or Zn particles in an alkaline medium can be ascribed to the graphene oxide sheets did not adhere to the surface of Al foil and dissolved or reduction of the Al foil and Zn powder varied from 20 min to 6 h, which can be attributed to the difference in the standard reduction potentials. The standard reduction potentials in acidic and alkali solutions are R1.66 and R2.33 eV, respectively, much lower than the R1.20 eV of Zn in an alkali solution; thus Al dissolves faster in both the HCl and NaOH solutions. Previous reports describe a phenomenon in which metal particles are bound and wrapped by graphene oxide sheets during the reduction of graphene oxide with metal powders.\textsuperscript{18-20} In contrast, the graphene oxide sheets did not adhere to the surface of the Al foil or Zn particles during the reduction processes in this study (Fig. 1 and Fig. S1). The fact that the graphene oxide sheets did not adhere to the surface of Al foil and Zn particles in an alkaline medium can be ascribed to the formation of a negative charge on the surface of these metals or through the reaction of Al and Zn with OH\textsuperscript{-} to produce Al\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} and ZnO\textsubscript{2}\textsuperscript{2-}, respectively. However, it is unclear why the graphene oxide sheets did not adhere to the Al foil surface in the acidic solution. Since there was no adhesion of the graphene oxide sheets to the Al and Zn surfaces, the reduction of graphene oxide by direct electron transport from Al and Zn to the graphene oxide sheets as reported in previous literatures can be excluded.\textsuperscript{18-20}

The extent of reduction of nHRGO is shown in Table 1. nHRGO\textsubscript{Al/HCl} and nHRGO\textsubscript{Zn/NaOH} were highly reduced with C/O ratios of approximately 21 and 18, respectively, which are comparable to that for RGO obtained via metal reduction of graphene oxide.\textsuperscript{18-20} However, nHRGO\textsubscript{Al/NaOH} was hardly reduced with a C/O ratio of only 5.35. The difference in the extent of reduction of nHRGO can be explained by the interaction between reactants in a heterogeneous reaction. Graphene oxide is well dispersed in an acidic solution as individual sheets, which facilitates contact between the graphene oxide sheets and nascent hydrogen, resulting in high reduction. In contrast, the graphene oxide agglomerates in basic solution, which diminishes the contact between the graphene oxide sheets and nascent hydrogen and results in less reduction. The difference in the C/O ratios for nHRGO\textsubscript{Al/HCl} and nHRGO\textsubscript{Zn/NaOH} can be attributed to the difference in reaction time. As illustrated in Figure 1, the reaction between Al and NaOH was very fast, the Al foil fully dissolved in 20 min, while the reaction between Zn and NaOH was significantly slower, taking 6 h to dissolve the Zn particles. Since the existence of nascent hydrogen is transient (nascent hydrogens combine to form dihydrogen, H\textsubscript{2}), the gradual production of nascent hydrogen would be most suitable for the reduction of graphene oxide.

The SEM images characterizing the nHRGO morphologies are shown in Fig. 2. nHRGOs consisted of folded and wrinkled sheets randomly aggregated to form a disordered solid. The visual observation suggests that the fold and wrinkle of the nHRGO sheets depended on the extent of reduction. The more reduced nHRGO had more folded and wrinkled sheets. Furthermore, the nHRGOs were very clean, without residual metal or salt particles.

<table>
<thead>
<tr>
<th>Table 1. Elemental composition of nHRGOs</th>
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<tr>
<td></td>
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<tr>
<td>C (wt. %)</td>
</tr>
<tr>
<td>---------------------------------------</td>
</tr>
<tr>
<td>Graphene oxide</td>
</tr>
<tr>
<td>nHRGO\textsubscript{Al/HCl}</td>
</tr>
<tr>
<td>nHRGO\textsubscript{Al/NaOH}</td>
</tr>
<tr>
<td>nHRGO\textsubscript{Zn/NaOH}</td>
</tr>
</tbody>
</table>

The process of graphene oxide reduction using nascent hydrogen is shown in Figure 1. By adding metals into the graphene oxide dispersion, vigorous effervescence of the hydrogen bubbles from the Al foil and a sparkle of hydrogen bubbles from Zn powder were observed. The color of the graphene oxide dispersions gradually changed from dark brown to black, and aggregated particles gradually appeared, indicating the graphene oxide was reduced to RGO. The RGOs obtained from the reduction of graphene oxide by nascent hydrogen generated \textit{in situ} from the reaction of Al foil with HCl, Al foil with NaOH and Zn powder with NaOH were denoted as nHRGO\textsubscript{Al/HCl}, nHRGO\textsubscript{Al/NaOH} and nHRGO\textsubscript{Zn/NaOH}, respectively. As shown in Fig. 1, the time for dissolution or reduction of the Al foil and Zn powder varied from 20 min to 6 h, which can be attributed to the difference in the standard reduction potentials. The standard reduction potentials of Al in acidic and alkali solutions are -1.66 and -2.33 eV, respectively, much lower than the -1.20 eV of Zn in an alkali solution; thus Al dissolves faster in both the HCl and NaOH solutions. Previous reports describe a phenomenon in which metal particles are bound and wrapped by graphene oxide sheets during the reduction of graphene oxide with metal powders.\textsuperscript{18-20} In contrast, the graphene oxide sheets did not adhere to the surface of the Al foil or Zn particles during the reduction processes in this study (Fig. 1 and Fig. S1). The fact that the graphene oxide sheets did not adhere to the surface of Al foil and Zn particles in an alkaline medium can be ascribed to the formation of a negative charge on the surface of these metals or through the reaction of Al and Zn with OH\textsuperscript{-} to produce Al\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} and ZnO\textsubscript{2}\textsuperscript{2-}, respectively. However, it is unclear why the graphene oxide sheets did not adhere to the Al foil surface in the acidic solution. Since there was no adhesion of the graphene oxide sheets to the Al and Zn surfaces, the reduction of graphene oxide by direct electron transport from Al and Zn to the graphene oxide sheets as reported in previous literatures can be excluded.\textsuperscript{18-20}

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| Fig. 2 SEM images of (a) nHRGO\textsubscript{Al/HCl}, (b) nHRGO\textsubscript{Al/NaOH} and (c) nHRGO\textsubscript{Zn/NaOH}. |
Fig. 3 (a) Raman spectra and (b) I(D)/I(G) ratios of graphene oxide and the nHRGOs

Raman spectroscopy is an important, non-destructive tool used to study the structural changes of graphene oxide during the reduction process. Fig. 3 shows the Raman spectra of graphene oxide and nHRGOs and the ratio of D and G peak intensities (I(D)/I(G)). The Raman spectrum of graphene oxide has two prominent peaks at 1343 and 1598 cm\(^{-1}\), corresponding to the D and G bands, respectively, and the I(D)/I(G) is approximately 1.01. The blue-shift of the G band of graphene oxide corresponding to graphite (1580 cm\(^{-1}\)) can be attributed to the presence of isolated double bonds, which resonate at frequencies greater than that of the G band of graphite. After reduction by nascent hydrogen, the G bands of the nHRGOs red-shifted toward the G band of the graphite and the I(D)/I(G) ratio significantly increased. The G band red-shifted from 1598 cm\(^{-1}\) in the graphene oxide spectrum to 1584, 1582 and 1582 cm\(^{-1}\) in the spectra for nHRGO\(_{\text{Al/NaOH}}\), nHRGO\(_{\text{Al/HCl}}\) and nHRGO\(_{\text{Zn/NaOH}}\), respectively, while the I(D)/I(G) ratio increased from 1.01 for graphene oxide to 1.36, 1.65 and 1.88 for nHRGO\(_{\text{Al/NaOH}}\), nHRGO\(_{\text{Al/HCl}}\) and nHRGO\(_{\text{Zn/NaOH}}\), respectively. Both the red-shift of the G band and the increase in I(D)/I(G) can be attributed to the recovery of sp\(^2\) domains in the graphitic structure.

Furthermore, the intensity of the 2D (2682 cm\(^{-1}\)) and S3 (2930 cm\(^{-1}\)) peaks in the nHRGO spectra, especially those of nHRGO\(_{\text{Al/HCl}}\) and nHRGO\(_{\text{Zn/NaOH}}\), significantly increased compared to that of graphene oxide, indicating good graphitization.

Fig. 4. C1s XPS spectra of (a) graphene oxide, (b) nHRGO\(_{\text{Al/HCl}}\), (c) nHRGO\(_{\text{Al/NaOH}}\) and (d) nHRGO\(_{\text{Zn/NaOH}}\)

X-ray photoelectron spectroscopy (XPS) analysis could provide direct evidence of graphene oxide reduction through the removal of oxygen functional groups. Fig. 4 shows the C1s XPS spectra of graphene oxide and the nHRGOs. In the C1s XPS spectrum of graphene oxide (Fig. 4(a)), there are clearly four peaks assigned to four types of carbon with different chemical valences, including non-oxygenated ring carbon (284.5 eV), carbon in C-O bonds (286.4 eV), carbonyl C (287.8 eV) and carboxylate C. After reduction, the oxygen functionality peaks remain in the C1s XPS spectra of the nHRGOs, but the intensity decreased noticeably, indicating that the graphene oxide was highly reduced by nascent hydrogen. The effective removal of oxygen functional groups was reflected in the increase of the C/O ratio from 2.1 for graphene oxide to 4.9, 12.1 and 12.8 for nHRGO\(_{\text{Al/NaOH}}\), nHRGO\(_{\text{Zn/NaOH}}\) and nHRGO\(_{\text{Al/HCl}}\), respectively, which is consistent with the elemental analysis results.
Fig. 5 (a) TGA and (b) DTG thermograms of graphene oxide and nHRGOs

Fig. 5 shows the thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) results for graphene oxide and the nHRGOS characterized in a nitrogen atmosphere. The TGA curve of graphene oxide shows approximately 5% mass loss at 100°C, which can be attributed to the evaporation of absorbed water. The DTG curve of graphene oxide reveals that the main mass loss occurred from 150 to 250°C, which can be ascribed to the decomposition of labile oxygen functional groups such as hydroxyl, epoxy and carbonyl. The graphene oxide loss was approximately 55 wt% at 800°C. The nHRGOS exhibited much higher thermal stability in comparison with graphene oxide due to the deoxygenation of graphene oxide during the reduction process, especially for nHRGO_{AHCl} and nHRGO_{ZnNaOH}. The TGA curves of nHRGO_{AHCl} and nHRGO_{ZnNaOH} show that the mass losses at 800°C were only 8–9 wt%. The DTG curves of these nHRGOS demonstrate that the decomposition peaks at 200°C disappeared, indicating effective removal of the labile oxygen functional groups of graphene oxide during the nascent hydrogen reduction process.

The high electrical conductivity of nHRGOS compared to that of graphene oxide is direct proof of the recovery of conjugated C=C bonds during the reduction process. The electrical conductivity of the nHRGO powder pellets compared to that of other RGOs is shown in Table 2. The electrical conductivity of the nHRGOS varied widely depending on the C/O ratio. Among the nHRGOS, nHRGO_{AHCl} exhibited the best electrical conductivity at greater than 12,500 S/m, which is a result of the highest graphitization at a C/O ratio greater than 21. The high electrical conductivity of the nHRGOS indicates that nascent hydrogen is a powerful reducing agent for the reduction of graphene oxide.

3.2 Possible mechanism for the chemical reduction of graphene oxide by nascent hydrogen

As previously mentioned, the reduction of graphene oxide by direct electron transport from Al or Zn to graphene oxide sheets can be excluded as the sheets did not adhere to the Al foil or Zn particle surfaces. The possible reducing agent for the reduction of graphene oxide is nascent hydrogen, which is generated in situ from the reaction of Al and HCl or NaOH and Zn with NaOH. To confirm this, a comparative experiment was performed. Graphene oxide was first spray-coated on a quartz substrate and then reduced by dipping the spray-coated specimens in beakers containing Al foil and a HCl solution or Zn powder and a NaOH solution, as shown in Fig. 6(a). To avoid contact between the graphene oxide and the metal, the quartz substrate was placed in the middle, while the metals were carefully placed at the bottom of the beaker. Al reacted vigorously with HCl to produce hydrogen bubbles that carried the Al foil to the surface within a few minutes and it was impossible to avoid random contact between the Al foil and graphene oxide film. However, the Zn powder reacted gently with NaOH and produced hydrogen bubbles that did not carry the Zn particles to the surface so the graphene oxide film was kept away from the Zn powder during the experiment. Fig. 6(b) shows the UV-vis spectra of graphene oxide and the nHRGO films on a quartz substrate (the inset of Fig. 6(b)). The UV-vis spectrum of graphene oxide exhibits a strong absorption peak at 232 nm and a shoulder at ~300 nm, which can be attributed to the π→π* transitions of aromatic C–C bonds and n→π* transitions of C=O bonds, respectively. After nascent hydrogen reduction, the absorption peak of the nHRGOS red-shifted to ~266–268 nm and the absorption in the whole spectra region increased, indicating that the conjugated C=C bonds and n→π* transitions of C=O bonds were further extended after nHRGO reduction.

### Table 2. The electrical conductivity of RGO prepared via the reduction of graphene oxide with various reducing agents

<table>
<thead>
<tr>
<th>RGO</th>
<th>Reducing agent</th>
<th>C/O ratio</th>
<th>Compression force (psi)</th>
<th>Electrical conductivity (S/m)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced GO</td>
<td>Hydrazine</td>
<td>10.3</td>
<td>-</td>
<td>2,420</td>
<td>4</td>
</tr>
<tr>
<td>CCG</td>
<td>NaBH₄ followed by concentrated H₂SO₄ at 120°C</td>
<td>8.57</td>
<td>4,000</td>
<td>1,660</td>
<td>31</td>
</tr>
<tr>
<td>RG-O_{H₂SO₄}</td>
<td>HI</td>
<td>15.27</td>
<td>10,000</td>
<td>30,400</td>
<td>14</td>
</tr>
<tr>
<td>RGO</td>
<td>Al</td>
<td>18.6</td>
<td>-</td>
<td>2,100</td>
<td>18</td>
</tr>
<tr>
<td>nHRGO_{AHCl}</td>
<td>Nascent hydrogen</td>
<td>21.11</td>
<td>4,000</td>
<td>12,530</td>
<td>This work</td>
</tr>
<tr>
<td>nHRGO_{ZnNaOH}</td>
<td>Nascent hydrogen</td>
<td>5.35</td>
<td>4,000</td>
<td>1,120</td>
<td>This work</td>
</tr>
<tr>
<td>nHRGO_{ZnNaOH}</td>
<td>Nascent hydrogen</td>
<td>17.96</td>
<td>4,000</td>
<td>7,540</td>
<td>This work</td>
</tr>
</tbody>
</table>
bonds were restored by reduction. The UV-vis spectra of the nHRGOs show clearly that the absorption in the whole spectra of nHRGO$_{Zn/NaOH}$ was significantly greater than that of nHRGO$_{Al/HCl}$, implying a higher degree of graphitization of nHRGO$_{Zn/NaOH}$. The sheet resistance of the nHRGO films was measured using a four-point probe to further confirm the reduction. The correlation between the sheet resistance and transmittance at 550 nm of the nHRGO$_{Al/HCl}$ and nHRGO$_{Zn/NaOH}$ films is shown in Table 3. The sheet resistance of the nHRGO$_{Zn/NaOH}$ film was significantly smaller than that of the nHRGO$_{Al/HCl}$ film, indicating that the nHRGO$_{Zn/NaOH}$ film was more highly reduced, which is consistent with the UV-vis spectra results. The greater reduction of the nHRGO$_{Zn/NaOH}$ film can be explained by the structure of the graphene oxide film that is composed of stacked graphene oxide sheets. The reducing agent first reduced the graphene oxide sheet on the film surface and it took time to penetrate and reduce the graphene oxide sheets underneath the surface sheet. As mentioned in Fig. 1, the Al foil reacted vigorously with HCl and the reaction was completed within 30 min, while the Zn powder reacted gently with NaOH and the reaction was completed within 6 h. As shown in Table 3, the sheet resistance of the nHRGOS was quite high, suggesting that just a few graphene oxide sheets on the film surface were reduced. Therefore, graphene oxide is reduced without contact to metal. The nascent hydrogen is only one candidate agent for the reduction of graphene oxide.

### Table 3. Correlation between the sheet resistance and transmittance at 550 nm of the nHRGO films

<table>
<thead>
<tr>
<th></th>
<th>Transmittance at 550 nm (%)</th>
<th>Sheet resistance (kΩ/□)</th>
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<tbody>
<tr>
<td>Graphene oxide</td>
<td>97</td>
<td>-</td>
</tr>
<tr>
<td>nHRGO$_{Al/HCl}$</td>
<td>91</td>
<td>144.7</td>
</tr>
<tr>
<td>nHRGO$_{Zn/NaOH}$</td>
<td>84</td>
<td>38.5</td>
</tr>
</tbody>
</table>

Scheme 1. Proposed reaction pathway for the reduction of graphene oxide by nascent hydrogen. (a) In situ generation of nascent hydrogen and (b) removal of oxygen functional groups by nascent hydrogen.

4. Conclusions

We have demonstrated that nascent hydrogen can be used to effectively reduce graphene oxide. The nascent hydrogen was generated in situ by reacting Al foil with HCl, Al foil with NaOH
and Zn powder with NaOH. The reduction efficiency of graphene oxide strongly depended on the medium and the rate of nascent hydrogen generation. The nascent hydrogen generated from the reaction between Al foil with HCl achieved the best graphene oxide reduction with a C/O atomic ratio greater than 21 and a bulk electrical conductivity as high as 12,500 S/m. The combination of XPS and TGA analyses suggested that most of the labile oxygen functional groups were removed during nascent hydrogen reduction. We also proposed a reaction pathway for the reduction of graphene oxide by nascent hydrogen. Since nascent hydrogen is naturally produced on the metal surface upon oxidation in solution, several metals that have a low standard reduction potential, such as Mg, Al, Mn, Zn, and Fe, can be used to reduce graphene oxide. Compared to other reducing agents, such as hydrazine, NaBH₄ or HI, the use of low cost, non-toxic metals for nascent hydrogen reduction of graphene oxide is a promising method for bulk preparation of high quality RGO.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Descriptions of graphene oxide synthesis and a photograph of graphene oxide reduction before and after washing with diluted HCl solution and XRD patterns of nHRGOS]. See DOI: 10.1039/b000000x/
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