Highly qualified reduced graphene oxides: the best chemical reduction†

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We report new step-by-step reduction methods by alternating two different reducing reagents with the order of hydrazine with NH₃ (NH₃/HI in acetic acid (HI) and the reverse order (HI/NH₃) to understand nitrogen incorporation and removal or reduction for providing highly qualified reduced graphene oxides (rGOs).

Graphene nanosheets (G) are novel materials which have unique electronic, mechanical, and chemical properties and potential applications in areas such as transparent conductive films, supercapacitors, solar cells, hydrogen gas storage media, bio-sensors, composites, and batteries.1 Reduced graphene oxides (rGOs) obtained via chemical reduction of mass producible graphene oxides (GOs) is a promising group of materials for electronic applications because of their superior properties and particularly, their suitability for flexible applications. Various chemical reduction methods of GOs have been introduced using hydrogen sulfide,2 hydrazine,3 NaBH₄,4 dimethylhydrazine,5 hydroquinone,6 sequential use of NaBH₄ and H₂SO₄,7 and aluminium powder.8 Until now, a hydrazine hydrate reducing agent with NH₃ (NH₃) has been the most widely used to obtain reduced GO (rGO-NH₃) in both solution and gas phases. One of the major advantages of using the NH₃ reducing agent is that it can be applied for the gas phase reduction of GO thin films on substrates. However, the NH₃ reducing agent results in a relatively high sheet resistance due to nitrogen impurities.9 Recently, a study on the incorporation of nitrogen impurities into rGOs has been reported.10 Until now, however, how to remove or reduce the nitrogen from the rGOs has not been addressed. Thus, when using the conventional hydrazine method, understanding of the nitrogen removal/reduction from the rGOs is becoming a crucial issue for further development of highly qualified rGOs. In addition, the answer to the remaining question on which is the best method to obtain the highest qualified rGOs has not been provided yet. Recently, we reported a novel reduction method without a nitrogen source in both solution and gas phases, which resulted in a high electrical conductivity.11 Hydroiodic acid in acetic acid (HI) was used as a reducing agent to synthesize rGO-HI. It is interesting to understand the role of the nitrogen atom and to find the best reduction method by combining the traditional method of NH with the HI method for the best reduction method. It is assumed that the introduction of the HI method to rGO-NH₃ can remove or reduce the nitrogen atom if the nitrogen atom is physically inserted.

Here, we focused our attention on new step-by-step reduction methods by alternating two different reducing reagents with the order of HI/NH₃ and NH₃/HI, as shown in Fig. 1, to understand the nitrogen incorporation and their removal or reduction resulting in highly qualified rGOs with a high electrical conductivity. With this in mind, we extended our study to investigate the preparation and characterization of the powder. We also compared the materials to rGOs that were investigated in ref. 11. It is expected that these new step-by-step reduction methods may provide insight on how to incorporate nitrogen into rGOs and remove the nitrogen out of rGOs in the case of using NH as well as how to find the best reduction method for highly qualified rGOs. Furthermore, it is also expected that these methods may result in rGOs with an increased electrical conductivity. The routes of the chemical step-by-step reduction steps are provided in Fig. 1.

Detailed analyses of the X-ray powder diffraction (XRD) data of the as-prepared powder reveal the presence of rGO-NH₃, rGO-HI, rGO-NH₃HI, and rGO-HI-NH₃ phases (Fig. 2, inset). As can be seen in the XRD patterns, the diffraction peaks of the rGOs are relatively weak and broad at around 24.4°. The peak of rGO-HI shows the most narrow width. Interestingly, after reduction of GO with NH₂NH₂, HI, and vice versa, the peaks of rGO-NH₂HI and rGO-HI-NH₃ became broader and each peak

![Fig. 1. Flow chart of 2 different step-by-step reductions for rGOs representing carbon (gray circle), nitrogen (blue dark circle), and oxygen atom (red dark circle), respectively.](image-url)
obtained an unsymmetrical shape. This effect is due to localized variations in the interlayer spacing leading to a certain degree of disorder in the size of the graphene nanosheets. Compared to the rGO powders, the diffraction angle also shifted toward the G powder (26.7°) with increased reduction conditions. The d-spacing and full width at half maximum (FWHM) of rGO powders prepared by each step-by-step method with NH/HI and HI/NH are shown in Fig. 2. In Fig. 2, it is seen that there was considerable restoration of π-conjugation onto the graphene nanosheets. Application of the Bragg equation to these diffraction peaks yields d-spacing values of 0.371 for rGO$_{\text{NH}}$, 0.368 for rGO$_{\text{NHHI}}$, 0.366 for rGO$_{\text{HI}}$, and 0.368 nm for rGO$_{\text{HINH}}$. Analyses of the normalized peaks revealed that the d-spacing and FWHM values of the rGOs after HI treatment sharply decreased, while those of rGO$_{\text{NH}}$ were higher. Interestingly, the d-spacing values changed depending on the different reduction routes of NH/HI and HI/NH, as shown in Fig. 2.

The d-spacing values with NH/HI reduction decreased from rGO$_{\text{NH}}$ (0.371) to rGO$_{\text{NHHI}}$ (0.368) while those with HI/NH increased from rGO$_{\text{HI}}$ (0.366) to rGO$_{\text{HINH}}$ (0.368). The d-spacing value after reduction using HI (rGO$_{\text{HI}}$) was the lowest value, indicating that the HI reduction method is superior to the NH method. It is concluded that the NH reducing agent influences to increase the d-spacing value while the HI reducing agent helps to reduce it. With increasing graphitization, the FWHM of the rGOs decreased due to the deoxygenation of GOS. The FWHM values were 5.219 for rGO$_{\text{NH}}$, 3.817 for rGO$_{\text{HI}}$, 3.661 for rGO$_{\text{NHHI}}$, and 3.623 for rGO$_{\text{HINH}}$. Both FWHM values with the NH/HI and HI/NH reduction routes decreased from rGO$_{\text{NH}}$ (5.219) to rGO$_{\text{NHHI}}$ (3.661) and from rGO$_{\text{HI}}$ (3.817) to rGO$_{\text{HINH}}$ (3.623), respectively. The FWHM with reduction with HI (rGO$_{\text{HI}}$) was lower than that with the NH method (rGO$_{\text{NH}}$).

The XPS analysis further revealed the surface compositions of GOS and the rGOs. Only carbon, oxygen and nitrogen species were detected as shown in the C/(O + N) atomic ratio results in Fig. S1 and Table S1 (ESI†). The quality of the rGOs was estimated from the atomic compositions of the C 1s, the O 1s and the N 1s (Fig. S1, inset, ESI†) and the ratio of the integrated intensity of the C 1s (Table S1) from their XPS spectra. As shown in Fig. S1 (ESI†), the C 1s spectra indicated the presence of oxygen in more than several components.

We considered five Gaussian curves centered at the following binding energies: C sp$^2$ (284.6 eV), C–OH (285.6 eV), epoxy/ether (286.7 eV), C–O (288.2 eV), and C(O)O (289.4 eV) attributed to sp$^2$ and sp$^3$ hybridized atoms, in agreement with Park et al. (Fig. 3). As given in Table S1, the order of the C/O atomic ratios with step-by-step reduction was rGO$_{\text{NH}}$ < rGO$_{\text{NHHI}}$ < rGO$_{\text{HI}}$ < rGO$_{\text{HINH}}$ and the peak areas of the C/(O + N) atomic ratios were obtained in the order of rGO$_{\text{NH}}$ < rGO$_{\text{NHHI}}$ < rGO$_{\text{HINH}}$ < rGO$_{\text{HI}}$ as depicted in the inset in Fig. S1 and Table S1 (ESI†). Herein, we were interested in the total decreased amount of the carbon–oxygen and carbon–nitrogen functional group content, which indicates the degree of reduction and the quality of the rGOs containing nitrogen impurity. The peak areas of the C 1s, the O 1s and the N 1s functional group were roughly in accordance with those expected on the basis of the molar ratio between these atoms in the graphene nanosheets. The C/(O + N) atomic ratios dramatically increased from 2.56% (GO) to 7.9–12.50% (rGOs). In particular, rGOs using HI were superior to those with NH$_2$NH$_2$ and further reduction using the step-by-step method is very effective to remove the oxygen in both reduction routes as shown by C/O atomic ratios in Table S1 (ESI†).

As depicted in Fig. 3, the deconvolution of the N 1s spectra of rGO$_{\text{NH}}$ yielded four peaks: a peak at 399.08 eV ascribed to the pyrrolic structure, a peak at 400.03 eV attributed to pyrrolic or amine moieties, a peak at 401.48 eV corresponding to quaternary nitrogens, and a peak at 402.73 eV reflecting pyridine-N oxides. Upon further reduction of rGO$_{\text{NH}}$ with HI, the peak intensity of the pyrrolic N 1s at 399.08 eV was sharply reduced while the peak intensities of the other 3 nitrogen peaks were not changed, as shown in Fig. 3b. As a result, the intensities of the N 1s peaks of rGO$_{\text{NHHI}}$ were reduced more than those of rGO$_{\text{NH}}$ as shown in Fig. 3a and b. Interestingly, with further reduction of rGO$_{\text{HI}}$ with NH, the peak intensities of the pyridinic, pyrrolic, and quaternary nitrogens of rGO$_{\text{HINH}}$ slightly increased while the peaks of the pyridine N oxides were not detected, as shown in Fig. 3c. Among them, the peak of the pyrrolic N 1s was the major component. These results reveal that treatment of rGO$_{\text{NH}}$ with HI resulted in partial removal of pyridinic N 1s, leading to a reduction of the nitrogen weight %. On the other hand, treatment of rGO$_{\text{HI}}$ with NH generally provided a nitrogen insertion. However, in the case of rGO$_{\text{HI}}$, a small amount of

**Fig. 2** Changes of d-spacing (black dark circle) and FWHM parameters (black dark rectangle) of the diffraction lines of prepared rGOs. The inset shows the XRD spectra of various rGOs.
nitrogen was inserted into the rGOHINH nanosheets due to hard exfoliation of rGOHI, which showed a similar trend as the nitrogen percentage determined by the elemental analyses (Table S2, ESI†).

Table S2 (ESI†) shows the elemental analyses of rGOH, rGOHI, rGOHINH, and rGOHINH. The rGONH, rGOHINH, and rGOHINH had 4.11%, 3.02%, and 1.46% nitrogen, respectively, while no nitrogen impurities were detected in the rGOHI. The order of the C/O atomic ratio was rGONH < rGOHINH < rGOHI < rGOH, which was well matched with the trend of the XPS C/O atomic ratio in Table S1 (ESI†). However, the order of the C/(O + N) atomic ratio was rGONH < rGOHINH < rGOHI < rGOH due to nitrogen incorporation, which showed a similar trend as the XPS C/(O + N) atomic ratio in Table S1 (ESI†). It was found that the nitrogen content of rGOHINH obtained from rGOH, after treatment with hydrazine decreased while that of rGOHINH obtained from rGOH increased, which is inversely related to the order of the XRD d-spacing, as shown in Fig. 2. It was assumed that the decreased amount of nitrogen from rGOH to rGOHINH (4.11–3.02 = 1.09%) may be physically intercalated between rGO nanosheets while the remaining nitrogen (3.02%) can be covalently bonded to rGOs.

In addition, the nitrogen incorporation of rGOHINH (1.46%) from rGOH (0%) increased much less than that of rGOH (4.11%) obtained from GO (0%). It was assumed that rGOH nanosheets closely packed by π–π interactions allow a small amount of nitrogen insertion into the rGO nanosheets.

Table 1 shows the electrical properties based on the reduction conditions of the rGO powders. It is well known that the electrical properties of powder pellets depend on a number of factors including the physicochemical structural parameters such as grain size, and the shape and size of the graphene nanosheets as well as the processing method and conditions. Surprisingly, the electrical conductivity order of the rGOs (rGONH < rGOHINH < rGOHINH < rGOH) demonstrated in Table 1 is well matched with the order of the elemental C/(O + N) ratios and inversely related to the d-spacing order (rGONH < rGOHINH ∼ rGOHINH < rGOH) depicted in Fig. 2. In addition, to some extent, it is related to the deoxygenation order (rGOHINH < rGOH). Thus, in considering possible reasons for the highest conductivity value of rGOHI, nitrogen incorporation and d-spacing values are the most important factors for the determination of the electrical conductivity. Therefore, nitrogen incorporation when using hydrazine, as confirmed in both step-by-step reduction methods, cannot be avoided and causes a reduction in the electrical conductivity.

In conclusion, the step-by-step reduction combining HI and NH as reducing agents provided high graphitization of graphene nanosheets at a relatively lower temperature than that of solvothermal reduction. The nitrogens of rGONH were partly removed after treatment with HI and those of rGOH were inserted after treatment with NH, confirmed by the step-by-step rGONH–rGOHINH and rGOH–rGOHINH reduction routes, respectively. Both step-by-step reduction routes provided the lowest FWHM and highest deoxygenation, leading to improvement of the electrical conductivity. The electrical conductivity order was well matched with the order of the C/(O + N) atomic ratio of XPS and the elemental analyses and inversely related to the d-spacing order. As a result, rGOs prepared by the HI method with no nitrogen impurities and the lowest d-spacing resulted in the highest conductivity. Our simple step-by-step reduction methods will guide how to improve the electrical conductivity. An investigation to increase the scope of this methodology is currently being conducted by our groups.

Notes and references

2. (d) N. Mohanty and V. Berry, Nano Lett., 2008, 8, 4469.