

# ***In-Situ* Synthesis of Hydrazine in Graphene Oxide Suspension and Stable Dispersion of Spontaneously Reduced Graphene Oxide Assisted by Hexamethyldisilazane**

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## **ABSTRACT**

The efficient reduction and a solution processability of graphene nanoplatelets are most important for its applications. Here we report for the first time that *in-situ* synthesis of hydrazine and spontaneous reduction of graphene oxide (GO) in solution can be achieved by addition of hexamethyldisilazane (HMDS) and hydrogen peroxide into GO solution just followed by step-wise heating. We demonstrated that hydrazine can be *in-situ* synthesized in the existence of GO by reacting with ammonia and hydrogen peroxide. The successful reduction of GO by *in-situ* synthesized hydrazine was confirmed by measuring x-ray photoelectron spectra (XPS) and Fourier transform infrared (FTIR) spectra of RGO powder and UV absorbance spectra of RGO solution. Moreover, importantly, trimethylsilanol molecules from HMDS contributed to a stable colloidal RGO solution even in ethanol.

**Keywords:** chemically-modified graphene, hydrazine, *in-situ* synthesis, dispersion, hexamethyldisilazane

## **1 INTRODUCTION**

Chemically modified graphene, which is produced through the oxidation of highly oriented pyrolytic graphite, is a typical two-dimensional (2D) particle attracting great interests in colloidal sciences and practical applications. The solution processability of graphene oxide (GO) permits application of GO to substrates *via* spin-coating, spray-casting, drop-casting, or inkjet printing for the large-scale production of graphene electronic circuits. The oxidized graphene nano-platelets should be reduced by chemical or thermal treatment for recovery of their electrical properties.[1-3] Hydrazine has been used as a efficient chemical reduction agent of GO, while unfortunately, hydrazine is a very hazardous chemical, both to the human health and to the environment.[4] We suggest that *in-situ* synthesis of hydrazine in GO suspension can be done by mimicking typical cycle reaction process, in which ketone molecules (catalyst), ammonia and hydrogen peroxide are used as reagents.

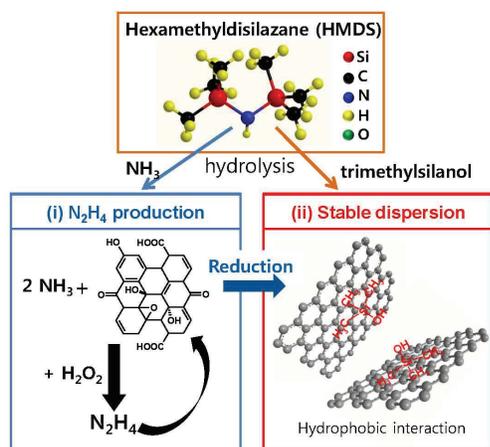
Another issue in advancing toward application is the difficulty in suspending reduced graphene oxide (RGO) in polar solvents owing to the easy irreversible stacking or

agglomeration of 2D RGO by  $\pi$ - $\pi$  interactions.[5-8] In particular, alcohol-based formulations of graphene are essential to graphene processing and fabrication of related devices when use of harsh organic solvents is not possible. In these context, our second suggestion is that hexamethyldisilazane (HMDS) can be used as a source of ammonia molecules for hydrazine synthesis and as a dispersant of RGO, because HMDS can be easily hydrolyzed into trimethylsilanol and ammonia in the presence of water molecules (Scheme 1). Generated trimethylsilanol from hydrolyzed HMDS can play like a dispersant of RGO in organic solvents (Scheme 1(ii)).

In this work, we therefore describe for the first time *in-situ* synthesis of hydrazine interacted by GO reacted with ammonia generated during hydrolysis of hexamethyldisilazane (HMDS) and hydrogen peroxide. We demonstrated the successful reduction of GO by *in-situ* synthesized hydrazine in GO solution by confirming X-ray photoelectron spectra (XPS) and Fourier transform infrared (FTIR) spectra of RGO powder and UV absorbance spectra of RGO solution. Importantly, a stable colloidal RGO suspension even in ethanol was fabricated assisted by trimethylsilanol hydrolyzed from HMDS via hydrophobic interaction. From our approach, we can achieve the environmentally friendly reduction of GO by *in-situ* synthesized hydrazine molecules in GO suspension and the stable dispersion of RGO in low boiling point and non-harsh solvents.

## **2 EXPERIMENTAL**

Graphene oxide was prepared from natural graphite (Alfa Aesar, 99.999% purity, -200 mesh) by a modified Hummers method. Briefly, 20 g graphite and 460 mL H<sub>2</sub>SO<sub>4</sub> were mixed in a flask. Then, 60 g KMnO<sub>4</sub> were slowly added over 1 h. Stirring was continued for 2 h in an ice-water bath. After the mixture was stirred vigorously for 18 h at room temperature, 920 mL deionized water was added, and the solution was stirred for 10 min in an ice-water bath. Fifty milliliters of H<sub>2</sub>O<sub>2</sub> (30 wt% aqueous solution) was then added, and the mixture was stirred for 2 h at room temperature. The resulting mixture was precipitated and filtered to obtain the graphite oxide powder. Graphite oxide was then exfoliated into graphene oxide (GO) nano-platelets (1g/L) in deionized water/dimethylformamide (DMF) (1/9 v/v) by bath sonication for 1 h.



Scheme 1: Roles of hexamethyldisilazane (HMDS): (i) ammonia source for GO-assisted production of hydrazine upon the addition of hydrogen peroxide; (ii) RGO dispersion agent in ethanol, via hydrophobic interactions.

For the reduction of GO in solution, hydrazine was in-situ synthesized in a GO solution by mimicking a typical reaction cycle involving GO (alternative ketone molecules as a catalyst) and ammonia and hydrogen peroxide as reagents. Hexamethyldisilazane (HMDS) molecules which can be easily hydrolyzed into ammonia and trimethylsilanol in the presence of water molecules were used as a source of ammonia molecules. First, HMDS was added into the GO solution at 25 °C and stirred for 30 min for hydrolysis and HMDS molecules into ammonia and trimethylsilanols, followed by addition of hydrogen peroxide and stirring at 50 °C for 10 h. The solution was then heated at 100 °C to reduce GO nano-platelets for 16h. Resulting reduced graphene oxide (RGO) solution was precipitated and redispersed in organic solvents by sonication with 120W for 5min.

GO and RGO films were fabricated at room temperature using an automatic spray coater (NCS Co., NCS400) with a nozzle 1.2 mm in diameter. The GO films were then reduced by heating under hydrazine fumes at 100°C for 2 h to fabricate RGO films as a control sample. Source and drain electrodes were then deposited by evaporating Au through a shadow mask. The channel length and width of a typical device were 100  $\mu\text{m}$  and 800  $\mu\text{m}$ , respectively. The transistor current–voltage characteristics were measured using Keithley 2400 and 236 source/measure units under vacuum (10–5 Torr).

The morphologies of the GO and RGO nano-platelets were imaged by AFM (DI Multi-modes), field emission scanning electron microscopy (FE-SEM, HITACHI S4800), and field emission transmission electron microscopy (FE-TEM, JEM2100F). The absorbance of the GO suspension during reduction was measured by UV-vis spectroscopy (Varian, Cary 5000). The structural characteristics of the RGO sheets were investigated by confocal Raman spectrometer (NTEGRA SPECTRA, NT-MDT) with an

excitation wavelength of 532 nm. To confirm the change in the carbon to oxygen atomic ratio in the functional groups of the films after reduction by hydrazine molecules synthesized in-situ, XPS analysis was conducted using a Multilab2000 (Thermo VG Scientific Inc.) spectrometer with monochromatized Al K X-ray radiation as the X-Ray excitation source. FT-IR spectroscopy (JASCO, 4200UP) analysis was performed to assign the functional group of GO and RGO.

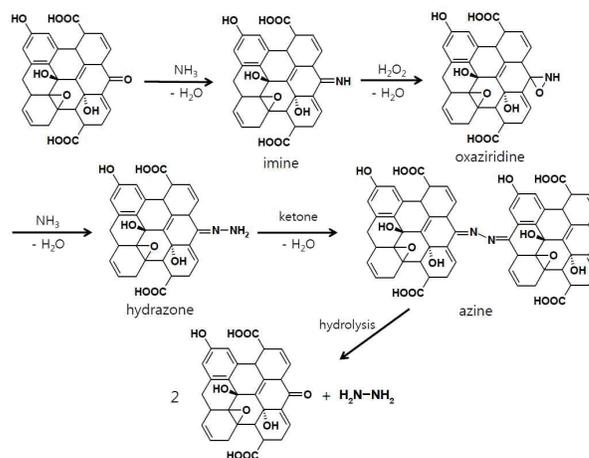


Figure 1: Synthesis scheme of hydrazine in graphene oxide, ammonia, hydrogen peroxide mixture solution.

### 3 RESULTS AND DISCUSSION

Hydrazine has been widely used for the production of RGO-based nano-platelets with excellent physical properties. Hydrazine is formed in a multitude of chemical reactions (Figure 1). In a typical process with acetone, ammonia, and hydrogen peroxide, acetone is treated with ammonia to give imine followed by oxidation with hydrogen peroxide resulting in 3,3-dimethyloxaziridine and then ammonolysis to the hydrazone, which reacts with one more equivalent of acetone. The resulting azine is hydrolysed to produce hydrazine and regenerating two molecules of acetone. In this study, GO nano-platelets having ketone groups were utilized as an alternative ketone molecule for in-situ production of hydrazine molecules and spontaneous reduction of GO in solution.

For the reduction of GO in solution, hydrazine was *in-situ* synthesized in a GO suspension by mimicking a typical reaction cycle involving GO (alternative ketone molecules as a catalyst) and ammonia and hydrogen peroxide as reagents. Hexamethyldisilazane (HMDS) molecules which can be easily hydrolyzed into ammonia and trimethylsilanol in the presence of water molecules were used as a source of ammonia molecules.

As shown in Figure 2a and the SEM image (Figure 2c), the GO nano-platelets underwent severe aggregation at low temperatures, even though the GO nano-platelets were not reduced. Moreover, the solution color did not change from dark brown. These results clearly supported that the

interconnected azine structure of GO formed mainly without the reduction of the GO nano-platelets. The intermediated GO was denoted GO-azine. The GO/HMDS/H<sub>2</sub>O<sub>2</sub> mixture solution was subsequently heated to 100 °C because the reduction of GO by hydrazine can usually be performed at elevated temperatures of 100 °C. The dark brown GO-azine suspension turned black within 30 min, indicating the production of hydrazine and the spontaneous reduction of GO. Importantly, step-wise heating at 50 °C and 100 °C was more efficient than a one-step process involving heating at 100 °C because at high temperatures, GO, which acts as a ketone molecule in the hydrazine synthesis, can be spontaneously reduced by the *in-situ* synthesized hydrazine molecules.

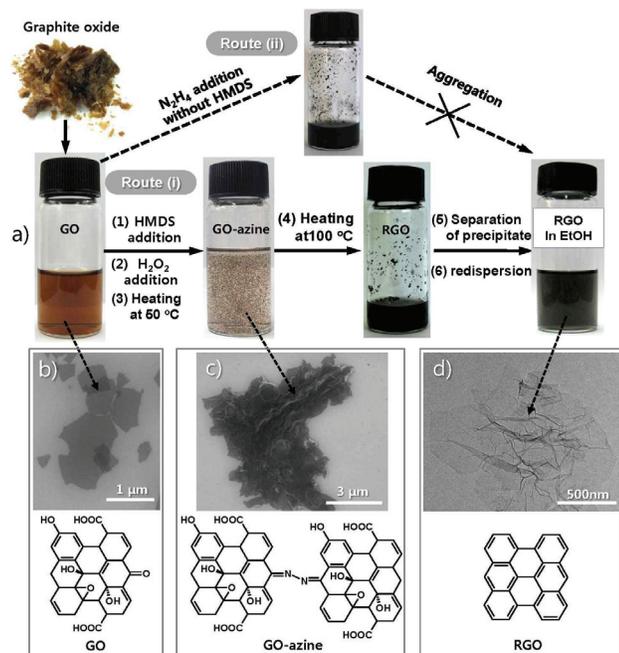


Figure 2: Reduction and dispersion of chemically-modified graphene nano-platelets. (a) Route (i): sequential addition of HMDS and hydrogen peroxide to a GO suspension at 50 °C, followed by stirring for 10 h and further heating at 100 °C for 16 h. The resulting aggregated RGO precipitate was redispersed in ethanol. Route (ii): Direct reduction with hydrazine monohydrate without any dispersant. (b, c) SEM images of well-exfoliated GO nano-platelets and aggregated GO-azine on SiO<sub>2</sub>, respectively. (d) TEM image of RGO nano-platelets well-dispersed with trimethylsilanol, showing the wrinkled structures produced via the route (i) method.

The reduction efficiency was investigated by monitoring the UV absorbance peak position of the RGO suspension. The XPS spectra of the films were also observed for varying concentrations of HMDS and for various heating conditions. The UV absorbance peak position of the graphene solution shifted from 232 to 273 nm upon an increase in the HMDS concentration (Figure 3a). Importantly, step-wise heating at 50 °C and 100 °C was

more efficient than a one-step process involving heating at 100 °C because at high temperatures, GO, which acts as a ketone molecule in the hydrazine synthesis, can be spontaneously reduced by the *in-situ* synthesized hydrazine molecules. Figure 3b shows the XPS spectra of the GO and RGO film reduced by the HMDS/H<sub>2</sub>O<sub>2</sub> mixture without other reduction agents. The addition of 4 moles HMDS and 2 moles H<sub>2</sub>O<sub>2</sub> per 100 mg GO (the stoichiometric yield of N<sub>2</sub>H<sub>4</sub> is 2 mol under these conditions) reduced the number of C-O bonds in the epoxides and hydroxyl groups, whereas carbonyl groups and C-O bonds remained. A ten-fold increase in the HMDS and H<sub>2</sub>O<sub>2</sub> concentrations dramatically reduced the remaining C-O and C=O bonds.

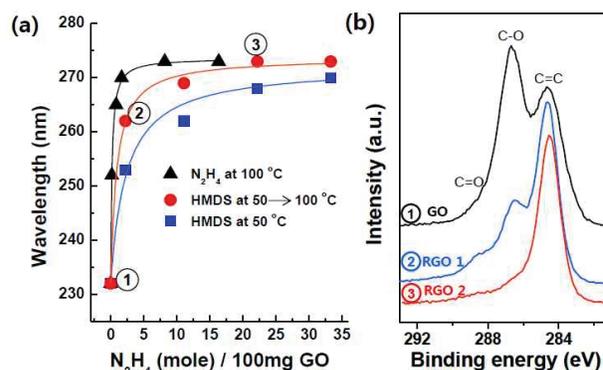


Figure 3: Characterization of GO and RGO. (a) The UV absorbance peak positions of the GO solution shifted upon step-wise heating at 50 °C and 100 °C (solid red), relative to the one-step heating at 100 °C. Star symbols indicate the RGO suspension reduced by the addition of N<sub>2</sub>H<sub>4</sub> at 100 °C. (b) C1s XPS spectra of GO, partially reduced GO (RGO1), and fully-reduced GO (RGO2) by the *in-situ* synthesized N<sub>2</sub>H<sub>4</sub>. The numbers shown in (a) correspond to those in (b).

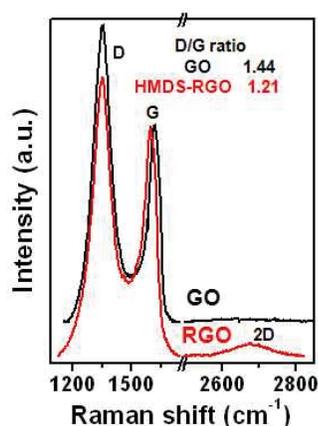


Figure 4. Raman spectra of the GO and RGO reduced by hydrazine molecules synthesized *in-situ* in a GO solution in the presence of ammonia (generated from hexamethyldisilazane) and hydrogen peroxide.

In addition, the D/G ratio decrease and the 2D peak increase in the Raman spectra of GO and RGO films (Figure 4) demonstrate the successful reduction of GO by the *in-situ* synthesized hydrazine.

## 4 CONCLUSIONS

We demonstrated that the *in-situ* synthesis of hydrazine in a GO suspension and the spontaneous reduction of GO nano-platelets in solution could be achieved in a reaction involving ammonia produced from hydrolyzed HMDS, hydrogen peroxide, and GO nanosheets. Intermediate oxaziridine and azine structure formation during the *in-situ* hydrazine synthesis and the spontaneous reduction of GO were supported by the FTIR and XPS spectra at low temperatures.

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