Hydrothermal Synthesis of Reduced Graphene Oxide Using Urea as Reduction Agent: Excellent X-band Electromagnetic Absorption Properties

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Abstract. We report a strong absorption of microwave energy at X-band (8 GHz to 12 GHz) by N-doped graphene. Attachment of nitrogen on the layered structure of GO improves the reflection loss of GO slab (2.0 mm, thickness) from ~10 dB to ~25.0 dB with a sharp bandwidth ~0.3 GHz. As for the broader bandwidth of about 1.4 GHz, reflection loss is ~10.5 dB. This significant absorption may take place by improvement of magnetic property of NG through high magnetic coupling of localized spins induced by a defect on the surface of graphene. N atoms play as the electron trapper, easily influenced by self-magnetic moments and incoming electromagnetic fields to produce electric and/or magnetic losses. Here, urea acts as the reducing agent and N atoms donor for graphene oxide in hydrothermal process at a temperature of 190 °C.

Keywords. Electronic adsorption, hydrothermal synthesis, reduction agent, and urea.

1. Introduction
Graphene has been produced using mechanical [1] or thermal exfoliation, chemical vapor deposition [2], and epitaxial growth [3]. Mechanical or thermal exfoliation process was limited to involving a small number of the product. CVD and epitaxial growth need a substrate for deposition graphene, restrict the applicability, and yet, the substrate may influence the properties of graphene. Due to the applicability of graphene in a wide range of applications and promising new technologies, people were searching for a cheaper, more straightforward, more efficient and better yielding method of processing graphene, that can be scaled up massively compared to current techniques, and be financially suitable for industrial or commercial applications. One of the most effective ways of synthesized graphene on a large scale could be by the chemical reduction of graphene oxide. Graphene oxide itself has been popularly produced by hummer method that involved oxidation process of graphite followed by exfoliation process.
As for chemical reduction of graphene oxide, in many cases, the active reduction agents were used [4–6]. Unfortunately, due to environmental safety aspects, strong acids cannot be utilized in the large-scale production facility. Using metals like Fe, Zn, and Al as reducing agents have also attracted significant interest in recent years [7]. However, to some extent, it was limited by the problem of a metal impurity.

Improvement of the magnetic property of graphene, in another side, was being an exciting issue in graphene research. Magnetism can take place in graphene via zig-zag structure, defect, or doped with the active substance. Doping graphene with sulfur or nitrogen [8, 9], for example, has proven enhancement of magnetic property of carbon or graphene. The existence of dopant on graphene surface can also change the electronic property of graphene.

In this report, doping of graphene oxide with nitrogen will be facilitated using urea as reduction agent through the hydrothermal process. It shows an excellent absorption of electromagnetic energy at X-band (8 GHz to 12 GHz).

2. Materials and methods
Graphene oxide (GO) was produced from fine graphite powder (particle size < 20 μm, Sigma Aldrich) following a modified of the Hummer’s method [10]. Typically, a 2 g of graphite powder was added, under stirring, to 98 mL of concentrated H₂SO₄ in an ice bath. Under robust agitation, KMnO₄ (8.0 g) and 4 g NaNO₃ were added wisely until the complete suspension formed. Stirring process was continued for additional 24 h at ~35 °C, followed by addition of 15 mL H₂O₂ where color changed from dark brown to yellow. After that, the mixture was centrifuged, filtered, washed with 10 ml HCl 37 % and several times with H₂O to remove the remaining metal ions. The resulting solid, graphite oxide was dried in air at 105 °C for 12 h. The resultant of graphite oxide was then diluted to 200 mL of aquades, stirred overnight and subsequently sonicated for 120 min at 53 kHz. Finally, GO was filtered and dried for 24 h at 105 °C.

Nitrogen-doped graphene (NG) was produced in situ via the hydrothermal reduction of GO in the presence of urea with a fixed weight ratio of urea and GO (3:1). The 1.8 g of urea and 0.6 g of GO were mixed in 160 mL of de-ionized water under stirring process. The mixture, then, was transferred to a 200 mL teflon lined hydrothermal chamber and heated for 12 h at 190 °C. The resulting powders were characterized by multiple techniques as described below.

Crystalline structure and phase purity of the as-prepared samples (NG and GO) were examined using powder X-ray diffraction (XRD). XRD pattern was recorded with graphite-monochromated Cu-Kα (γ = 1.54056 Å) radiation on Rigaku RINT UltimaIII ranging from 10° to 70° (20) with a scanning speed of 2° per min. The surface morphology of the resulting products was investigated by a scanning electron microscopy (SEM) TESCAN. Transmission electron microscope (TEM) images were collected from TEM device of JEOL JEM 1400 USA. Fourier transforms infrared spectroscopy (FTIR) spectra were recorded on a Fourier transform infrared spectrometer (Bruker Vertex V70). Reflection loss of samples at X-band (8 GHz to 12 GHz) were measured using vector network analyzer (VNA) Advantest R3770 Network Analyzer

3. Results and discussion
3.1. Crystal structure
XRD patterns are shown in Figure 1a. GO diffraction spectrum exhibits a usual sharp peak of (002) crystal phase at 11.0° that corresponds to an interlayer distance of about ~0.80 nm. On the contrary, XRD peak of NG shows a board shape centering at ~24.78° that is a layer by layer distance of about 0.36 nm. Shifting of this peak from a strong peak of (100) GO crystal phase at 26.8°, reflecting a self-healing of graphitic crystal structure related to nitrogen embedding. The (002) reflections, corresponding to the coherent and parallel stacking of graphene like-sheets, become broader, signifying the increase of amorphous nature. However, the (100) reflection corresponds to the honeycomb structure which is formed by sp² hybridized carbons [11]. The heteroatom (N) doping in
graphene facilitates defect site formation and destruction in the carbon lattice which, then, results in low crystallinity.

FTIR spectrum of GO and NG are shown in Figure 1b. In the range of GO, the peaks located at 3418 and 1111 cm\(^{-1}\) are attributed to the stretching vibration of hydroxyl groups \([12]\). The peaks at 1720 and 1219 cm\(^{-1}\) are assigned to the stretching vibrations of C=O and C–O–C in conjugated graphene, respectively. After hydrothermal reaction, the peak at 3418 cm\(^{-1}\) decreases accordingly. A disappearing peak at 1720 cm\(^{-1}\) can be assigned to a complete reduction of GO taking place where C=O groups are suppressed completely. More importantly, the peak at 1592 cm\(^{-1}\), corresponding to the in-plane vibration of C=C, shifts to 1586 cm\(^{-1}\). The disappearance is due to the superposition of the vibrations of C=C and C=N, which gives the evidence of the embedding of nitrogen-containing groups.

![Figure 1](image1.png)

**Figure 1.** Spectroscopic measurement data of GO and NG, (a) XRD diffraction pattern and (b) FTIR spectra

### 3.2. Surface morphology

Morphology of GO and NG are presented in Figure 2. As for GO, the clump layered GO is shown in Figure 2a and Figure 2c. Morphology of NG surface in Figure 2b and Figure 2d is resulting from the considerable folding of an individual graphene sheet. The dark spots appeared on Figure 2c can be attributed to the evidence of destructive parts of carbon lattice.

![Figure 2](image2.png)

**Figure 2.** Images of SEM and low magnification TEM; SEM images of (a) GO and (b) NG; TEM images of (c) GO and (d) NG

### 3.3. Absorption capability

Absorption capabilities of GO and NG through measurement of reflection loss \((R_L)\) of sample backed by copper plate are shown in Figure 3. Sample thickness of 1.0 and 2.0 mm are involved in analyses at X-band with frequency ranging from 8 GHz to 12 GHz. Attachment of nitrogen on the layered
structure of GO improves absorption capability by a factor of 2.5 compared to absorption of GO only. In the case of only 2 mm NG thickness, $R_L$ is $-25.0$ dB (bandwidth $\sim 0.3$ GHz) corresponding to power absorption of 91.8 %, or $R_L$ is $-10.6$ dB (bandwidth $\sim 1.5$ GHz) related to 65.4% of absorption of incoming microwave power. These achievements are very significant compared to another result [13]. They used graphene having a thickness of 4 mm. However, $R_L$ was only in the order of comparable to graphene having a thickness of $\sim -4.3$ dB. A similar absorption, in [13], was achieved by 2 mm of Fe-doped graphene. Significant absorption of microwave energy may occur from self-doping effect took place by lattice defects in graphene and also some carriers induced into graphene through replacement of oxygen sites by nitrogen atoms [14]. A defect in graphene can only produce a small quantity of carrier, and hence, it would not substantially change the dielectric effect and absorption capability as shown in [15]. This significant absorption may take place by improvement of magnetic property of NG.

![Figure 3](image_url)

**Figure 3.** Reflection loss measurements data of GO and NG at different thickness, (a) 1.0 mm and (b) 2.0 mm.

3.4. Discussions
Magnetic properties of graphene can be investigated through intra-molecular and inter-molecular magnetic interaction. Intramolecular magnetic interaction arises from magnetic exchange interaction between unpaired electrons in a molecule. The typical interaction producing magnetism is between unpaired electron $d$ or $f$ orbital and graphene $\pi$ electron. However, the unusual interaction creating the magnetic moment was shown by calculation which took place by unpaired $2p$ electrons of nitrogen atoms at a low concentration of nitrogen atoms [16]. This mechanism is one of the reasonable sources of magnetism responsible for strong absorption of microwave energy. Introducing nitrogen doping would possibly perform the spin symmetry breaking, resulting in energy degeneracy at some doping configurations. The spin symmetry breaking would cause spin-polarized effects, which induce a magnetic response in graphene.

Intermolecular magnetic interaction arises when ferromagnetic (FM) or antiferromagnetic (AFM) molecules approach each other. Defects in the structure of graphene can facilitate evidence of localized spin in the form of the armchair and/or zigzag structure. The localized spin on the armchair and zig-zag structure interact each other to form a ferromagnetic and antiferromagnetic state, respectively. Experimental studies have been performed to understand intermolecular interactions [17]. Unfortunately, the intermolecular ferromagnetic spin couplings are rather weak. Thermal vibration effect marked it. Recently, the magnetic property of pure graphene was demonstrated experimentally at room temperature. The room temperature magnetism was ascribed to the ferromagnetic order of spin magnetic moment arrangement at the graphene layer edges [18]. Evidence of self-magnetism in graphene film plays a vital role in that experiment. In the case of NG, number
defects can be multiplied in comparison to undoped graphene. Figure 4 shows indication of defect in high-resolution TEM image of NG with three probable formations of N atoms on the structure of graphene (pyrrolic, pyridinic, and graphitic attachments).

Other detailed and clear explanations can be found in [13]. The magnetic coupling between the magnetic moments may appear via Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions by delocalized $\pi$ electrons, which is expected to decay as $D^r$, where $D$ is the distance between the magnetic moments and $r$ is the decay exponent. In this case, the increasing of localized magnetic moments of graphene because of doping, the gap between the magnetic moments will decrease. As for the decay exponent $r$, enhancing of electron-electron interaction may reduce the value of $r$, and hence, increasing magnetic coupling. Instead of RKKY interactions, the bound magnetic polaron (BMP) may responsible for the existence of ferromagnetism in graphene. Ferromagnetic coupling is derived from shallow donor electrons that form BMPs, which overlap to create a spin-split impurity band. The N atoms act as BMP and trapping the free electrons. The electrons trapped in these BMPs tend to get easily polarized under the influence of the magnetic field and, resulting in ferromagnetism. It should be noted, here, that an appropriate amount of N atoms should be required for establishment of ferromagnetic graphene at room temperature.

![Figure 4](image_url)

**Figure 4.** Evidence of defect on NG, (a) TEM image and (b) Three possible attachment of N atoms on graphene surface (pyrrolic, pyridinic, and graphitic)

### 4. Conclusions

N-doped graphene has been synthesized successfully by the hydrothermal process at 190 °C and 12 h using urea as reduction agent and N atom donors. Absorption capability of NG was investigated through measurement of reflection loss of metal backed graphene slab at X-band. In the case of only 2 mm of NG thickness, $R_L$ is $-25.0$ dB (bandwidth $\sim 0.3$ GHz) corresponding to power absorption of $91.8$ % or $-10.6$ dB (bandwidth $\sim 1.5$ GHz) comparable to absorption of $65.4$ % of incoming microwave power. These achievements are very significant compared to $-4.3$ dB reflection loss of 4 mm graphene slab in [13]. The defect of graphene has been identified via a moderate magnification of TEM image. Defect and attachment of N atoms play an important role in the improvement of electric and/or magnetic losses which responsible for excellent absorption of X-band microwave energy.

### Acknowledgments

This work was partially supported by the Fundamental Research Grant in 2017 from the Ministry of Research and Higher Education Republic of Indonesia, contract no. 065/ADD/SP2H/LT/DRPM/VIII/2017.

### References

[1] Novoselov K S *et al* 2004 Electric Field Effect in Atomically Thin Carbon Films *Science* **306** 666–669

[2] Yang W *et al* 2013 Epitaxial growth of single-domain graphene on hexagonal boron nitride *Nature Materials* **12** 792–797
[3] Chen G, Wen W G, and Wu D J Preparation and characterization of graphite nanosheets from ultrasonic powdering technique 2004 Carbon 42 753–759
[4] Stankovich S et al 2007 Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide Carbon 45 1558–1565
[5] Wang G et al 2008 Facile Synthesis and Characterization of Graphene Nanosheets J. Phys. Chem. C 112 8192–8195
[6] Muszynski R, Seger B, and Kamat P V 2008 Decorating Graphene Sheets with Gold Nanoparticles J. Phys. Chem. C 112 5263–5266
[7] Fan Z J et al 2011 Facile synthesis of graphene nanosheets via Fe reduction of exfoliated graphite oxide ACS Nano. 5 191–198
[8] Gao H et al 2012 Synthesis of S-doped graphene by liquid precursor Nanotechnology 23 p 275605
[9] Wang H, Maiyalagan T, and Wang X 2012 Review on Recent Progress in Nitrogen-Doped Graphene: Synthesis, Characterization, and Its Potential Applications ACS Catal. 2 781–794
[10] Agusu L et al 2017 Transmission characteristic of graphene/TiO2 paper measured at Ka-band AIP Conference Proceedings 1801 p 050006
[11] Geng D et al 2011 Nitrogen doping effects on the structure of graphene Applied Surface Science 257 9193-9198
[12] Zhang Y et al 2015 Nitrogen-doped graphene as a cathode material for dye-sensitized solar cells: effects of hydrothermal reaction and annealing on electrocatalytic performance RSC Adv. 5 p 10430
[13] Zhao X et al 2013 Excellent microwave absorption property of Graphene-coated Fe nanocomposites Scientific Reports 3 p 3421
[14] Huard B et al 2008 Evidence of the role of contacts on the observed electron-hole asymmetry in graphene Phys. Rev. B 78 p 121402
[15] Wang Z, Qin S, and Wang C 2014 Eur. Phys. J. B 87 p 88
[16] Liu Y et al 2013 Realization of ferromagnetic graphene oxide with high magnetization by doping graphene oxide with nitrogen Scientific Reports 3 p 2566
[17] Rajca A 1994 Organic Diradicals and Polyradicals: From Spin Coupling to Magnetism? Chem. Rev. 94 871-893
[18] Wang C and Diao D 2017 Self-magnetism induced large magnetoresistance at room temperature region in graphene nanocrystallized carbon film Carbon 112 162-168