A Green Approach for Highly Reduction of Graphene Oxide by Supercritical Fluid

著者	Kong Chang Yi, Shiratori Yuuki, Sako Takeshi, Iwata Futoshi
journal or publication title	Advanced Materials Research
volume	1004-1005
page range	1013-1016
year	2014-08
出版者	Trans Tech Publications
権利	(C) (2014) Trans Tech Publications, Switzerland
URL	http://hdl.handle.net/10297/8098

doi: 10.4028/www.scientific.net/AMR.1004-1005.1013

A Green Approach for Highly Reduction of Graphene Oxide by Supercritical Fluid

Chang Yi Kong^{1,*}, Yuuki Shiratori¹, Takeshi Sako¹ and Futoshi Iwata²

¹Department of Applied Chemistry and Biochemical Engineering, Graduate School of Engineering, and Research Institute of Green Science and Technology, Shizuoka University, 3-5-1 Johoku Naka-ku, Hamamatsu 432-8561, Japan

²Department of Mechanical Engineering, Graduate School of Engineering, Shizuoka University, 3-5-1 Johoku Naka-ku, Hamamatsu 432-8561, Japan

*tcykong@ipc.shizuoka.ac.jp

Keywords: Graphene oxide, reduced graphene oxide, graphene, supercritical fluid, reduction.

Abstract. A green method to synthesize the reduced graphene oxide using supercritical fluid has been developed, which is an environmentally friendly and efficient route. The reduced graphene oxide has been examined by X-ray diffraction, Raman spectroscopy. We have also studied the effects of reduction temperatures and supercritical fluids on the electrical properties of reduced graphene oxide. It was found that ethanol has higher reducing capability than CO₂ at all temperatures (200 - 400 °C) examined in this study for graphene oxide reduction. As a result, reduced graphene oxide (6300 S/m) from supercritical ethanol treatment has 5 times as high conductivity as that from supercritical CO₂ treatment at the reduction temperature of 400 °C. This green process is applicable for large scale production of reduced graphene oxides for various practical applications.

Introduction

Graphene, one atom thick two dimensional layers of sp² bonded carbon, is predicted to have the superior electrical, optical, chemical, mechanical, thermal and catalytic properties as the next wonder material [1-3]. Recently, graphene has attracted much attention as a potential material for a wide range of applications in various fields. In view of this, a large scale and cost effective method for the production of graphene is necessary in order for it to be used in industry [4,5]. The current state of graphene production is divided to two routes of the bottom up and top down. The bottom up approach seeks to synthesize graphene sheets from simple carbon molecules such as methane and ethanol. And the top down approach is started from graphite. The top down approach via grapheme oxide (GO) from graphite and its reduction is the most convenient method to date. This top down method can easily provide a large scale production of reduced GO (rGO), which can be used for many applications such as solar cells [6], fuel cells [7], Lithium ion batteries [8], capacitors [9], sensors [10], electrocatalysis [11], photocatalysis [12], drug delivery [13]. Although the chemical reduction route from GO to graphene is the most promising method, but this technique still has several limitations which hinder its use in commercial implementation. To realize the mass production of high quality rGO from GO prepatterned on a substrate, the development of new chemical reduction methods at lower temperature is needed. In addition, until now, hydrazine, the most widely used reducing agent for chemical reduction of GO. Unfortunately, the reducing agent gave rise to high sheet resistance because of the nitrogen impurities incorporated during the reduction process. Further, nowadays, the problems in graphene synthesis and their processing are the handling of waste (such as solvents, sub-products and unreacted precursors) and the search for environmental tolerable procedures. Thus, it would be much more efficient if both processes synthesis and processing could be green method. Therefore, a green and one pot process to restore the graphene structure is still to be developed for obtaining high quality rGO for mass production. Supercritical fluid (SCF) having a liquid-like solvating power and gas-like transport properties has been found successful applications not only in extraction and fractionation but also in chemical reaction process, which is of great interest for

designing green systems. In this study, rGO was synthesized by an environmentally friendly method using the SCF fluids. Further, we have investigated the effects of the supercritical treatment temperatures and fluids (CO₂ and ethanol) on the electrical conductivity of the obtained rGO.

Experimental

Materials. Graphite (45 μ m, 98.0%), analytical grade (NH₄)₂S₂O₈, P₂O₅, KMnO₄, 98% H₂SO₄, 30% H₂O₂ aqueous solution and 99.5% ethanol were from Wako Japan, and used without further purification. CO₂ (99.95%) was obtained from Air Gases Tokai Ltd., Japan. Polyvinylidene fluoride (PVDF) membrane filters (0.22 μ m pore size) were supplied by Merck Millipore Ltd. Ultra pure water (18 M Ω ·cm) was produced by a Merck Millipore ultrapure water system.

Synthesis of GO. GOs were prepared from graphite using the Hummers method [14] with minor modification, which included two steps. Typically, in the preoxidation step, 0.9 g P₂O₅, 0.9 g (NH₄)₂S₂O₈ and 10 mL concentrated H₂SO₄ were sequentially introduced into a 500 mL flask and then vigorously stirred at 80 °C until the reagents were completely dissolved. 1.0 g graphite was added to the mixture and kept stirring at 80 °C for 4.5 h. After the preoxidation, cooling down to lower 10 °C, the mixture was diluted carefully with 250 ml ultrapure water, and kept stirring for whole night at room temperature. It was then filtrated and washed repeatedly with ultrapure water, followed by drying in air. In the oxidation step, the pretreatment graphite was added to concentrated 50 mL H₂SO₄ in a 500 mL flask cooled in an ice bath. 4 g KMnO₄ was introduced into the mixture slowly and kept stirring at lower than 10 °C. Then, the mixture temperature was raised up to 35 °C and still stirred for 2 h. then, the temperature was cooled down to 10 °C, 85 mL ultrapure water was slowly added. The temperature was then increased to 35 °C again and further stirring for 2 h, then 250 mL ultrapure water and 3 mL 30% aqueous H₂O₂ were added. The mixture turned into a brilliant yellow solution with bubbling. The mixture was stirred for 2 h and then allowed to settle down for whole night, and, the mixture was filtrated and washed repeatedly with 1000 mL 10 % HCl solution, then, with ultrapure water.

Fabrication of free standing GO film. Aqueous GO was vacuum filtrated using a PVDF membrane. The GO film was allowed to dry at room temperature, then, peeled come off by itself when the GO film was dried completely. Further, it was dried again in a vacuum oven at 45 °C for one night before reducing treatments.

Reduction of GO film. All reducing the GO films with SCF were performed in a stainless-steel reactor with an inner volume of 75 ml. In a typical experiment, the GO films were placed in the vessel with a heater and a pressure sensor, then, the vessel was sealed and after replaced the air in the reactor, pressure transducer, connected tubing and valves, followed by filling with CO₂ or ethanol, after that, controlled the targeted temperature (up to 400 °C) and pressure (up to 9 MPa). After the GO were annealed in the SCF for a defined period of time, the vessel was cooled down to room temperature using ice bath and depressurized, and then the film was used for characterization.

Results and Discussion

GO consists of intact graphitic regions interspersed with sp³ hybridized carbons containing hydroxyl and epoxide functional groups on the top and bottom surfaces of the sheet and sp² hybridized carbon containing carbonyl and carboxyl functional groups mostly at the sheet edges. Hence, GO is hydrophilic and readily disperse in water to form stable colloidal suspensions (Fig. 1a). Aqueous GOs appeared like colored solutions, from dark brown at high concentration to yellow brown at lower concentration. The optical transmittance corresponding to the GO is shown in Fig. 1b, which shows a higher 90% transmittance in the visible region. A typical UV/vis spectrum of GO in a stable aqueous dispersion is shown in Fig. 1c. The GO has a bands peak at about 230 nm. Also, a similar shoulder around 300 nm is observed and can be attributed to n- π^* transitions of the carbonyl groups.

The X-ray diffraction patterns for the parent graphite, GO and rGO after supercritical CO₂ treatment at 400 °C and 9 MPa for 4 h are shown in Fig. 2. The featured diffraction peak of GO appears at 10.12 ° is observed with interlayer space (d-spacing) of 8.73 Å. The value is larger than the d-spacing (3.35 Å) of graphite at 26.56 °, as a result of the introduction of oxygenated functional groups on carbon sheets. In the peak of rGO, the sharp XRD peak of GO at 10.12 ° disappeared, but a new broad diffraction peak appeared and shows a obvious shift to higher 2θ angles (24.60 °, 3.62 Å), which is closer to that of graphite, suggesting that the reduction of GO to graphene resulted in structural change, especially the distance between the layers, and was well ordered with two dimensional sheets with removal of surface functional groups [5].

Fig. 3 shows the Raman spectra of graphite and the rGO after supercritical CO₂ treatment at 400 °C and 9 MPa for 4 h. The rGO had a G peak at 1583 cm⁻¹, D peak at 1350 cm⁻¹ and 2D peak at 2706 cm⁻¹, which is well consistent with graphite (G peak at 1352 cm⁻¹, D peak at 1577 cm⁻¹ and 2D peak at 2708 cm⁻¹). The I_D/I_G ratio of rGO is 0.85, which is similar to what was typically observed in the Raman of rGOs [15].

The above studies reveal that GO can be effectively reduced by supercritical CO₂ without any reducing agents. In order to further investigate the GO reduction mechanisms, we have examined the effects of reduction temperatures and supercritical fluids on electrical property. Fig. 4 shows that the conductivities increased substantially with increasing reduction temperatures. Note that the conductivity of GO does not show conduction. Significantly, the conductivities of the rGO films from supercritical ethanol are higher than those from in supercritical CO₂ at all temperatures (200 - 400 °C) examined in this study. It means that ethanol has higher reducing capability than CO₂ for GO reduction. The treatment in supercritical ethanol is more effective in restoring the properties intrinsic to graphene sheets, as reflected in significantly improved performance in electrical conductivities. The effectiveness might also be attributed to some contribution from reductive effect by the ethanol. As a result, the rGO (6300 S/m) from supercritical ethanol treatment has 5 times as high conductivity as the rGO (1250 S/m) from supercritical CO₂ treatment at 400 °C, which is mainly due to much more significant restoration of π-conjugated system in the rGO from supercritical ethanol treatment. The restored electrical conductivities in this study are comparable to the rGO from using the reduction agents [5]. The results in this study presented that the SCFs (CO₂ and ethanol) under relatively mild conditions are apparently capable of converting GO into rGO and taking advantage of the unique properties of SCFs (low density and viscosity and diminishing surface tension). It is interesting that substantial conversion of GO could be achieved in supercritical CO₂ and ethanol environmentally friendly, offering opportunities in various applications for green processing.

Fig. 1. Optical characterizations of the aqueous GO. a, Photographs of aqueous dispersion of GO in higher (left) and lower (right) concentrations. b, Optical transmittance spectrum of GO. c, The UV/vis spectrum of GO.

Fig. 2. XRD patterns of GO and rGO, and their parent graphite. rGO produced through the GO after supercritical CO₂ treatment at 400 °C and 9 MPa for 4 h.

Fig. 3. Raman spectra of graphite (gray) and the rGO films from the supercritical CO₂ treatment (blue) at 400 °C and 9 MPa for 4 h.

Summary

A green approach using SCF to synthesis of rGO is developed. The rGO has been confirmed by X-ray diffraction, Raman spectroscopy. We have also examined the effects of supercritical reduction temperature and fluids (CO_2 and ethanol) on the conductivities of rGO. It was observed that ethanol has higher reducing capability than CO_2 at all studied temperatures from 200 to 400 °C. This green route using supercritical ethanol treatment results in rGO with high conductivity (up to 6300 S/m). The advantage of this method is that the SCF can be applied to the conversion of GO to rGO without any reduction agents, offering not only an environmentally friendly option but also relatively simple and facile processing conditions. This green process is applicable for large scale production of rGOs on industrial scale.

Fig. 4. Electrical conductivity results for the rGO films from the supercritical CO_2 and ethanol treatments at various temperatures.

Acknowledgements

This research was supported by the Ministry of Education, Sports, Culture, Science and Technology of Japan (24360305) and the research project from Shizuoka University.

References

- [1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, *Science* 306 (2004) 666-669.
- [2] A.K. Geim and, K.S. Novoselov, *Nat. Mater.* 6 (2007) 183-191.
- [3] Y.W. Zhu, S. Murali, W.W. Cai, X.S. Li, J.W. Suk, J.R. Potts, R.S. Ruoff, *Adv. Mater.* 22 (2010) 3906-3924.
- [4] R.S. Edwards, K.S. Coleman, *Nanoscale* 5 (2013) 38-51.
- [5] C.K. Chua, M. Pumera, *Chem. Soc. Rev.* 43 (2014) 291-312.
- [6] L. Kavan, J.H. Yum, M. Grätzel, *ACS Nano* 5 (2011) 165172.
- [7] L.Y. Feng, Y.G. Chen, L. Chen, *ACS Nano* 5 (2011) 9611-9618.
- [8] E. Yoo, H. Zhou, *ACS Nano* 5 (2011) 3020-3026.
- [9] Y.W. Zhu, S. Murali, M.D. Stoller, K.J. Ganesh, W.W. Cai, P.J. Ferreira, A. Pirkle, R.M. Wallace, K.A. Cychosz, M. Thommes, D. Su, E.A. Stach, R.S. Ruoff, *Science* 332 (2011) 1537-1541.
- [10] S. Myung, A. Solanki, C. Kim, J. Park, K.S. Kim, K.B. Lee, *Adv. Mater.* 3 (2011) 2221-2225.
- [11] S.B. Yang, X.L. Feng, X.C. Wang, K. Müllen, *Angew. Chem. Int. Ed.* 50 (2011) 5339-5343.
- [12] S.M. Sher, A.R. Park, K. Zhang, J.H. Park, P.J. Yoo, *ACS Appl. Mater. Interfaces* 4 (2012) 3893-3901.
- [13] C.S. Wang, J.Y. Li, C. Amatore, Y. Chen, H. Jiang, X.M. Wang, *Angew. Chem. Int. Ed.* 50 (2011) 11644-11648.
- [14] W. Hummers, R.E. Offeman, *J. Am. Chem. Soc.* 80 (1958) 1339.
- [15] A.M. Dimiev, L.B. Alemany, J.M. Tour, *ACS Nano* 7 (2013) 576-588.