Green reduction of graphene oxide by ascorbic acid

Zahra Khosroshahi, Mahshid Kharaziha, Fathallah Karimzadeh, and Alireza Allafchian

---

Articles you may be interested in

Development of an electrochemical biosensor for vitamin B12 using D-phenylalanine nanotubes
AIP Conference Proceedings **1920**, 020032 (2018); 10.1063/1.5018964

Green Reduction of Graphene Oxide by Ascorbic Acid

Zahra Khosroshahi[1, a)], Mahshid Kharaziha[1, b)], Fathallah Karimzadeh[1, c)], Alireza Allafchian[2, d)]

[1]Department Materials Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran.
[2] Researcher Institute for Nanotechnology and Advanced Materials, Isfahan University of Technology, Isfahan 84156-83111, Iran.

a) Corresponding author: z.khosroshahi@ma.iut.ac.ir
b) karimzadeh_f@cc.iut.ac.ir
c) kharaziha@cc.iut.ac.ir
d) allafchian@cc.iut.ac.ir

Abstract. Graphene, a single layer of sp2-hybridized carbon atoms in a hexagonal (two-dimensional honey-comb) lattice, has attracted strong scientific and technological interest due to its novel and excellent optical, chemical, electrical, mechanical and thermal properties. The solution-processable chemical reduction of Graphene oxide (GO is considered as the most favorable method regarding mass production of graphene. Generally, the reduction of GO is carried out by chemical approaches using different reductants such as hydrazine and sodium borohydride. These components are corrosive, combustible and highly toxic which may be dangerous for personnel health and the environment. Hence, these reducing agents are not promising choice for reducing of graphene oxide (GO). As a consequence, it is necessary for further development and optimization of eco-friendly, natural reducing agent for clean and effective reduction of GO. Ascorbic acid, an eco-friendly and natural reducing agents, having a mild reductive ability and nontoxic property. So, the aim of this research was to green synthesis of GO with ascorbic acid. For this purpose, the required amount of NaOH and ascorbic acid were added to GO solution (0.5 mg/ml) and were heated at 95 ℃ for 1 hour. According to the X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and electrochemical results, GO were reduced with ascorbic acid like hydrazine with better electrochemical properties and ascorbic acid is an ideal substitute for hydrazine in the reduction of graphene oxide process.

INTRODUCTION

Graphene, a single layer of sp2-hybridized carbon atoms in a hexagonal (two-dimensional honey-comb) lattice, has attracted strong scientific and technological interest since its discovery in 2004. Graphene has shown great potential application in numerous fields, consisting of electronic devices, nanocomposite materials, sustainable energy storage and conversion (ultracapacitors, batteries, fuel cells, solar cells), bioscience/biotechnologies and tissue engineerng due to its excellent optical (transmittance of 97.7%), chemical, electrical (high conductivity ~104 Ω-1 cm-1), mechanical (Young's modulus=1.0 TPa) and thermal properties (thermal conductivity=5000Wm^{-1}K^{-1}) [1-4]. Among techniques have been developed to produced graphene so far, chemical vapor deposition (CVD), epitaxial growth on electrically insulating surfaces and chemical reduction of graphene oxide (GO) are considered as the most favorable methods regarding mass production of graphene [2]. Even though the epitaxial growth and CVD techniqus are particulary promising in the terms of providing the large area, high quality graphene for applications in electronics, the chemical reduction is currently considered the most attractive option for many applications. The main advantage of this route is its cost effective, massive scalability, versability for chemical functionalization [5]. Reduction method involves exfoliation of the GO in a suitable solvent (usually water) and chemical reduction of the dispersed GO sheets with using different reductants such as hydrazine [6-8], dimethylhydrazine [9], hydroquinone [10], sodium borohydride [11, 12], hydrohalic acids [13], and strong alkali [14]. All these reducing agents are corrosive, combustible and highly toxic which may be dangrous for human health and environment. Results reveal that trace

amounts of hydrazine could be harmful for various applications such as organic solar cells [2]. Hence, these reducing agents are not promising choice for reducing of GO. As a consequence, it is necessity for further development and optimisation of eco-friendly, natural reducing agent for clean and effective reduction of GO [15]. Recently, various types of eco-friendly and natural reducing agents have been offered to reduce various kinds of metals, metal oxides and GO consisting of wild carrot root [16], phyto extracts [17], tea solution [18], Chrysanthemum extract [19], alanine [20], and ascorbic acid [5, 21, 22]. Between them, ascorbic acid having a mild reductive ability and nontoxic property [21]. Ascorbic acid (vitamin C) is a natural antioxidant which is vital for many metabolic functions in living organisms and extensively used as a food additive [5]. Fernandez-Merino et al. [5] observed that vitamin C is an innocuous and effective reagent that can replace hydrazine for reduction of graphene oxide. Li et al. [22] prepared Cu_2O/rGO nanocomposite by a green and facile one pot wet-reduction process process by using ascorbic acid instead of hazardous chemical. Results showed that nanocomposite have enhanced photocatalytic and effective charg transportation from Cu_2O to rGO.

The aim of this research was to green chemical reduction of GO using inexpensive, ecofrendly and nontoxic reducing agents of ascorbic acid and evalution of difference with reduction of GO by hydrazine (uaual reductant agent). Moreover, the effect of reducing agent type on the electrochemical properties of rGO were evluated. It could be hypothesis that GO reduced with ascorbic acid could be more appropriate for electrochemical applications.

EXPERIMENTAL

Materials

GO powder (purity>99%, thickness: 3.4-7 nm, 6-10 layers) was bought from Nanosay Co., Iran. Hydrazine hydrate (N_2H_4, purity$\geq$80%), L(+)-ascorbic acid ($C_6H_5O_6$, purity$\geq$99.7%), and sodium hydroxide (NaOH, purity$\geq$99%) were obtained from Merck Co., Germany. Glassy carbon electrode (GCE) was prepared from Azar Electrode Co., Iran.

Chemical Reduction of GO

GO nanopowder was dispersed in dionized water (0.5 mg/ml) using ultrasonication for 1 h. subsequently, required amount of NaOH and reductant agent (hydrazine or ascorbic acid) were added to the GO susension under vigorous stirring, respectively. The mixture was heated to 95℃ and maintained for 1 hour. The precipitation extracted from solution using centrifuse (5 min, 1600 rpm) was washed three times with DI water and ethanol and, finally, dried in oven at 50-60 °C for 15 hours. Shematic of this precedure is shown in Fig. 1. The as prepared rGO with ascorbic acid and hydrazine were named rGOa and rGOh sequently.
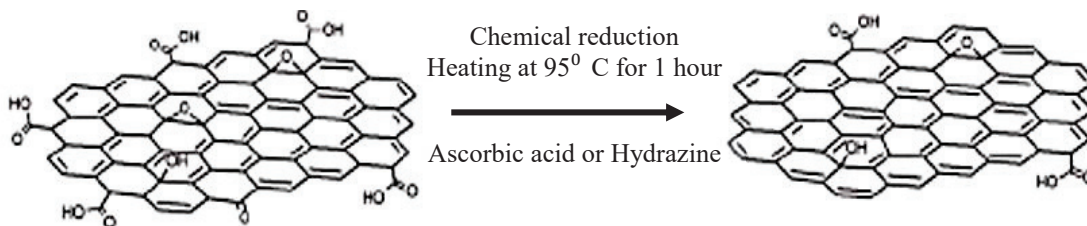

FIGURE 1. Schematic of chemical reduction of GO

Characterization of Powders

The crystal structure and phase analysis of GO and as-prepared samples were performed using X-ray diffraction (XRD, Philips X'Pert-MPD, Holland) with Cu Kα radiation (λ=0.542) and time per step 1.25 second. Results were analyzed by X'Pert High Score software. The surface morphology of powders were characterized using scannig electron microscopy (SEM, Philips XL30 SERIES) and particle sizes were characterized with ImageJ software. Brfore immaging, the samples were coated with a thin layer of gold.

Electrochemical Evaluation of the Powders

Before analysis, GCE was polished with 0.05 μm alumina slurries and washed with dionized water. 10 μL of rGO solution (1 mg/ml in ethanol) was deposited on GCE at room temperature. Schematic of this precedure is presented in Fig. 2. Cyclic voltametry (CV) test (Potential window: -0.2-0.8 V, Scan rate:100 mV/s) and electrochemical impedance spectroscopy (EIS) test (Frequency window: 0.01 mHz -100000 Hz) were run on Autolab (204 SERIES) electrochemical work station and in 0.1 M $[Fe(CN)_6]^{3-/4-}$ aqueouse solution with a convertional three-electrode system at room temperature. rGO on GCE, a saturated calomel electrode (SCE), and Pt electrode were used as working, reference, and counter electrodes, respectivly.
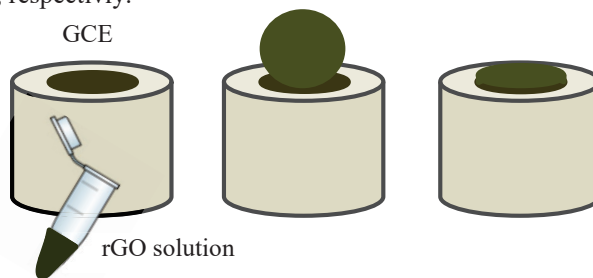

FIGURE 2. Schematic of modified GCE for electrochemical evaluation

RESULTS AND DISCUSSION

Characterization of As-prepared Samples

The XRD of GO, rGOa, and rGOh are shown in Fig. 3. XRD pattern of GO showed two characteristic peaks centered at 2θ of 10.7 and 42.4 degreecorresponding to (001) and (100), respectivly. XRD of rGOa and rGOh showed two small and broad peaks at 23.8 and 42.5 degree that were related to (002) and (100), respectively. These peaks are related to the disordered stacking of rGO sheets [23, 24]. So the GO is correctly reduced with both reductant agents correctly and ascorbic acid might be an appropriate substitute for hydrazine in the reduction of GO.
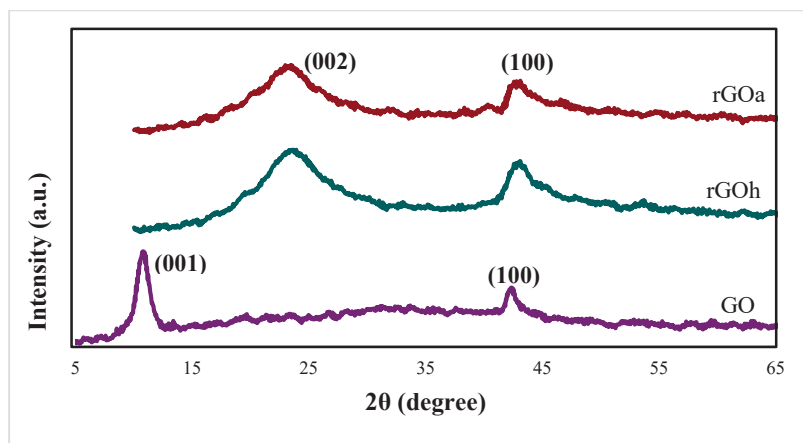

FIGURE 3. XRD patterns of GO, rGOa, and rGOh

SEM image of GO sheets is presented in Fig. 4. GO powder consisted of smooth nanosheets with folded shapes at the edges. The surface of the GO sheets is very smooth and no obviously aggregations are observed. The wrinkled GO sheets are loosely connected to each other. SEM images of the as-prepared rGOa and rGOh sheets are shown in Fig. 5. In both samples, rGO consisted of several layers stacked on top of one another with wrinkled and thin morphology. Also, rGO sheets have more edges than GO for better reaction with other materials. So, the srface morphology of rGO didnt changed with using ascorbic acid instead of hydrazine in reducing precuder but the amount of wrinkled of rGO sheets is increased with using ascorbic acid.
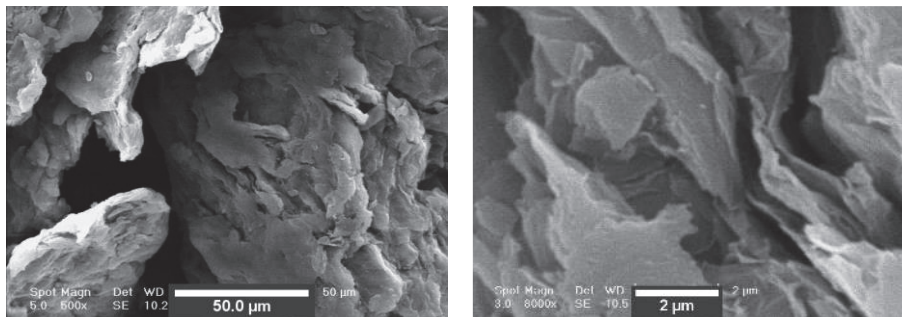
FIGURE 4. SEM image of GO powder at different magnifications.
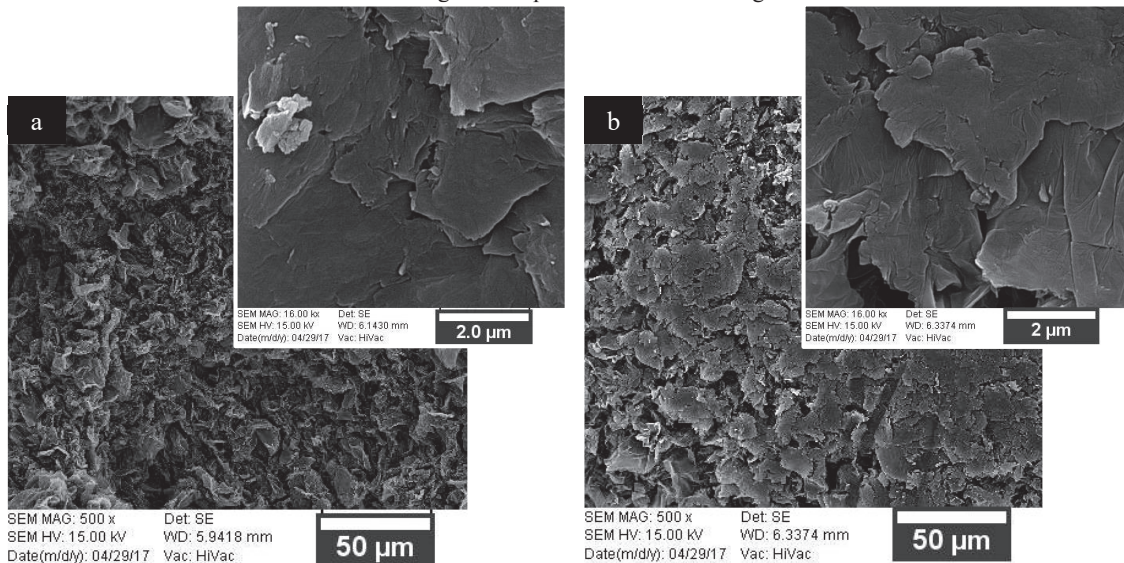
FIGURE 5. SEM image of (a) rGOa, (b) rGOh at different magnifications

Electrochemical Evaluation of the Powders

EIS can reflect the impedance changes of the electrode surface during the modification process and was employed to investigate the electron transfer ability between electrode surface and electrolyte. Normally, EIS can be divided into two regions: the semicircular region and the linear region. The semicircular portion at higher frequencies corresponds to the charge transfer limiting process and is ascribed to the double-layer capacitance in parallel with the charge transfer resistance at the contact interface between electrode and electrolyte solution and its diameter is equal to the charge transfer resistance (Rct). The linear portion at low frequency was ascribed to the diffusion limit process. As seen in Fig. 6 as well as corresponding to the Warburg circuit fitted plot with Nova software (Fig. 7) and calculated Rct with it (Table 1), diameter of semicircular region (Rct) of rGOh > rGOa, thus implying that the electron transfer ability sequence was: rGOa > rGOh. This phenomenon manifested that type of reduction agent has an effect on charge mobility and electron transfer of rGO. So, the electron transfer of rGO is more when using the ascorbic acid instead of hydrazine in reducing precedure. These result is corresponding to structure of rGO that previously explained. Therefore, rGOa is more suitable for electrochemical applications compared with rGOh due to more electron transfer.
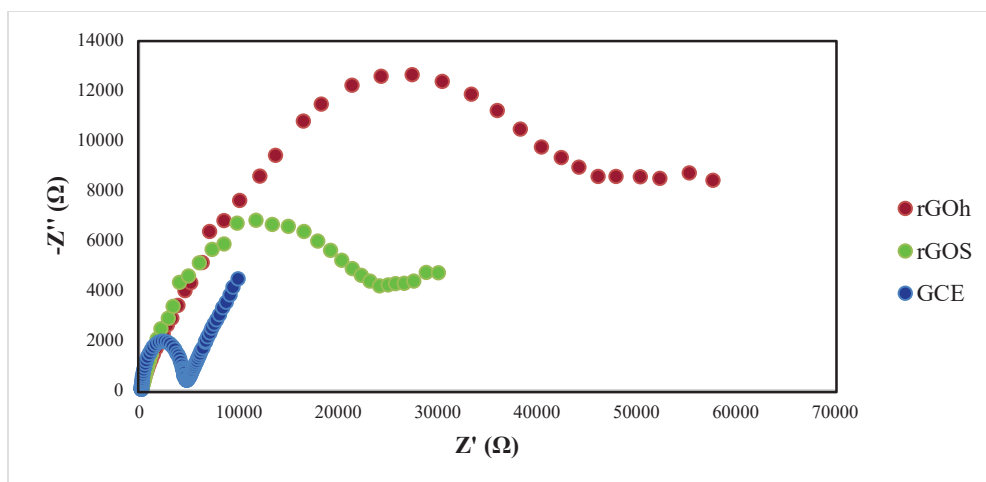
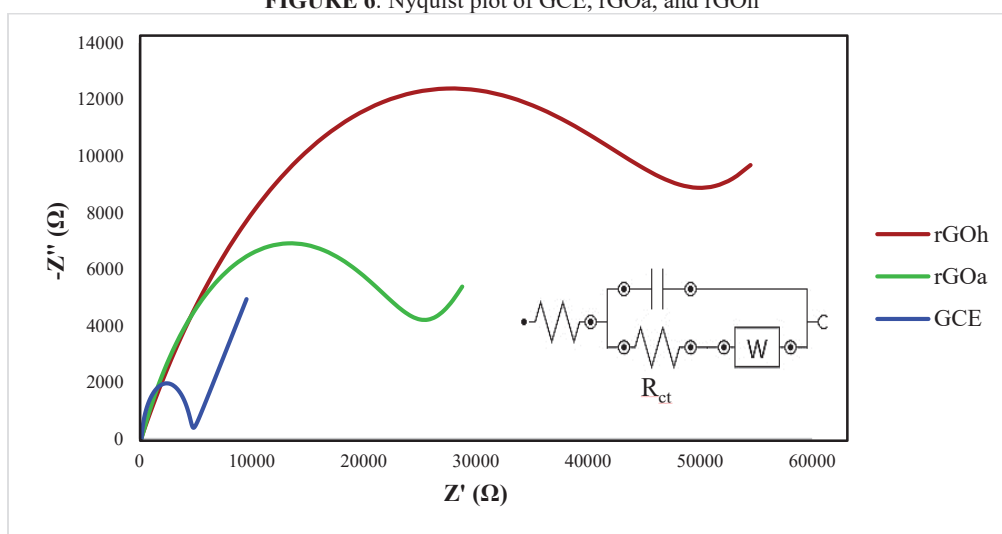**FIGURE 6**. Nyquist plot of GCE, rGOa, and rGOh

FIGURE 7. Nyquist plot of GCE, rGOa, and rGOh corresponding to equivalent Warburg circuit. Insert equivalent Warburg circuit for electrodes

TABLE 1. Rct calculated with equivalent Warburg circuit for GCE, rGOa, and rGOh

Sample	GCE	rGOh	rGOa
R_{ct} (kΩ)	4.425∓0.001	52.453∓0.003	25.378∓0.003

CV has been considered to be a suitable tool for estimating the difference between the non-Faradic and Faradic reaction. Figure 8 presents CV curves of GCE, rGOa, and rGOh in the potential range of -0.2 to 0.8 V (vs. SCE) at the scan rate of 100 mV.s-1. CV curves consist of a pair of redox peak that were corresponding to an electrochemical transform between $Fe[(CN)_6]^{4-}$ and $Fe[(CN)_6]^{3-}$. The type of modified electrode has an effect on speed of electron transfer and electrochemical response. Generally, the higher current output at the redox peak of CV curve indicating enhanced electrical conductivity and facile ion transfer. Peak current is rGOa > rGOh. So, thus implying that electrochemical surface sequence is rGOa > rGOh. However the sample have more electrochemical surface, it can better acts as a promoter to enhance the electrochemical reaction. So the electrochemical response of samples sequence is rGOa > rGOh and however electrochemical response of nanocomposite is better, it's more suitable for electrochemical analysis. Therefore the rGOa is better for electrochemical application.
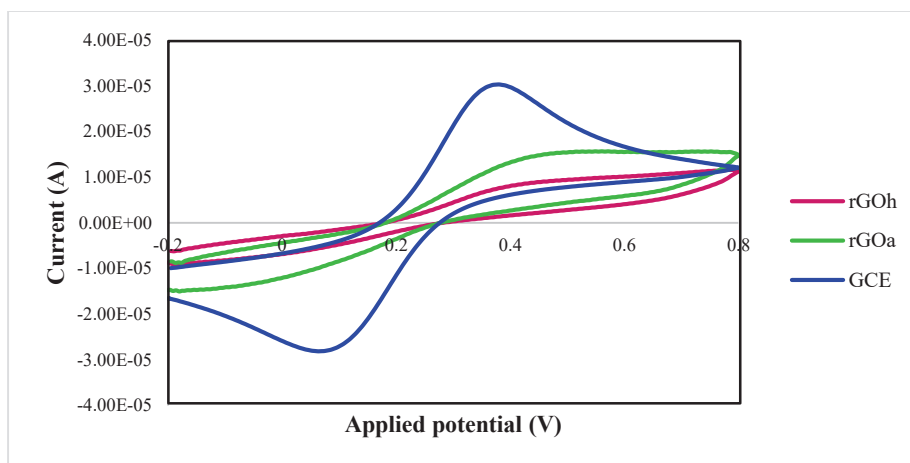
FIGURE 8. CV curves of GCE, rGOa, and rGOh

CONCLUSION

A comparison between deoxygenation efficienty of GO by hydrazine and ascorbic acid has been done. Among the XRD and SEM result, GO were reduced with ascorbic acid like hydrazine but with a more aggregation sheets structure. Electrochemical results revealed that electron conductivity and electrochemical response of rGO is better with using ascorbic acid as reductant agents in reducing precedure. So this rGO (reduced with ascorbic acid) is more suitable for applications that are corresponding to electrochemical response such as electronic devices, nanocomposite materials, sustainable energy storage and conversion (ultracapacitors, batteries, fuel cells, solar cells), bioscience/biotechnologies, and tissue engineerng. In addition to the above mentioned, ascorbic acid is a natural, clean, and effective reducing agent compared to high toxic hydrazine. Therefore, ascorbic acid is an ideal substitute for hydrazine in the reduction of GO.

REFERENCES

1. W. Chen, L. Yan, and P. R. Bangal, "Preparation of graphene by the rapid and mild thermal reduction of graphene oxide induced by microwaves," *Carbon,* vol. 48, no. 4, pp. 1146-1152, 2010.
2. Q. Yan, Q. Liu, and J. Wang, "A simple and fast microwave assisted approach for the reduction of graphene oxide," *Ceramics International,* vol. 42, no. 2, pp. 3007-3013, 2016.
3. Y. Shao, J. Wang, M. Engelhard, C. Wang, and Y. Lin, "Facile and controllable electrochemical reduction of graphene oxide and its applications," *Journal of Materials Chemistry,* vol. 20, no. 4, pp. 743-748, 2010.
4. G. Álvarez- Romero, G. Alarcon- Angeles, and A. Merkoçi, "Graphene: insights of its application in electrochemical biosensors for environmental monitoring," *Biosensors Nanotechnology,* pp. 111-140, 2014.
5. M. J. Fernández-Merino *et al.*, "Vitamin C is an ideal substitute for hydrazine in the reduction of graphene oxide suspensions," *The Journal of Physical Chemistry C,* vol. 114, no. 14, pp. 6426-6432, 2010.
6. S. Park, J. An, J. R. Potts, A. Velamakanni, S. Murali, and R. S. Ruoff, "Hydrazine-reduction of graphite-and graphene oxide," *Carbon,* vol. 49, no. 9, pp. 3019-3023, 2011.
7. C. K. Chua and M. Pumera, "The reduction of graphene oxide with hydrazine: elucidating its reductive capability based on a reaction-model approach," *Chemical Communications,* vol. 52, no. 1, pp. 72-75, 2016.
8. X. Gao, J. Jang, and S. Nagase, "Hydrazine and thermal reduction of graphene oxide: reaction mechanisms, product structures, and reaction design," *The Journal of Physical Chemistry C,* vol. 114, no. 2, pp. 832-842, 2009.
9. S. Stankovich *et al.*, "Graphene-based composite materials," *nature,* vol. 442, no. 7100, pp. 282-286, 2006.
10. G. Wang *et al.*, "Facile synthesis and characterization of graphene nanosheets," *The Journal of Physical Chemistry C,* vol. 112, no. 22, pp. 8192-8195, 2008.
11. Y. Si and E. T. Samulski, "Synthesis of water soluble graphene," *Nano letters,* vol. 8, no. 6, pp. 1679-1682, 2008.
12. H. J. Shin *et al.*, "Efficient reduction of graphite oxide by sodium borohydride and its effect on electrical conductance," *Advanced Functional Materials,* vol. 19, no. 12, pp. 1987-1992, 2009.

13. S. Pei, J. Zhao, J. Du, W. Ren, and H.-M. Cheng, "Direct reduction of graphene oxide films into highly conductive and flexible graphene films by hydrohalic acids," *Carbon,* vol. 48, no. 15, pp. 4466-4474, 2010.
14. X. Fan *et al.*, "Deoxygenation of exfoliated graphite oxide under alkaline conditions: a green route to graphene preparation," *Advanced Materials,* vol. 20, no. 23, pp. 4490-4493, 2008.
15. Y. Sudhakar, H. Hemant, S. Nitinkumar, P. Poornesh, and M. Selvakumar, "Green synthesis and electrochemical characterization of rGO–CuO nanocomposites for supercapacitor applications," *Ionics,* pp. 1-10.
16. T. Kuila, S. Bose, P. Khanra, A. K. Mishra, N. H. Kim, and J. H. Lee, "A green approach for the reduction of graphene oxide by wild carrot root," *Carbon,* vol. 50, no. 3, pp. 914-921, 2012.
17. S. Thakur and N. Karak, "Green reduction of graphene oxide by aqueous phytoextracts," *Carbon,* vol. 50, no. 14, pp. 5331-5339, 2012.
18. Y. Wang, Z. Shi, and J. Yin, "Facile synthesis of soluble graphene via a green reduction of graphene oxide in tea solution and its biocomposites," *ACS applied materials & interfaces,* vol. 3, no. 4, pp. 1127-1133, 2011.
19. D. Hou, Q. Liu, H. Cheng, K. Li, D. Wang, and H. Zhang, "Chrysanthemum extract assisted green reduction of graphene oxide," *Materials Chemistry and Physics,* vol. 183, pp. 76-82, 2016.
20. J. Wang, E. C. Salihi, and L. Šiller, "Green reduction of graphene oxide using alanine," *Materials Science and Engineering: C,* vol. 72, pp. 1-6, 2017.
21. J. Zhang, H. Yang, G. Shen, P. Cheng, J. Zhang, and S. Guo, "Reduction of graphene oxide via L-ascorbic acid," *Chemical Communications,* vol. 46, no. 7, pp. 1112-1114, 2010.
22. B. Li, T. Liu, L. Hu, and Y. Wang, "A facile one-pot synthesis of Cu 2 O/RGO nanocomposite for removal of organic pollutant," *Journal of Physics and Chemistry of Solids,* vol. 74, no. 4, pp. 635-640, 2013.
23. X. Wang, E. Liu, and X. Zhang, "Non-enzymatic glucose biosensor based on copper oxide-reduced graphene oxide nanocomposites synthesized from water-isopropanol solution," *Electrochimica Acta,* vol. 130, pp. 253-260, 2014.
24. S. Yu, J. Liu, W. Zhu, Z.-T. Hu, T.-T. Lim, and X. Yan, "Facile room-temperature synthesis of carboxylated graphene oxide-copper sulfide nanocomposite with high photodegradation and disinfection activities under solar light irradiation," *Scientific reports,* vol. 5, 2015.