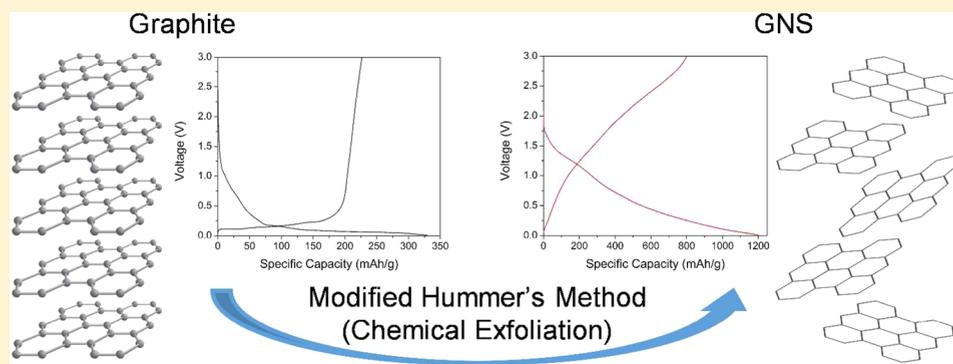


# Chemical Fabrication and Electrochemical Characterization of Graphene Nanosheets Using a Lithium Battery Platform

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**S** Supporting Information



**ABSTRACT:** Graphene has opened up new opportunities for scientific and technological innovations because of its astonishing electrical, mechanical, chemical, and thermal properties. For instance, graphene-based nanocomposites have found extensive applications in Li-ion batteries (LIBs) as scientists and engineers seek to achieve superior electrochemical performances. The laboratory module reported herein includes both chemical fabrication and electrochemical characterizations of graphene nanosheets (GNSs). The GNS powders are fabricated through the chemical exfoliation of graphite, and the resulting morphological and structural changes are evaluated by means of scanning electron microscopy and X-ray diffraction. Li storage electrochemical characteristics of GNSs are then assessed via galvanostatic chronopotentiometry and compared with that of graphite, a commonly used anode material in LIBs. This novel laboratory module, suitable for a wide range of students with a general chemistry background, has been successfully implemented in a multidisciplinary laboratory and lecture course entitled Experimental Nanomaterials and Nanoscience. Because the laboratory connects chemistry and materials engineering to a real-world application, it raises students' interest in and awareness of nanomaterials' contribution to the renewable and clean energy field.

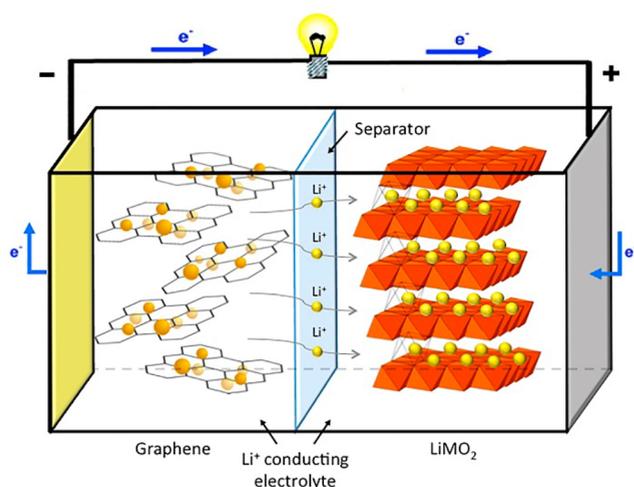
**KEYWORDS:** *Second-Year Undergraduate, Graduate Education/Research, Interdisciplinary/Multidisciplinary, Hands-On Learning/Manipulatives, Electrochemistry, Materials Science, Nanotechnology, Upper-Division Undergraduate, Laboratory Instruction*

## INTRODUCTION

Nanomaterials, nanotechnology, and nanoscience play a key role in the advancement of modern technologies from nanosensors<sup>1</sup> to biomedicine,<sup>2,3</sup> renewable energies,<sup>4</sup> and more. The National Science Foundation (NSF) projected that the nanotechnology sector will employ six million workers by 2020, and over 80% of the jobs will require trained workforces in nanoscience and nanotechnology.<sup>5,6</sup> Therefore, the introduction of nanomaterials and nanotechnology aspects to undergraduate students is a growing science and engineering educational trend for meeting the future demand. Graphene, since first reported in 2004,<sup>7</sup> has opened up new opportunities for scientific and technological innovations because of its astonishing electrical, mechanical, chemical, and thermal properties.<sup>7–9</sup> For instance, graphene nanosheets (GNSs) and graphene-based nanomaterials have found extensive applications in Li-ion batteries (LIBs),<sup>10,11</sup> supercapacitors,<sup>12,13</sup> and

fuel cells,<sup>14–16</sup> which have been widely utilized in the renewable energy field.<sup>17,18</sup> The objective of this laboratory is not only to introduce students the GNS and LIB related concepts, but also provide students with hands-on experiences to connect the state-of-the-art materials with real-world applications. Meanwhile, their chemical and electrochemical knowledge can be enhanced through the experimental practices and data analyses.

The LIB, relying on the migration of Li-ions through an electrolyte and reversible storage in cathode and anode during discharge/charge (Figure 1), is a simple yet comprehensive educational platform that encompasses fundamental principles of many aspects in chemistry. Several educational modules involving LIB chemistry have been published in this journal. Treptow briefly summarized the practical application of chemical principles in various Li battery electrochemical



**Figure 1.** Schematic illustration of LIB consisting of GNS anode and layer-structured lithium transition-metal oxide  $\text{LiMO}_2$  cathode.

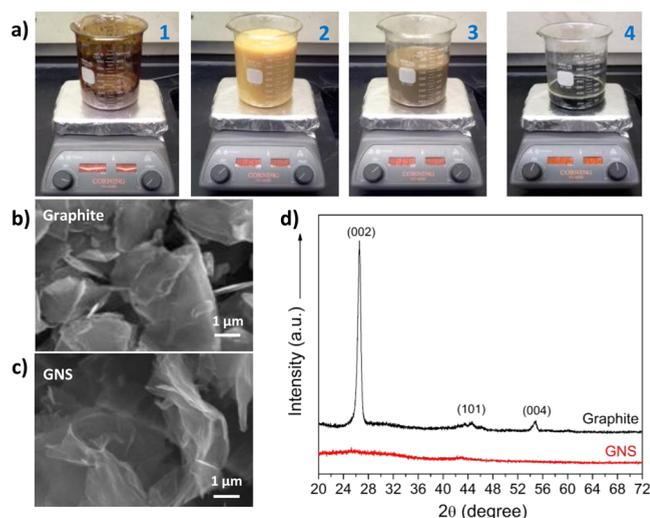
reactions.<sup>19</sup> Compton et al. reported a laboratory experiment to demonstrate periodic trends through correlating electrolyte conductivity with ionic radius.<sup>20</sup> Summerfield proposed a model of lithium-ion motion to compute transport phenomena.<sup>21</sup> In the laboratory module reported here, activities include chemical fabrication and structural characterizations of GNSs, electrochemical half-cell assembly, and a series of electrochemical analyses of the lithium storage characteristics in GNSs. Through this practice, students will gain the insights on how the electrode materials influence the practical battery performances and how nanomaterials can alter the reaction mechanism and kinetics. This laboratory effectively connects chemistry, materials engineering, nanoscience, and real-world applications.

This laboratory module is suitable for any students who have completed general chemistry and has been successfully implemented in two terms (fall 2012 and fall 2013) in the multidisciplinary lecture/laboratory course entitled “Experimental Nanomaterials and Nanoscience”, newly developed at Wright State University. As manifested by the anonymous participating student evaluations, the novel laboratory module raises students’ interest in, awareness of, and experiences with nanotechnology.

## ■ EXPERIMENTAL ASPECTS

### Fabrication of Graphene Nanosheets

GNS powders were chemically fabricated via a modified Hummer’s method<sup>22,23</sup> through in situ oxidation, intercalation, and exfoliation of natural graphite powders in an aqueous solution of sodium nitrate ( $\text{NaNO}_3$ ), potassium permanganate ( $\text{KMnO}_4$ ), and sulfuric acid ( $\text{H}_2\text{SO}_4$ ). Figure 2, panel (a) displays color evolution that students observed during the synthesis. The color change from purple to yellow, light brown, and black indicates oxidation/intercalation, cease of oxidation, exfoliation, and formation of graphene oxide (GO), respectively. After the as-prepared GO powders were effectively washed and dried, they were subjected to thermal reduction at  $250\text{ }^\circ\text{C}$ , which resulted in the desired GNS powders. Detailed synthesis procedure is depicted in the Supporting Information.



**Figure 2.** (a) Color changes in the suspension observed during the fabrication of GNSs (from 1 to 4, color changes from purple to yellow, light brown, and black, which indicates oxidation/intercalation, cease of oxidation, exfoliation, and formation of GO intermediates, respectively). Student results for (b) SEM image of graphite; (c) SEM image of thermally reduced GNSs; and (d) XRD profile of graphite and GNS.

### Morphological and Structural Characterizations

The morphology and structure of graphite and GNSs were distinguished with the help of scanning electron microscopy (SEM) and X-ray diffraction (XRD). Morphologically, graphite exhibits large, thick flake structures (Figure 2b), while the GNS shows wave-like corrugated characteristics (Figure 2c). Seen in Figure 2, panel d, the characteristic diffraction peaks of graphite essentially disappeared for the GNS, which indicates the transition from graphite’s 3D long-range order stacking to 2D disordered nanosheets as a result of the chemical exfoliation process.

### Electrode Preparation and Electrochemical Cell Assembly

The GNS powders were mixed with polyvinylidene fluoride (PVDF) in *N*-methyl-2-pyrrolidone (NMP) solvent to obtain a uniform slurry with an appropriate viscosity. The slurry was then coated onto a copper substrate and dried under vacuum at  $110\text{ }^\circ\text{C}$ . A graphite electrode was prepared using the same procedure for comparison in the following electrochemical characterizations. The coated electrode was cut into 1 cm diameter disks, pressed, massed, marked, and then transferred into an argon-filled glovebox that limits the water and oxygen levels to less than 0.5 ppm. A Swagelok-type electrochemical Li/carbon half-cell, consisting of a working electrode disk (either GNS or graphite), a porous separator (polypropylene,  $25\text{ }\mu\text{m}$  thick) soaked with liquid electrolyte (1 M  $\text{LiPF}_6\text{-EC/DEC}$ ), and a reference/counter electrode (Li-foil), was assembled in the glovebox.

### Electrochemical Characterizations

For the Li/carbon half-cells, the open circuit voltage (OCV) should be around 3.1 V because the electrode potential of  $\text{Li/Li}^+$  is  $-3\text{ V}$ , whereas  $\text{C/Li}^+$  is slightly above standard hydrogen electrode (SHE) potential ( $\sim 0.1\text{ V}$ ). The assembled half-cells with a satisfactory and stable OCV value were transported out of the glovebox and connected to a battery testing station. The electrochemical tests for both the graphite and GNS half-cells were carried out at current densities of  $0.05\text{ mA/cm}^2$  and  $0.2$

mA/cm<sup>2</sup> for two discharge/charge (d/c) cycles, respectively. The electrochemical performance data (voltage, current, and time) were automatically saved on the computer. After the tests were completed, the students exported the data for analyzing and reporting.

## HAZARDS

Potassium permanganate and concentrated sulfuric acid (98%) are highly corrosive and will cause severe burns if they come into contact with eyes, skin, or mucous membranes. Hydrogen peroxide aqueous solution (30 wt %) is a toxic substance that can cause irritation upon contact with skin and eyes. Therefore, care should be utilized when handling these chemicals.

## BASIC FIGURES OF MERIT OF AN ELECTRODE MATERIAL

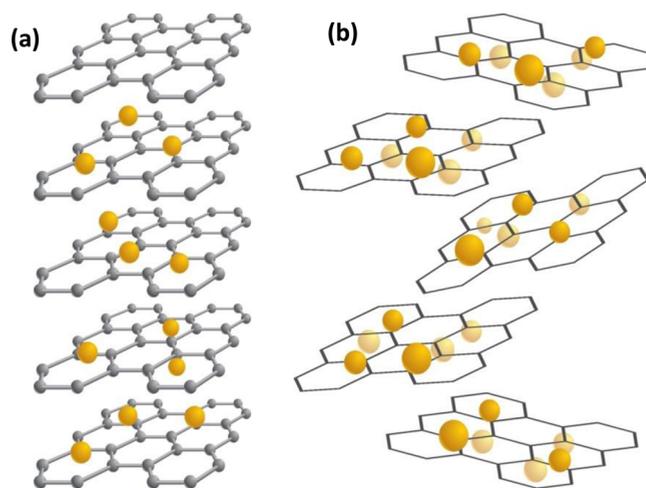
In the battery industry, the specific capacity, Coulombic efficiency (CE), and rate capability are three basic figures-of-merit to assess an electrode material. The specific (gravimetric) capacity is the Coulombic capacity (total deliverable charge) per unit mass, which can be theoretically derived based on the Faraday principle, that is,  $q = ((nF)/(M_w))$ . Here,  $q$  is specific capacity,  $n$  is the number of electrons transferred,  $F$  is the Faraday constant, and  $M_w$  is the molecular weight of the active electrode material. CE is the ratio of the specific capacity obtained during the d/c cycle, while rate capability is a measure of the deliverable reversible capacity at increased current drain. The words “discharge” and “charge” correspond to the lithiation and delithiation of carbon in the half-cell configuration, respectively. The structural difference between graphite and GNSs will have impacts not only on the specific capacity, but also the CE and rate capability.

## RESULTS AND DISCUSSION

In this laboratory, students are requested to complete two figures that plot the voltage profile as a function of the specific capacity for both graphite and GNSs from their electrochemical data. One is the profile obtained at 0.05 mA/cm<sup>2</sup> during the first d/c cycle in order to determine the values of reversible specific capacity and CE. The other is the voltage profiles obtained at the current densities of 0.05 mA/cm<sup>2</sup> and 0.2 mA/cm<sup>2</sup> to compare the rate capability of the two materials. Since the electrochemical tests are conducted at a constant current, the practical specific capacity can be calculated by multiplying the operating current by the time and dividing by the electrode mass. The two figures shown in the following sections are representative results obtained by students.

### Specific Capacities and Coulombic Efficiencies of Graphite and GNSs

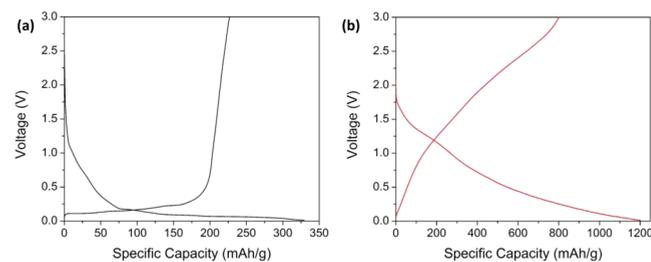
In the 3D-structured graphite, lithium is intercalated between the stacked layers (Figure 3a), and the maximum lithium storage results in the formation of the compound LiC<sub>6</sub>. The electrochemical redox reaction can be expressed as  $6C + Li^+ + e^- \leftrightarrow LiC_6$ . Accordingly, the theoretical specific capacity of graphite is 372 mAh/g. Practically, defects existing in the graphite's 3D crystal structure will cause a reduced capacity value in the range of 250–350 mAh/g.<sup>24</sup> By contrast, the 2D-structure of graphene renders the capability of storing Li ions on both sides of an individual honeycomb sheet (Figure 3b), which leads to formation of LiC<sub>3</sub> and hence, twice the theoretical capacity of graphite, that is, 744 mAh/g for graphene.<sup>25</sup> The nanocavities and functional groups on the



**Figure 3.** Schematic illustrations showing the differences of the structure of and lithium storage in (a) graphite (b) and GNSs. Yellow spheres represent lithium ions.

surface of GNSs can further increase the lithium storage capacity up to 900 mAh/g.<sup>26</sup> It is well-known that when electron transfer occurs on the surface of any carbon anode, a stable solid electrolyte interlayer (SEI) will inevitably form due to the irreversible reaction between the electrolyte and lithium,<sup>27</sup> which is usually predominant during the first d/c process that results in the CE in the first cycle being around 60–70%.

Figure 4 shows the first d/c profiles of graphite and the as-prepared GNS. The two profiles are completely different and



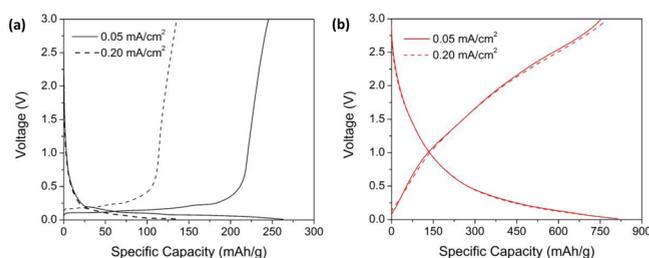
**Figure 4.** First discharge/charge profiles obtained from lithium half-cells with the working electrode of (a) graphite and (b) GNSs. The current density is 0.05 mA/cm<sup>2</sup>.

originate from distinct structures of graphite and GNSs. For graphite, a long plateau in the vicinity of 0.2 V is observed during the first discharge. This electrode potential is associated with lithium intercalation into the 3D stacked structure and the coexistence of two-phase lithiated graphite.<sup>28,29</sup> Upon charging, lithium is reversibly removed from the graphite structure, which also occurs in the vicinity of 0.2 V. The graphite electrode delivers an initial discharge and charge capacity of 330 mAh/g and 227 mAh/g, and hence the corresponding CE is 69%. By contrast, the GNS cell potential reduces/increases continuously with no apparent potential plateau, where the midpoint d/c voltages are 0.25 and 1.67 V, respectively. This phenomenon is associated with a gradual absorption/removal of lithium ions onto GNS surfaces without distinguished phase transformation. Specific d/c capacities of GNSs are 1200 mAh/g and 780 mAh/g, which are over three times higher than those of graphite due to the lithium storage on both sides of GNSs as well as the

functional groups on GNSs.<sup>26</sup> Besides the reaction between lithium and electrolyte, lithium may also irreversibly react with the defects and functional groups on GNSs, resulting in a slightly lower efficiency (65%) than that of graphite.

### Rate Capability

Figure 5, panels a and b compare the lithium storage/removal characteristics in graphite and GNSs at two different current



**Figure 5.** Discharge/charge profiles of (a) graphite and (b) GNS obtained at the two different discharge current densities, that is, 0.05 mA/cm<sup>2</sup> and 0.2 mA/cm<sup>2</sup>.

densities. In the case of the graphite, the reversible capacity drastically decreased from 250 mAh/g to 60–70 mAh/g as the current increased from 0.05 to 0.2 mA/cm<sup>2</sup>. For the GNS, however, there is no significant capacity reduction with the increase of current rate. Seen in Figure 5, panel b, the GNS voltage profiles show almost no difference at the two current densities. The rapid lithium storage kinetics in GNSs, distinguished from those in graphite, are rooted from the difference in lateral dimension, structure, and lithium storage mechanism.<sup>25</sup> As lithium is inserted into the stacked layers of graphite, lithium must overcome the van der Waals force and transport through a few micrometer-long path hindered by the preoccupied lithium ions. On GNSs, lithium ions only need to adsorb in the open surface and diffuse through nanoscale paths, which is more kinetically favorable.

The obtained results corroborate well with the chemistries and structures of these two materials. From this set of electrochemical experiments, students learned that GNSs have higher lithium storage capacity and much better rate capability than does graphite. When GNSs are adopted in LIBs, they can significantly increase the capacity and reduce the charging time.

### FORMATIVE ASSESSMENT

A formative assessment was administered during the fall 2012 and fall 2013 courses, with emphasis on the students' learning interest and awareness of nanotechnology before and after their completion of this laboratory module, the overall laboratory experiences with GNSs and LIBs, and the laboratory content ratings in terms of nanotechnology and practical application. Apparently, the students' awareness of and learning interest in

nanotechnology increased significantly after their completion of the experiments (Table 1). The students truly appreciated the laboratory practicum with GNSs and LIBs, manifested by their consistently high ratings (9.32–9.53). On the basis of the students' comments received in fall 2012, the arrangement and schedule of the laboratory activities were further improved, which resulted in an increased rating in fall 2013. The impacts of this laboratory module on the aspects of chemical synthesis skills, electrochemical analysis, and relevance to nanotechnology were also positively commented. The entire class responded affirmatively about the benefits of implementing this laboratory into other chemistry or nanotechnology courses. Overall, this laboratory module proved to sustain and enhance intellectual enthusiasm and passion for both education and research in chemistry, materials, and nanotechnology.

### ASSOCIATED CONTENT

#### Supporting Information

Additional experimental instructions, notes for instructors, and safety and hazards information. This material is available via the Internet at <http://pubs.acs.org>.

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#### Notes

The authors declare no competing financial interest.

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**Table 1.** Formative Assessment Results Obtained

Formative Assessment Categories	Mean Score <sup>a</sup> (N = 16)	
	Fall 2012	Fall 2013
Interest and awareness of nanotechnology before the experiment	8.60	9.09
Interest and awareness of nanotechnology after the experiment	9.37	9.47
Laboratory experience with the graphene and Li-ion batteries	9.32	9.52
Laboratory content in relation to nanotechnology and application	9.40	9.53

<sup>a</sup>The assessment is based on a scale from 1–10, with 1 being extremely poor and 10 being excellent.

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