

Toward Green Synthesis of Graphene Oxide Using Recycled Sulfuric Acid via Couette–Taylor Flow

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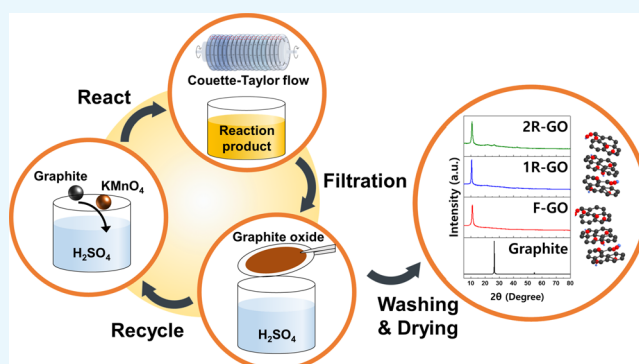
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S Supporting Information

ABSTRACT: Developing eco-friendly and cost-effective processes for the synthesis of graphene oxide (GO) is essential for its widespread industrial applications. In this work, we propose a green synthesis technique for GO production using recycled sulfuric acid and filter-processed oxidized natural graphite obtained from a Couette–Taylor flow reactor. The viscosity of reactant mixtures processed from Couette–Taylor flow was considerably lower (~ 200 cP at 25 °C) than that of those from Hummers' method, which enabled the simple filtration process. The filtered sulfuric acid can be recycled and reused for the repetitive GO synthesis with negligible differences in the as-synthesized GO qualities. This removal of sulfuric acid has great potential in lowering the overall GO production cost as the amount of water required during the fabrication process, which takes a great portion of the total production cost, can be dramatically reduced after such acid filtration. The proposed eco-friendly GO fabrication process is expected to promote the commercial application of graphene materials into industry shortly.



INTRODUCTION

Graphene is a free standing, two-dimensional monolayer carbon-based nanomaterial with remarkable physical properties, which has been studied in various applications such as transistor, transparent electrode, supercapacitor, sensor, and polymer composite.^{1–11} Typical synthesis routes of graphene include mechanical exfoliation from bulk graphite (the “Scotch-tape” method),⁴ chemical vapor deposition (CVD) through the reaction of metal catalysts and precursors,^{12–16} or chemical exfoliation of graphite using strong oxidants.^{9,17–29} For practical industrial applications of graphene, the synthesis routes should guarantee high-quality, low-cost, and high-yield eco-friendly processes. The mechanical exfoliation method can yield the highest quality of graphene, but the associated process is not suitable for the mass production.⁴ Although large-area as well as single-layered graphene sheets can be produced by the CVD method, the fabrication process is rather complex and requires metal catalysts, which can potentially raise the overall production costs.^{12–16} On the other hand, the solution-processed chemical exfoliation technique is desirable for the

large-scale production process with relatively lower costs,^{9,17–29} and various functional composite structures can also be readily constructed utilizing the oxygen-containing functional groups created on the basal plane and edge sites of graphene.^{17,21}

In chemical exfoliation processes, strong acids are typically used, and graphene oxide (GO) produced from Hummers' method is one of the most widely studied graphene derivatives synthesized by such an approach. Sulfuric acid (H_2SO_4) is frequently used in the oxidation process of GO,^{30–32} which raises serious environmental concerns and also increases the overall production cost due to the large amount of water required to handle the discharged acid waste and to purify the resulting GO from the acid. A few studies suggested adjusting the concentration and volume of the applied acid to mitigate the aforementioned issues.^{31–33}

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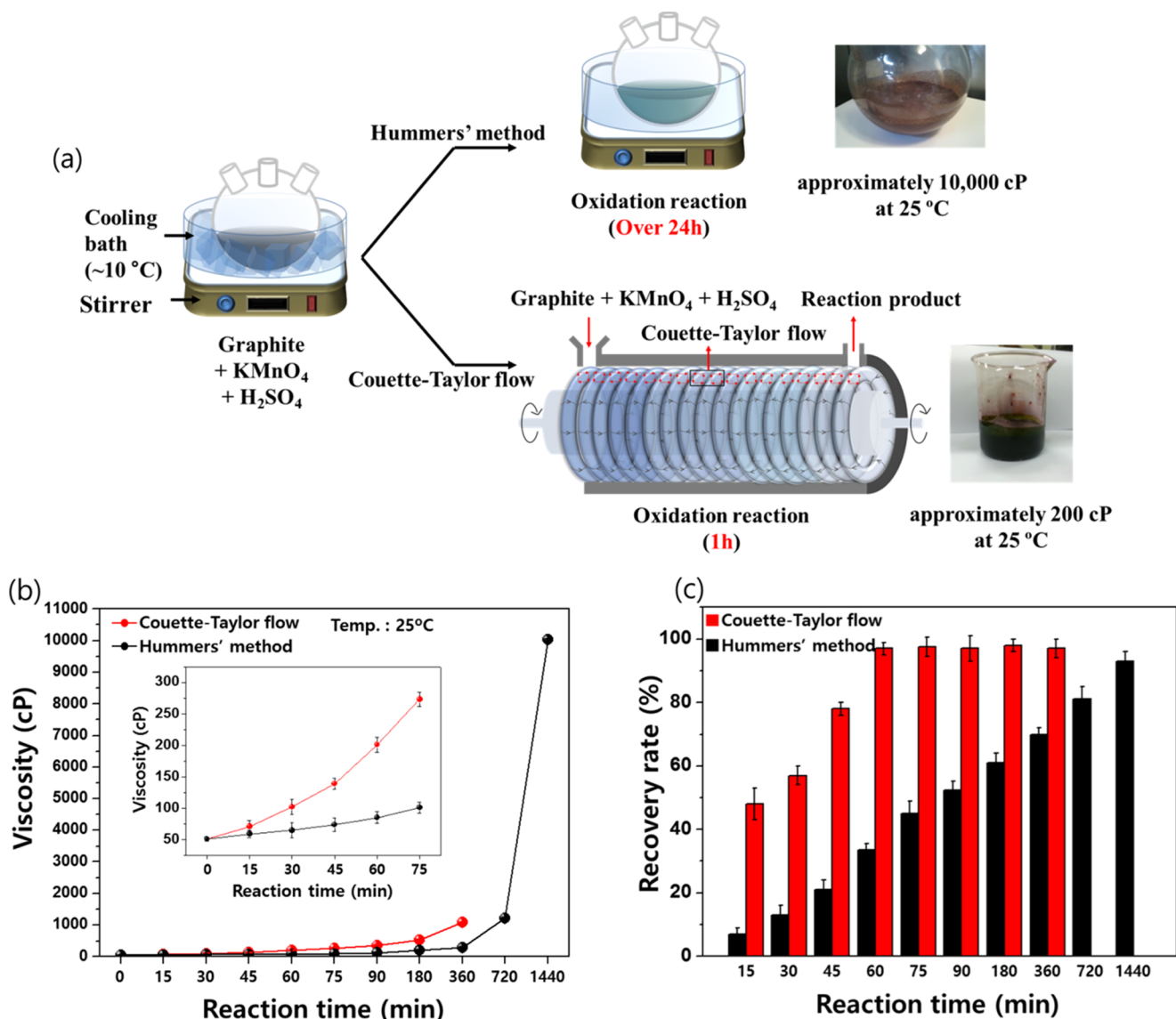


Figure 1. Comparison of the Hummers and Couette–Taylor flow methods. (a) Schematic of the GO synthesis process. (b) Viscosity of the graphite oxide mixture with varying reaction times. (c) Recovery rate of GO in accordance with the reaction time.

Herein, we report a facile filter system to recycle the H_2SO_4 and reduce the amount of water required for the GO production process, which can facilitate the reduction of overall production cost and commercialization of GO-based materials with alleviated environmental concerns. H_2SO_4 and graphite oxide were separated through the filter system after the oxidation of graphite using the Couette–Taylor reactor and before the washing process. The Couette–Taylor flow reactor is equipped with rotating inner and fixed outer coaxial cylinders. Toroidal vortices are generated and evenly spaced along the axis at a critical rotating speed of the inner cylinder.^{34–36} In our previous study, the toroidal flow of solutions led to excellent blending of graphite with oxidants (KMnO_4 and H_2SO_4), thus enhancing the oxidation efficiency with high yields of single- and few-layered GO production.³⁷ The Couette–Taylor flow reactor comprises two coaxial cylinders. Whereas the outer cylinder remains standstill, the inner one rotates at controlled speed. When the rotational speed of the inner cylinder reaches a threshold value, doughnut-shaped vortices are generated, which rotate in opposite directions with constant arrays along

the cylinder axis. This Couette–Taylor vortex induces highly effective radial mixing and uniform fluidic motion within each vortex cell, enabling enhanced mass transfer of the reactants. The toroidal motion also generates high wall shear stress, which can facilitate GO fabrication.^{34–37} The key parameter that renders the acid filtration process possible is the viscosity of the reactant mixtures, which shows distinctive characteristics between the Hummers and Couette–Taylor methods as discussed later. The filtered acid can also be recycled in subsequent GO production processes, and such consecutive oxidation reactions from the Couette–Taylor flow reactor were successfully demonstrated utilizing the recycled H_2SO_4 .

RESULTS AND DISCUSSION

The modified Hummers method has been widely adopted as the standardized synthesis technique for GO production because of its relatively simple approach.^{30–32} However, the long reaction time and use of large volume of water in Hummers' method have been the major bottleneck to its widespread industrial applications. In our previous work, we

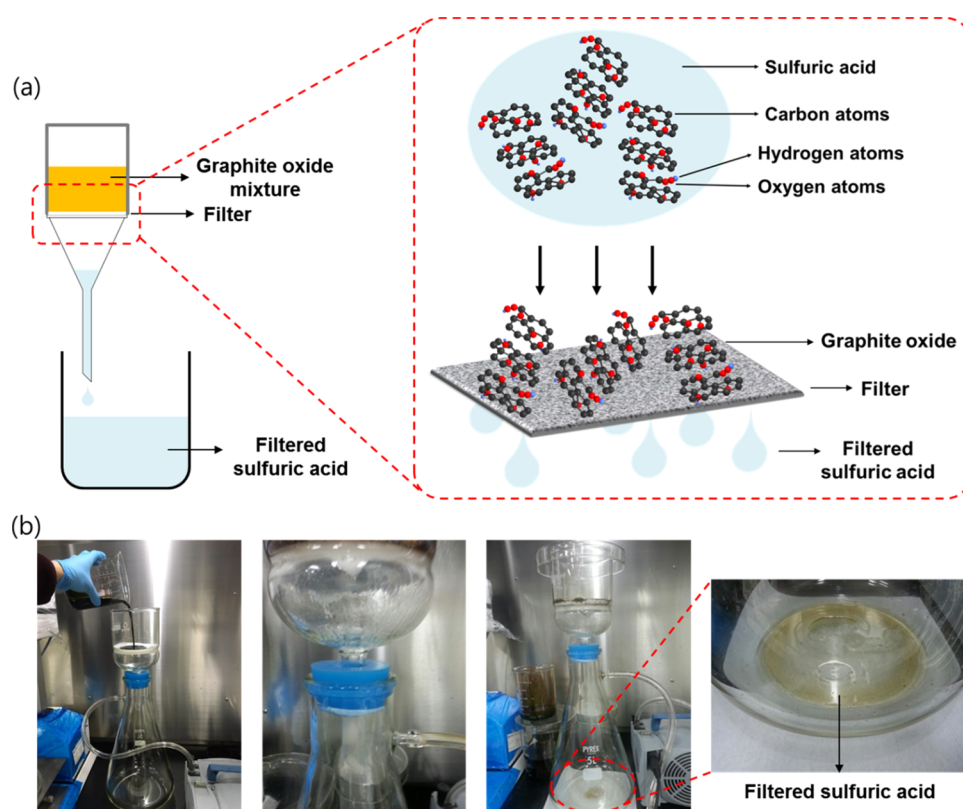


Figure 2. H_2SO_4 filtration process of the graphite oxide mixture produced by the Couette–Taylor flow reactor: (a) schematic and (b) digital image.

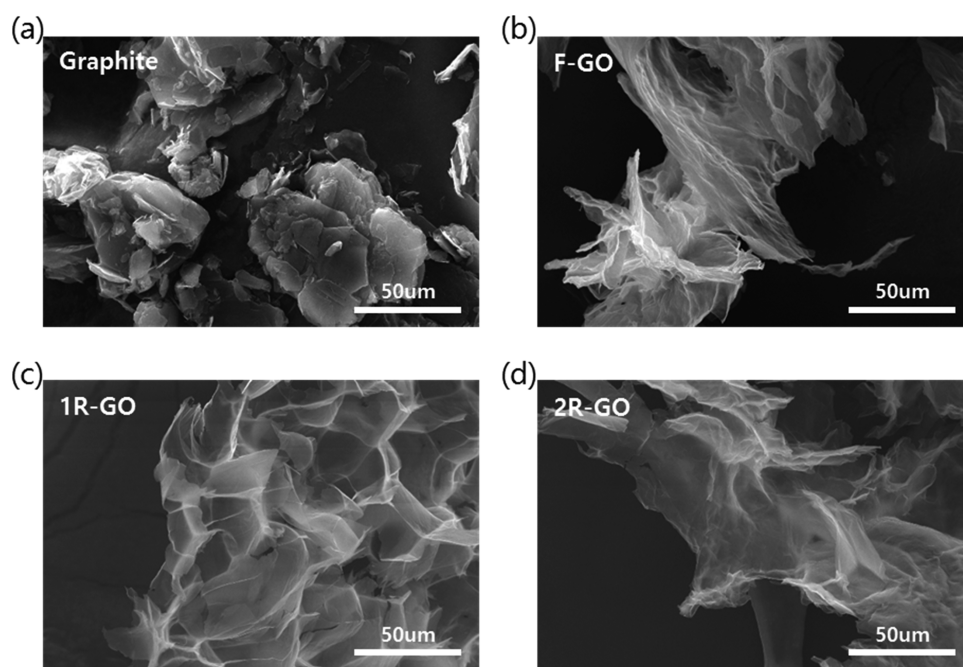


Figure 3. SEM pictures of (a) natural graphite, (b) F-GO, (c) 1R-GO, and (d) 2R-GO.

demonstrated that the Couette–Taylor flow reactor can dramatically reduce the process time with high yield of single- and few-layered GOs (Figure 1a).³⁷ In a typical GO synthesis process, the dissolved oxidizing agent (KMnO_4) in acid (H_2SO_4) is diffused into the graphite interlayer during the oxidation reaction of graphite, which leads to increase in the viscosity of the mixture (graphite, KMnO_4 , and H_2SO_4).³² As shown in Figure 1b, the viscosity of the mixture before the

oxidation reaction is ~ 50 cP at 25°C , which increases to ~ 85 and ~ 200 cP for the Hummers and Couette–Taylor flow methods, respectively, after the oxidation reaction of 60 min. For this reaction time, the recovery rate of GO prepared by Couette–Taylor flow is $\sim 98\%$, indicating that the graphite oxides are mostly well-oxidized and exfoliated into single- and few-layered GOs, whereas the recovery rate is only $\sim 34\%$ for Hummers' method, implying inefficient oxidation and exfolia-

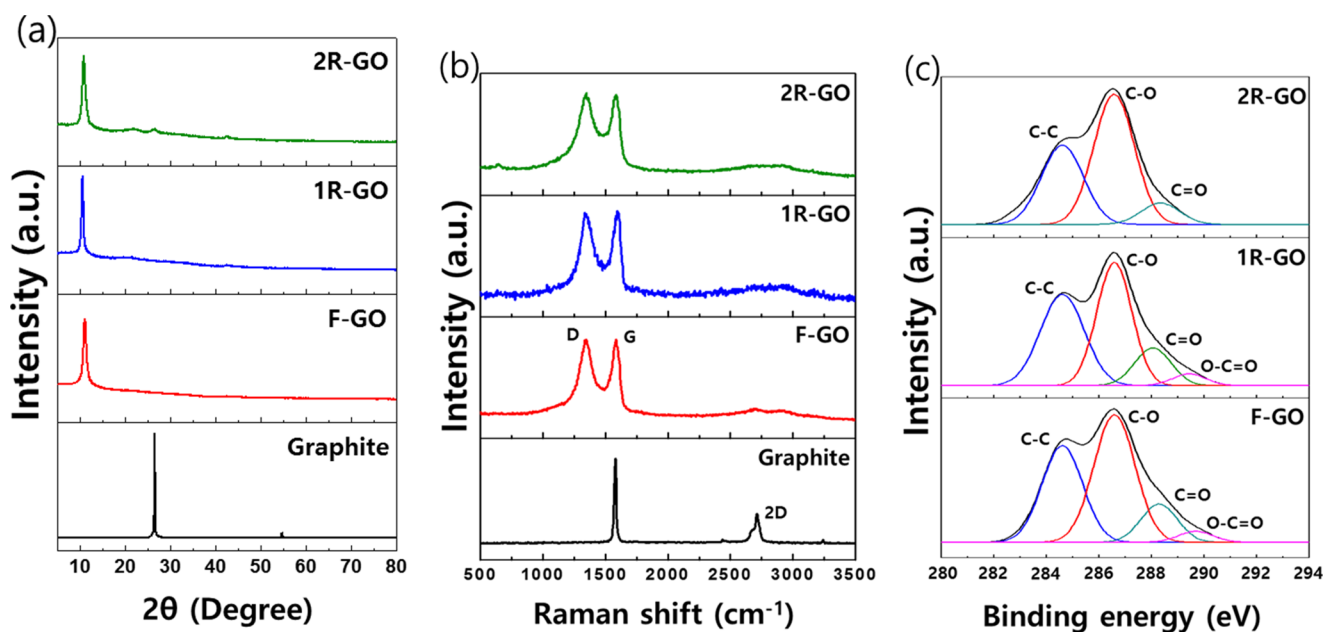


Figure 4. Spectroscopic characterizations of natural graphite and three types of GOs (F-GO, 1R-GO, and 2R-GO). (a) XRD patterns, (b) Raman spectra (514 nm laser excitation), and (c) C1s XPS spectra.

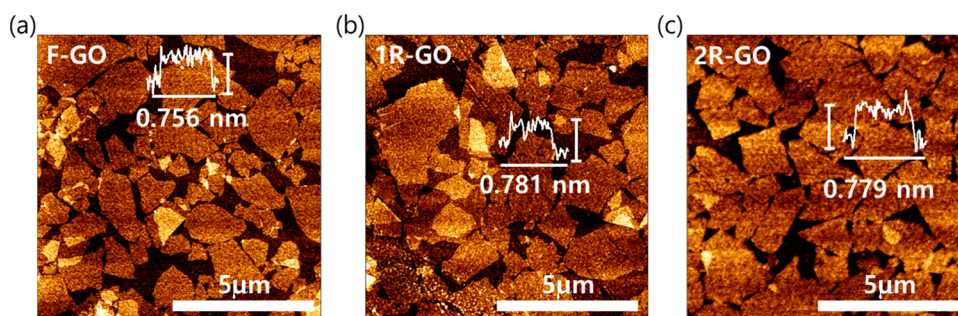


Figure 5. AFM pictures and thickness profiles of GO sheets. (a) F-GO, (b) 1R-GO, and (c) 2R-GO. The measured thickness of all three types of GO sheets was ~ 0.8 nm.

tion. Although the recovery rate of Hummers' method ($\sim 93\%$) becomes comparable to that of Couette–Taylor flow after prolonged treatment time (1440 min), the viscosity of the mixture is extremely increasing (10 000 cP), which impedes the acid filtration. Therefore, the Couette–Taylor flow method enables the acid filtration process by producing the reactant mixtures with relatively low viscosity (<200 cP) and can achieve the high recovery rate at the same time, whereas in Hummers' method, these two important conditions cannot be realized simultaneously. We note that the graphite oxide mixture prepared from Hummers' method for 60 min of reaction time can be used in the filtering process with its low viscosity (~ 85 cP). However, the low recovery rate of the resulting GO ($\sim 34\%$) is limiting the efficacy of Hummers' method in the filtration process. On the basis of these results, for the filtering process of H_2SO_4 , the oxidation reaction of 60 min by the Couette–Taylor flow method was used for the following sets of analysis.

H_2SO_4 filtration in the graphite mixture was conducted before washing with water during the GO production process using the Couette–Taylor flow reactor. Figure 2a illustrates the schematic diagram of the suggested acid filtering process, in which the viscosity of the reactants affects the filtration efficiency. Because of the low viscosity of the reactant mixture

manufactured from the Couette–Taylor flow reactor, the oxidized graphite slurries were successfully separated into H_2SO_4 and graphite oxide, as shown in Figure 2b. After filtering the H_2SO_4 , the remaining graphite oxide slurries could then be washed with a significantly reduced amount of water compared to that required in the existing Hummers method (decreased by 75%). Furthermore, the filtered H_2SO_4 could be recycled for the repetitive GO synthesis in the Couette–Taylor flow reactor. In the following, various types of GO products, GO with fresh H_2SO_4 (F-GO), one-time recycled H_2SO_4 (1R-GO), and two-time recycled H_2SO_4 (2R-GO), were comparatively analyzed.

Figure 3 shows SEM pictures of the natural graphite and three different types of GOs. Thick-layered platelets are mostly observed in natural graphite (Figure 3a). On the contrary, GO samples were well-exfoliated and exhibited a wrinkled thin sheet form for both the fresh and recycled H_2SO_4 cases (Figure 3b–d). These results suggest that the recycled H_2SO_4 can also effectively oxidize the graphite as the fresh H_2SO_4 .

The progression of oxidation reaction in the Couette–Taylor flow reactor was spectroscopically examined as shown in Figure 4. Figure 4a shows XRD patterns of F-GO, 1R-GO, and 2R-GO compared to those of natural graphite. The interlayer spacing was originally ~ 0.34 nm ($2\theta = \sim 26.4^\circ$) for the natural graphite,

which widened to ~ 0.75 nm ($2\theta = \sim 10.6^\circ$) for the three GO flake cases, typical value for highly oxidized graphite oxide, thus confirming the reliable oxidation capability of the recycled H_2SO_4 . Raman spectra of GO flakes exhibited G peaks at ~ 1590 cm^{-1} and D peaks at ~ 1350 cm^{-1} in all cases (Figure 4b), with broadened G-band and increased D-band characteristics compared to those of the graphite flake, indicating the existence of oxidized graphitic states. Figure 4c shows C1s X-ray photoelectron spectroscopy (XPS) spectra of GO samples with typical results in accordance with those for oxygen functional groups on carbon: 284.5, 286.8, and 288.7 eV related to sp^2 carbon in aromatic rings, epoxy/hydroxyl groups (C–O), and carbonyl groups (C=O), respectively.

For the thickness characterization of the exfoliated GO sheet, GO flakes were coated on silicon substrates and then analyzed by via AFM. GO sheets are typically thicker than the pure graphene because of various functional groups, such as hydroxy, epoxide, and carboxy groups, present on the basal planes and edges of the graphene. The height profiles of F-GO, 1R-GO, and 2R-GO sheets reveal uniform flake thicknesses of ~ 0.8 nm, normal of sufficiently oxidized GO sheet (Figure 5). These observations suggest that high-quality, single- and few-layered GOs can be successfully produced using the recycled H_2SO_4 during the synthesis process.

The efficacy of filtration process using recycled H_2SO_4 was further examined after separating the non- or low-oxidized graphite flakes. The resulting recovery rates of the three different types of GOs are presented in Figure 6. The recovery

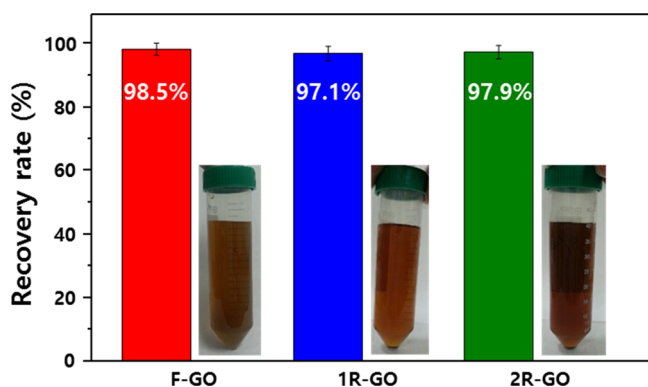


Figure 6. Recovery rate of the GO obtained using fresh and first- and second-recycled H_2SO_4 . Photograph: Dispersed GO solution after sonication and centrifugation. Precipitates in the bottom of the conical tube represent non- or low-oxidized graphitic particles.

rates were ~ 98.5 , ~ 97.1 , and ~ 97.9 % for F-GO, 1R-GO, and 2R-GO, respectively, indicating that the graphite was successfully exfoliated into single- or few-layered GO in all three cases. These results again support the fact that the recycled H_2SO_4 can be used to fabricate GO as the fresh H_2SO_4 .

The amount of water consumption during the GO synthesis, which accounts for the large portion of the production cost, needs to be considered for practical industrial applications of GO. In the following, we compared the amount of water spent during the washing process from Hummers' method and that from the proposed filter process (Table 1). In the case of Hummers' method, 1600 mL of water was required to reach pH 5 for 1 g of the graphite oxide mixture. After the first filtration process, the volume of rinsing water used was dramatically reduced to 400 mL for the same amount of

Table 1. Comparison of the Amount of Water Used in the Washing Process for the Hummers and Filtration Methods

method	amount of mixture (g)	volume of water (mL)	final pH
Hummers' method	1	1601 \pm 11	5
first filtration (fresh H_2SO_4)	1	400 \pm 7	5
second filtration (one-time recycled H_2SO_4)	1	399 \pm 3	5
third filtration (two-time recycled H_2SO_4)	1	402 \pm 6	5

mixture to reach pH 5 and similarly for the one- and two-recycled cases. Therefore, the suggested filter system in conjunction with the Couette–Taylor flow reactor can selectively filter H_2SO_4 from graphite oxide mixtures, which can significantly reduce the amount of water required during the purification process, a critical requirement for the commercialization of the solution-based graphene synthesis approach.

CONCLUSIONS

In this study, we introduced a feasible filtering system for recycling sulfuric acid during the GO synthesis process by the Couette–Taylor flow reactor. Successful filtration of the acid enabled dramatic reduction of purifying water content required in the synthesis process. After the filtration process, the impurities present in the graphite oxide mixture were effectively rinsed and removed by only 25% of the purifying water required in the conventional Hummers method. Moreover, the filtered sulfuric acid could be reused for the repetitive GO synthesis processes, contributing to save the overall fabrication cost. By adopting the filtration process, the single- and few-layered GOs have also been successfully produced in high efficiency. In terms of mass commercial production, our approach for eco-friendly fabrication of GO demonstrates obvious advantages over the existing technique and may find its usefulness in diverse industrial applications.

EXPERIMENTAL SECTION

Materials. Graphite flakes (150 μm) were obtained from Alfa Aesar. Potassium permanganate (KMnO_4), sulfuric acid (H_2SO_4 , 95%), and hydrogen peroxide (H_2O_2 , 30%) were purchased from Sigma Aldrich. Membrane filter (25 μm of pore size) was obtained from CS Technofil Co., Ltd. (South Korea).

Synthesis of GO Using Fresh and Recycled H_2SO_4 . GO was synthesized from natural graphite using the Couette–Taylor flow reactor (Figure S1). Graphite flakes (7 g) were added to 250 mL of H_2SO_4 , and then, 35 g of KMnO_4 was slowly added while stirring for 30 min at $\sim 10^\circ\text{C}$. This mixture was loaded into the Couette–Taylor flow reactor for oxidation reaction and intercalation. The 500 mm long reactor consists of two coaxial cylinders: a 120 mm diameter rotating inner cylinder and a 130 mm diameter fixed outer cylinder. When the mixture is injected into the space between the two cylinders, the inner cylinder is rotated. In this work, the rotating speed was 1000 rpm with the reaction time of 60 min. Oxidation of graphite resulted in brown-colored pasty slurry. The color change of mixture from greenish black to brown indicates that the oxidation and intercalation are fully occurred. The obtained slurry was filtrated through a 25 μm pore size poly-(tetrafluoroethylene) (polypropylene) membrane to extract the H_2SO_4 . During the filter process, 171, 167, and 159 mL of H_2SO_4 came out in each cycle. It means 79, 83, and 91 mL of

H₂SO₄ was lost in first (using fresh sulfuric acid), second (using first-recycled sulfuric acid), and third (using second-recycled sulfuric acid) cycles, respectively. Then, 250 mL of ultrapure water and 15 mL of H₂O₂ were poured into the filtered slurry, and the mixture was stirred for 30 min. Centrifuge was used to purify the filtered graphite oxide from the impurities, which was then freeze-dried for characterization and mass measurement. The filtered H₂SO₄ was reused for the repetitive GO synthesis following similar processes as described above. After drying, the graphite oxide was dispersed in water followed by sonication. After sonication, non- or low-oxidized graphite was precipitated by centrifugation at 4000 rpm for 30 min. The supernatant containing single- and few-layered GOs was freeze-dried for characterization and mass measurement of the GO. The efficiency of the recycling process was evaluated by the characterization of the produced GOs and a recovery rate defined by the mass ratio between the single- or few-layered GO and the initial graphite oxide.

Characterization. Microstructures of the GO were investigated by field emission scanning electron microscopy (JSM-7600F, JEOL). The thickness of GO sheets was determined via atomic force microscopy (SPA-300HV, SII). To analyze the further characteristics of GO and graphite oxide, X-ray diffraction (D8 ADVANCE, BRUKER), Raman (Bruker FRA 160/S, BRUKER), and X-ray photoelectron (VG Microtech ESCA2000, JEOL) spectroscopy were used.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00352.

Illustration of the oxidation and the intercalation process of graphite flakes in the Couette–Taylor flow reactor and viscosities of the initial reactant mixture and reaction product (PDF)

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Notes

The authors declare no competing financial interest.

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based on 900 × 1600 mm² large, less than 1 nm thick graphene film synthesis technique) funded by the Korea Government Ministry of Knowledge Economy and the Ministry of Trade, Industry and Energy through Technology Innovation Program (Grant No. 10067449).

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