Material Processing of Chemically Modified Graphene: Some Challenges and Solutions

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CONSPECTUS

Graphene-based sheets show promise for a variety of potential applications, and researchers in many scientific disciplines are interested in these materials. Although researchers have developed many ways of generating single atomic layer carbon sheets, chemical exfoliation of graphite powders to graphene oxide (GO) sheets followed by deoxygenation to form chemically modified graphene (CMG) offers a promising route for bulk scale production. The materials processing, which we broadly define as the physical and chemical means to tailor a material's chemical and microstructures, enables us to control the properties in bulk CMG materials. For example, by processing CMG sheets in different solvents, we can make thin films, blend CMG sheets with other materials, and modify them by chemical reactions. Materials processing methods also allow us to control the interactions between CMG sheets for the assembly of large scale two- or three-dimensional structures with desirable microstructures.

This Account highlights a few problems associated with large scale production and processing of GO and CMG. First, we briefly discuss the potential fire risk of GO and CMG when alkaline salt byproducts are not completely removed. These impurities can catalyze carbon combustion. We introduce an improved purification procedure that effectively removes the byproducts and speeds up the production. Next, we address the challenges of imaging GO and CMG sheets on common substrates such as glass and plastics using standard microscopy methods. We have introduced a new technique fluorescence quenching microscopy (FQM), which allows us to observe graphene-based sheets with both high throughput and high contrast on arbitrary substrates and even in solution. Then we focus on how to prevent aggregation in CMG. Aggregation greatly reduces the material processability and accessible surface area, which degrades the material properties. We introduce two strategies to reduce aggregation by (i) reducing the lateral dimension of the sheets to nanometer range to enhance their colloidal stability and (ii) crumpling the sheets into paper ball-like, fractal-dimensional particles to make them aggregation-resistant in both solvents and solid state, even after mechanical compression.

Solutions to these material processing challenges can pave the way for further research and development. We hope that the tools and strategies presented in this Account can facilitate the processing and property control of this promising material.

1. Introduction

Chemically modified graphene (CMG) usually refers to the deoxygenation product of graphene oxide (GO) sheets,[1−4] which is made by solution chemical exfoliation of graphite powders using strong oxidizing reactants (Figure 1a−d).[5,6] Compared with "pristine" graphene,[7] CMG (a.k.a., reduced GO, r-GO) is still derivatized with chemical functional groups and thus more defective and less conductive (Figure 1e,f). But GO-derived graphene still holds great promise because it has low cost and high single layer yield, and can be made in bulk. Since GO is dispersible in water and many other polar solvents and can be readily reduced to CMG such as by chemical, thermal, and photo treatments, CMG can be used in many forms such as transparent few layer thin films, thicker paper-like materials, and three-dimensional porous monoliths (Figure 1g−i). Potential applications of GO and CMG have been demonstrated in many areas such as transparent conductors,[8,9] sensors,[10,11] polymer composites,[12] in energy storage and conversion,[13−17] and as surfactant for dispersing other insoluble carbon materials.[18,19] As a result, industrial manufacturing of GO and CMG has emerged.[20]
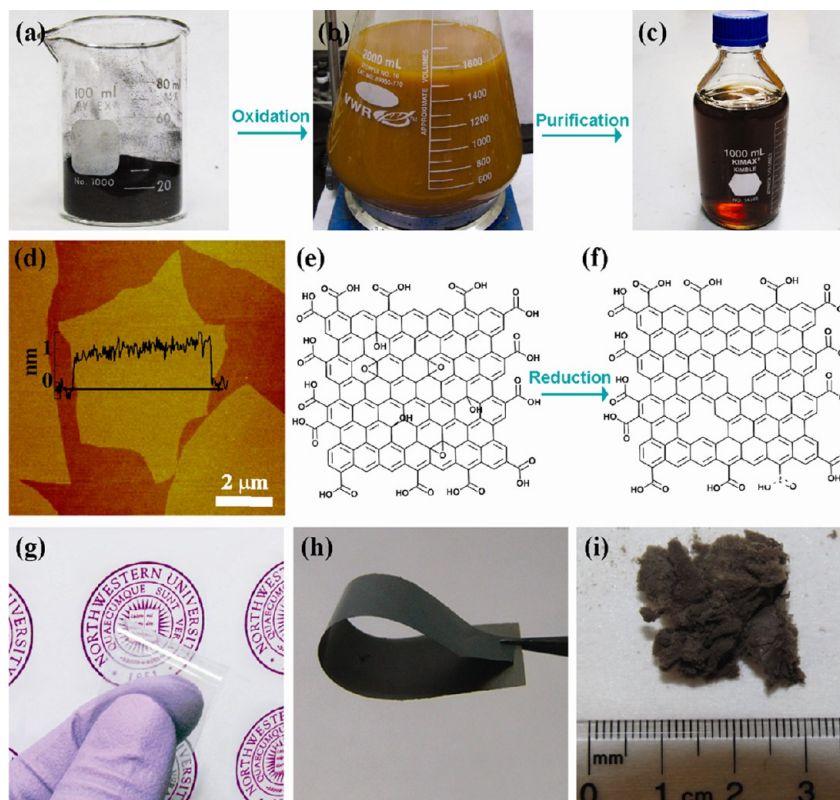
FIGURE 1. (a−c) Synthesis of GO. (d) AFM image of a GO single layer showing apparent thickness of around 1 nm. (e, f) molecular structural model of GO and CMG. GO has been processed and used in a form of (g) few layer thin films on plastic substrate, (h) paper-like materials, or (i) fluffy high surface area foams.

Materials processing, here broadly defined as the physical and chemical means to tailor materials' chemical and micro-structures for achieving desirable properties, is the enabling factor for any material application. For CMG, proper material processing strategies, including the synthesis and assembly of these single atomic layers, are needed to control the chemical functionality at single sheet level, as well as the microstructures of their ensemble such as those shown in Figure 1g−i. Since chemical functionalization of CMG has been extensively discussed in other reviews,[1,2,4,9,11] this Account will focus on three important material processing challenges, which have not been well addressed yet in literature. First, GO is easy to synthesize but hard to purify due to gelation. So the residual alkaline salt byproducts can turn it and its CMG product from a flame retardant to a potential fire hazard. An improved sample purification procedure can help to avoid this problem. Second, it is quite challenging to see these world's thinnest materials, making it hard to evaluate the shape, size and conformation of GO and CMG and the microstructures of their thin films. A general imaging tool that allows high-throughput observation of GO and CMG can greatly

enhance the capability to design better processing techniques. Finally, CMG sheets have strong tendency to aggregate, which will significantly reduce their processability as well as degrading their properties such as surface area. Strategies to prevent CMG aggregation would allow their single or few layer properties to be retained even in bulk quantities of materials, which can help to standardize the CMG materials. In the following sections, we will start with a very brief introduction to the first two problems since they have been discussed in much greater detail elsewhere.[21,22] Next, we will review a few ideas to make GO or CMG resist aggregation in solution, at interfaces, and even in solid state.

2. Potential Fire Risk of GO and CMG Due to Salt Contamination

GO can be readily converted to CMG by heating, a process that is often referred to as thermal "reduction". However, this deoxygenating reaction is actually *disproportionation* rather than *reduction* since some carbon atoms are also oxidized to carbonaceous gases, leaving carbon vacancies in the basal plane. The disproportionation reaction is highly exothermic. If the reaction heat is not properly dissipated, it can trigger
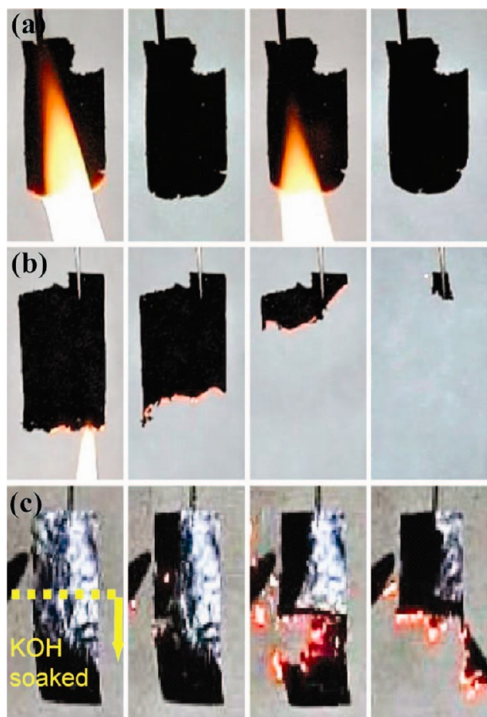
FIGURE 2. Snapshots showing salt induced flammability of GO and its graphene product. (a) Purified CMG is quite stable in natural gas flame. (b) KOH (ca. 1 wt %) contaminated CMG can burn away after brief exposure to a flame. (c) Upon tapping by a hot soldering iron, KOH (ca. 1 wt %) contaminated GO (bottom half) undergoes violent self-propagating combustion, producing flying debris carrying a slow burning hotspot, while clean GO turns into CMG similar to the one shown in panel a.

FIGURE 3. (a) GO tends to gel during washing by water, making purification procedures tedious and increasing the likelihood of salt contamination. (b) Gelation can be greatly suppressed in strong acid or acetone. Therefore, a two-step, acid–acetone washing procedure is developed to greatly accelerate the purification process.

self-propagating reduction in a GO solid. We have discovered that residual alkaline salt byproducts (e.g., Na$^+$, K$^+$) generated from the oxidation of graphite powders can catalyze the combustion of GO and CMG, making them highly flammable.[23] Figure 2a shows a CMG (a.k.a., r-GO) film being repeatedly exposed to a natural gas flame. Although the exposed edge turned red hot, combustion cannot be initiated even after prolonged flame treatment. However, when contaminated by potassium salts, CMG becomes much more prone to combustion (Figure 2b). As shown in Figure 2c, if GO is contaminated by these salts, it can burst into flames upon gentle heat treatment on local spots since the heat released from the deoxygenation reaction is sufficient to trigger combustion. In contrast, purified GO would merely undergo reduction, producing incombustible CMG. If the salt byproducts are not completely removed from GO, an accidental spark, excessive exposure to light, or a local hot spot generated by heat accumulated from slow self-reduction could trigger rapid, catastrophic total combustion of the solid product, which poses a serious fire
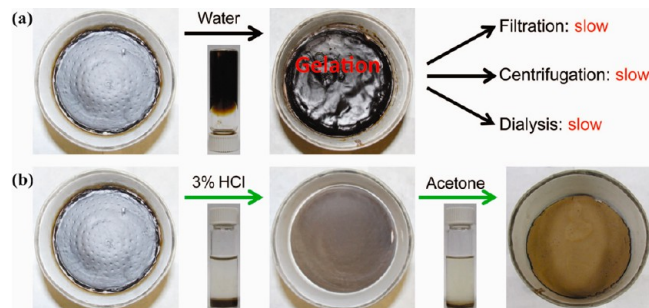
hazard. This is particularly alarming for the fire safety of large scale production, processing, and storage of GO materials. Although these salt byproducts are very soluble in water, it is not trivial at all to remove them from GO, since GO dispersions tend to gel as the pH value increases during washing (Figure 3a). Gelation makes common purification techniques, such as dialysis, centrifugation, and especially filtration, very tedious and inefficient. In fact, the filtration of GO gels can become so slow that actually more solvent is removed by evaporation from the filter! This will increase the likelihood of trapping metal salt byproducts in GO.

If the gelation of GO is suppressed, it can be washed more easily. To address this problem, we have developed a two-step, acid–acetone washing procedure to avoid gelation and speed up the purification process.[23] First, excess amount of hydrochloric acid (3 wt %) is used to remove the salts, followed by acetone to remove the acid (Figure 3b). In the first step, the solution pH is maintained around 0 to keep GO from gelling. HCl is chosen because it is effective at removing alkaline metal salts and can vaporize without leaving solid residue. After three to four times of HCl washing, the filter cake is dried in air or under vacuum, and then washed again with acetone to remove any trapped HCl or salts. Since GO tends to aggregate in acetone, filtration can be done conveniently. Acetone also readily evaporates without leaving solid residue. With this two-step washing procedure, filtration of GO at tens of grams scale can be done in a matter of minutes to hours rather than days. GO dispersions in various solvents can then be obtained through solvent exchange after the final acetone-washing step or by directly dispersing the dried solid in the solvent of choice. Such purified GO samples produce graphene products with potassium content less than 0.1 wt % based on energy-dispersive X-ray spectroscopy,[23] which are very stable against combustion,

like those shown in Figure 2a. While we independently developed the purification procedure,[22,23] later we found that a report in 1974 had already mentioned purifying GO by two-step washing using strong acid and acetone.[24] Unfortunately, the citation record of ref 24 suggests that the GO purification method reported there had not been noted at all. Therefore, our coincidental rediscovery[23] actually proved the effectiveness of the two-step washing procedure.

3. Seeing GO and CMG on Arbitrary Substrates

Imaging is an indispensable characterization tool for working with graphene-based materials. For example, we need microscopy techniques to validate material processing strategies to see whether sheets with suitable size and conformation are obtained or whether a graphene coating has the desirable microstructures such as coverage, thickness (a.k.a., number of layers), and roughness (e.g., wrinkles or overlaps). However, being single atomic layers, they are hard to visualize by absorption based optical microscopy techniques. There are a number of microscopy techniques for seeing graphene-based sheets, but all of them require the use of special substrates.[21] For example, graphene can be made visible by eye under an optical microscope operated under reflectance mode. However, this only works for samples deposited on dielectric coated Si wafers with a set of parameters optimized including the thickness of the dielectric layer, the dielectric constant, and the illuminating wavelength. Atomic force microscopy (AFM) requires the use of atomically smooth substrates and is quite low throughput. Scanning electron microscopy (SEM) offers higher throughput but requires the use of conductive substrates and is operated in vacuum. Raman microscopy has been quite successful for imaging pristine graphene but places limits on the type of substrates due to concerns of laser heating and background autofluorescence that may overwhelm the Raman signal. Laser heating could also be a problem for GO because it can be readily reduced by photothermal heating (Figure 4).[25] There are urgent imaging needs that cannot be met by current microscopy techniques. For example, graphene-based sheets can be deposited on plastic substrates to make flexible transparent conductor. Yet no current microscopy techniques are suitable for high-throughput imaging of these single atomic sheets on plastic surfaces! Therefore, there is an urgent need for a rapid, low cost, general imaging technique that allows quick evaluation of graphene materials on arbitrary substrates.

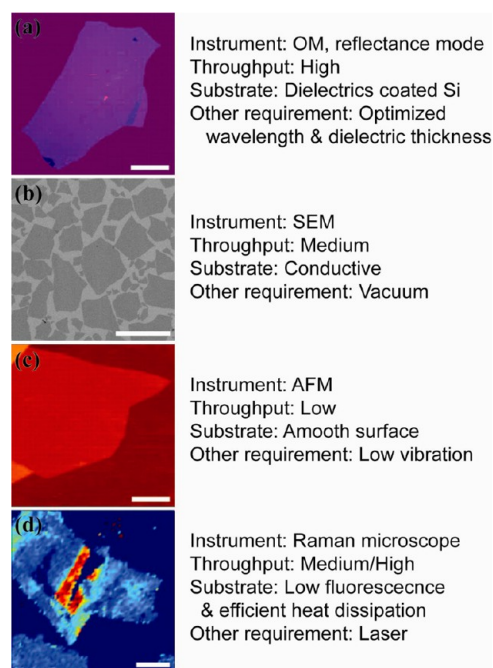To address this challenge, we have developed fluorescence quenching microscopy (FQM) for seeing graphene-based

FIGURE 4. Common microscopy techniques for imaging graphene-based sheets and their limitations. Scale bars for images take by (a) optical microscopy, (b) SEM, (c) AFM, and (d) Raman microscopy are 20, 20, 1 and 3 μm, respectively.

sheets.[26] In common fluorescence microscopy, the objects of interest are labeled with dye to light up in a dark background. However, in FQM, dye molecules are applied everywhere and the graphene materials appear dark in a bright background since they can quench the fluorescence of nearby dye molecules (Figure 5a). Figure 5b shows an FQM image of GO sheets deposited on a SiO_2/Si substrate. Even though GO is a weaker fluorescence quencher than pristine graphene or r-GO, the quenching effect is strong enough to generate stark contrast, the quality of which is far beyond the optical microscopy image (Figure 5c) and comparable to those taken by AFM (Figure 5d) and SEM (Figure 5e), but with much simpler and cheaper instruments and higher throughput. The layer contrast in FQM images is due to the long-range energy transfer between graphene-based sheets and the dye molecules, which can be separated by tens of nanometers.[21,26] This long-range quenching capability has been predicted by theory[27] and experimentally confirmed for the first time by us[26] using FQM as a tool.

FQM can visualize graphene-based sheets on arbitrary substrates (e.g., plastic, glass, or metal), which has not been possible with current techniques. For example, FQM can readily image GO sheets on common glass substrates, generating high contrast, SEM-quality images (Figure 5f), while neither SEM nor AFM can be used. Under the bright field
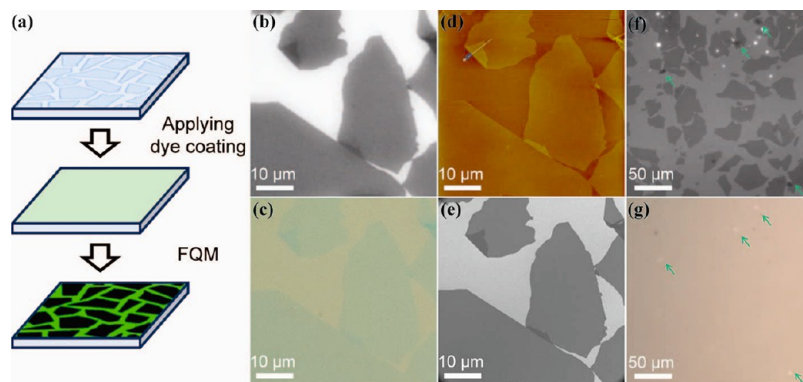
FIGURE 5. High-throughput imaging of graphene-based sheets on arbitrary substrates can be achieved by FQM. (a) In FQM, graphene layers appear darker than the bright background by quenching the fluorescence of nearby dye molecules. (b−e) Images of the same GO sample on SiO$_2$/Si obtained by FQM, OM, AFM, and SEM, respectively. (f) FQM can generate high contrast images for samples deposited on glass, which cannot be imaged by (g) OM or SEM (not shown). As indicated by the arrows in panels f and g, OM can only resolve the much thicker, heavily wrinkled part in the GO sample.

reflectance mode of optical microscopy, only the thick, multilayer aggregates can be seen (Figure 5g). Thus FQM finally offers a tool for routine evaluation of the morphology of GO or CMG sheets, and the microstructures of graphene-based thin films, especially on insulating, transparent, or rough substrates.[28]

FQM also offers a few new niche capabilities. For example, FQM is capable of visualizing GO and CMG sheets in solutions, helping to reveal their solution conformation and dewetting induced behaviors.[21,26] With dye-doped photoresist as the imaging layer, FQM allows projection lithography to see and define patterns on graphene-based sheets on a fluorescence microscope.[21] Taking advantage of the different quenching capability of CMG with different degrees of graphitization,[26] FQM can easily reveal chemical patterns on graphene sheets,[29] which is again hard to do with current imaging techniques. By developing suitable fluorescent substrates, one can eliminate the step of applying a dye layer, making FQM even more widely accessible.

4. Making CMG Resist Aggregation

4.1. Aggregation Problem of Graphene-Based Materials. Although GO can form stable colloidal dispersions, CMG tends to aggregate due to the strong van der Waals attraction between graphene sheets, which can be expressed by

$$E \approx \frac{S}{d^4} \qquad (1)$$

where E is the interacting potential, S is the overlapping area between two sheets, and d is the separating distance.[30] The restacking of sheets is largely uncontrollable and irreversible, thus it not only reduces their processability but also compromises properties such as accessible surface area (Figure 6a). Moreover, since materials typically experience some form of compressive stress during processing steps such as drying and pelletizing, their aggregation state would also vary by processing history. Making graphene-based materials aggregation-resistant will help to standardize the materials and their properties, which are especially critical for applications using bulk quantities of CMG.

Strategies based on colloidal chemistry[31] have been successfully applied to keep CMG dispersed in solvents. For example, electrostatic repulsion between CMG sheets can be introduced to overcome van der Waals attraction. Figure 6b shows the DLVO stability curves for three classical types of colloidal behaviors: stable colloids (red line), reversible flocculation (blue line) and irreversible aggregation.[31] CMG sheets will form stable dispersion in solvent if the repulsive interaction is dominating, which can be achieved by chemically modifying their surface with charged functional groups or fine-tuning the CMG−solvent interaction to shift the balance of DLVO stability toward repulsive interaction. Alternatively, eq 1 suggests that the van der Waals attraction between graphene sheets can be greatly weakened by inserting spacers to increase the intersheet spacing. Many spacer materials have been demonstrated ranging from small molecules or grafted polymer chains to nanostructures. Many papers on dispersing CMG or graphene platelets have been published in these two areas, which have already been extensively reviewed.[1,9,13] This Account will focus on some very different ideas that can prevent CMG aggregation without extensively modifying the material or introducing foreign spacer materials.
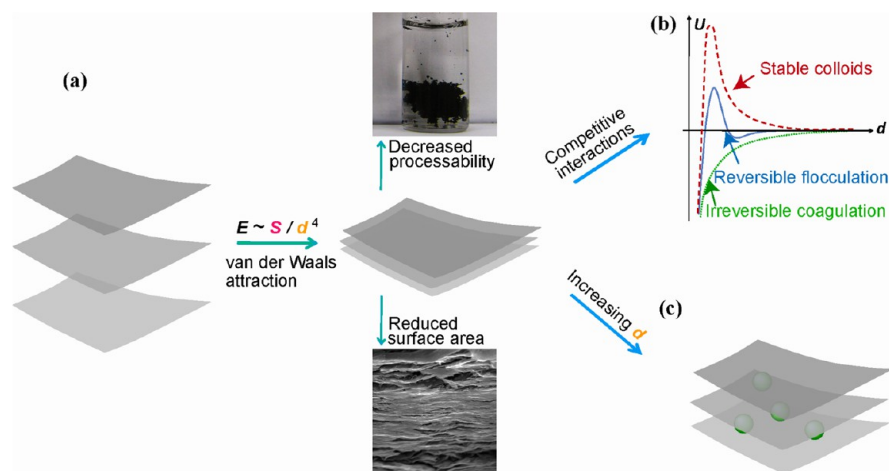
FIGURE 6. (a) Graphene sheets tend to restack due to strong van der Waals attraction, which leads to decreased processability and degraded properties such as surface area. To prevent aggregation, (b) competitive interactions such as electrostatic repulsion can be introduced to balance the attractive interaction, a typical strategy in the colloidal chemistry paradigm, which is represented by the classic DLVO colloidal stability curves. (c) Alternatively, spacer materials can be used to increase the spacing between graphene sheets and disrupt their overlapping.

4.2. Enhanced Stability of GO and CMG Nanocolloids.

Although S is a less pronounced factor than d, eq 1 also suggests that the van der Waals potential decreases with reduced overlapping area S between sheets. For CMG, reducing the lateral dimension from micrometer to nanometer scale should greatly enhance their colloidal stability due to several reasons (Figure 7a). First, CMG nanosheets would have orders of magnitude smaller overlapping area compared with regular micrometer-sized sheets. Second, nanocolloids have higher edge-to-center ratio and thus higher charge density due to the ionizable —COOH groups on their edges.[3] Third, kinetically nanocolloids can stay dispersed longer due to smaller probability to interact. Figure 7b shows the synthesis of GO nanocolloids by chemically exfoliating graphite nanofibers, in which the graphene sheets are coinstacked along the fiber length.[32] Although nanometer sized GO sheets can be made by fracturing the larger micrometer sized ones, the direct synthesis eliminates the extensive postsynthetic processing steps needed to cut, sort, and collect GO by sizes, which could adversely affect the colloidal stability or introduce impurities to the highly absorbing GO sheets. Using graphite nanofibers as the precursor, the upper size limit of the resulting nanocolloids is predetermined by the diameter of the nanofibers, thus the size of the GO product can be more uniform and controllable. For example, nanofibers with average diameter of about 130 nm yielded uniform GO nanosheets with average size around 50 nm after 2 h reaction (Figure 7c). The size of GO nanocolloids can be tuned by the diameter of the nanofibers and the oxidation time. In terms of spectroscopic characteristics and chemical properties, these nano-GO sheets are very similar to regular micrometer sized GO. However, the nanocolloids have much enhanced colloidal stability as shown in centrifugation tests (Figure 7d,e). After being reduced by hydrazine, the resulting CMG nanocolloids can form self-stabilized colloidal solutions in water over a wide range of pH values between 4 and 10 (Figure 7f). In contrast, regular micrometer-sized CMG sheets are only stable at pH between 8 and 10. The enhanced colloidal stability of GO and CMG nanocolloids over a wide range of pH values makes them especially promising for spectroscopy-based biosensing applications.[33]

4.3. Aggregation Resistant Crumpled Graphene Particles.

In many of its potential applications, CMG is used in a compact bulk solid form, in which the sheets would still tend to restack no matter how well they were dispersed in solutions. One way to prevent CMG from stacking in solid state is to fundamentally minimize its van der Waals attraction. Solution to this problem can be inspired from our daily life experience with crumpled paper balls. While flat paper sheets readily stack and reduce surface area, crumpled paper balls can resist aggregation and maintain their high surface area even under mechanical compression.[34] Moreover, crumpled paper balls are much more "processable" because they do not stick to each other or to any surface like flat paper sheets do. With eq 1 used as a model, such behaviors are not at all surprising since crumpling two thin sheets into balls minimizes their attraction: large overlapping area S is prohibited due to the uneven surfaces, and the intersheet separation d is increased by orders of magnitude, that is, from around the thickness of the sheets to around the
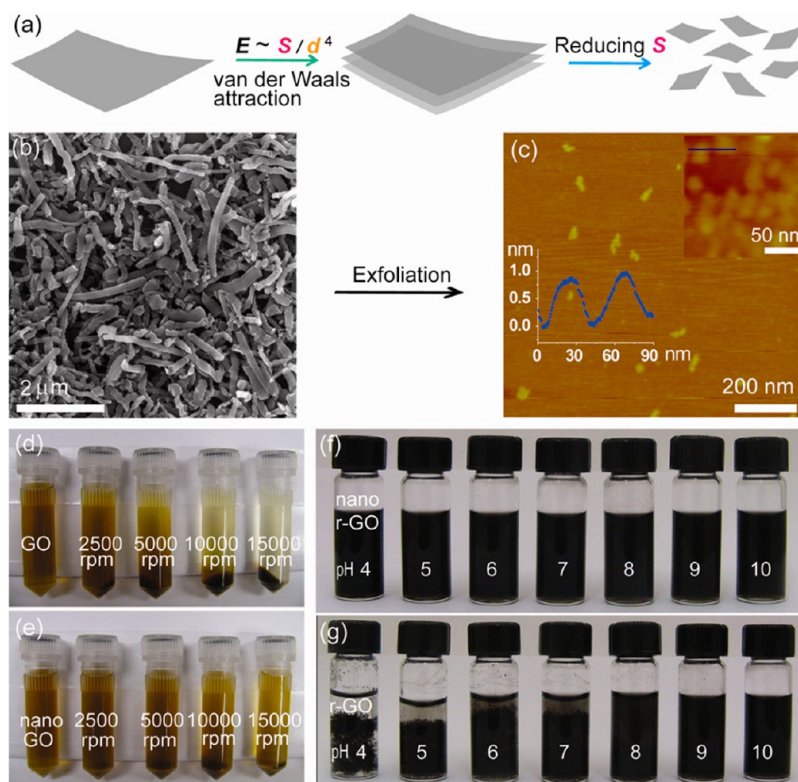
FIGURE 7. (a) Smaller sheets are less likely to aggregate due to decreased van der Waals attraction. (b, c) GO nanocolloids with sub-100 nm lateral dimension and much more uniform size distribution can be obtained by exfoliating graphite nanofibers, in which graphene sheets are coin stacked along the long axis. Compared with (d) regular GO made from graphite powders, (e) GO nanocolloids have much higher colloidal stability as shown in the centrifugational test. After being reduced, the (g) r-GO nanocolloids are also more stable than (f) their micrometer counterparts, as shown in the dispersion test under different solution pH values.

diameter of the balls. If graphene-based sheets can be made into this fractal dimensional morphology,[35] they could also become aggregation-resistant with enhanced processability.

Paper balls are made by isotropically compressing the flat sheets.[34] In an earlier work, we observed with FQM that GO sheets can be wrinkled and folded by capillary force during solvent evaporation.[21,26] To isotropically squeeze the sheets, GO sheets are suspended in aerosol droplets, which are then rapidly evaporated to crumple the sheets into particles with near-spherical contours.[36] As shown in Figure 8a, aqueous dispersion of micrometer-sized GO sheets is nebulized to generate aerosol droplets, which are blown through a preheated tube furnace. Rapid evaporation causes shrinkage of the droplets, first concentrating the GO sheets and subsequently compressing them into crumpled balls with average contour diameters at submicrometer scale. The GO sheets can also be thermally reduced to CMG during the flight. Each aerosol droplet produces one crumpled particle, the size of which and the degree of crumpling can be tuned by the concentration of GO in the initial dispersion. The crumpled morphology is very open but also very robust because it can sustain common material

processing conditions such as solution processing, thermal shock, microwave heating, and hydrazine treatment, without unfolding or collapsing. Since the crumpled ball morphology minimizes van der Waals attraction, the crumpled CMG particles would not form permanent aggregates regardless of the nature of the solvents in which they are dispersed in. As shown in Figure 9a, the crumpled CMG powders can be readily dispersed in 10 very different solvents in terms of density and polarity after just gentle shaking by hand. Note that some of these solvents such as toluene, acetone, and cyclohexane are known to be otherwise incapable of dispersing graphene-based materials. In contrast, CMG sheets precipitate in most of these solvents even after sonication (Figure 9b).

In addition to the much improved solvent processability, the crumpled graphene particles can even resist aggregation after being compressed in solid state.[36] As shown in Figure 10a,b, after being pelletized under 55 MPa, crumpled graphene balls form an isotropic, black solid with similar microstructures at both the surface and the cross section. In contrast, sheet-like CMG yields an anisotropic, shiny pellet with a smooth, nearly featureless surface but laminated microstructure at the cross section (Figure 10c,d). The pellet

of crumpled particles can be readily redispersed in solvents such as water (Figure 10e), methanol, tetrahydrofuran, toluene, acetone, and cyclohexane, upon shaking by hand. SEM image of redispersed sample (Figure 10 f) clearly shows individual particles and their crumpled morphology were
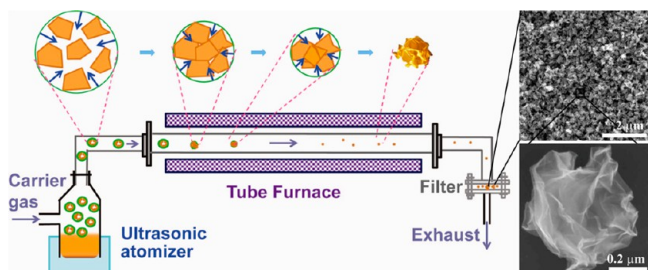

FIGURE 8. Schematic drawing illustrating that CMG particles with crumpled paper-ball like structure (right, SEM images) can be made by isotropic capillary compression in rapidly evaporating aerosol droplets.
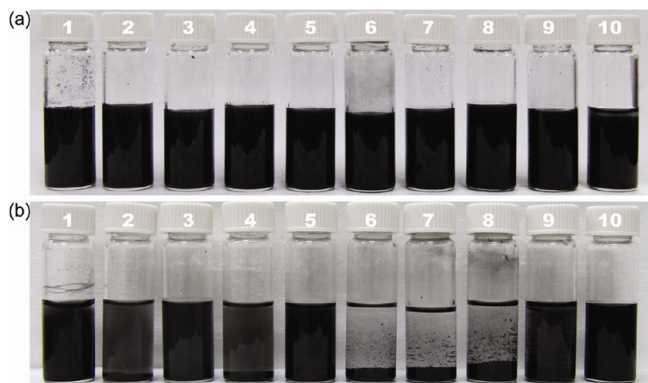

FIGURE 9. (a) Powders of crumpled graphene balls can be dispersed in many solvents by gentle shaking with hand, while (b) graphene sheets aggregate in most of these solvents even after sonication. The solvents in 1 to 10 are water, methanol, isopropanol, acetone, chloroform, tetrahydrofuran, toluene, cyclohexane, dichlorobenzene, and ethylene glycol, respectively.
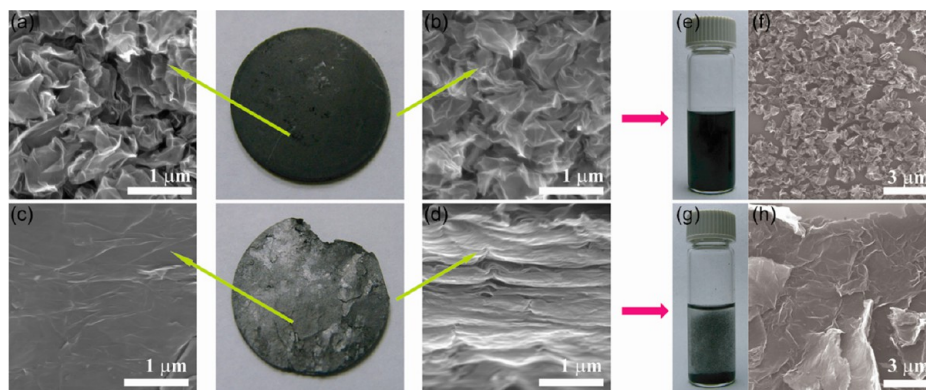
largely unaffected by the compression. In contrast, pellets of the CMG sheets prepared under the same pressure cannot be redispersed at all even after extensive sonication (Figure 10g) since they have heavily restacked into thick graphite-like flakes (Figure 10h). The ease of aggregation of flat sheets makes their properties, especially the surface area, extremely sensitive to their processing history. The flowchart in Figure 11 shows the specific surface areas of CMG powders after various treatments. The surface area of the graphene product was 407 m^2/g after thermal shock of a GO paper, which was reduced by 44% to 226 m^2/g after just one step of solution processing (i.e., dispersing and drying) in methanol. Pelletizing the product at 55 MPa eliminated 84% of its original surface area, resulting in a low value of only 66 m^2/g. In contrast, crumpled balls had consistently higher and much more stable surface areas after the same processing steps. This suggests that crumpled graphene balls can help to standardize the bulk CMG materials since their properties are now less dependent on the materials' processing history. The crumpled graphene balls shown here are not entirely made of single sheets. With pure single-sheet crumpled graphene balls, the surface area could approach 60% of the theoretical value of graphene.[37]

Since crumpled graphene particles can pack tightly without significantly losing accessible surface area, they offer two advantages over their flat counterparts in applications requiring high surface area such as energy storage and conversion.[14,16,38] First, their higher surface area leads to higher device performances. For example, microbial fuel cell electrodes modified with crumpled graphene particles generated significantly higher short-circuit currents and maximum power densities than those covered with regular sheet-like CMG.[36,39] Crumpled graphene particles are also

FIGURE 10. Crumpled graphene balls can resist aggregation even after pelletization. Panels a,b and c,d are SEM images showing the surface and cross-sectional morphologies of graphene pellets of crumpled particles and wrinkled sheets compressed at 55 MPa, respectively. (e,f) The pellet of crumpled graphene can be readily redispersed in water as individual particles by hand-shaking, while (g,h) the pellet of sheets cannot be redispersed even after sonication due to extensive aggregation.
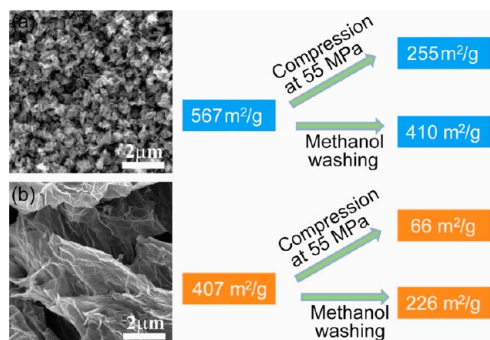
FIGURE 11. Evolution of the BET specific surface areas of (a) crumpled CMG particles and (b) heavily wrinkled sheets made by thermal shock after one step of solution processing or compression. The wrinkled sheets can resist overlapping initially but restack after washing or compression, as indicated by the significant decrease in surface area. In contrast, the crumpled graphene balls are much more resistant to aggregation.
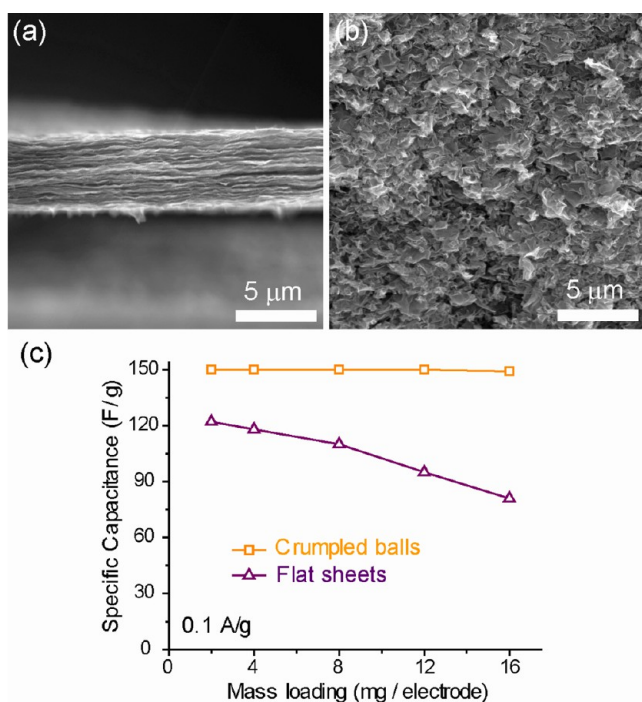

FIGURE 12. Effect of mass loading level on graphene-based ultracapacitors. (a,b) SEM images showing the cross-sectional morphology of graphene pellets made from flat sheets and crumpled particles, respectively. (c) Specific capacitance of the two types of graphene electrodes as a function of mass loading level at current density of 0.1 A/g.

an excellent catalytic support for inorganic nanoparticles[40] and can act as expandable coating for Si nanoparticle anodes in Li ion batteries.[41] Second, the aggregation-resistant property of crumpled CMG particles solves the scaling problem[42] encountered with sheet-like graphene, in which the device performance significantly decreases as the mass loading level increases. For example, to make ultracapacitors with high energy density, the active material

with high specific capacitance also needs to be used at high mass loading level. However, for sheet-like graphene materials (Figure 12a), higher loading levels lead to a higher degree of aggregation, decreasing the specific surface area and thus specific capacitance. Figure 12c shows that at low current rate of 0.1 A/g, the specific capacitance of flat graphene sheets decreases from 122 to 81 F/g when the electrode loading increases from 2 to 16 mg. In contrast, the specific capacitance of the crumpled graphene balls (Figure 12b) is not only higher (150 F/g) but also remains consistent as the loading level increases. At higher current rates, the difference between the performances of these two types of devices becomes even greater. This clearly illustrates the importance of making graphene resist aggregation in applications using bulk quantities of materials.

5. Conclusions and Outlook

To further the research and realize applications of CMG-based materials, material processing challenges must be overcome to let bulk materials retain single layer properties as much as possible or generate unique controllable, collective properties. Here we highlight a few material processing problems associated with the scaled-up production, high-throughput imaging, and ease of aggregation of CMG-based materials. To address these challenges, some solutions are provided including improved purification procedures to speed up the production of the CMG precursor GO and mitigate its potential fire risk, fluorescence quenching microscopy for rapidly screening of GO and CMG sheets on arbitrary substrates and even in solution, and aggregation-resistant CMG made with uniformly sized nanocolloids or crumpled sheets. We hope these new tools and strategies can help inspire new ideas that advance the field. Looking forward, perhaps applications of CMG will be limited by the manufacturing of GO. With many post-GO-synthesis material processing strategies highlighted here and reported elsewhere in place, greener and inexpensive strategies that allow scalable production of GO under chemically less harsh conditions but without significantly decreasing its processability, single layer yield, and lateral dimensions should be able to finally let GO and CMG to be used in commercial applications.

BIOGRAPHICAL INFORMATION

Jiayan Luo is a Ph.D. candidate in Materials Science and Engineering at Northwestern University. His current research focuses on designing graphene-based materials and energy storage. He is a recipient of the 3M Graduate Fellowship, the Ryan Fellowship in Nanoscience at Northwestern, the Chinese Government Award for Outstanding Students Abroad, and the Materials Research Society Graduate Student Gold Award.

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FOOTNOTES

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