3 Size Control Methods and Size-Dependent Properties of Graphene

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ABSTRACT
Graphene, one of whose lateral sizes is confined to being one-atom thick, has grabbed enormous attention ever since the discovery of this atomic thin layer of carbon crystal or polymer which was theoretically proved to be thermodynamically unstable. Size effects of the other two dimensions were then found and investigated. To precisely control the planar size of graphene and chemically convert graphene into nanoribbons or nanoshapes with regularity remains a challenge in this field. A few research groups including ours have pioneered some fundamental work on the size control of this atomic thin carbon layer, which we will summarize and expand in details here in this section. Meanwhile, variations in corresponding properties between different lateral sizes will be depicted. Furthermore, some unsolved problems preventing further progress will be illuminated and possible solutions to them will be given.

3.1 INTRODUCTION
When the lateral size of materials is reduced down to the critical size of nanoscale, the nanomaterials normally behave distinctly other than the bulk. For instance, quantum dots, the nanoscale semiconductor particles, emit photons with different wavelengths upon the same excitation. This intriguing variation is termed as the small size effect. Unlike semiconductors, graphene behaves as zero-band gap semiconductor due to the huge $\pi$ system in the basal plane which can greatly facilitate the carrier mobility. The massless carriers, Dirac fermions, can move without scattering as long as there is no confinement at the boundaries. Measurements show graphene has room-temperature mobilities of $10^4 \text{ cm}^2\text{s}^{-1}\text{V}^{-1}$. Meanwhile, an unusual half-integer quantum Hall effect (QHE) for both electron and hole carriers in graphene has been observed by adjusting the chemical potential using the electric field effect. In addition, graphene is highly transparent, with an absorption of only $\sim 2.3\%$ per layer toward visible light. Its thermal conductivity, $k$, is measured with a value of 5000 W mK$^{-1}$ for a single-layer sheet at room temperature. Graphene also possesses excellent mechanical strength. The intrinsic mechanical properties of free-standing monolayer graphene membranes were measured by nanoindentation under an atomic force microscope. The breaking strength was found to be 42 N m$^{-1}$ and Young’s modulus 1.0 TPa, indicating it is one of the strongest materials ever measured.

Till now, hundreds of papers have revealed a definite relationship existing between the properties and the morphologies of graphene, where the morphologies can be ascribed to both sizes and shapes. The sizes and shapes of graphene were shown dictating their electrical, optical, magnetic, and chemical properties. Ever since the finding of graphene by Novoselov et al., numerous papers had reported the methodologies to fabricate graphene with various sizes and morphologies as well as how its properties are governed by its different sizes and shapes. In this chapter, methods to obtain size-controlled graphene and several cases of graphene nanostructures with size-dependent properties will be discussed.
3.2 SIZE CONTROL METHODOLOGY

One prerequisite for specific practical use is the availability of graphene with appropriate sizes. A few efficient pathways have been established and applied to certain areas such as devices fabrication, biomaterials, and so forth. Effective methods to control the size and shape of graphene are initially summarized in Table 3.1 together with their advantages and disadvantages, which will be expanded on later. Graphene with different sizes and shapes will also be discussed and it will be elaborated how their given size is related to concerned properties.

3.2.1 NANO SCALE CUTTING

Sonication is widely used to disperse nanoparticles and cut nanomaterials down to nanorange in liquid media. Acoustic waves in liquids can generate small cavitation bubbles; the cavitation bubble nuclei then quickly grow through rectified diffusion and coalescence. After reaching a critical size, these bubbles collapse violently, creating a strong hydrodynamic flow field in the surrounding liquid. This phenomenon, known as cavitation, can explain the efficiency of sonication in disrupting nanoparticle aggregates and even at exfoliating or cutting nanomaterials. Sonication to reduce the size of graphene oxide (GO) was shown to be remarkably useful. With the initial GO size of $1.573\, \mu m$, 4 min of horn sonication (~400 W) can reduce the lateral size (LS) down to an average size of 400 nm. Continual sonication brings the size reducing effect further till a size limit is reached at about 170 nm, whose tendency is shown in Figure 3.1. The $\ln(\text{LS}/\text{nm})$ function (LS stands for lateral size) was further shown to depend on the $\ln(t/\text{min})$ which is in line with the equation

$$
\ln \left( \frac{\text{LS}}{\text{nm}} \right) = 6.53 - 0.36 \ln \left( \frac{t}{\text{min}} \right)
$$

Surprisingly, the sonication method can also be used to produce graphene nanoribbons (GNRs), as reported by Li et al. As schematically shown in Figure 3.2, they firstly exfoliated commercial expandable graphite by 60-s heating to 1000°C to form gas (3% hydrogen in argon). The resulting exfoliated graphite was dispersed in a 1,2-dichloroethane (DCE) solution of poly($m$-phenylenevinylene-$co$-$2,5$-dioctoxy-$p$-phenylenevinylene) (PmPV) by sonication for 30 min to form a homogeneous suspension. Centrifugation was done to remove large pieces of materials from the supernatant. The GNRs were solution phase-derived, stably suspended in solvents with noncovalent polymer functionalization, and exhibited ultrasmooth edges with possibly well-defined zigzag or armchair-edge structures. Electrical transport experiments showed that, unlike single-walled carbon nanotubes (CNTs), all of the sub-10-nm GNRs produced were semiconductors and afforded graphene field-effect transistors with on-off ratios of about $10^7$ at room temperature.

Yet sonication methods inevitably loosely control the aspect of size distribution as revealed by the long error bar of each data point in Figure 3.1a. Normally, it is hard to narrow the

### TABLE 3.1

<table>
<thead>
<tr>
<th>Method</th>
<th>Defect Degree</th>
<th>Repeatability</th>
<th>Damage</th>
<th>Size Control</th>
<th>Layer Control</th>
<th>Shape Control</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanoscale cutting</td>
<td>Low</td>
<td>Good</td>
<td>Low</td>
<td>100 nm$^{-1}$ mm</td>
<td>No</td>
<td>Yes</td>
<td>9,10</td>
</tr>
<tr>
<td>Chemical control</td>
<td>Medium</td>
<td>Poor</td>
<td>Medium</td>
<td>10–100 nm</td>
<td>No</td>
<td>No</td>
<td>11–18</td>
</tr>
<tr>
<td>Chemical synthesis</td>
<td>Low</td>
<td>Good</td>
<td>N/A</td>
<td>10 nm–100 μm</td>
<td>Yes</td>
<td>Yes</td>
<td>19–24</td>
</tr>
<tr>
<td>Differential separation</td>
<td>High</td>
<td>Good</td>
<td>Very low</td>
<td>10–100 μm</td>
<td>No</td>
<td>No</td>
<td>31</td>
</tr>
<tr>
<td>Density gradient separation</td>
<td>High</td>
<td>Good</td>
<td>Very low</td>
<td>5 nm–5 μm</td>
<td>Yes</td>
<td>No</td>
<td>35,37</td>
</tr>
</tbody>
</table>

**FIGURE 3.1** (a) The lateral size of aqueous GO in the function of sonication duration time under the power of ~400 W. Then the initial size of GO is approximately 1.573 μm. (b) The log of lateral sizes of GO based in e is found having a linear relationship with that of the duration of sonication. The slope is $-0.36$ and 6.53 for the intercept. (Unpublished data of the authors of this chapter.)
distribution as well as to achieve a desirable shape. To control the shape more precisely without compromising the surface chemistry, the diamond-edge-induced nanotomy technique was developed. The sharp diamond knife can cut graphene into graphite blocks of nanoscale with designed shapes; and then, those graphite blocks are intercalated by solvent and exfoliated forming graphene, which was pioneered by Berry et al. Schematically shown in Figure 3.3, the diamond edge is kept perpendicular to the graphene planes of the highly oriented pyrolytic graphite (HOPG), which is subsequently cleaved via C-C bond stretching and crack formation in the direction of cleavage. Depending on the desired shape/size, the HOPG is cut several times, at controlled thicknesses and in different directions to produce graphite nanostructures of defined dimensions and shape. By this method, various kinds of graphene with desirable shape and size can be fabricated, including nanoribbon, -square, -rectangle, and -triangle. Results showed that the edges of the produced graphene nanostructures were straight and relatively smooth with an I_D/I_G of 0.22–0.28 and a roughness <1 nm. Further, thin films fabricated from ribbons exhibited a band gap evolution with width reduction (0, 10, and ~35 meV for 50, 25, and 15 nm width, respectively). Along with the effectiveness of achieving designed shape and size, another advantage of the nanotomy technique is providing a size precisely without compromising the surface.

3.2.2 Chemical Control

The one-atom thin graphene, all of whose atoms are on the surface, is very reactive and sensitive when exposed to oxidants or metal catalysts. Oxidants like oxidative acids are frequently used, including H_2SO_4, HNO_3, HMnO_4, and HIO_4. Pan et al. have reported a facile approach for cutting graphene into surface-functionalized zero-dimensional graphene quantum dots (GQDs) under sonication in mixed acids of H_2SO_4 and HNO_3. The functionalized GQDs of approximate 9.6 nm mean size were found to exhibit ~430 nm bright blue photoluminescence (PL), which has never been observed in bigger graphene nanostructures.

The size and the edge structure of GO can also be tailored by the oxidation of periodic acid. The edges were verified to be dominant quinone structures. Under the same excitation wavelength of 365 nm, samples of S1, S2, S3, and S4, whose mean size are respectively 43, 22, 13, and 8 nm, displayed a strong emission peak and the peak shifted from 550 nm of S1, 526 nm of S2, 488 nm of S3 to 470 nm of S4, indicating a size-dependent PL behavior. However, when the lateral size of GQDs reduces down to less than 5 nm and GO is gets fully oxidized, their PL properties become constant, as shown in Sun’s report. GQDs with different sizes afforded similar PL, which may due to the contained similar small aromatic domains. The domain size was inhomogeneous and ranged from small aromatic molecules to large macromolecular domains. The former was responsible for fluorescence in the visible range, while the latter gave PL in the IR range. Fujii and Enoki reported a simple approach to produce nanosized graphene on the basis of chemical oxidation followed by cutting of the sheet using a scanning probe microscopic (SPM) manipulation technique. The linear defects present in GO were observed to have a spacing of 5–10 nm and a length of >100 nm, which resulted from the linear arrangement of epoxide functional groups. The cutting experiments are directly performed on graphene sheets and cutting is initiated by a point contact between the preoxidized sheet and the atom force microscope (AFM) probe. The local mechanical stress caused by the point contact leads to rupture of the sheet, which proceeds linearly along the linear defect of the epoxide groups. They further noticed that the cut edge shape could have a well-defined alignment along the zigzag direction, which is based on a theoretical prediction that the linear epoxide groups have preferential alignment along a zigzag direction in the graphene lattice.

A systematic study of strain-induced breakage of graphene was promoted by Wang and Ding. They used ab initio calculations to demonstrate that graphene could be cut into graphene nanoribbon, -rectangle, and -triangle on oxidation with the assistance of a uniaxial external tensile strain. The external strain is used to break the symmetry of the graphene honeycomb lattice and is applied along two directions: armchair (AM) and zigzag (ZZ). They found with external strain that the 90° epoxy chain has the highest binding energy and the 0° has the lowest. Further they claimed that there is an energetically preferred orientation for the epoxy chains on graphene if an external uniaxial strain is applied, indicating that linear defect formation resulting from linear epoxy chain was favorable and may benefit cutting graphene into nanostructure of desirable shape and size.
Excepting oxidants, metal atoms and nanoparticles that are intimate with carbon can also be used for cutting preoxidized graphene into well-defined shapes. Typically, Ni nanoparticles were first deposited on HOPG plates by a dip-drawing process. Afterward, the sample was annealed at 500°C in Ar/H₂ flow (normally 1300 sccm, 15 vol% hydrogen) for 1 h, and then the temperature was immediately increased up to the cutting set point (850–1000°C). By applying a multistage cutting, they could obtain ribbons, rectangle, rhomboid, and triangle. Experimental observations and theoretical analysis indicate that the cutting directions in the graphene planes can be controlled by the size of the metal particles, in principle allowing graphene pieces to be cut with discrete armchair or zigzag edges. It is also observed several turns for the channels during cutting. All the angles for these turns are 120°, or 60°. This indicates that the particles move, while cutting, along symmetric directions along the graphene lattice. This catalyst cutting method provides a feasible pathway to fabricate size-, shape-, and edge structure-controllable graphene nanostructures, which may accelerate their usage in electronic devices.

Shape-controlled graphene, especially one-dimensional (1D) GNR, can be alternatively fabricated by unzipping a diameter-selected CNT. Unzipping multwalled CNTs by plasma etching of nanotubes partly embedded in a polymer film, Jiao et al. proposed a facile approach to obtain GNRs with smooth edges and controllable widths with relative high yields (Figure 3.4a through f). The GNRs have smooth edges and an arrow width distribution (10–20 nm). Raman spectroscopy and electrical transport measurements reveal the high quality of the GNRs. The average $I_D/I_G$ values were, respectively, 0.38, 0.30, and 0.28 for the single-, bi-, and trilayer GNRs with 10- to 20-nm widths. Unzipping CNTs with well-defined structures in an array allow the production of GNRs with controlled widths, edge structures, placement, and alignment in scalable fashion for device integration. By using gas-phase oxidation, pristine few-layer nanoribbons can be produced by unzipping mildly gas-phase oxidized multiwalled CNTs using mechanical sonication in an organic solvent. The nanoribbons are of very high quality, with smooth edges, low ratios of disorder to graphitic Raman bands, and very high electrical conductance and mobility (up to 5 e² h⁻¹ and 1500 cm² V⁻¹ s⁻¹ for ribbons 10–20 nm in width).

### 3.2.3 Chemical Synthesis

Precise control over graphene is highly demanded nowadays because it is crucial for probing their fundamental physical properties and introducing them in promising applications.
Considering practical uses that need repeatability and scalability, bottom-up graphene synthesis with precise control over sizes and chemical compositions has an indispensable position in the fabrication of fine graphene nanostructures. Remarkable progress on chemical vapor deposition (CVD) graphene synthesis has been achieved in the last 10 years.\textsuperscript{19} To date, Zhang et al.\textsuperscript{20} developed a new method to grow uniform small graphene directly on various substrates, such as insulators, semiconductors, and even metals, without using any catalyst, as visually and graphically depicted in Figure 3.4. The growth was carried out using a remote plasma enhancement chemical vapor deposition (r-PECVD) system at relatively low temperature. Scanning tunneling microscopy (STM) confirmed that the films are made up of nanocrystalline graphene particles of tens of nanometers in lateral size.

Liu et al.\textsuperscript{21,22} reported a CVD approach that allowed the direct synthesis of uniform single-layered, large-size (up to 10,000 \(\mu\)m\(^2\)), spatially self-aligned, and single-crystalline hexagonal graphene flakes (HGFs) by using liquid copper as the substrate (Figure 3.5). These HGFs showed an average two-dimensional resistivity of 609 \(\pm\) 200 \(\Omega\) and saturation current density of 0.96 \(\pm\) 0.15 mA/\(\mu\)m, demonstrating their good conductivity and capability for carrying high current density. Size control could be achieved by differing the annealing temperature and time to vary the nucleation distribution and density.

Müllen et al. devoted much effort to the atomically precise synthesis of nanographene and GNRs for decades. Nanographene and GNRs of various sizes and shapes have been obtained in bulk scale, thus offering an opportunity for additional solution/vacuum processing and device fabrication. The bottom-up synthesis of graphene was initiated through the versatile organic chemistry of polycyclic aromatic hydrocarbons (PAHs).\textsuperscript{23,24} By far, the largest synthesized nanographene molecule consists of 222 carbon atoms with a disk diameter of 3.2 nm, while one of the smallest has a size of approximately 1.4 nm.\textsuperscript{25} By appropriately choosing the synthetic units, normally the high-molecular-weight oligophenylene precursors, we can obtain various types of graphene nanostructure: the triangle, the ribbon, and Chevron-like shape.

### 3.2.4 Post Synthesis Separation (Chemically Converted Graphene)

#### 3.2.4.1 Differential Separation

Differential separation comes up as one time-efficient and low-cost way to get graphene sheets with wide size distribution. The sedimentation rate of particles in a medium with given density \(\rho_m\) and viscosity \(\eta_m\), in a centripetal force field \(g'\), can be described as\textsuperscript{27}

\[
U = \frac{2g'(\rho_p - \rho_m)(r + t)^2}{9\eta_m}
\]  

(3.2)

Here \(r\) denotes the radius of the core particle, \(t\) is the thickness of the solvated shell,\textsuperscript{28} and \(\rho_p\) denotes the apparent density of the particle. Equation 3.1 indicates that the colloid
sedimentation rate $U$ depends on both the colloid core radius $r$ (that is why large particles sediment faster than small ones) and the properties of the medium ($\rho_p$ and $\eta_m$). The density difference between $\rho_p$ and $\rho_m$ is the dominant term. The particles stop sedimentation when they reach the medium of the same density (i.e., $\rho_p - \rho_m = 0$). This is how we estimate the apparent density of colloids by differential separation. As long as the graphene, mostly chemically converted graphene (CCG), can be solvated by given solvents such as the polar solvents like water (H$_2$O), N-methyl-2-pyrrolidone (NMP), and dimethyl formamide (DMF), or the nonpolar solvents like tetrachloromethane (CCl$_4$) and cyclohexane, those graphene derivatives can be sorted by adjusting separation rate and time. After combining the solvated shell and balancing the buoyancy, graphene will sedimentate down to the bottom if the buoyancy cannot match the centrifugal force; or they will stay where the buoyancy matches the centrifugal force, forming the supernatant. The CCG staying in the supernatant is definitely more easily solvated than the remnant left in the bottom. Further, the ability of contacting solvents or being solvated by them will diversify their applications. This strategy is almost universally available for all kinds of CCG. For the case of low oxidized GO, they normally have a very thin solvated shell, which means they can be easily separated from the liquid phase. All we need is to adjust the rate to a lower level in order to achieve a smaller centrifugal force.\textsuperscript{29} The above-mentioned separation is based on the neutral aqueous system. If CCG has very small $I_D/I_G$, we should use other solvents to alter the aqueous system. For instance, NMP and DMF, two very strong polar solvents, are capable of solving small $I_D/I_G$ CCG and sorting CCG according to their size when combining differential separation. Now that buoyancy is highly related to the solvated shell, the overall separation effect should be influenced by thinning or expanding the solvated shell like adjusting the pH value.\textsuperscript{30}

By analyzing the zeta potentials of GO with two kinds of sizes under varied pH values, Shi et al.\textsuperscript{31} found that there existed a certain pH range at which two kinds of GO (Figure 3.6), f1 and f2, had right opposite zeta potential, which means f1 the small GO remains soluble while f2 the big GO is protonated so f2 can be easily expelled from the suspension. Meanwhile, they found f1 had more oxygen content than f2. This size effect inherited into the Langmuir–Blodgett (LB) film and greatly influenced the films’ resistance and transmittance; higher oxygen content leads to higher sheet resistance. Because of lower oxygen content in bigger GO, the LB film fabricated from f2 showed to have lower resistance and higher transmittance. Generally speaking, the differential separation methods are effective and of low cost as long as we do not put too much emphasis on the precise size distribution. Besides, they fit the practical usages well due to the scalable production of CCG with rough size distribution. Yet there are some occasions that need precise control of the size distribution, aiming at more advanced research. Then we should probably use a modified version of differential separation, that is, density gradient separation (DGS).
3.2.4.2 Density Gradient Separation

3.2.4.2.1 Zonal Centrifugation

By using a differential separation, rough size distributions can be achieved by either a one-step or multistep separation process. For more precise cases, the researchers may turn to DGS, which originate from the separation of biomacromolecules. Once this method was transplanted to sort inorganic nanomaterials, hundreds of investigated cases had shown this strategy effective for nearly all nanocrystals including zero-dimensional FeCo@C, gold nanoparticles, CdSe nanodots, 1D CdS nanorods, CNTs, and of course, 2D CCGs. Schematically shown in Figure 3.7, gradients of different densities are first layered bottom up. Then the analyst suspension with appropriate solvent is placed on top of the gradients. Once the centrifugation begins, the analyst particles start to move down to the bottom. The larger and heavier particles have a higher sedimentation rate after balancing the centrifugal force against buoyancy and viscous drag. Higher density and viscosity could slow down the smaller graphene sheets while allowing larger and heavier sheets to pass through.

FIGURE 3.6 Separation of graphene oxide by adjusting pH value. Size of graphene oxide can greatly affect properties of GO, such as resistance and transparency. (Reprinted with permission from Wang, X., Bai, H., and Shi, G. Size fractionation of graphene oxide sheets by pH-assisted selective sedimentation. J. Am. Chem. Soc. 133(16): 6338–42. Copyright 2011 American Chemical Society.)

FIGURE 3.7 Schematic illustration of the mechanism of DGUR separation of CMG sheets with different sizes. (Reprinted with permission from Sun, X. et al. Monodisperse chemically modified graphene obtained by density gradient ultracentrifugal rate separation. ACS Nano 4(6): 3381–9. Copyright 2010 American Chemical Society.)
In the case of CCG, the apparent density of the CCG is highly dependent on both the sheet size and the degree of solvation. The apparent density of the CCG is given by the following formula:

$$\rho_p = \frac{1 + (\rho_s - 1)}{[1 + (t/r)]^2(1 + 2(t/h))}$$  (3.3)

Equation 3.3 indicates how the density difference between CCGs allows separation: when the CCG sheets are large \((r^\uparrow)\) or multilayered \((h^\uparrow)\), the apparent density increases and promotes sedimentation. As the solvation degree increases, it results in the solvated shell thickening \((t^\uparrow)\), so that the apparent density of the CCG decreases, which results in the colloids being retained in the upper gradient layers. Given appropriate separation time and rate, particles with different sizes will stop at a corresponding layer of gradient with the matchable buoyancy, viscosity, and centrifugal force. The more the gradient layers, the higher resolution of the analyst’s size, and also, more uniform the morphology of analysts will be.

Sun et al.\(^{35}\) systematically conveyed a study of CCGs upon DGS. Environment-friendly sucrose–water solutions with different densities and viscosities were used as the gradients. The as-made gradients and the uppermost analyst layer were centrifuged at 50,000 rpm for 15 min, and consequently, CCGs were separated into different zones along the centrifuge tube. Different fractions were collected after centrifugation and characterized to have a lateral size variation error of less than 5%. Besides, uniform morphology was found by AFM (Figure 3.8). The XPS spectrum of f30 showed a much weaker C–O peak (at ca. 286.5 eV) than upper fractions like f10 or that reported for GO.\(^{36}\) This corresponds to a reduced number of epoxide and hydroxyl functional groups in the former, that is, a lower degree of oxidation (Figure 3.9b and d). Differences in extent of chemical functionalization also induced significant differences in fluorescence properties. F5 was the only fraction showing strong PL in the visible range, which is consistent with the presence of GO sheets with extremely small size and a high degree of oxidation.\(^7\) After UV–vis curves being normalized to the absorbance of the peak around 230 nm, UV–vis curves of different fractions showed a clear tendency that the ratio of absorbance intensity at 400 nm to that at 800 nm (Abs\(_{400\text{ nm}}\)/Abs\(_{800\text{ nm}}\)) decreased markedly with fraction number increasing, that is, the surface state of different fractions varied much with different sizes, which came from the variation of oxidation degree (Figure 3.9a and c).

### 3.2.4.2.2 Isopycnic Centrifugation

Isopycnic centrifugation, a DGS branch, is an effective pathway for separating graphene of low defect according to their layer numbers, proved by Hersam et al.\(^7\) Sodium chloride (SC) was first mixed with graphene aqueous solution to reach a SC concentration of 2% w/v, then the suspension was horn-sonicated to force SC to attach onto the graphene surface and intercalate into graphene interlayers. Collective data about thickness histograms of graphene fractions as well as the concentrated and sedimented graphene dispersions is comprehensively shown in Figure 3.10a and b. Compared to the sediment and concentrated graphene, f4 showed a much more sharpening distribution in thickness. Meanwhile, f4 contained nearly 80% single-layered graphene in contrast with 20% for f16 and 5% for f28. A buoyant density model of few-layered SC-encapsulated graphene was established (Figure 3.10c). A flake of thickness \(N\) is coated by a surfactant with packing density \(\sigma\) and effective thickness \(t_s\) and a hydration layer of thickness \(t_h\). The resulting buoyant density \(\rho(N)\) is then\(^{37}\)

$$\rho(N) = \rho_s N + 2m_{sc}\sigma + 2\rho_{H_2O}t_h \frac{(N + 1)t^r + 2t_s + 2t_h}{(N + 1)t^r + 2t_s + 2t_h}$$  (3.4)

where \(\rho_s = 7.66 \times 10^{-8} \text{ g cm}^{-2}\) is the sheet density of graphene, \(m_{SC} = 7.15 \times 10^{-22} \text{ g}\) is the mass of one SC molecule, and \(\rho_{H_2O}\) is the density of water. Further analysis of DGS of the SC-encapsulated graphene yield graphene sheets with mean thicknesses (i.e., layer numbers) that increase as a function of their buoyant density.

### 3.3 SIZE-DEPENDENT PROPERTIES OF GRAPHEME

Starting from graphene and CNT, different types of \(sp^2\) graphitized carbon networks can be fabricated: nanoribbons,\(^{14,17,18,38–41}\) dots,\(^{7,11–13}\) nanomeshes,\(^{42,43}\) and other designed
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FIGURE 3.9 (a) UV–vis absorption spectra of GO in different fractions showing in Figure 3.13. (b, d) XPS spectra of f10 and f30 GO fractions. (c) Ratio of absorption at 400 nm to that at 800 nm of GO in different fractions. (Reprinted with permission from Sun, X. et al. Monodisperse chemically modified graphene obtained by density gradient ultracentrifugal rate separation. ACS Nano 4(6): 3381–9. Copyright 2010 American Chemical Society.)

FIGURE 3.10 (a) Mean flake thickness histograms for sedimented, concentrated, and DGU fraction f4 graphene solutions calculated using AFM. (b) Mean flake thickness histograms plotted by relative frequency (mode thickness scaled to unity) for DGU fractions f4, f16, and f28. (c) Buoyant density model for SC-encapsulated graphene in which a flake of thickness \( N \) is coated by a surfactant with packing density \( \sigma \) and effective thickness \( t_A \) and a hydration layer of thickness \( t_H \). (d) Fit of the geometrical density model to the experimental data. The uncertainty in graphene flake thickness was taken as the full-width at half maximum (FWHM) of the flake thickness distribution. (Reprinted with permission from Green, A. A. and Hersam, M. C. Solution phase production of graphene with controlled thickness via density differentiation. Nano Lett. 9(12): 4031–6. Copyright 2009 American Chemical Society.)
shapes. These graphene nanstructures are expected to possess distinct electrical and optical properties because of the variation in size and geometry and the confinement in specific dimensions. Meanwhile, edge structure and heteroatom dopant may also influence the final performance. With the decreasing of size, confined behavior of graphene gradually occurs. The electronic sea model was substituted with an electronic “lake” model, charge carriers became confined in certain areas enclosed by the defective boundaries. Resistance between sheets rises sharply owing to the high binding energy as well as the impediment over the charge carrier crossing the boundaries. Therefore, sp² domain size can dramatically influence the properties of graphene.

### 3.3.1 Zero-Dimensional Graphene (Quantum Dots)

Unlike 1D and 2D confinement of graphene by forming nanoribbons and small graphene sheets, the electrons in these graphene nanostructures can be strictly confined in a very small dot called GQD. The zero-dimensional GQDs can be carved from graphene as reported by Novoselov et al. or oxidized from carbon fiber by electrochemical methods. Quantum dot devices were then fabricated by Novoselov et al. based on the as-obtained GQDs. They found the electron transfer in these devices behaved like chaotic neutrino billiards. At large sizes (>100 nm), they behave as conventional single-electron transistors, exhibiting periodic Coulomb blockade peaks. For quantum dots smaller than 100 nm, the peaks become strongly nonperiodic, indicating a major contribution of quantum confinement.

Small size GO is a functionalized graphene and an important precursor for GQDs and other CCG. Dai et al. proposed a kind of GQD with high oxidation degree and given size distribution, which possessed excellent aqueous solubility. The modified small GO was first sorted to obtain GO of appropriate size by DGS and found to exhibit PL. With further functionalization of polyethylene glycol, those very small GO can be compatible for physiological conditions. Therefore, fluorescent GO can be used as an indicator in physiological conditions (Figure 3.11). Anticancer drugs were loaded onto nanographene oxide (NGO) with high capacity and selectively transported into specific cancer cells by antibody-guided targeting. Meanwhile, small GO can not only emit PL but also strongly absorb NIR light.

By utilizing the strong optical absorbance of NGS in the near-infrared (NIR) region, we can use nanosize NGS in vivo photothermal therapy. First, GO were polyethylene glycosylated (PEGylated) to gain better solubility and biological compatibility. Then NGO–PEG was sorted by zonal DGS (Figure 3.12). Specific size is the key to guarantee long-term circulation in the vessel, and proper functionality can facilitate better absorb NIR light. Results showed that ultraefficient tumor ablation can be achieved after intravenous administration of NGS and low-power NIR laser irradiation on the tumor. New fur grew right on the spot of old tumor’s location. Those mice using NGO–PEG photothermal therapy can survive for another 40 days while the others in the control experiments all died with no exception (Figure 3.13). The graphene-based in vivo photothermal therapy, if combined with chemotherapeutic drugs also delivered by NGS as demonstrated in our

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earlier in vitro work, could bring novel opportunities to the next generation of combined cancer treatment.

Pan et al. have developed a hydrothermal route for cutting preoxidized graphene sheets into GQDs (9.6 nm in average diameter) with blue emissions. The blue luminescence and newly forming UV–vis absorption bands at 320 nm (Figure 3.14c) are directly induced and affected by the edge state. When pH is switched between 13 and 1, pH-dependent PL properties can be reversibly achieved (Figure 3.14).

By reducing the size of GO, GQDs with strong fluorescence emission can be obtained. The optical properties can be further tuned by chemical reduction. Shen et al. proposed a hydrazine hydrate reduction of GO method or the fabrication of GQDs with upconverted emission. Zhuo et al. presented


![FIGURE 3.13](image-url) In vivo photothermal therapy study using intravenously injected NGS–PEG. (a) Tumor growth curves of different groups after treatment. The tumor volumes were normalized to their initial sizes. There were 6 mice in the untreated, 10 mice in the “laser only,” 7 mice in the “NGS-PEG only,” and 10 mice in the “NGS-PEG + laser” groups. While injection of NGS-PEG by itself or laser irradiation on un.injected mice did not affect tumor growth, tumors in the treated group were completely eliminated after NGS-PEG injection and the followed NIR laser irradiation. (b) Survival curves of mice bearing 4T1 tumor after various treatments indicated. NGS-PEG injected mice after photothermal therapy survived over 40 days without any single death. (c) Representative photos of tumors on mice after various treatments indicated. The laser irradiated tumor on NGS injected mouse was completely destructed. Error bars in (a) were based on standard deviations. (Reprinted with permission from Yang, K. et al. Graphene in mice: Ultrahigh in vivo tumor uptake and efficient photothermal therapy. Nano Lett. 10(9): 3318–23. Copyright 2010 American Chemical Society.)
a facile ultrasonic method to prepare GQDs, which exhibited bright PL in an aqueous solution. Most interestingly, the as-prepared GQDs possessed excitation-independent downconversion and upconversion PL properties. The PL spectra showed a strong peak at 407 nm. By taking advantage of superb optical and electrical properties, GQDs can expand their use in many hot fields like: in vivo tracking,7 fuel cells,45 solar cells,49 and so on.

3.3.2 One-Dimensional Graphene Nanoribbons

Small graphene nanostructures with various kinds of edges functionalization have attracted tremendous attention due to the convenience of changing their edges and basal planes. Carriers in two-dimensional small graphene are typically confined. Their behaviors can be further confined in one-dimensional systems by creating GNRs. The GNRs could exhibit different edge geometries including zigzag and armchair and mix types, which will determine their electronic structures and the properties. Particularly, narrowing the width of GNRs and heteroatom-doped edges will lead the band gap formation, which will make them suitable for applications in semiconductor devices. However, the band gap of GNRs will decrease with increasing ribbon width.50

Fujita et al. have discussed the effect of the system size and edge shape on the special edge state by varying the width of the graphene ribbons.51 They found that the nanoscale size effect is crucial for determining the edge state. They also had extended the GNRs to have different edges, which was defined as a mixture of zigzag and armchair sites. Such an edge shape with three or four zigzag sites per sequence is sufficient to show an edge state when the system size is on a nanometer scale. They also found that the special characteristics of the edge state play an important role in determining the density of states near the Fermi level for graphite networks on a nanometer scale.51 If the width goes larger than 10 nm, GNRs will again behave like a metallic ribbon.

Yang and Murali52 characterized the impact of line width scaling on GNR transport. GNR mobility is found to be severely limited by line-edge roughness (LER) scattering for width < 60 nm. While a mobility of more than 3000 cm2 V−1 s−1 can be achieved for width > 60 nm, the value decreases to less than 200 cm2 V−1 s−1 for width < 20 nm. This trend agrees well with the expected impact of LER-limited mobility.

3.3.3 Two-Dimensional Graphene Nanosheets

Single-layer GO can be viewed as an unconventional type of soft material and has recently been recognized as a promising material for composite and electronics applications. It is of both scientific and practical importance to know how these atomically thin sheets assemble and by what interaction an individual sheet can form a desirable infrastructure. Bulk sources for making GO are abundant as long as the original materials have a high degree of graphitization. For instance, GO can be derived from graphene nanofiber and

FIGURE 3.14  (a) UV–vis absorption (ABS) and PL (at 320 nm excitation) spectra of the GQDs dispersed in water; UV–vis absorption (ABS) spectrum of oxidized GSs. Inset: Photograph of the GQD aqueous solution taken under visible light. (b) PL spectra of the GQDs at different excitation wavelengths. (c) PLE spectrum with the detection wavelength of 430 nm and PL spectrum excited at 257 nm. Inset: Photograph of the GQD aqueous solution taken under UV light in a fluorescence spectrophotometer. (d) pH-dependent PL spectra when pH is switched between 13 and 1. (Pan, D. et al.: Hydrothermal route for cutting graphene sheets into blue-luminescent graphene quantum dots Adv Mater. 2009. 22(6). 734–8. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)

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show uniform size distribution, as reported by Huang et al. Size variation of this kind of GO can be facilely achieved by controlling the oxidation time. All of this GO was shown to be capable of dispersing graphitized carbon materials with less functional groups in water using the undamaged zone of GO as the hydrophilic part and the functionalized zone as the hydrophobic part. Even reduced GO (RGO) sheets are stable under a wide range of pH values with the help of this kind of uniform GO. They also show promising dispersing ability toward the insoluble, aromatic SWCNTs, without causing any hazards. By varying the ratio of the hydrophilic and hydrophobic zones, the capability of dispersing carbon materials into either aqueous or oil solution can be achieved.

By applying the edge-to-edge electrostatic repulsion, monolayer GO aqueous dispersion can be readily formed. Meanwhile, the undisturbed area of GO induce each other by aromatic sp² region, causing a face-to-face interaction. The strong edge-to-edge and the weak face-to-face interactions lead to 2D monolayer assembly when the GO solution was induced to the air–liquid interface, that is, an LB film can be formed. Surface roughness, film porosity, and packing density of the LB film may dictate the properties of the film. These characters are highly related to GO’s size, which has been reflected in Shi’s research, and also GO’s functionality, which can be semiempirically analyzed by XPS, XRD, and Raman spectroscopy. By controlling the size and the functionality of precursive GO, we can create a large-area monolayer GO film via the LB assembly technique. These GO films are important precursors for graphene-based electronics applications.

### 3.4 SUMMARY AND PROSPECT

Although many methods, including nanoscale-cutting, chemical oxidation, and bottom-up synthesis, have been effective for narrowing the size distribution of chemically converted graphene, a scalable and general strategy to obtain high-quality size-controlled graphene nanostructures still needs to be sought by extensive study. Further research can be focused on how to functionalize graphene with specific size distribution in certain dimensions while keeping them highly conductive or luminescent. Besides, fabricating a hierarchical graphene network for practical applications is also an important issue.

### REFERENCES