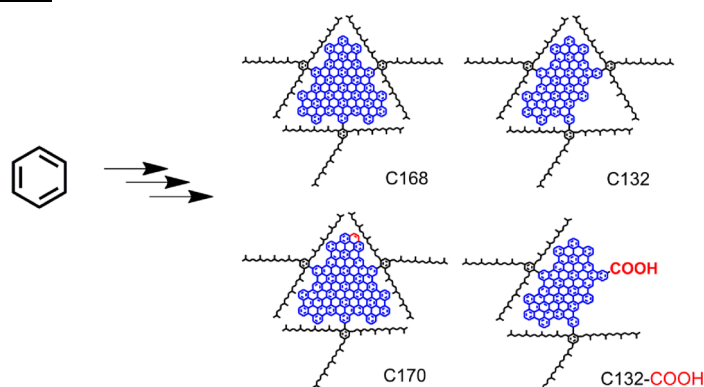


Colloidal Graphene Quantum Dots with Well-Defined Structures

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CONSPECTUS



When the size of a semiconductor crystal is reduced to the nanometer scale, the crystal boundary significantly modifies electron distribution, making properties such as bandgap and energy relaxation dynamics size dependent. This phenomenon, known as quantum confinement, has been demonstrated in many semiconductor materials, leading to practical applications in areas such as bioimaging, photovoltaics, and light-emitting diodes.

Graphene, a unique type of semiconductor, is a two-dimensional crystal with a zero bandgap and a zero effective mass of charge carriers. Consequently, we expect new phenomena from nanometer-sized graphene, or graphene quantum dots (QDs), because the energy of charge carriers in graphene follows size-scaling laws that differ from those in other semiconductors. From a chemistry point of view, graphene is made of carbon, an element for which researchers have developed a whole branch of chemistry. Thus, it is possible to synthesize graphene QDs through stepwise, well-controlled organic chemistry, achieving structures with an atomic precision that has not been possible for any other semiconductor materials.

Recently, we developed a new solubilizing strategy that led to synthesis of stable colloidal graphene QDs with more than 100 conjugated carbon atoms, allowing us to study their properties in a new size regime. In this Account, we review our recent progress working with the colloidal graphene QDs, including their synthesis and stabilization, tuning of their properties, and new phenomena in energy relaxation dynamics. In particular, we have observed extraordinarily slow “electron cooling”—the relaxation of electrons from high excited states to lower ones. With further investigation, these high-energy electrons could potentially be harvested in solar energy applications, for example, creating more efficient photovoltaic cells.

We discuss additional emerging opportunities with these new materials and current challenges, hoping to draw the interest of researchers in various fields to overcome these obstacles.

Introduction

Nanometer-sized semiconductor crystals, or “quantum dots”, have been intensively investigated in the past decades for their novel properties resulted from quantum confinement.^{1–5} Colloidal semiconductor quantum dots (QDs) made of solution chemistry, in particular, not only can be made with tightly controlled size and shape in large

quantities,⁵ but also can readily interface with other active components for complex functions, leading to practical applications in bioimaging, photovoltaics, and light emitting diodes. Graphene, a zero-bandgap semiconductor, provide further opportunities to explore size-induced properties that are unique in many aspects. Especially, bulk graphene is a two-dimensional crystal and has

charge carriers with zero effective masses at band edges. As a result, energy of carriers in graphene follows scaling laws with respect to size that are different from those in other semiconductors. From a chemistry point of view, graphene is primarily made of carbon atoms which can adopt various geometries when forming chemical bonds. Therefore, on one hand, synthesis of colloidal graphene QDs requires well-defined chemistry, and on the other hand it is possible to synthesize graphene QDs through stepwise, well-controlled organic chemistry to achieve structures with atomic precision that has not been possible for any other semiconductor materials.

Chemically graphene belongs to the family of polycyclic aromatic hydrocarbons; and there has been a long history of making larger conjugated compounds by fusing smaller aromatic compounds.^{6,7} Previous work, most notably by Müllen and co-workers, has demonstrated versatile chemistry to achieve large aromatic compounds⁷ (containing up to 222 conjugated carbon atoms⁸) with excellent yield. However, the strong tendency of the compounds to aggregate turns them into intrinsically graphite, altering their electro-optical properties and preventing systematic studies of their properties. It was not until the development of a new solubilizing strategy⁹ that stable colloidal graphene QDs could be synthesized with more than 100 conjugated carbon atoms,¹⁰ making it possible to study properties of polycyclic aromatic hydrocarbons in a new size regime.

Colloidal graphene QDs with well-defined structures provide unique opportunities to study the evolution of properties with size in a two-dimensional crystal, and may lead to useful applications. In addition, since more complex carbon materials including graphite, activated carbon, carbon fibers, and carbon black have been widely used for various purposes ranging from electronics to catalysis, colloidal graphene QDs could serve as a model system for mechanistic studies and lead to a better understanding of these complex materials. In this Account, we discuss our recent progress with colloidal graphene QDs and the emerging opportunities. We also outline challenges in the research of these new materials, hoping to draw the interest of researchers in various fields to overcome these obstacles.

Stabilization of Colloidal Graphene Quantum Dots

Stabilization of graphene is an integral part of graphene synthesis because unstabilized graphene forms graphite. Even though remarkable progress has been made in forming carbon–carbon bonds and making extended conjugated

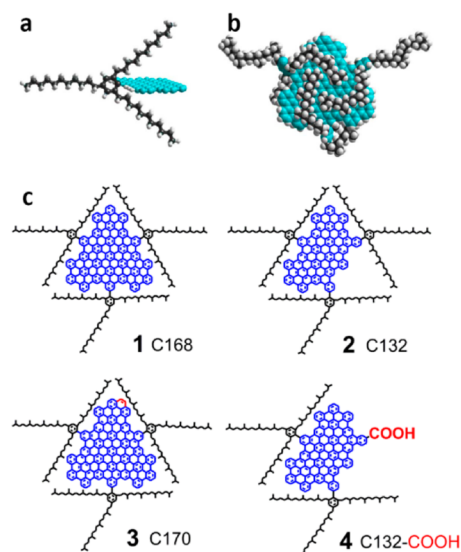


FIGURE 1. Solubilization of colloidal graphene quantum dots. (a) A 2',4',6'-trialkylphenyl moiety (black) is covalently attached to the edges of the graphene (blue) so that the crowdedness on the edges forces the peripheral phenyl groups to twist from the plane of the graphene, resulting in the alkyl chains at 2',6'-positions extending out of the plane and the one at 4'-position extending laterally. (b) An energy-minimized geometry of graphene QD **1** (in c), showing the "caging" around the graphene core (blue) by the alkyl chains (black) in three dimensions. (c) Structures of examples of colloidal graphene QDs synthesized so far, with the graphene core containing 168, 132, 170, and 132 conjugated carbon atoms. The structures of the QDs are controlled with stepwise solution chemistry so that they have excellent size uniformity. (Adapted with permission from refs 9, 10, 16. Copyright 2010, 2011 American Chemical Society.)

systems,⁷ the rapidly decreasing solubility of graphenes with increasing size poses a tremendous challenge for the solution-chemistry approach to large graphene nanostructures. A traditional strategy to solubilize conjugated systems is lateral attachment of flexible side chains, which has been very successful in solubilizing small graphene molecules. The affinity between solvents and the flexible chains overcomes intergraphene attraction, resulting in the graphenes to be entropically pushed apart. However, since the maximum number of the flexible side chains and thus the chain-solvent interaction scales with perimeter of the graphenes ($\sim a$, with a being the diameter) while the intergraphene attraction scales with area ($\sim a^2$), for graphenes with increasing size the intergraphene attraction rapidly overtakes the solubilization forces, making the traditional strategy less and less effective.

We recently developed a new solubilization strategy for large graphene QDs by creating a three-dimensional "cage" around the graphene core.^{9,11} This was based on covalent attachment of multiple 2',4',6'-trialkylphenyl moieties to the periphery of the graphene (Figure 1). The crowdedness on the edges forces the peripheral phenyl groups to twist from

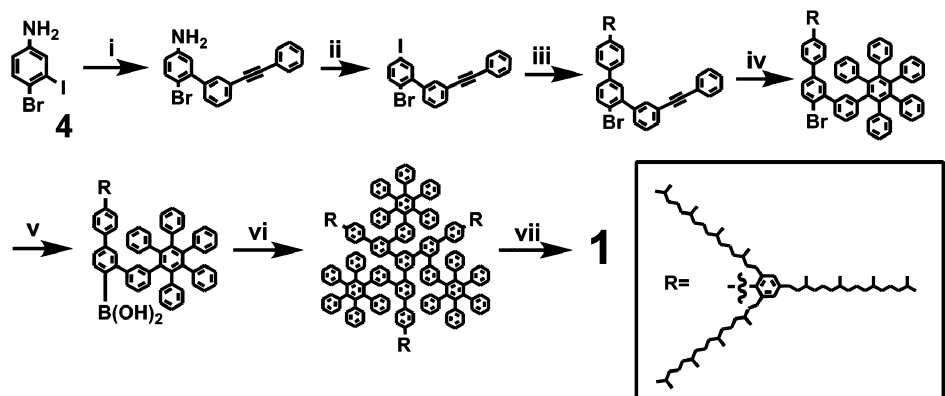


FIGURE 2. Synthetic route for colloidal graphene QD **1**. The QD is synthesized with stepwise organic reactions and has excellent size uniformity. Conditions: (i) 3-(phenylethynyl)phenylboronic acid, Pd(PPh₃)₄, K₂CO₃, toluene, EtOH, H₂O, 80 °C (94%); (ii) I₂, *t*-butyl nitrite, benzene, 5 °C (54%); (iii) 4-(2',4',6'-trialkylphenyl)phenylborate, Pd(PPh₃)₄, K₂CO₃, toluene, EtOH, H₂O, 80 °C (92%); (iv) tetraphenylcyclopentadienone, diphenyl ether, reflux (61%); (v) (a) *n*-BuLi, THF, −78 °C, (b) B(*i*-PrO)₃, (c) HCl, H₂O (60%); (vi) 1,3,5-triiodobenzene, Pd(PPh₃)₄, K₂CO₃, H₂O, toluene, 80 °C (52%); (vii) FeCl₃, CH₂Cl₂, CH₃NO₂ (100%). (Adapted with permission from ref 10. Copyright 2010 American Chemical Society.)

the plane of the graphene, resulting in the alkyl chains at 2', 6'-positions extending out of the plane and the one at 4'-position extending laterally. This leads to increased inter-graphene distance in all three dimensions, and greatly reduces the short-ranged intergraphene attraction.¹² This approach is reminiscent of the well-known intercalation of graphite,¹³ in which inserting atoms or molecules between graphene layers significantly reduces the interlayer binding energy.

With the new solubilization approach, we have demonstrated synthesis of stable graphene QDs that contain 132, 168, and 170 conjugated carbon atoms (**1–3** in Figure 1c).¹⁰ They were synthesized from small aromatic compounds through stepwise organic reactions (e.g., synthesis of QD **1** shown in Figure 2) and have excellent size uniformity. The intermediates to the QDs are purified with chromatography and confirmed with standard organic characterization techniques. In the last step, a polyphenylene dendrimer precursor is oxidized to fuse the phenyl rings, leading to the graphene QDs, which are then purified with repetitive precipitation and dissolution. To ensure the solubility of the final products, the dendrimeric precursors have the solubilizing trialkylphenyl groups preinstalled. The resultant QDs are highly soluble in common solvents such as chloroform and toluene. Dynamic light scattering shows that the QDs are dispersed in forms of reversible oligomers, indicating the presence of residual intergraphene attraction in solution despite the introduction of the solubilization groups.⁹

Tuning Properties of Graphene Quantum Dots

The tight structural control enabled by solution chemistry offers us unique opportunities to control the properties of graphene QDs for various purposes. As is well established

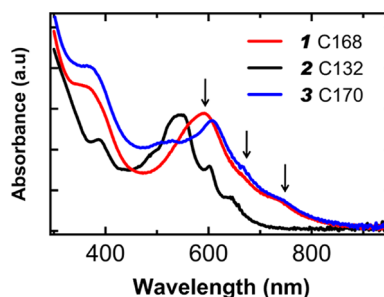


FIGURE 3. UV-vis absorption spectra of graphene QDs **1–3** in toluene. Marked by arrows are the α , p , and β bands of **1** (right to left). The α and p transitions, which in **1** are only weakly dipole-allowed due to the high molecular symmetry, are significantly more pronounced in **2** and **3** as the symmetry reduces; and the β transition that is doubly degenerate in **1** appears as two separate bands in **2** or **3** since the reduced symmetry lifts its degeneracy. (Reproduced with permission from ref 10. Copyright 2010 American Chemical Society.)

for other semiconductor nanoparticles,⁵ size and shape are important parameters for graphene nanostructures as well. By changing size and shape, in principle, we can tune the bandgap of graphene from 0 eV (bulk material) to ~ 6 eV (benzene), a wide range that is not possible in any other semiconductor materials. Further, unique to graphenes are parameters such as edge geometry^{14,15} and functionalization¹⁶ that can be explored to tune their properties.

An example for the edge-dependence of the graphene QD properties is the symmetry effect imposed by the edge geometry that determines selection rules of electronic transitions.¹⁰ Figure 3 shows the UV-vis absorption spectra of QDs **1–3**, demonstrating the edge-dependence of the intensity and degeneracy of the lowest-energy electronic transitions (traditionally labeled as α , p , and β bands in ascending order,^{17,18} marked with arrows in Figure 3).

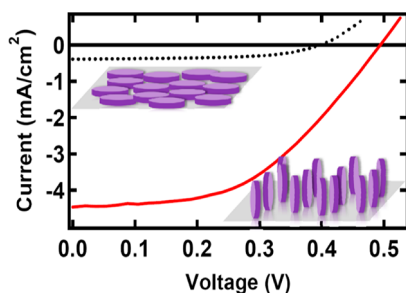


FIGURE 4. Current–voltage characteristics of solar cells sensitized by QDs **1** (dotted curve) and **4** (solid curve) under a simulated AM 1.5 Global light. For the devices, the electrolyte solution was composed of 0.02 M iodine, 0.04 M lithium iodide, 0.5 M 1,2-dimethyl-3-hexylimidazolium iodide, and 0.5 M *tert*-butylpyridine that was dissolved in acetonitrile. The insets illustrate the orientation of the QDs on TiO₂ cathode surfaces, with the QDs represented by the disks.

Remarkably, the two carbon atoms **3** has (marked red in Figure 1) more than **1** change the molecular symmetry, causing an effect disproportionate to the number of the extra atoms. This level of structural control in graphene so far can be achieved only with solution chemistry.

We have further demonstrated that bandgaps and redox potentials of graphene QDs can be independently tuned, the former by size and the latter by functionalization.¹⁶ With increasing size, as expected from quantum confinement, the graphene QDs have smaller bandgaps. Attaching electron-withdrawing functionalities such as carboxylic acids (e.g., QD **4** in Figure 1) to the peripheries of the QDs suppresses their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels simultaneously relative to the vacuum level, thus changing their redox potentials. By comparing the experimentally determined HOMO and LUMO energy levels with those calculated with tight-bind (TB) calculations, we showed that the TB calculations could satisfactorily reproduce the experimental values,¹⁶ providing a simple tool to predict the bandgap and redox potentials of the graphene nanostructures.

The independent tuning of bandgap and redox potential of graphene QDs is especially useful for optoelectrical applications such as solar energy conversion or light emitting diodes, where the bandgap determines the light that can be harvested or emitted while the redox potentials dictate charge transfer processes.⁹ The attachment of functional groups can also be taken advantage of to control the interaction between the graphene and other active components in the devices. For example, our research group has applied colloidal graphene QDs as sensitizers in dye-sensitized solar cells.⁹ When we used **4** (Figure 1) as the sensitizer, much greater energy conversion efficiency was

observed than that of devices sensitized by **1** despite the larger bandgap of **4** (Figure 4). This was partly because the carboxylic acid group in **4** leads to the QDs aligning vertically (i.e., “edge-on”) on cathode (i.e., TiO₂) surfaces.¹⁹ This results in higher sensitizer packing density than the “face-on” orientation **1** adopts on surfaces. Further, the covalent binding between **4** and the TiO₂ surface due to the “edge-on” geometry also leads to much faster electron transfer when the sensitizers are photoexcited; whereas with the “face-on” geometry the charge transfer occurs through space and is less efficient.

Electronic Structures and Energy Relaxation Dynamics in Graphene Quantum Dots

To describe their electronic and optical properties, it is natural to compare the graphene QDs with other semiconductor QDs.^{1–4,11,20} In semiconductor QDs, the electronic energy levels are dictated by quantum-size energy E_q caused by quantum confinement, carrier–carrier Coulombic interaction E_C , and exchange interaction E_X . In QDs of semiconductors with massive carriers confined in three dimensions, the scaling of the three terms versus the diameter of the QDs a follows: $E_q \sim (h^2/8m^*a^2) \sim 1/a^2$, $E_C \sim (e^2/4\pi\epsilon a) \sim 1/a$, and $E_X \sim 1/a^3$, where m^* is the effective mass of the carriers, h is Planck's constant, e is the charge of an electron, and ϵ is the dielectric constant of the semiconductor. In contrast, because of the dimensionality of graphene and its massless carriers, within the zeroth-order approximation, the scaling for graphene QDs is $E_q \sim (v_F h/2a) \sim 1/a$, $E_C \sim 1/a$, and $E_X \sim 1/a^2$, where $v_F \approx 10^6$ m/s is the Fermi velocity in graphene.²¹ By assuming a dielectric constant of 1 for graphene,²² we obtain $E_q/E_C \sim 1$. Thus, E_q and E_C are equally important and excitonic effects are significant for graphene QDs of all sizes; whereas in very small particles of semiconductors with massive carriers the Coulombic interaction E_C is only a small correction to E_q or E_X . As an example, for a graphene QD with diameter of 2.0 nm, the Coulombic term $E_C \sim 0.8$ eV, much greater than those for CdSe or CdS,²⁰ and thus, distinct excitonic features can be readily observed spectroscopically at room temperature.

Graphene QDs share some important characteristics with small aromatic hydrocarbons and carbon nanotubes: they all consist of light atoms and have weak spin–orbit coupling.^{22,23} This results in electronic states with well-defined spin multiplicity. However, the energy difference between the two spin states (i.e., singlet–triplet splitting), determined by the exchange interaction, decreases with increasing size ($E_X \sim 1/a^2$). As a result, according to the

“energy-gap law” in radiationless energy relaxation,²⁴ the reduced singlet–triplet splitting enhances spin–orbit coupling and thus the coupling between the singlet and triplet manifolds.²⁵ In small polycyclic aromatic molecules ($a \sim 0.5$ nm), E_x is in the order of 1 eV.¹¹ For graphene QDs of a few nanometers in size, it is in the order of 100 meV, comparable to vibrational frequencies in the aromatic systems (e.g., stretching frequencies of C=C bonds ~ 1600 cm^{-1} or 200 meV). Thus, when vibronic coupling is considered, the singlet and triplet manifolds overlap significantly in energy, leading to enhanced intersystem crossing. This was experimentally observed in photoexcited graphene QDs of ~ 2.5 nm in diameter.²⁵ The singlet–triplet splitting was determined to be ~ 175 meV, and intersystem crossing is so efficient that it competes with internal conversion among the states with the same multiplicity. As a result, the QDs emit both fluorescence and phosphorescence at room temperature, with their relative intensity depending on the excitation energy.

Internal conversion rates in the graphene QDs are of great interest because, as in other quantum confined systems, the size-dependent, discrete excitonic levels could significantly slow down the relaxation of high excited states (i.e., “electron cooling”), a phenomenon known as “phonon bottleneck”.^{26–29} The reduced electron cooling rates could potentially enable the high-excited-state electrons to be harvested, for example, for solar energy utilization, and thus increase energy conversion efficiency. Recently, we have observed extraordinarily slow electron cooling (up to ~ 100 ps) in graphene QDs, 2 orders of magnitude slower than that in bulk graphene,³⁰ which we preliminarily attribute to the “phonon bottleneck”. Its exact origin, however, is still being investigated.

The slow electron cooling in the graphene QDs prompts us to search for other relaxation pathways that may be useful for solar energy utilization. For example, the high-excited-state electrons can potentially be extracted for electricity or solar fuel generation before their energy in excess to the bandgap gets dissipated and wasted in the form of heat, a phenomenon known as “hot-electron” transfer.³¹ In addition, the strong carrier–carrier interactions in the graphene QDs could lead to generation of more than one exciton with one photon absorbed, a process particularly useful for improving the efficiency of photovoltaics which is under debate.³²

Assemblies of Graphene Quantum Dots

Assemblies of semiconductor or metal nanoparticles, often considered as “artificial atoms”, not only provide a way to bridge nanoscale objects with macroscopic length scales,

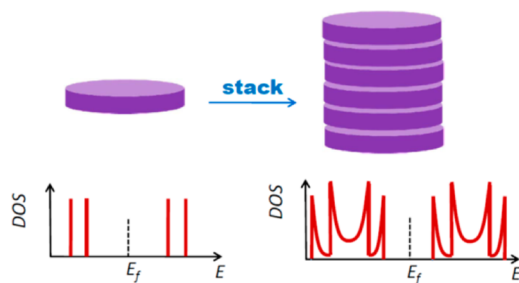


FIGURE 5. Evolution of electronic density of states (DOS) for a 0D system to a 1D system. The disks represent the graphene QDs which tend to stack into 1D “nanographite”. E_f represents the Fermi level of the semiconductors.

but also may give rise to novel properties due to interparticle coupling.³³ Since the colloidal graphene QDs are among the most structurally uniform semiconductor nanoparticles synthesized so far, their assemblies may enable some properties that would otherwise be impossible. It has been well established in solids that nonuniformity in constituent atoms or molecules can significantly alter the electron density of states and lead to dramatically different transport properties, a phenomenon known as Anderson localization.^{34,35}

Not only the structures of graphene QDs but also their interactions can be controlled with solution chemistry, drastically different from other nanoparticles where excluded volume mostly dictates the assembled structures. Previous work on discotic liquid crystalline phases of smaller aromatic compounds,^{36,37} for example, has demonstrated this versatility, leading to structural hierarchy from the molecular level to the macroscopic scale. This was shown to result in extraordinarily high charge mobilities for solution-cast semiconductor organic films.^{38,39} Similarly, we anticipate that the graphene QDs could form discotic liquid crystalline phases as well, containing one-dimensional (1D) superstructures (i.e., “nanographite”) that form a new type semiconductors. A simple picture based on a 1D atomic chain illustrates the evolution of the electronic density of states from a zero-dimensional (0D) character to a 1D one (Figure 5). The singularities in the density of states in the 1D system can profoundly affect its transport properties,^{40,41} a topic currently being investigated in our research group.

Model Systems for Complex Carbon Materials

Various carbon materials, including activated carbon, carbon fibers, carbon black, nanotubes, and graphene, have been widely used or studied for a wide range of applications. Notable examples are carbon-supported metal particles^{42–44} for, for example, catalysis, sensing, and fuel cells. More recently, heteroatom-doped carbon has drawn

enormous interest because it can catalyze reactions such as reduction of oxygen in fuel cells and oxidative dehydrogenation of hydrocarbons that are typically done with transition metals or metal oxides.^{45,46} However, due to the complexity and inhomogeneity of the carbon materials used, mechanistic studies of these processes have been difficult, preventing further improvement of these functions. In contrast, colloidal graphene QD have well-defined structures and properties and, thus, can provide model systems to study the more complex carbon materials. Their uniform, defect-free structures greatly simplify the interpretation of experimental results, and their high solubility in common solvents enables us to apply ensemble characterization techniques in the studies with great sensitivity.

We recently used the colloidal graphene QDs to study the interaction between metal nanoparticles and carbon supports.⁴⁷ Our goal was to understand the role of the carbon in carbon-supported metal particles used for various applications so that we could rationally improve these functions by modifying the carbon supports. In our studies, we observed formation and attachment of palladium nanoparticles on the colloidal graphene QDs. The metal–graphene interaction is sufficiently strong so that the Pd nanoparticles can be stabilized by the graphene QDs without the needs for extra stabilizing agents. In addition, infrared (IR) spectroscopy revealed the covalent nature of the interaction between the metal particles and the carbon surface, which had been proposed by density functional theory calculations yet never directly experimentally proven before.

To provide model systems to study heteroatom-doped carbon that has shown promising catalytic activities,^{45,46} we are currently developing doped colloidal graphene QDs with solution chemistry.⁴⁸ Well-defined doped QDs could provide homogeneous chemical environments for the catalysis and thus help elucidate the structures that are responsible for the catalytic activities.

Toward Graphene Nanostructures with Increasing Size and Tightly Controlled Structures

The solubilizing strategy we have developed naturally can be applied to much larger conjugated systems. Nevertheless, making solution-processable graphene structures that are significantly larger than a few nanometers with solution chemistry still remains a challenge. Obviously, this task encounters some fundamental challenges in synthetic chemistry,^{49,50} including the need to form a large number of

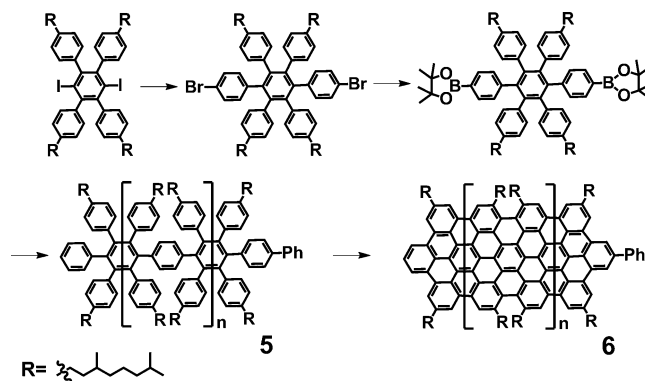


FIGURE 6. An example of previous work on synthesizing graphene nanoribbons with solution chemistry. Precursor polymer **5** is synthesized with Suzuki polycondensation, followed by oxidative dehydrogenation to yield the nanoribbons **6**. (Adapted with permission from ref 58. Copyright 2008 American Chemical Society.)

covalent bonds with high efficiency and to control the molecular shape against a quickly increasing conformational space. Thus, making these structures is fundamentally intriguing. Meanwhile this could lead to important applications due to the reduced bandgap of larger graphenes down to the infrared region and emerging transport properties as their sizes get larger.

The challenge in making larger graphene QDs is best illustrated in the synthesis of graphene nanoribbons, which broadly can be considered as elongated QDs. These elongated structures are of particular interest because of their nonzero bandgaps and their great potentials for high-precision microelectronics.^{51–53} Theoretical calculations have shown the properties of the nanoribbons depend not only on their widths but also on their edge structures.^{14,15} Therefore, solution chemistry holds a unique position since it could enable the large-scale synthesis of graphene nanoribbons with tightly controlled structures.

Chemically graphene nanoribbons belong to ladder polymers, which are often synthesized by intramolecular condensation reactions within single-stranded precursor polymers.^{50,54,55} With this approach, the lengths of the ladder polymers are determined by the lengths of the single-stranded precursor polymers, and the structural perfection of the ladder polymers is determined by the efficiency of the intramolecular condensation. Previous efforts to graphene nanoribbons have been focused on oxidative dehydrogenation of polymeric phenylene precursors, remarkably leading to nanoribbons with lengths reaching 60 nm.^{56–58} An example is shown in Figure 6. The precursor polymer **5** was synthesized with Suzuki polycondensation, which is subsequently subject to dehydrogenation to afford graphene nanoribbon **6**.⁵⁸

Previous work has revealed challenges and necessary steps for achieving structurally uniform graphene nanoribbons with lengths that can interface with lithographic techniques (e.g., ~100 nm). For example, to obtain long nanoribbons with the oxidative dehydrogenation approach developed by Müllen and co-workers,^{7,58} precursor polymers (e.g., **5** in Figure 6) should be synthesized with high molecular weight and carefully designed connectivity. To achieve a high molecular weight, the precursor polymers should be made from sterically unchallenging monomers^{56,58} with highly efficient reactions.⁵⁹ High solubility of the precursor polymers can be enormously helpful, so that in the course of the step-growth polymerization the low-weight intermediate can further react to increase the molecular weight.⁶⁰ To ensure a high yield in the subsequent oxidative dehydrogenation, the precursor polymers should have connectivity that avoids isomer formation due to either the various conformations of the precursors or rearrangement of phenyl groups.^{61,62} In addition, they should have readily accessible planar conformations, since the transition states for the products are likely to be near planar. For this purpose, templating techniques that prearrange the precursors in the planar geometries can obviously greatly facilitate the oxidation.⁵⁰ For these reasons, synthesis of nanoribbons of each size and structure requires careful planning from the very beginning, unlike nanostructures of other semiconducting materials where varying reaction conditions or reaction time is usually sufficient.⁵

Characterization of Graphene Nanostructures

Equally challenging in developing large graphene nanostructures is their structural characterization, as the graphene QDs we have made have already reached such a range that unambiguous structural characterization becomes difficult.^{9,11} While scanning tunneling microscopy (STM)⁵⁷ and transmission electron microscopy (TEM)⁶³ can determine graphene structures with atomic resolution on an individual basis, on an ensemble level currently there is not a single technique existing that can work to this effect. Therefore, multiple techniques, in combination with pre-existing knowledge about the graphene nanostructures, for example, obtained from their precursors and the chemical reactions involved, are necessary.

Because of the large size and the high rigidity of graphene nanostructures, many structural characterization techniques commonly used for organic or nanostructure characterization become ineffective.¹¹ In conventional liquid NMR techniques, the most important structural information for the

graphenes, contained in the aromatic proton resonance region that covers a narrow chemical shift range of ~2 ppm, is prone to suppression by peak broadening due to the slow tumbling of the graphenes and the fast spin–spin relaxation in the rigid structures. Dynamic aggregation of the graphenes in solution was also observed,⁹ further limiting the usefulness of these techniques. Elemental analysis of the graphenes suffers from incomplete combustion and the difficulty in determining the hydrogen content with sufficient accuracy. TEM techniques often used for screening semiconductor nanostructures are hindered by the low contrast from the carbon-containing graphenes, making it necessary to use large graphene sheets as the substrates for the imaging. In addition, since the properties of the graphene nanostructures are determined not only by their sizes and shapes but also by the edges, atomic resolution is necessary and thus TEM, as well as STM, becomes impractical for ensemble analysis.

High-resolution MALDI-mass spectroscopy (MALDI-MS) has been so far the best way to survey graphene QDs^{9–11} and in some cases nanoribbons⁵⁸ on the ensemble level. Within a certain mass range (typically for m/z in the order of 10 000 or smaller), isotope-resolved MALDI-MS spectra can be readily obtained experimentally and compared with simulated ones from proposed structures, yielding mass accuracy up to a fraction of an atomic mass unit. Since the species of concern are all large aromatics that differ little in structure, they are likely to have comparable ionization probabilities and thus MALDI-MS can yield a reasonable, yet not quantitative, estimate of the composition.

IR vibrational spectroscopy can provide important local structural information to prove or disprove graphene nanostructures derived from known precursors. Especially, aromatic C–H out-of-plane bending frequencies provide a fingerprint for identifying the substitution patterns of phenyl groups and thus the edges of the QDs.⁶⁴ It is particularly useful for highly symmetric graphene QDs with few functional groups (such as **1** in Figure 1) where the number of resonance peaks can confirm the molecular symmetry.⁹ For graphene QDs with lower symmetry or more functional groups, however, theoretical calculation of vibrational frequencies is necessary to assist with the structural determination, which is challenging because of the size of the systems. Raman spectroscopy also provides information related to the vibrational motion of graphene.⁶⁵ However, it is predominantly determined by motion of the highly polarizable conjugated carbon backbones, and is not sensitive to the edge geometry of graphene nanostructures.⁶⁶

Summary and Outlook

A new addition to quantum confined systems, colloidal graphene QDs are different from QDs of any other semiconductors in many aspects. Therefore, we expect many new phenomena to be discovered and possibly novel applications. With stepwise solution chemistry, it is possible to synthesize the graphene QDs with atom precision in large quantities. However, some challenges persist especially in synthesis of larger colloidal graphene nanostructures and their ensemble characterization, calling for the collective efforts of scientists in multiple disciplines. In a broader context, since graphene can be considered as the basic architecture for more complex graphitic carbon materials, including graphite, activated carbon, carbon fibers, carbon black, nanotubes, and so forth, which have played extremely important roles in our society, synthesis and investigation of well-defined graphene nanostructures could greatly enhance our understanding of the processes based on these complex carbon materials. Better understanding and control of these materials has enormous practical significance and undoubtedly could lead to new applications.

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BIOGRAPHICAL INFORMATION

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FOOTNOTES

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