J|A|C|S
COMMUNICATIONS

Synthesis of Large, Stable Colloidal Graphene Quantum Dots with Tunable Size

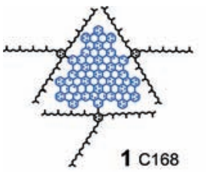
Xin Yan, Xiao Cui, and Liang-shi Li*

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

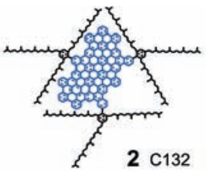
Received February 2, 2010; E-mail: li23@indiana.edu

Synthesis of colloidal semiconductor nanocrystals (or "quantum dots") with uniform sizes that approach bulk-material exciton Bohr radius played an important role in our understanding of quantum confinement.[1] It has led to various practical applications in bioimaging,[2a−c] lasing,[2d−f] photovoltaics,[3a−c] and light emitting diodes.[3d−f] Graphene, consisting of a single atomic layer of graphite, is a unique type of zero band gap semiconductor with an infinite exciton Bohr radius due to a linear energy dispersion relation of the charge carriers.[4] As a result, quantum confinement could take effect in graphenes of any finite size and is expected to result in many interesting phenomena not obtainable in other semiconductor materials.[5] However, in comparison with conventional semiconductors, the synthesis of graphene quantum dots is less developed. The increasing face-to-face attraction between graphenes with increasing size leads to rapidly decreasing solubility, which has seriously limited the sizes achievable for stable colloidal graphene nanostructures and prevented systematic studies of quantum confinement in them.[6]

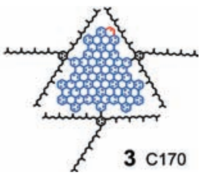
Here we report the synthesis of large colloidal graphene quantum dots with a uniform and tunable size, e.g., **1**−**3**, through solution chemistry. They consist of graphene moieties containing 168, 132, and 170 conjugated carbon atoms, respectively, and are the largest stable colloidal graphene quantum dots reported so far. Our work is based on oxidative condensation reactions developed by Scholl, Müllen, and others,[6a,7] with a new solubilization strategy recently developed in our research group.[8] The oxidation of polyphenylene dendritic precursors that were synthesized through stepwise solution chemistry led to fused graphene moieties. The stabilization of the resultant graphenes is achieved by multiple 2′,4′,6′-triakyl phenyl groups covalently attached to the edges of the graphene moieties. The crowdedness on the edges of the graphene cores twists the substituted phenyl groups from the plane of the core, leading to alkyl chains closing the latter in all three dimensions. This results in reduced face-to-face interaction between the graphenes, thus effectively increasing their solubility and allowing us to make stable graphene quantum dots larger than previously achieved.



1 C168



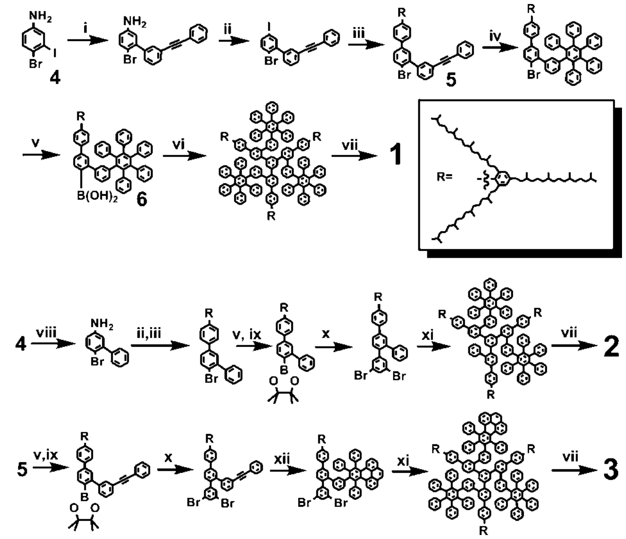
2 C132



3 C170

The synthesis of **1**−**3** is outlined in Scheme 1. We started from small-molecule precursors, such as 3-iodo-4-bromoaniline (**4**) and other substituted benzene derivatives, to synthesize two key intermediates **5** and **6** (details in the Supporting Information). Subsequent stepwise Suzuki coupling reactions led to polyphenylene dendritic precursors for **1**−**3**, which were then exposed to an excess of FeCl$_3$ in a dichloromethane/nitromethane mixture, yielding the graphene quantum dots. All the intermediates to the quantum dots were purified with silica gel chromatography and confirmed with standard characterization methods. To ensure good yields for the final products, the connectivity among the phenyl groups in the dendritic precursors was designed to avoid unwanted phenyl rearrangement under the oxidative conditions.[6a−c,8] The solubilizing trialkyl phenyl groups were installed prior to the oxidation, thus preventing aggregation of the final products when they were formed. The oxidation reactions were stopped by quenching with methanol after 2−3 h. Repetitive centrifugation, dissolution with toluene, and precipitation with methanol led to quantum dot **2** as a deep red and **1**, **3** as black waxy solids. Here the synthetic routes are derived from one we reported earlier that is applicable only for synthesizing highly symmetric quantum dots.[8] We have significantly improved it so that we can tune the properties of the graphenes by varying their symmetry, as well as increase the yield for **1**.

Scheme 1. Synthesis of Graphene Quantum Dots **1**−**3**[a]



[a] Conditions: (i) 3-(phenylethynyl)phenylboronic acid, Pd(PPh$_3$)$_4$, K$_2$CO$_3$, toluene, EtOH, H$_2$O, 80 °C; (ii) I$_2$, *tert*-butyl nitrite, benzene, 5 °C; (iii) 4-(2′,4′,6′-trialkylphenyl)phenylborate, Pd(PPh$_3$)$_4$, K$_2$CO$_3$, toluene, EtOH, H$_2$O, 80 °C; (iv) tetraphenylcyclopentadienone, diphenyl ether, reflux; (v) (a) *n*-BuLi, THF, −78 °C; (b) B(*i*-PrO)$_3$, (c) HCl, H$_2$O; (vi) 1,3,5-triiodobenzene, Pd(PPh$_3$)$_4$, K$_2$CO$_3$, H$_2$O, toluene, 80 °C; (vii) FeCl$_3$, CH$_2$Cl$_2$, CH$_3$NO$_2$; (viii) phenylboronic acid, Pd(PPh$_3$)$_4$, K$_2$CO$_3$, toluene, EtOH, H$_2$O, 80 °C; (ix) pinacol; (x) 1,3-dibromo-5-iodobenzene, Pd(PPh$_3$)$_4$, K$_2$CO$_3$, toluene, H$_2$O, EtOH, 60 °C; (xi) **6**, Pd(PPh$_3$)$_4$, K$_2$CO$_3$, toluene, H$_2$O, 80 °C; (xii) 1,3-diphenylcyclopenta[*e*]pyren-2-one, diphenyl ether, reflux.

Quantum dots **1**−**3** were identified with isotope-resolved mass spectroscopy (MS), indicating their excellent uniformity in size. They all are highly soluble in common organic solvents such as chloroform, toluene, THF, etc. However, with conventional liquid phase NMR spectroscopy no aromatic protons in **1**−**3** could be detected, presumably because of dynamic aggregation of the quantum dots in the NMR time scale. This is similar to soluble

10.1021/ja1009376

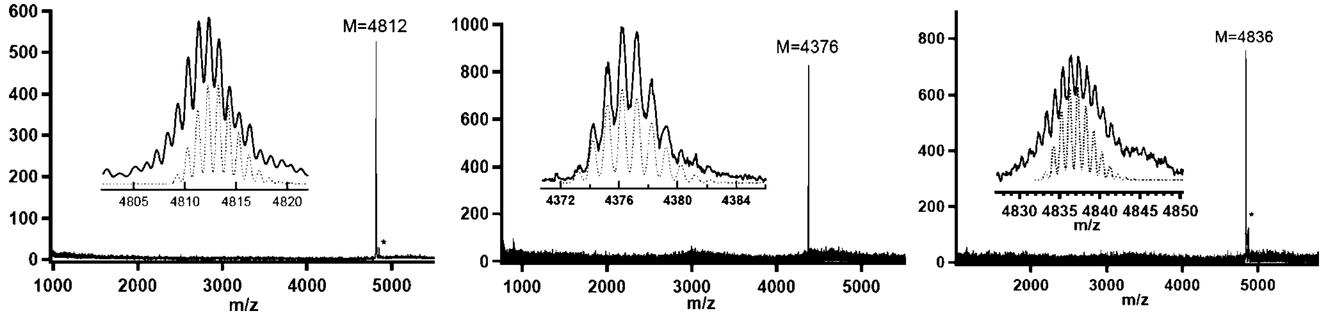


Figure 1. MALDI-TOF MS spectra of quantum dots **1**−**3** (left to right), respectively. In the insets are the isotope-resolved patterns experimentally measured (solid curves) with ones calculated (dotted curves) from the molecular structures of the quantum dots. In the spectra of **1** and **3**, the small peaks marked by asterisks are due to monochlorinated byproducts (M+34) in the last oxidation step.

nanographenes previously reported that contain fewer conjugated carbon atoms.[10a] As a result, isotope-resolved MS with mild ionization methods (e.g., MALDI-TOF) have been the only applicable techniques for ensemble characterization of large graphene nanostructures.[10] Figure 1 shows the MALDI-TOF MS results of **1**−**3**, respectively. The comparison with spectra calculated with the molecular formula of the quantum dots indicates the elimination of the desired numbers of hydrogen atoms during the oxidative condensation and the excellent size uniformity achieved in the quantum dots. The structure of **1** was further confirmed with infrared vibrational spectroscopy because of its high structural symmetry and therefore the easy interpretation of the spectrum.[8]

As expected **1**−**3** have size- and shape-dependent optical properties. Figure 2 shows their absorption spectra in dichloromethane. Because of their larger sizes **1** and **3** have absorption edges appearing at significantly longer wavelengths than **2**. In addition, all the spectra show α, *p*, and *β* bands in the order of increasing energy from the absorption edges (e.g., marked by arrows for **1** in Figure 2), a classic pattern observed in many polycyclic aromatic hydrocarbons.[11] The α and *p* transitions, which in **1** are only weakly dipole-allowed due to the high molecular symmetry, become significantly more pronounced in **2** as the symmetry reduces (details in the Supporting Information), and the *β* transition that is doubly degenerate in **1** appears as two separate bands in **2** or **3** since the reduced symmetry lifts the degeneracy.

Our work demonstrates the versatile synthesis of large, stable colloidal graphene quantum dots with desired sizes and structures enabled by a new solubilization strategy. Quantum dots **1** and **3** presented here, in particular, have large extinction coefficients (Figure 2) in a wide spectral range from UV to near-infrared and, thus, can serve as a new type of light harvesting media for photovoltaics.[8] We can further reduce the band gap of the graphenes by increasing their sizes and tune their redox potentials by chemical functionalization to tailor their properties for the devices. In addition, both theoretical and experimental studies have shown that novel electronic and magnetic properties may emerge as results of well-defined edge structures in graphenes.[5] Therefore the graphene quantum dots may see a wide range of applications in optoelectronics and molecular magnetism.

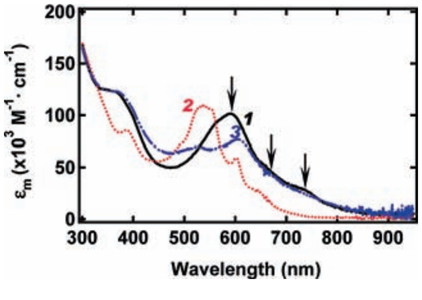


Figure 2. UV−vis absorption spectra of quantum dots **1**−**3** in solution. Marked by arrows are the α, *p*, and *β* bands of **1**, from right to left, respectively.

Acknowledgment. This work is supported by Indiana University and the National Science Foundation (Grant 0747751).

Supporting Information Available: Detailed procedure for synthesis and characterization of intermediates, IR spectra, and analysis of UV−vis absorption bands of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Brus, L. E. *Appl. Phys. A: Mater. Sci. Process.* **1991**, *53*, 465. (b) Efros, A. L.; Rosen, M. *Annu. Rev. Mater. Sci.* **2000**, *30*, 475. (c) El-Sayed, M. A. *Acc. Chem. Res.* **2004**, *37*, 326.

(2) (a) Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013. (b) Chan, W. C. W.; Nie, S. M. *Science* **1998**, *281*, 2016. (c) Alivisatos, A. P.; Gu, W.; Larabell, C. *Annu. Rev. Biomed. Eng.* **2005**, *7*, 55. (d) Klimov, V. I.; Mikhailovsky, A. A.; Xu, S.; Malko, A.; Hollingsworth, J. A.; Leatherdale, C. A.; Eisler, H. J.; Bawendi, M. G. *Science* **2000**, *290*, 314. (e) Eisler, H. J.; Sundar, V. C.; Bawendi, M. G.; Walsh, M.; Smith, H. I.; Klimov, V. *Appl. Phys. Lett.* **2002**, *80*, 4614. (f) Kazes, M.; Lewis, D. Y.; Ebenstein, Y.; Mokari, T.; Banin, U. *Adv. Mater.* **2002**, *14*, 317.

(3) (a) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* **2002**, *295*, 2425. (b) Nozik, A. J. *Physica E* **2002**, *14*, 115. (c) Gur, I.; Fromer, N. A.; Geier, M. L.; Alivisatos, A. P. *Science* **2005**, *310*, 462. (d) Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P. *Nature* **1994**, *370*, 354. (e) Coe, S.; Woo, W. K.; Bawendi, M.; Bulovic, V. *Nature* **2002**, *420*, 800. (f) Tessler, N.; Medvedev, V.; Kazes, M.; Kan, S. H.; Banin, U. *Science* **2002**, *295*, 1506.

(4) (a) Geim, A. K.; Novoselov, K. S. *Nat. Mater.* **2007**, *6*, 183. (b) Geim, A. K. *Science* **2009**, *324*, 1530.

(5) (a) Nakada, K.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. *Phys. Rev. B* **1996**, *54*, 17954. (b) Son, Y. W.; Cohen, M. L.; Louie, S. G. *Phys. Rev. Lett.* **2006**, *97*, 216803. (c) Iyengar, A.; Luo, T.; Fertig, H. A.; Brey, L. *Phys. Rev. B* **2008**, *78*, 235411. (d) Wang, X. R.; Li, X. L.; Zhang, L.; Yoon, Y.; Weber, P. K.; Wang, H. L.; Guo, J.; Dai, H. J. *Science* **2009**, *324*, 768. (e) Fernandez-Rossier, J.; Palacios, J. J. *Phys. Rev. Lett.* **2007**, *99*, 177204. (f) Wang, W. L.; Meng, S.; Kaxiras, E. *Nano Lett.* **2008**, *8*, 241. (g) Ritter, K. A.; Lyding, J. W. *Nat. Mater.* **2009**, *8*, 235.

(6) (a) Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718. (b) Simpson, C. D.; Brand, J. D.; Berresheim, A. J.; Przybilla, L.; Rader, H. J.; Müllen, K. *Chem.—Eur. J.* **2002**, *8*, 1424. (c) Wu, J. S.; Tomovic, Z.; Enkelmann, V.; Müllen, K. *J. Org. Chem.* **2004**, *69*, 5179. (d) Sakamoto, J.; van Heijst, J.; Lukin, O.; Schlüter, A. D. *Angew. Chem., Int. Ed.* **2009**, *48*, 1030.

(7) (a) Scholl, R.; Mansfeld, J. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1734. (b) Rempala, P.; Kroulik, J.; King, B. T. *J. Am. Chem. Soc.* **2004**, *126*, 15002.

(8) Yan, X.; Cui, X.; Li, B.; Li, L.-S. *Nano Lett.* (Accepted).

(9) Ormsby, J. L.; Black, T. D.; Hilton, C. L.; Bharat; King, B. T. *Tetrahedron* **2008**, *64*, 11370.

(10) (a) Tomovic, Z.; Watson, M. D.; Müllen, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 755. (b) Yoshimura, K.; Przybilla, L.; Ito, S. J.; Brand, J. D.; Wehmeir, M.; Rader, H. J.; Müllen, K. *Macromol. Chem. Phys.* **2001**, *202*, 215. (c) Przybilla, L.; Brand, J. D.; Yoshimura, K.; Rader, H. J.; Müllen, K. *Anal. Chem.* **2000**, *72*, 4591.

(11) (a) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: London, 1964; Vol. 1. (b) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970.

JA1009376