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Bottom-Up Fabrication of Photoluminescent Graphene Quantum Dots with Uniform Morphology

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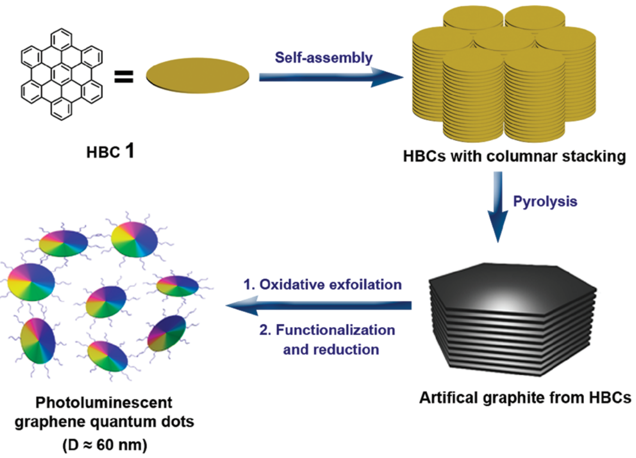
Supporting Information

ABSTRACT: Multicolor photoluminescent graphene quantum dots (GQDs) with a uniform size of ~60 nm diameter and 2−3 nm thickness were prepared by using unsubstituted hexa-*peri*-hexabenzocoronene as the carbon source. This result offers a new strategy to fabricate monodispersed GQDs with well-defined morphology.

Graphene, a two-dimensional (2D) honeycomb network of sp^2-hybridized carbon atoms, has received much attention because its unique properties, including high surface area, electronic conductivity, and mechanical stability, make it very attractive in physics, chemistry, and material science.[1,2] It has been both theoretically predicted and experimentally proved that the morphology of graphene sheets, including their size, shape, and thickness, can effectively determine their properties.[3−5] For instance, graphene sheets smaller than 100 nm, generally called graphene quantum dots (GQDs),[4] possess strong quantum confinement and edge effects, which make them excellent materials for the construction of nanoscaled optical and electronic devices. To fabricate GQDs, Novoselov et al. used high-resolution electron-beam lithography to carve graphene crystallites to desired sizes;[4] this method is limited by the requirement for special equipment and an extremely low yield. On the other hand, GQDs with sub-10 nm diameter were prepared from large graphene oxide (GO) sheets via a hydrothermal route,[6,7] a reoxidization method,[8] or an electrochemical avenue.[9] However, these approaches involve a nonselective "top-down" chemical cutting process, which does not allow precise control over the morphology and the size distribution of the products. Alternatively, cyclodehydrogenation of polyphenylene precursors can lead to GQDs with uniform shape through solution chemistry,[10,11] but these GQDs are usually smaller than 4 nm, which is below the processable scale of state-of-the-art lithography technology (10 nm). Very recently, Loh et al. reported the fabrication of geometrically well-defined GQDs by the cage-opening of fullerene on ruthenium surfaces.[12] However, a solution-processable and scalable method toward monodispersed GQDs with precisely tailored morphology and size ranging from 10 to 100 nm is still lacking.

Scheme 1. Processing Diagram for the Preparation of Photoluminescent GQDs by Using HBC (1) as Carbon Source



Hexa-*peri*-hexabenzocoronene (HBC) and other large polycyclic aromatic hydrocarbons (PAHs) are generally regarded as nanoscaled fragments of graphene.[10] Similar to graphene, these large PAHs have high thermal stability and a strong tendency to stack with each other via $\pi-\pi$ interactions. Recently, our group prepared a series of unprecedented carbon materials by the pyrolysis of structure-defined aromatic molecules.[13−15] The composition, degree of graphitization, and physical and chemical properties of these materials can be easily tuned by the selection of pyrolysis conditions and precursors with different aromatic frameworks. Inspired by these results, we envision that the fabrication of GQDs by controlled pyrolysis of large PAHs could be experimentally feasible.

Herein, we report for the first time the preparation of monodispersed disk-like GQDs of ~60 nm diameter and 2−3 nm thickness with unsubstituted HBC (**1**, Scheme 1) as precursor by a process of carbonization, oxidization, surface functionalization, and reduction. To the best of our knowledge, these graphene disks are the largest GQDs reported so far. Optical property characterization indicates that the resultant GQDs possess a high photoluminescence (PL) efficiency of 3.8%, which make these graphene nanodisks promising candidates for biolabeled carriers and nanodevices.

In this work, **1** was synthesized conveniently by the gram-scale cyclodehydrogenation of commercially available hexaphenylbenzene with high purity (Supporting Information). The wide-angle X-ray scattering (WAXS) pattern for the as-made powder of

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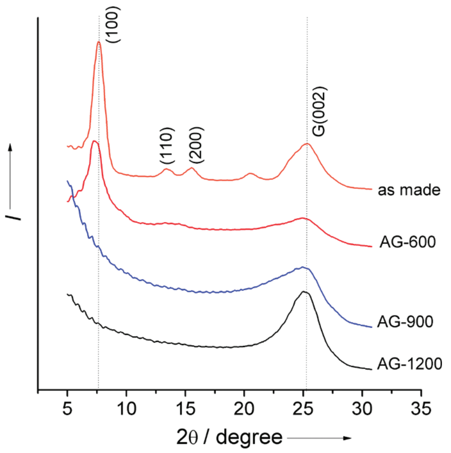

Figure 1. WAXS patterns of as-made HBC, AG-600, -900, and -1200.

1 (Figure 1) depicts three well-resolved scattering peaks at 7.7, 13.5, and 15.5°, associated with 100, 110, and 200 reflections, respectively, of 2D hexagonal symmetry with space group *P6mm*. The unit cell parameter a_0 is calculated to be 1.32 nm, consistent with the length (1.35 nm) of **1**.[16] Additionally, a strong diffraction peak with $2\theta = 25.3°$ is observed, corresponding to the $\pi-\pi$ stacking distance between two overlapped molecules of **1** (0.35 nm). By comparison with HBC derivatives with functional groups, the condensed stacking of **1** can be attributed to the absence of steric hindrance from the substituents, which favors the formation of a graphitic framework with fewer defects during the carbonization process.

The overall procedure for the preparation of GQDs is illustrated in Scheme 1. To prepare the artificial graphite, the as-made powder of **1** was first pyrolyzed at different temperatures, 600, 900, and 1200 °C, for 5 h with a heating rate of 1 °C/min; the products are denoted as AG-600, AG-900, and AG-1200, respectively. As indicated by their WAXS patterns, the characteristic peak of graphite at 25.3° was observed in each case (Figure 1), which clearly suggests that the artificial graphite was generated by elimination of hydrogen and fusion to larger graphitic structures. This scattering peak becomes narrower and more intense as the pyrolysis temperature is increased from 600 to 1200 °C, indicating an increase in the degree of crystallinity. Wide-angle X-ray diffraction (XRD) and Raman analysis further confirmed the high degree of crystallinity of AG-1200 (Figure S1). In the second step, the artificial graphite was oxidized and exfoliated with a modified Hummers method.[17] Subsequently, aqueous solutions of the resultant GOs were heated to reflux for 48 h with oligomeric poly(ethylene glycol) diamine (PEG_{1500N}) and then reduced with hydrazine. The FT-IR spectrum of the resultant graphene nanodisks provides direct evidence of successful surface modification with PEG_{1500N} (Figure S2). According to the starting artificial graphite, the final products are denoted as GQD-600, GQD-900, and GQD-1200, respectively. Owing to their PEG substituents, the graphene sheets prepared in this work exhibit very good dispersibility in water. To investigate their morphologies, the suspensions of graphene sheets were transferred to the surfaces of freshly exfoliated mica and characterized by atom force microscopy (AFM). It was found that GQD-600 consisted mainly of disordered particles, while GQD-900 contained both particles and disk-shape nanosheets (Figure S3). For GQD-1200, homogeneous nanodisks of ~60 nm diameter and 2−3 nm thickness were found (Figure 2A,B). The thickness of these nanodisks is 3−4 times higher than that of reduced GO, which suggests that they contain more than one layer of graphene.[6] Dynamic light scattering (DLS) and transmission electron microscopy (TEM) studies of GQD-1200 further confirmed the disk-like morphology. As shown in Figure 2C, the average hydrodynamic diameter of GQD-1200 in water is 59.6 nm.

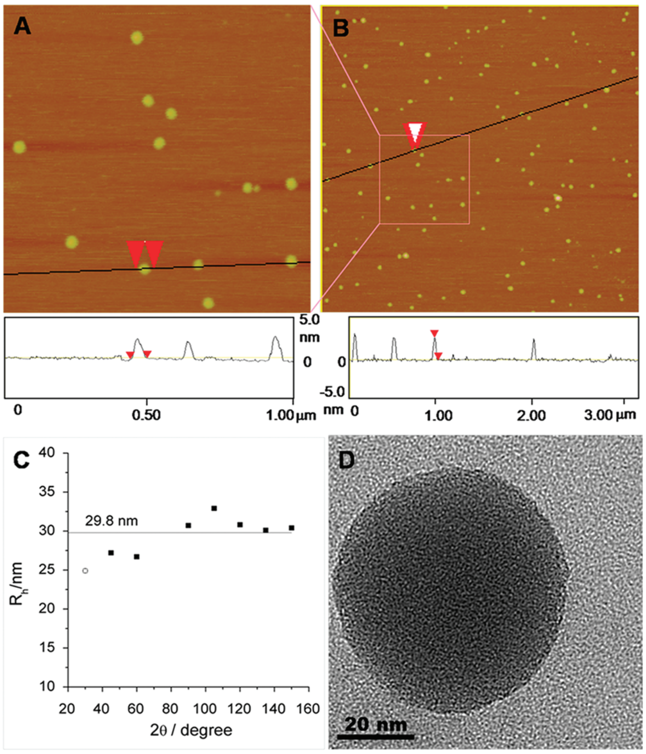

Figure 2. (A,B) AFM topography images of GQD-1200 on mica substrates with the width and height profiles along the line in the images. (C) DLS and (D) TEM images of GQD-1200.

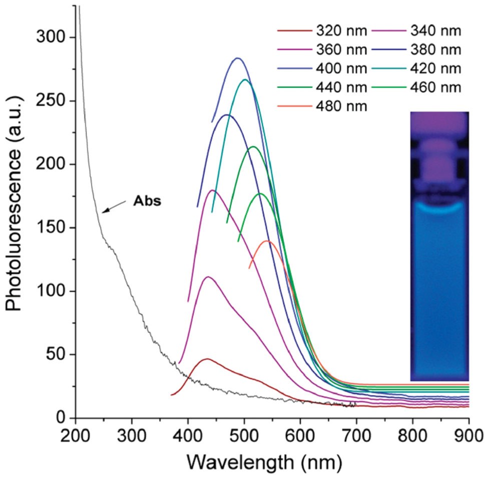

Figure 3. UV−vis absorption and PL emission spectra (recorded for progressively longer excitation wavelengths from 320 to 480 nm in 20 nm increments) of GQD-1200 in water solution. Optical photograph obtained under excitation at 365 nm.

Round graphene nanodisks of ~60 nm diameter can also be observed in the TEM image (Figure 2D).

According to the WAXS patterns of the artificial graphite (Figure 1), the temperature of the thermal treatment is very important for reorganizing **1** into more ordered architectures, which subsequently decides the morphology of the graphene nanodisks. With the elevated pyrolysis temperature, the continuous graphitic domains in the artificial graphite grow gradually by fusing **1** with neighboring molecules at different directions in-plane. This might be the reason for the formation of round nanodisks from AG-1200.

The optical properties of GQDs hold the key for their future applications in optoelectronic devices[7,9] and biological sensors. With this in mind, we recorded the UV−vis absorption and PL emission spectra of GQD-1200. The GQD-1200 suspension shows a broad UV−vis absorption with a weak shoulder at 280 nm (Figure 3), similar to chemically reduced graphene.[18] Subsequent PL characterization indicated that the GQDs can emit strong blue PL under excitation at 365 nm. As shown in Figure 3, GQD-1200 exhibits an excitation-dependent PL behavior, very similar to previously reported GQDs.[6−9] When the excitation wavelength changes from 320 to 480 nm, the PL peak correspondingly shifts from 430 (violet) to 560 nm (yellow). The most intense PL from the nanodisks appears under 400 nm excitation and has a maximum at 510 nm. The bright and colorful PL may be attributed to the chemical nature of the graphene edges,[6−9] although the exact mechanisms responsible for the PL from GQDs, especially blue to ultraviolet emission, remain to be elucidated.[19] The quantum yield at 400 nm excitation was calculated to be ~3.8% by calibrating against quinine sulfate.[20] The suspension of graphene nanodisks also shows extra-high stability. Even after being kept for 1 year in air at room temperature, it still exhibits a transparent appearance and strong PL, which offers another advantage for its future applications.

In conclusion, we have developed an unprecedented strategy to prepare multicolor PL GQDs with a uniform size of ~60 nm diameter and 2−3 nm thickness by using unsubstituted HBC as the precursor. For the first time, our results demonstrate that GQDs with ordered morphology can be obtained by pyrolysis and exfoliation of large PAHs, and the morphology of the GQDs can be influenced by the pyrolysis temperature. It is expected that the shape, size, and composition of the GQDs from this method can be further controlled by using different aromatic molecules, and such work is now under way in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental details, XRD and Raman spectra of AG-1200, FT-IR spectra of PL GQD-1200, and AFM images of GQD-900. This material is available free of charge via the Internet at http://pubs.acs.org.

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