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Nitrogen-Doped Graphene Quantum Dots with Oxygen-Rich Functional Groups

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Supporting Information

ABSTRACT: Graphene quantum dots (GQDs) represent a new class of quantum dots with unique properties. Doping GQDs with heteroatoms provides an attractive means of effectively tuning their intrinsic properties and exploiting new phenomena for advanced device applications. Herein we report a simple electrochemical approach to luminescent and electrocatalytically active nitrogen-doped GQDs (N-GQDs) with oxygen-rich functional groups. Unlike their N-free counterparts, the newly produced N-GQDs with a N/C atomic ratio of ca. 4.3% emit blue luminescence and possess an electrocatalytic activity comparable to that of a commercially available Pt/C catalyst for the oxygen reduction reaction (ORR) in an alkaline medium. In addition to their use as metal-free ORR catalysts in fuel cells, the superior luminescence characteristic of N-GQDs allows them to be used for biomedical imaging and other optoelectronic applications.

The development of new type of quantum dots (QDs) with controllable properties provides opportunities for fabrication and design of new devices with extraordinary properties and functions. Recently, significant advancement on both the experimental and theoretical fronts has been made in the synthesis of zero-dimensional (0D) graphene quantum dots (GQDs) having marvelous properties associated with quantum-confinement and edge effects.[1] As a consequence, tremendous attention has been paid to the development of various chemical methods for the controllable synthesis of GQDs.[1,2] Recently, we also reported a facile electrochemical approach for the large-scale preparation of functional GQDs[3] with unexpected green luminescence and electron-accepting properties.

Doping carbon nanomaterials with heteroatoms can effectively tune their intrinsic properties, including electronic characteristics, surface and local chemical features.[4,5] The N atom, having a comparable atomic size and five valence electrons for bonding with carbon atoms, has been widely used for chemical doping of carbon nanomaterials. For instance, N-doped carbon nanotubes (N-CNTs) showed highly effective electrocatalytic activities for the oxygen reduction reaction (ORR).[5,6] Similarly, doping of graphene with substituent N heteroatoms could effectively modulate the band gap of graphene to introduce new properties for device applications.[4b,7] Along with various methods developed for the preparation of N-doped graphene materials,[4a,8−13] we have used chemical vapor deposition (CVD) to create N-doped few-layer graphene sheets, which showed superior electrocatalytic activity similar to that of N-doped CNTs.[14]

In view of the remarkable quantum-confinement and edge effects of 0D GQDs, doping GQDs with chemically bonded N atoms could drastically alter their electronic characteristics and offer more active sites, thus producing new phenomena and unexpected properties. As far as we are aware, however, no attempt has been made to synthesize N-doped GQDs (N-GQDs), and hence, their unique optoelectronic properties are almost completely unknown. In line with the intensive research on GQDs and N-doped carbon nanomaterials, we for the first time report here an electrochemical approach for the facile preparation of N-GQDs. Unlike their green-luminescent N-free counterparts of similar size (2−5 nm),[3] the N-GQDs with a N/C atomic ratio of ca. 4.3% emit a distinct blue luminescence. In addition, N-GQDs supported by 2D graphene sheets can be used as a new class of metal-free electrocatalysts for the ORR comparable to those of commercial Pt/C electrodes, N-doped CNTs, and N-doped graphene sheets.

To prepare N-GQDs with a N-enriched circumstance, we modified our previously reported electrochemical approach for preparing N-free GQDs[3] by using N-containing tetrabutylammonium perchlorate (TBAP) in acetontrile as the electrolyte to introduce N atoms into the resultant GQDs in situ. The N-GQDs were continuously produced by cyclic voltammogram (CV) scanning over a potential window of ±3.0 V [Figure S1 in the Supporting Information (SI)]. The as-produced N-GQDs were dissolved in the electrolyte solution while increasing the number of scan cycles, and the solution color changed from colorless to yellow (Figure S2).

The electrochemical process for the formation of N-GQDs is shown in Figures S1 and S3. Just as in the oxidation of other carbon materials by an oxidant with a high redox potential (e.g., $KMnO_4$),[15] the applied potential of 3 V in the current study was high enough to drive the electrolyte ions into the graphene layers and oxidize the C−C bonds of the graphene sheets. The physical and/or chemical defects along the starting filtration-

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formed graphene film[16] provide a myriad of active sites for preferential electrochemical oxidation at the defect sites[17] (Figures S3d,e), leading to breakage of the graphene film into tiny graphene dots.

The as-prepared N-GQD solution was found to exhibit a long-term homogeneous phase without any noticeable precipitation at room temperature (Figure S2). Transmission electron microscopy (TEM) images (Figure 1a,b) showed fairly uniform N-GQDs with diameters of ca. 2−5 nm, which are much smaller than those of the N-free counterparts synthesized hydrothermally (~10 nm)[1a] but well-consistent with those of N-free GQDs prepared electrochemically.[3] The corresponding atomic force microscopy (AFM) image (Figure 1c) revealed a typical topographic height of 1−2.5 nm (Figure 1d), suggesting that most of the N-GQDs consist of ca. 1−5 graphene layers.[1a,3] High-resolution TEM observations confirmed a 0.34 nm interlayer spacing for the few-layer N-GQDs (Figure S4).

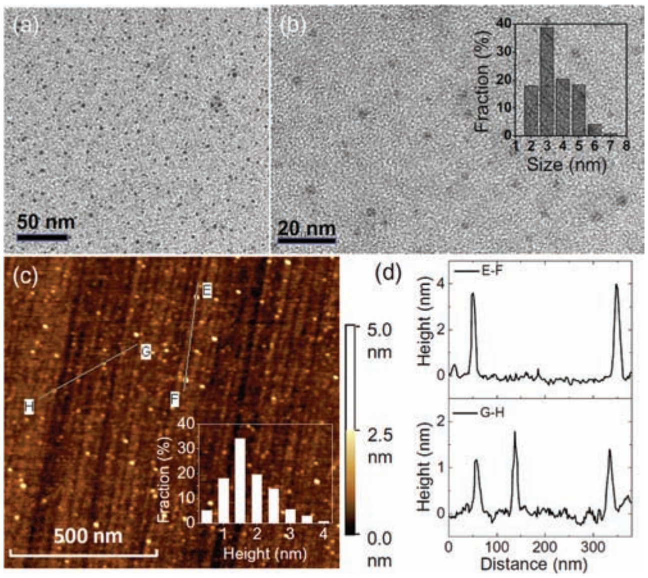

Figure 1. (a, b) TEM images of the as-prepared N-GQDs under different magnifications. (c) AFM image of the N-GQDs on a Si substrate. (d) Height profile along the lines in (c). The insets in (b) and (c) show the size and height distributions of N-GQDs.

X-ray photoelectron spectroscopy (XPS) measurements were performed to determine the composition of the as-produced N-GQDs. The XPS survey spectra of the graphene starting material and the resultant N-GQDs (Figure 2a) show a predominant graphitic C 1s peak at ca. 284 eV and an O 1s peak at ca. 532 eV. The O/C atomic ratio for the N-GQDs is ca. 27%, similar to that of the N-free GQDs[3] and higher than that of the graphene film (ca. 15%). A pronounced N 1s peak was observed for the resultant N-GQDs, whereas no N signal was detected on the graphene film (Figure 2a). This confirmed the successful incorporation of N atoms into the GQDs by electrochemical cycling in the N-containing electrolyte. The N/C atomic ratio was calculated to be 4.28%, which is close to that of the N-doped CNTs[5] and graphene[14] reported previously. The high-resolution N 1s spectrum of the GQDs (Figure 2b) reveals the presence of both pyridine-like (398.5 eV) and pyrrolic (401 eV) N atoms.[14] In addition to the C−N bond (285.2 eV), the high-resolution C 1s spectrum of the N-GQDs (Figure 2c) further confirmed the presence of O-rich groups, such as C−O (286.6 eV), C═O (288.3 eV), and O−C═O (289 eV),[3,13b,18] which is consistent with the corresponding FT-IR spectra (Figure S5). Control experiments (Figure S6) demonstrated that TBAP and/or acetonitrile used for the electrochemical synthesis served as the N sources for doping GQDs. A possible structure of an O-rich N-GQD based on the above analysis is shown in Figure 2d.

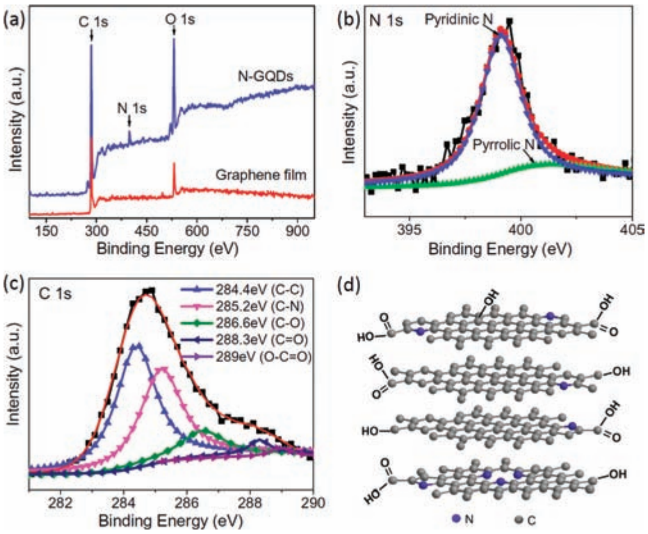

Figure 2. (a) XPS spectra of the original graphene film (red) and the as-produced N-GQDs (blue). (b, c) High-resolution N 1s (b) and C 1s (c) peaks of N-GQDs. (d) Possible structure of an O-rich N-GQD (not drawn to scale).

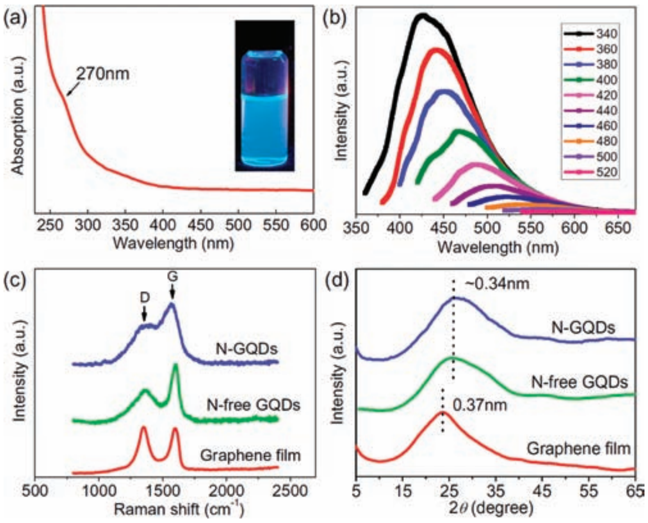

Figure 3. (a) UV−vis absorption and (b) PL spectra of N-GQDs in water. (c) Raman spectra and (d) XRD patterns of the original graphene film, N-free GQDs, and N-GQDs. The inset in (a) is a photograph of the N-GQD solution in water under 365 nm UV irradiation.

The UV−vis absorption spectrum of the resultant N-GQDs shows an absorption band at ca. 270 nm (Figure 3a), which is blue-shifted by ca. 50 nm with respect to that of N-free GQDs of similar size.[3] Under irradiation by a 365 nm lamp (16 W), the N-GQDs emitted intense blue luminescence (Figure 3a inset), which is different from the green luminescence of their N-free counterparts.[3] It has been reported that isolated sp^2-hybridized clusters with a size of ca. 3 nm within the carbon−

oxygen matrix could yield band gaps consistent with blue emission due to the localization of electron−hole pairs,[19] which, along with the previous observation of blue photoluminescence (PL) from nanosized graphene oxides,[20] suggests that in addition to the size and surface effects, the O-rich groups make an important contribution to the observed blue shift in the PL emission from N-GQDs. The relatively strong electron affinity of N atoms in the N-GQDs could also contribute to the PL blue shift. Indeed, previous experimental observations and quantum-mechanical calculations have proved the strong electron-withdrawing ability of the N atoms within the conjugated C plane.[5,6b] Like GQDs, N-GQDs show excitation-dependent PL emission (Figure 3b). These results indicate that the as-prepared N-GQDs possess unique optoelectronic properties due to the N-doping-induced modulation of the chemical and electronic characteristics of the GQDs.

Raman spectra of the original graphene film, N-free GQDs, and N-GQDs are included in Figure 3c for comparison. The peaks centered at ca. 1365 and 1596 cm^{-1} are attributed to the D and G bands, respectively, of carbon materials. It was observed that both the N-GQDs and their N-free counterparts[3] have an I_D/I_G ratio of ca. 0.7, which is much lower than that of the original graphene film (∼1.05) (Figure 3c). This indicates that relatively high quality GQDs were produced by the electrochemical method. In comparison with GQDs, however, the N-GQDs exhibit a broader D band, suggesting that the intercalation of N atoms into the conjugated carbon backbone has led to somewhat disordered structures.

Figure 3d shows typical X-ray diffraction (XRD) profiles for the original graphene film, N-free and N-GQDs. Just like their N-free counterparts,[3] the N-GQDs showed a broader diffraction peak at ca. 25°, which is substantially higher than that of the graphene film (ca. 23.5°). The more compact interlayer spacing (ca. 0.34 nm) in the N-GQDs than in the original graphene film (ca. 0.37 nm) as probed by XRD is consistent with the TEM observations (Figure S4). The reduced interlayer spacing in N-GQDs could be attributed to the effective $\pi-\pi$ stacking of tiny graphenes with few structural defects (Figure 2d). On the other hand, the possible formation of hydrogen bonding between the O-containing functional groups surrounding the edges of the graphene layers in the N-GQDs (Figure 2d and Figures S7 and S8) may further facilitate the compact stacking of graphene layers (Figure S4). It is also noteworthy that the N-GQDs thus prepared did not show any diffractions in the $2\theta \approx 10°$ region characteristic of graphene oxides,[21] evidently indicating that the N-GQDs are different from graphene oxide, though both contain oxygen-enriched functional groups (Figure 2).

N-doped carbon nanomaterials such as N-CNTs[5] and N-graphene[14] have been demonstrated to hold promise as metal-free electrocatalysts to replace the commercially available Pt-based catalysts for the ORR. Apart from their unique luminescence properties, N-GQDs are also expected to possess electrocatalytic activity for the ORR. To avoid any possible effect of the glassy carbon (GC) base electrode (Figure S9), we used a large-area, electrically conductive graphene assembly to support the N-GQDs as ORR catalysts. The graphene-supported N-GQDs (N-GQD/graphene) were prepared by hydrothermal treatment of a suspension of well-dispersed graphene oxides with N-GQDs (Figure S10). This mild process ensured the formation of N-GQD/graphene assemblies without acutely changing the intrinsically chemical nature of the N-GQDs (Figures S11 and S12). The N-GQD/graphene film (Figure S13) thus formed was demonstrated to exhibit a good conductivity of ca. 40 S/cm and superior electrocatalytic ability for the ORR (see below).

Figure 4a,b depicts CVs for O_2 reduction on N-GQD/graphene in comparison with a commercial Pt/C catalyst (20 wt % Pt on carbon black). Similar to the commercial Pt/C (Figure 4b), a well-defined cathodic peak clearly occurred in the O_2-saturated but not N_2-saturated KOH solution for N-GQDs/graphene (Figure 4a). The ORR onset potential was at ca. −0.16 V with a reduction peak at ca. −0.27 V, which are close to those of the commercial Pt/C catalyst (Figure 4b) and comparable to those of N-containing CNT-based[6b] or graphene-based[14] metal-free electrocatalysts, indicating the great catalytic ability of N-GQD/graphene for the ORR.

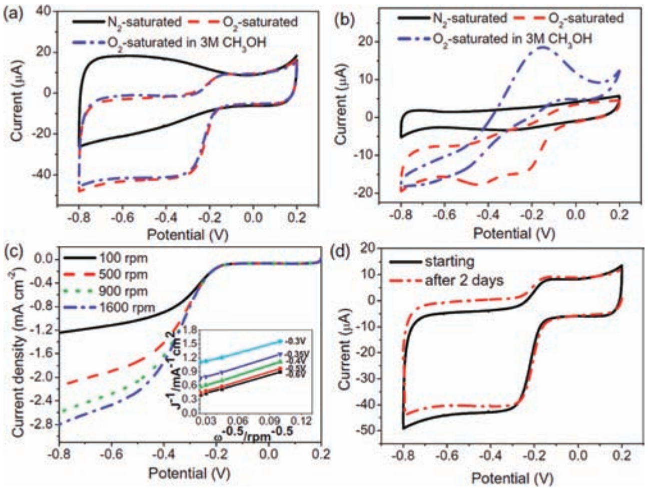

Figure 4. (a, b) CVs of (a) N-GQD/graphene and (b) commercial Pt/C on a GC electrode in N_2-saturated 0.1 M KOH, O_2-saturated 0.1 M KOH, and O_2-saturated 3 M CH_3OH solutions. (c) Rotating disk electrode (RDE) curves for N-GQD/graphene in O_2-saturated 0.1 M KOH with different speeds. The inset shows the Koutecky−Levich plots derived from the RDE measurements. (d) Electrochemical stability of N-GQD/graphene as determined by continuous cyclic voltammetry in O_2-saturated 0.1 M KOH.

Unlike the commercial Pt/C electrode, for which the cathodic peaks for oxygen reduction disappear in the O_2-saturated electrolyte containing 3 M methanol (a typical fuel molecule) coupled with one pair of peaks characteristic of methanol reduction/oxidation,[22] the N-GQD/graphene electrode exhibits a stable ORR without any electroactivity specific to methanol in the methanol-containing electrolyte, suggesting the remarkable tolerance to possible crossover effects. As a control, ORR tests on pure graphene and N-free GQD/graphene were performed in O_2-saturated KOH solution, and no obvious ORR electrocatalytic activity was found (Figure S14). Therefore, the observed electrocatalytic activity for N-GQDs can be exclusively attributed to the N-doping effect.

Linear-sweep voltammetry (LSV) curves of the ORR for N-GQD/graphene in an O_2-saturated 0.1 M KOH solution measured on a rotating disk electrode (RDE) are shown in Figure 4c for different electrode rotation rates. The measured current density shows the typical increase with increasing rotation rate due to the enhanced diffusion of electrolytes.[5,22] The transferred electron number per O_2 molecule involved in the ORR process was determined using the Koutecky−Levich equation (eq S1 in the SI),[5,14] and the corresponding curves are plotted for different potentials in the Figure 4c inset. The parallel and straight fitting lines imply a first-order reaction with respect to dissolved oxygen. The *n* value for N-GQD/graphene was derived to be 3.6−4.4 over the potential range from −0.3 to −0.6 V (Figure S15), suggesting a four-electron process for the ORR on the N-GQD/graphene electrodes.[5,14] This was further confirmed by the negligible ring current recorded at a Pt rotating ring−disk electrode (Figure S16).[5] As shown in Figure 4d, no obvious decrease in current was observed after 2 days of continuous cycling in O_2-saturated 0.1 M KOH, indicating no loss of catalytic activity for the N-GQD/graphene electrode.

In summary, we have developed a simple yet effective electrochemical strategy for generating N-doped GQDs with O-rich functional groups, which show unique optoelectronic features distinctive from those of their N-free counterparts. N-GQDs supported by graphene sheets have been demonstrated to possess superior electrocatalytic ability. Apart from the use of N-GQDs as a metal-free catalyst for the ORR, their unique luminescence properties indicate their potential for use in bioimaging and light-emitting diodes, among many other potential applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details for preparation of N-GQDs and N-GQD/graphene, electrode fabrication, related characterization, and supporting results and discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

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