

Communication

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

Yan Li,^{†,‡} Yang Zhao,^{†,‡} Huhu Cheng,[†] Yue Hu,[†] Gaoquan Shi,[‡] Liming Dai,[§] and Liangti Qu^{*,†}

[†]Key Laboratory of Cluster Science, Ministry of Education of China, School of Chemistry, Beijing Institute of Technology, Beijing 100081, P. R. China

[‡]Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China

[§]Department of Macromolecular Science and Engineering, Case School of Engineering, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, Ohio 44106, United States

*Corresponding author: lqu@bit.edu.cn. [‡]These authors contributed equally.

ABSTRACT: Graphene quantum dots (GQDs) represent a new class of quantum dots with unique properties. Doping GQDs with heteroatoms provides an attractive means to effectively tune their intrinsic properties and to exploit 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%, exhibit blue luminescent emissions and possess electrocatalytic activities comparable to that of commercially available Pt/C catalyst for 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 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 in both the experimental and theoretical fronts has been made in the synthesis of zero-dimensional (0D) graphene quantum dots (GQDs) of marvelous properties associated with the quantum confinement and edge effects.¹ As a consequence, tremendous attention has been paid to the development of various chemical methods, including hydrothermal route,¹ solution chemistry,^{1b-1d,2} transforming C₆₀,^{1e} for controllable synthesis of GQDs. In this regard, we have recently reported a facile electrochemical approach to large scale preparation of functional GQDs³ with unexpected green luminescence and electron-accepting properties for various potential applications in optoelectronic devices (*e.g.*, as new electron-acceptors for photovoltaics).

Doping carbon nanomaterials with heteroatoms can effectively tune their intrinsic properties, including electronic characteristics, surface and local chemical features.^{4,5} In this context, the nitrogen (N) atom, having a comparable atomic size and five valence electrons for bonding with carbon atoms, has been widely used for chemically doping carbon nanomaterials. For instance, N-doped carbon nanotubes (N-CNTs) showed highly effective electrocatalytic activities for oxygen reduction reaction (ORR)^{5,6} through the electron-transfer from adjacent carbon atoms to N-atoms in the conjugated CNT carbon-network. Similarly, doping of graphene with substituent N heteroatoms could effectively modulate the band gap of graphene to introduce new properties for novel de-

vice applications.^{4b,7} Along with various methods developed for the preparation of N-doped graphene materials, such as electrothermal reactions,⁸ thermal annealing,⁹ plasma treatment,^{4a,10} arc discharge,¹¹ hydrothermal,¹² and solvothermal synthesis,¹³ we have used chemical vapor deposition (CVD) to create N-doped few-layered graphene sheets, which showed the superior electrocatalytic activity similar to that of N-doped CNTs.¹⁴

In view of the remarkable quantum confinement and edge effect 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 we are aware, however, no attempt has been made to synthesize the 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 to the facile preparation of N-GQDs. Unlike its green-luminescent N-free counterparts with a similar size (2–5 nm),³ the as-prepared N-GQDs with a N/C atomic ratio of *ca.* 4.3 % exhibited a distinct blue luminescent emission. In addition, the N-GQDs, supported by 2D graphene sheets, can be used as a new class of metal-free electrocatalysts for ORR with the electrocatalytic activities comparable to those of commercial Pt/C electrodes, N-doped CNTs, or N-doped graphene sheets.

To prepare the N-GQDs with a N-enriched circumstance, we modified our previously-reported electrochemical approach to N-free GQDs³ by using N-containing tetrabutylammonium perchlorate (TBAP) in acetonitrile as the electrolyte to effectively introduce N atoms into the resultant GQDs in-situ during the GQD production. Briefly, a graphene film, formed by filtration of an aqueous suspension of chemically-reduced graphene oxides, was used as the starting material and working electrode.³ Pt wire and Ag/AgCl acted as counter and reference electrodes, respectively. The electrolyte was 0.1 M TBAP in acetonitrile. The N-GQDs were continuously produced by cyclic voltammogram (CV) scanning over a potential window of ± 3.0 V at a scan rate of 0.5 V/s (Figure S1). The as-produced N-GQDs were dissolved in the electrolyte solution with increasing the scan cycles, and the solution color changed from colorless to yellow. The water soluble N-GQDs were then collected and dialyzed for several days to fully remove the electrolyte. The purified N-GQDs were finally obtained by filtering the resulting solution through a 20-nm filter membrane (AAO, Whatman), and then re-dispersed in deionized water for subsequent characterization (Figure S2). The above process could be scaled up by simply using large-area graphene films as the working electrode and increasing the CV cycles.

The electrochemical process for the formation of N-GQDs is shown in Figures S1 and S3. Just like the oxidation of other carbon materials by an oxidant (e.g., KMnO_4) with a high redox potential,¹⁵ the applied potential of 3V in current study should be high enough to drive the electrolyte ions into the graphene layers and oxidize the carbon-carbon bonds of graphene sheets. However, unlike the oxidation of graphite (a perfect stacking of defect-free graphene layers), the physical and/or chemical defects along the starting filtration-formed graphene film¹⁶ provide a myriad of active sites for preferential electrochemical oxidation at the defect sites¹⁷ (Figures S3,d&e), leading to the breakage of the graphene film into tiny graphene dots.

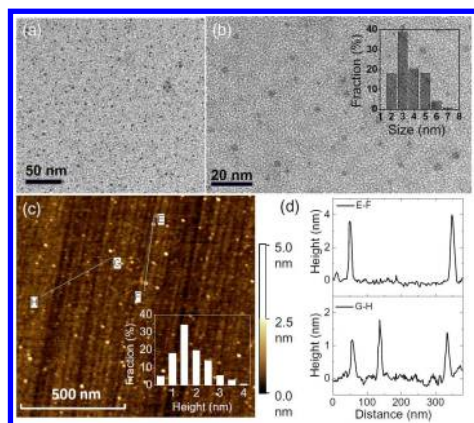


Figure 1. (a, b) TEM images of the as-prepared N-GQDs under different magnifications, (c) AFM image of the N-GQDs on a Si substrate, and (d) the height profile along the lines in (c). Insets in (b) and (c) show the size and height distribution of N-GQDs.

The as-prepared N-GQD solution was found to exhibit a long-term homogeneous phase without any noticeable precipitation at room temperature (Figure S2). TEM images (Figures 1a&b) show fairly uniform N-GQDs with diameters in the range of ca. 2–5 nm, which are much smaller than those of the N-free counterparts (~10 nm) synthesized hydrothermally^{1a} but well consistent with those of the N-free GQDs prepared electrochemically.³ The corresponding AFM image (Figures 1c&d) reveal a typical topographic height of 1–2.5 nm, suggesting that most of the N-GQDs consist of ca. 1–5 graphene layers.^{1a,3} High-resolution TEM observation confirms a 0.34-nm interlayer spacing for the few-layered N-GQDs (Figure S4).

XPS measurements were performed to determine the composition of the as-produced N-GQDs. As can be seen in Figure 2a, the XPS survey spectra of both the graphene starting material and the resultant N-GQDs show predominant graphitic C 1s peak at ca. 284 eV and 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 synthesized electrochemically³ and higher than that of the graphene film (ca. 15%), indicating the occurrence of oxidation reaction during the electrochemical process. 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 CNTs⁵ and graphene¹⁴ 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 The electrolyte solution contains acetonitrile and TBAP. The absence of Cl peak associated with TBAP in Figure 2a, together with the highly volatile nature of acetonitrile, indicates that the possible physical adsorption and/or intercalation of N-

containing species is negligibly low. Therefore, the observed N 1s peak in Figure 2b is mainly attributed to the electrochemical doping of GQDs with N. In addition to the C–N bond (285.2eV), 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). Controlled experiments (Figure S6) demonstrated that TBAP and/or acetonitrile used for the electrochemical synthesis serve as the N sources for doping GQDs. A possible structure of O-rich N-GQD is shown in Figure 2d on the basis of the analysis above.

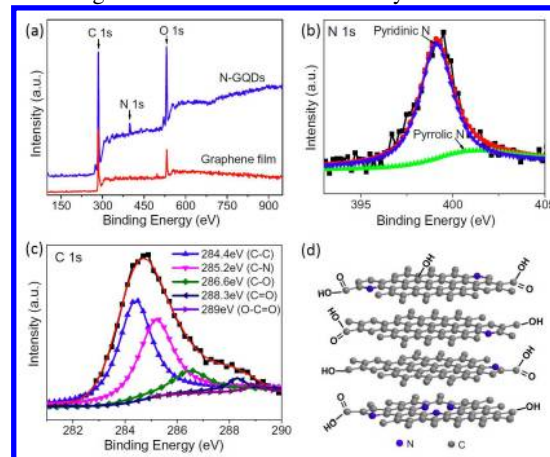


Figure 2. XPS spectra of the original graphene film and the as-produced N-GQDs (a), and high resolution N 1s (b) and C 1s (c) peaks of N-GQDs. (d) is the possible structure of O-rich N-GQD (not drawn to scale).

UV-vis absorption spectrum of the resultant N-GQDs shows an absorption band at ca. 270 nm (Figure 3a), which is ca. 50 nm blue shift with respect to that of the N-free GQDs of a similar size.³ Under the irradiation of 365-nm lamp (16W), the N-GQDs exhibited an intensive blue luminescent emission (Figure 3a, inset), which is different from the green-luminescence of their N-free counterparts synthesized electrochemically³ but similar to that of the hydrothermally-synthesized N-free GQDs with a large size of ca. 10 nm.^{1a} It has been reported that isolated sp^2 clusters 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 PL from nanosized graphene oxides,²⁰ suggests an important role of the O-rich groups, in addition to the size and surface effects, 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 have contribution to the PL blue-shift. Indeed, previous experimental observations and quantum mechanics calculations have proved the strong electron-withdrawing ability of the N atoms within the C conjugated plane,^{5,6b} which may restrict the electron delocalization and thus induce the spectroscopic blue shift of N-GQDs. Like GQDs, N-GQDs show the 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 chemical and electronic characteristics of the GQDs.

Raman spectra of the original graphene film, the N-free and N-GQDs are included in Figure 3c for comparison. The peaks centered at ca. 1365 cm^{-1} and ca. 1596 cm^{-1} are attributed to the D band and G band of carbon materials. It is observed that both the N-GQDs and their N-free counterparts³ have a I_D/I_G ratio of ca. 0.7, a value which is much lower than that of the original graphene film (~1.05) (Figure 3c). This indicates that relatively high quality GQDs have been produced by the electrochemical meth-

ods. Comparing with GQDs, however, 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.

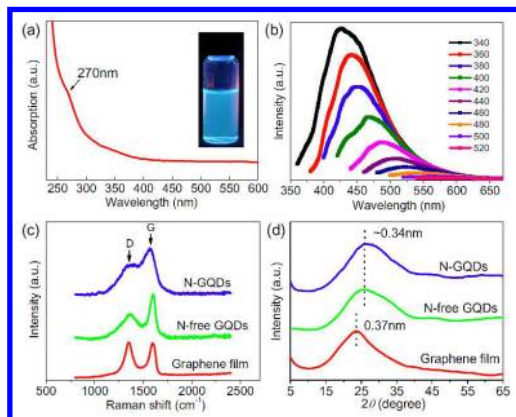


Figure 3. (a and b) UV-vis absorption and photoluminescence (PL) spectra of N-GQDs in water, respectively. (c) Raman spectra and (d) XRD patterns of the original graphene film, the N-free and N-GQDs. Inset in (a) is a photo of the N-GQD solution in water under 365nm UV irradiation.

Figure 3d shows typical XRD profiles for the original graphene film and the as-prepared N-free and N-GQDs. Just like their N-free counterparts,³ the N-GQDs show a broader diffraction peak at around 25° , which is substantially higher than that of the graphene film (*ca.* 23.5°). The more compact interlayer spacing (*ca.* 0.34 nm) probed by XRD for N-GQDs than the original graphene film (*ca.* 0.37 nm) is consistent with the TEM observation (Figure S4). The reduced interlayer spacing in N-GQDs could be attributed to the effective π - π stacking of tiny graphenes with few structure 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 N-GQDs (Figures 2d, S7 and S8) may further facilitate the compact stacking of graphene layers (Figure S4). It is also worth to note that N-GQDs thus-prepared do not show any diffractions in the region of *ca.* 10° (2θ) 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-CNTs⁵ and N-graphene¹⁴ have been demonstrated to hold promise as metal-free electrocatalysts in replacing the commercially-available Pt-based catalyst for ORR. Apart from their unique luminescent properties, N-GQDs are also expected to possess the electrocatalytic activities for ORR. To avoid any possible effect of the glassy carbon (GC) base electrode (Figure S9), we used a large-area and electrically conductive graphene assembly to support the N-GQD as ORR catalysts. The graphene supported N-GQDs (N-GQDs/graphene) were prepared by hydrothermal treatment of the 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 N-GQDs (Figures S11 & 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 ORR (see below).

Figures 4a and b depict CVs for O_2 reduction on the N-GQD/graphene in comparison with a commercial Pt/C catalyst (20wt% platinum 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 the N-GQDs/graphene (Figure 4a). The onset potential of ORR is 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 that of N-containing CNT-based^{6b} or graphene-based¹⁴ metal-free electrocatalysts, indicating the great catalytic ability of N-GQD/graphene for ORR.

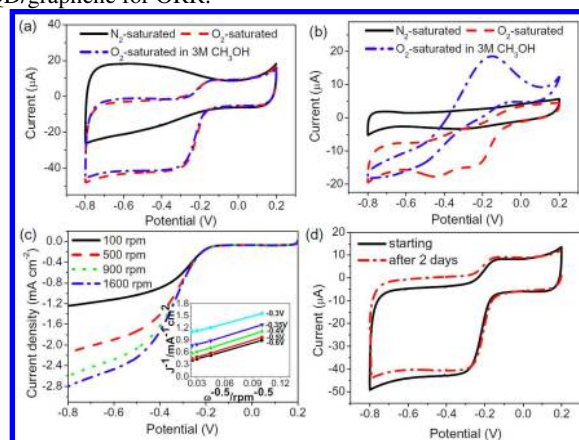


Figure 4. (a, b) CVs of N-GQDs/graphene (a) and commercial Pt/C (b) on a GC electrode in N_2 -saturated, O_2 -saturated 0.1M KOH, and O_2 -saturated 0.1M KOH and 3M CH_3OH solutions. (c) Rotating disk electrode (RDE) curves of the N-GQDs/graphene in O_2 -saturated 0.1M KOH with different speeds (the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

Unlike the commercial Pt/C electrode that the cathodic peaks for oxygen reduction disappear in the O_2 -saturated electrolyte containing 3M 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 effect. As a control, the ORR test on pure graphene and N-free GQDs/graphene was performed in O_2 -saturated KOH solution, which shows no obvious ORR electrocatalytic activity (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 ORR for the N-GQD/graphene in an O_2 -saturated 0.1M KOH solution measured on a rotating disk electrode (RDE) are shown in Figure 4c with 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 oxygen molecule involved in the ORR process was determined by the Koutecky-Levich equation (Equation S1),^{5,14} and the corresponding curves were plotted for different potentials in the inset of Figure 4c. The parallel and straight fitting lines imply a first-order reaction toward dissolved oxygen. The n value for the N-GQD/graphene is derived to be 3.6–4.4 at 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} and the reduction of oxygen yielding water as the main product. This is further confirmed by the negligible ring current recorded at a Pt rotating ring-disk electrode (Figure S16).⁵ We also performed continuous potential cycling to investigate the stability of the N-GQD/graphene toward ORR. As can be seen in Figure 4d, no obvious decrease in current was observed after two-day continuous cycling between -0.8 and 0.2 V in O_2 -saturated 0.1M KOH, indicating no loss of catalytic activity for the N-GQD/graphene electrode.

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

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Supporting Information. The experimental details for preparation of N-GQDs, N-GQD/graphenes, electrode fabrication, related characterization, and supplementary results and discussion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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