Communication

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

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The electrochemical process for the formation of N GQDs is shown in Figures S1 and S . Just like the oxidation of other carbon materials by an oxidant

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.

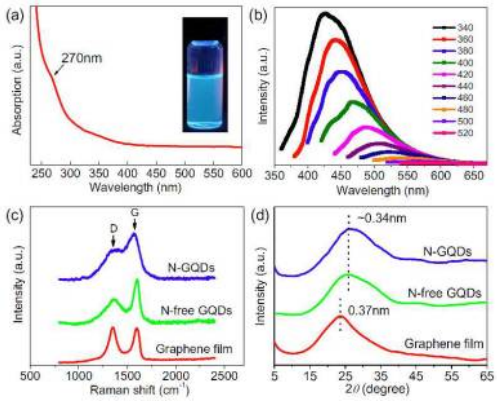

Figure 3. a and b, UV-vis absorption and photoluminescence (PL) spectra of N-GQDs in water, respectively. c, Raman spectra and d, XRD patterns of the original graphene film, the N-free and N-GQDs. Inset in a is a photo of the N-GQD solution in water under 365 nm UV irradiation.

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, the N-GQDs show a broader diffraction peak at around 25° which is substantially higher than that of the graphene film (*ca.* 24.5°). 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 3d). 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 3d, S3, and S5) 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,[12] 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 and N-graphene,[14] 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 S11) 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). Sim[illegible] 110 f[illegible] o[illegible] r

In summary we have developed a simple yet effective electro chemical strategy to generate N doped GQDs with O rich func tional groups which show unique optoelectronic features distinc tive 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 prepara tion of N GQDs N GQD graphenes electrode fabrication re lated 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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