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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 7. Just like the oxidation of other carbon materials by an oxidant

ods⁴ 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 structures⁴

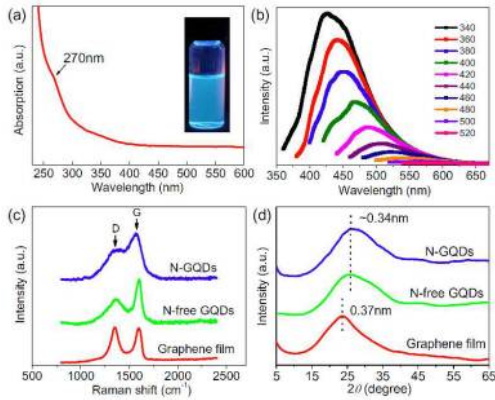


Figure 3. a and b UV vis absorption and photoluminescence PL spectra of N GQDs in water respectively⁴ c Raman spectra and d XRD patterns of the original graphene film the N free and N GQDs⁴ Inset in a is a photo of the N GQD solution in water under 270 nm UV irradiation⁴

Figure d shows typical XRD profiles for the original graphene film and the as prepared N free and N GQDs⁴ Just like their N free counterparts the N GQDs show a broader diffraction peak at around $2\theta \approx 25^\circ$ which is substantially higher than that of the graphene film *ca.* 20° ⁴ 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 4⁴ The reduced interlayer spacing in N GQDs could be attributed to the effective $\pi-\pi$ stacking of tiny graphenes with few structure defects Figure d⁴ 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 d S₉ and S₁₀ may further facilitate the compact stacking of graphene layers Figure 4⁴ It is also worth to note that N GQDs thus prepared do not show any diffractions in the region of *ca.* 10° θ characteristic of graphene oxides¹ evidently indicating that the N GQDs are different from graphene oxide though both contain oxygen enriched functional groups Figure 4⁴

N doped carbon nanomaterials such as N CNTs and N graphene⁴ have been demonstrated to hold promise as metal free electrocatalysts in replacing the commercially available Pt based catalyst for ORR⁴ Apart from their unique luminescent properties N GQDs are also expected to possess the electrocatalytic activities for ORR⁴ 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 catalysts⁴ 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 S10⁴ This mild process ensured the formation of N GQD/graphene assemblies without acutely changing the intrinsically chemical nature of N GQDs Figures S11 S12⁴ The N GQD/graphene film Figure S13 thus formed was demonstrated to exhibit a good conductivity of *ca.* 0.40 S cm and superior electrocatalytic ability for ORR see below⁴

Figures 4 a and b depict CVs for O₂ reduction on the N GQD/graphene in comparison with a commercial Pt/C catalyst

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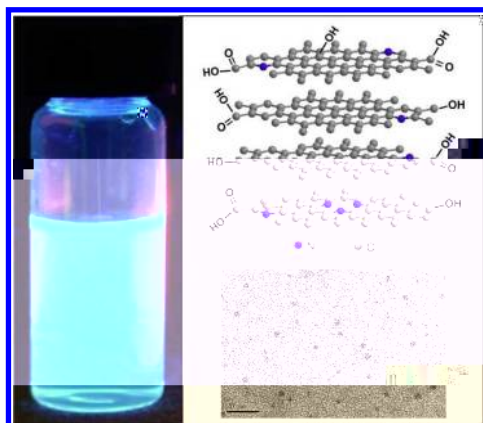
Supporting Information. The experimental details for preparation of N GQDs N GQD graphenes electrode fabrication related characterization and supplementary results and discussion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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