

Single- and Multi-Doping in Graphene Quantum Dots: Unraveling the Origin of Selectivity in the Oxygen Reduction Reaction

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EXPERIMENTAL DETAILS

S1. Chemicals

The chemicals here employed were high purity reagents and they were used as received without further operations. The Deionized water (DI, $\rho=18.2 \text{ M}\Omega\cdot\text{cm}$) used for the experiments was previously bi-distilled in KMnO_4 .

S2. Preparation of GO

The preparation of Graphene Oxide (GO) was performed using the modified Hummer's oxidation reaction.^{1,2} 1g of ultra-pure graphite micrometric powder ($d < 150 \text{ }\mu\text{m}$, Aldrich) was slowly added to 25 mL of a 9:1 mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (96% and 65% respectively, Aldrich), in ice-water bath. Then, operating in ice-water bath ($T \sim -15^\circ \text{C}$), 3 g of KMnO_4 (Aldrich) were gradually added into the mixture under vigorous stirring. After stirring for 1 hour at room temperature, the mixture was heated at 35°C for 1 hour in ultrasonic bath. After that, of 50 mL of deionized water was slowly added to the mixture causing the temperature to increase to about 98°C . The mixture was maintained at this temperature for 15-20 min. The reaction was terminated by adding 140 mL of deionized water at 60°C followed by 1 mL of 30% H_2O_2 solution (Fluka). After stirring for 30 min and 30 min of ultrasonication, the yellow product was collected after several cycles of centrifugation-water washing, to obtain a dispersion of GO in water with a pH of 5.5. This weak acid environment is suitable to achieve an optimum time stability of the GO dispersions. Prior to each use, few mL of a GO dispersion (15 mg/mL) were dialyzed

over five days with osmotic membranes (Spectra/Por, Molecular Weight Cut-Off (MWCO) of 7 kD) in MilliQ water ($p=18.2 \text{ M}\Omega\cdot\text{cm}$), to remove eventual residual contaminations.

The obtained GO dispersion was characterized by UV-VIS, Raman and X-ray Photoelectron Spectroscopies (XPS). Furthermore, the Z-potential of the obtained GO dispersions in water (measured by a Zetasizer (Nano-ZS) from Malvern Instruments) was equal to -44.8 mV.

Figure S1 and S2 report spectroscopic (XPS, IRAS, UV-Vis and Raman) and morphological characterizations (SEM) of the obtained-pristine GO, respectively.

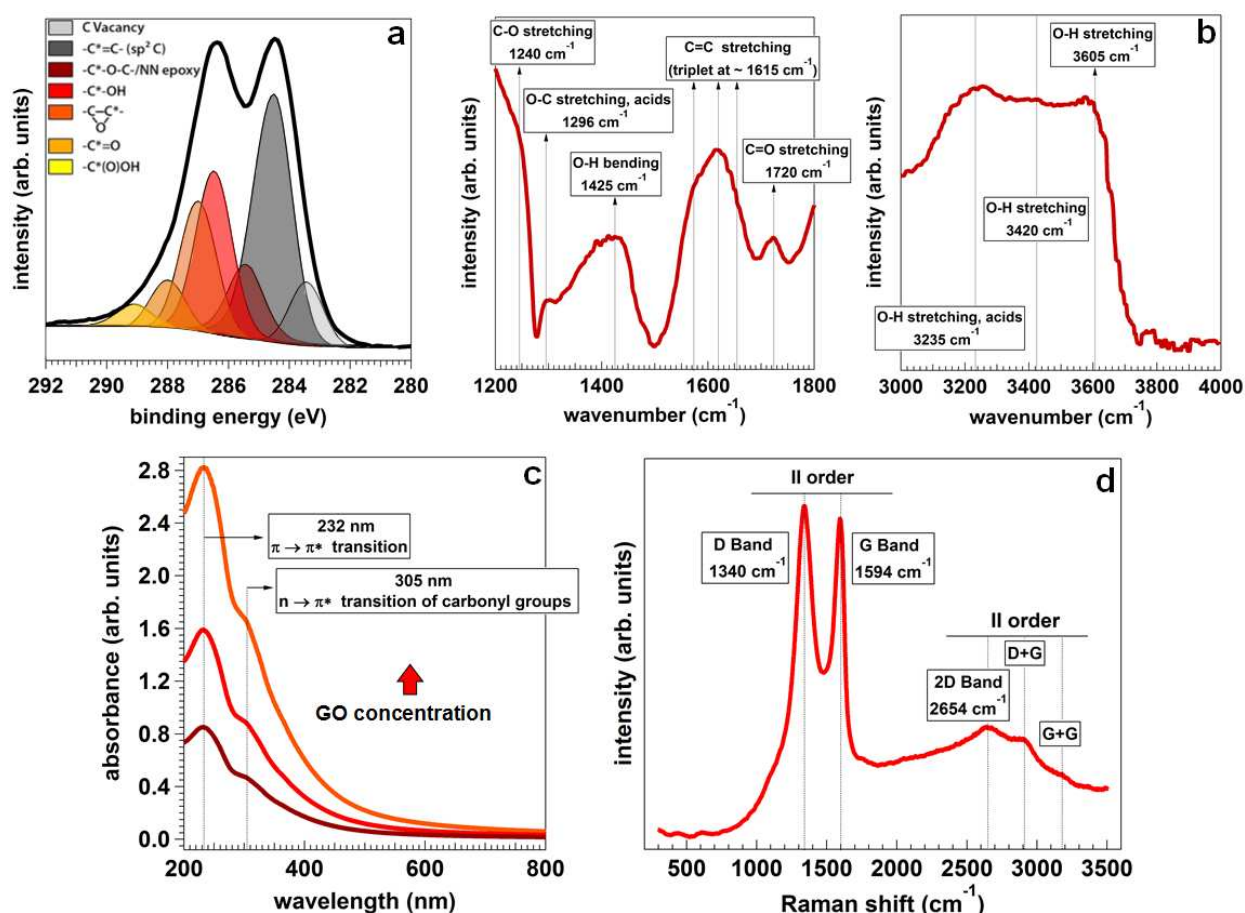


Figure S1. Spectroscopic characterization of the pristine GO obtained by the modified-Hummers' synthesis; a: multi-component fitting of the C 1s photoemission line (XPS was taken on a thick film of GO drop-casted on Cu foil); b: Fourier Transform Infrared Reflection Absorption Spectroscopy (FT-IRAS) measurements on a GO thin film deposited by dropcasting on Cu foil; c: UV-Visible absorption spectroscopy of GO aqueous dispersions at different GO concentrations; d: Raman spectroscopy on GO thick film drop-casted on Cu foil.

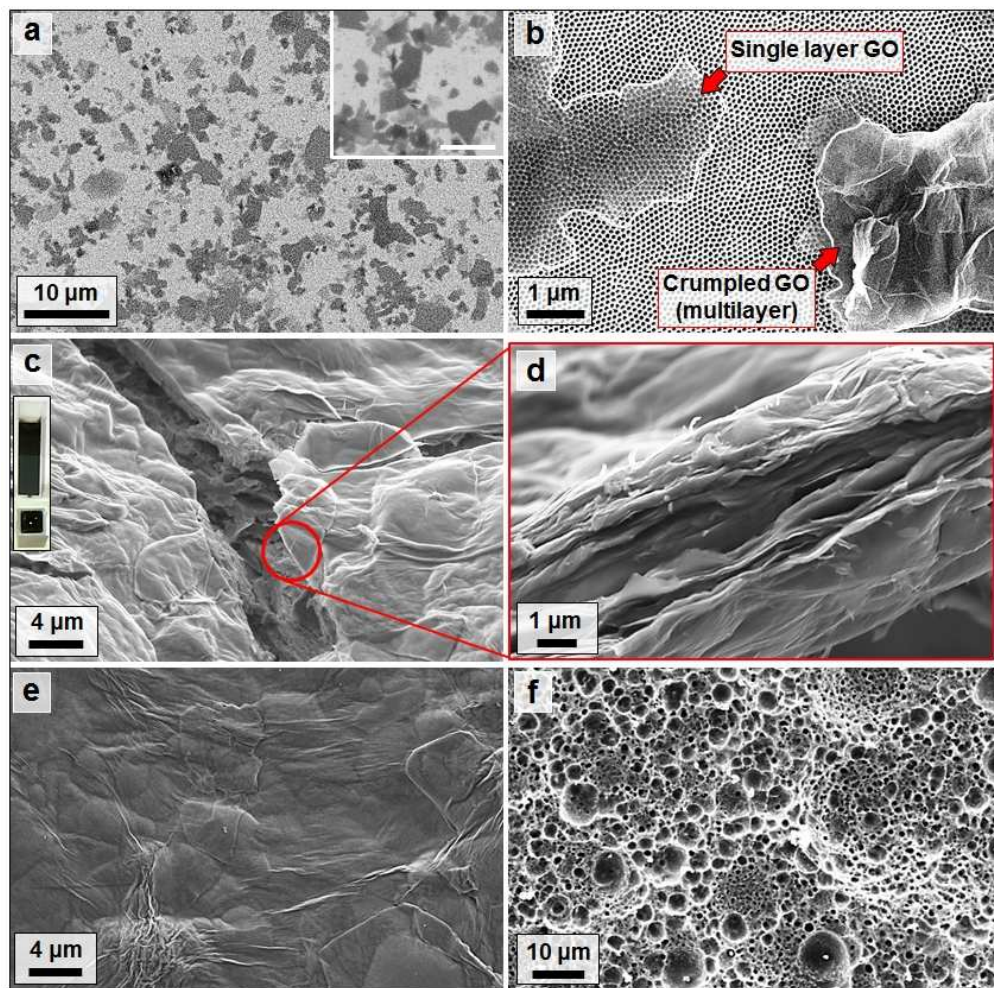


Figure S2. a: Morphological characterization of the pristine GO microflakes deposited on P:Si (110) via electrophoretic deposition (the scale bar in the inset is 5 μm .); b: Electrophoretic deposition of GO microflakes on an anodic aluminium oxide membrane, in which it is possible to see both GO single layers and crumpled GO papers made by several GO layers; c, d, e: GO thick paper supported on GC, used as WE during the GOQDs synthesis; f: example of the GO WE surface after the electrochemical synthesis of the GOQDs (for more details, see ref. 3).

S3. Synthesis of pure and doped-GOQDs

Electrochemical (EC) preparations of GOQDs^{4, 5} were carried out in a standard three-electrode EC cell, using a Pt ring as Counter Electrode (CE) and a saturated Ag/AgCl/ Cl^- as Reference Electrode (RE). The electrodes were assembled in an EC cell with a 30° degrees configuration and an interelectrode gap of 1 cm. The electrolytic solutions (constant volume of 50 mL) were kept at 25 °C during the synthesis by a thermostatic water bath. A magnetic stirrer provided the stirring of the electrolytic medium during the reactions. All the Cyclic Voltammeteries (CVs) were acquired with the same disk area exposed to the electrolytic medium (1.5 cm^2), by enveloping

the samples with Teflon tape and contacted them from the back with a copper plate. The electrochemical measurements were carried out with a EG&G PARC 173 potentiostat/galvanostat.

The Working Electrodes (WE) were built from a Glassy Carbon (GC) plate (Tokai GC-20), polished to a mirror finish with silicon carbide papers of decreasing grain size (Struers, grit: 500, 1000, 2400, 4000) followed a refinishing on soft cloth with diamond pastes (3, 1 and 0.25 μm particle size). The samples were cleaned by ultrasonic treatment in a mixture of isopropanol/ethanol (Aldrich, 1:1) for 10 min. Finally, 150 μL of a concentrated dispersion of GO in water (15 mg of GO/mL) were drop casted on these GC substrates (GO/GC) and then annealed in a tubular furnace at 150 $^{\circ}\text{C}$ for 30 minutes under an overpressure flow of N_2 (500 sccm). The EC synthesis of doped-GOQDs were conducted adding to a 0.1 M Phosphate Buffer Solution (PBS) the molecular precursor that was chosen as dopant source.

The potential was cycled between $\pm 3.000\text{ V}$ (vs. $\text{Ag}/\text{AgCl}/\text{Cl}^-_{(\text{sat})}$, $-2.803\text{ V} \div +3.197\text{ V}$ vs. SHE) at a scan rate of 500 mV/s. Figure S3 shows the polarization curves obtained during the synthesis of the different prepared systems.

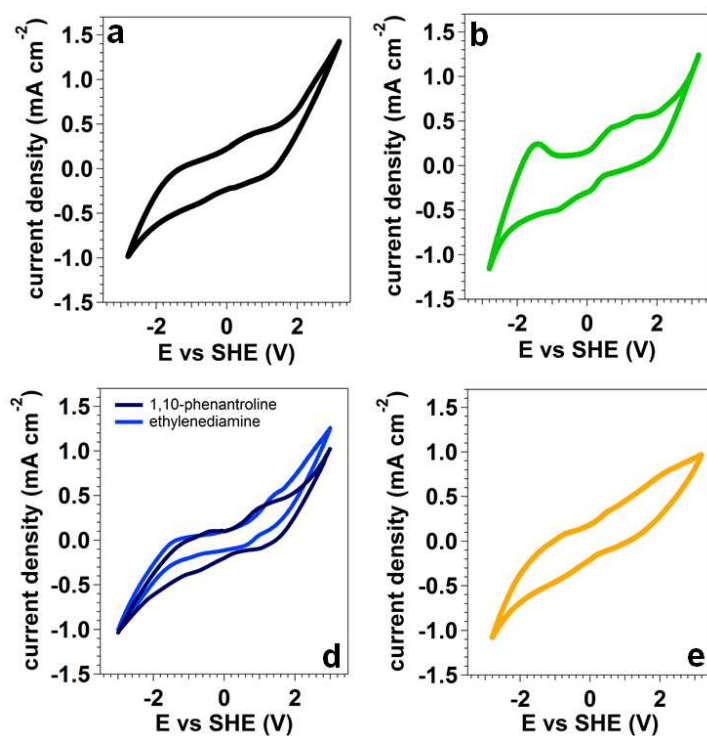


Figure S3. Cyclic voltammeteries acquired with a scan rate of 500 mV/s of a GO paper WE in presence of the different dopant molecules used in this study (for detail about the electrolyte, see Table 1 reported in the text).

After 2000 CVs the obtained solutions were filtered twice using cellulose acetate membranes with a porosity size of 400 and 200 nm, respectively. Then, the filtered solutions were dialyzed for five days with osmotic membranes (Spectra/Por, Molecular Weight Cut-Off (MWCO) of 1 kD) to remove the supporting electrolyte and the dopant source and finally they were lyophilized (Edwards, Modulyo) at a pressure of 10^{-1} mbar and at an initial temperature (reached with an acetone/dry ice bath) of -76 °C).

S4. XPS, UV-Vis, photoluminescence, STM and SEM characterizations

The pure and doped-GOQDs were re-dispersed in bi-distilled water ($\rho=18.2 \text{ M}\Omega\cdot\text{cm}$) for further characterizations.

The samples for the *X-ray photoemission spectroscopy* (XPS) were prepared by drop casting pure and doped-GOQDs concentrated solution on Cu polycrystalline substrates.

Core level photoemission spectra were taken on a VG ESCALAB MKII spectrometer using the Mg anode of a conventional non-monochromatized X-ray source ($K\alpha=1253.6 \text{ eV}$) and with the analyzer pass energy set to 20 eV. The measurements were taken at room temperature (r.t.) in normal emission. The calibration of the Binding Energy (BE) scale was carried out using the Au 4f photoemission peak as reference. In order to characterize the chemical states of carbon and the dopant heteroatoms, the relative peaks were de-convoluted into chemically-shifted components (after Shirley background removal) using a Doniach-Šunjić shape for the C sp^2 component and symmetrical Voigt functions for the other species. The χ^2 minimization was ensured by the use of the nonlinear least squares routines.

The *UV-VIS absorption spectroscopy* was carried out using an Agilent CARY 100 UV-visible spectrophotometer, thermostated at 25 °C. The *photoluminescence* (PL) spectra were taken with a Perkin-Elmer LS 50B spectrophotometer, thermostated at 25 °C and using an excitation wavelength of 340 nm.

Scanning Tunnelling Microscopy (STM) measurements were performed in the constant current mode with an Agilent 5500 SPM. Vibration insulation was provided by a bungee system enclosed in a sound dumping chamber. STM tips were mechanically cut from a Pt/Ir (80:20) wire with a diameter of 0.25 mm. The graphite used was HOPG ZYB 12x12 mm, SPL. STM measurements were performed at the HOPG/air interface at room temperature (RT). STM data were analyzed with the WSxM software.⁶ The topography measurements were background corrected. All mentioned bias voltages correspond to the sample voltage, relative to the grounded tip.

Surface preparation was performed by adhesive tape cleaving of the HOPG surface and the surface cleaning was accurately checked prior each deposition of graphene oxide quantum dots (GOQD). The deposition technique chosen for all the observation was the drop-coating method.⁷ This method consists of heating separately the pure and doped-GOQDs solutions (~ 1 mg/mL) and the substrate at 90°C. Then, 30-50 μL were deposited on the surface, maintained at 90°C until the solvent was completely evaporated. With this preparation technique, relatively neat samples were obtained which could be observed for several days, albeit, to limit ambient contamination, STM investigations were performed just after completion of the drop-coating process.

The nano- and micro-scale micrographs of the materials here reported were performed using *Scanning Electron Microscopy* (SEM). The instrument used in this work was a field emission SEM equipped with a GEMINI column in a Zeiss Supra 35VP system. Micrographs have been taken with an acceleration voltage of 5 kV and using InLens high-resolution detection.

S5. ORR catalytic tests on pure and doped-GOQDs

The electrochemical activity measurements toward the ORR were carried out by CVs and rotating disk electrode (RDE), using an Autolab PGstat 101 potentiostat. A conventional three-electrode configuration consisting of a Pt wire as CE and a saturated Ag/AgCl/ $\text{Cl}^-_{(\text{sat.})}$ as RE was used (standard electrode potential $E^\ominus_{\text{Ag/AgCl}(\text{sat.})} = 0.197 \text{ V}$ with respect to the standard hydrogen electrode, SHE). All the potentials reported in this work are referred to the SHE.

In order to prepare the catalyst ink, 4 mg of pure or doped-GOQDs were dissolved in 1 mL of bi-distilled water; after the addition of perfluorinated Nafion alcoholic solution (5%, Aldrich), the so- obtained solutions were ultra-sonicated for 30 min. Then, the WEs were prepared depositing 15 μL of the desired ink onto a polished (see 2.1) GC disk mounted in a RDE tip (Autolab RDE-2), which exposed an area of 0.071 cm^2 to the electrolytic medium. Finally, the drop-cast films were dried in air at r.t. for about 12 h. The CV and RDE measurements were performed in 0.1 M KOH purging the solutions with Ar before each measurement, while the ORR tests were carried out in an O_2 saturated solution.

The transferred electron number per O_2 molecule involved in the ORR process and, therefore, the predominant reaction pathway, was determined using the Koutecky-Levich formalism. The equation that relates the current density j to the angular rotation speed (ω) of the electrode is given by Eq. 1:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\sqrt{\omega}} \quad (1)$$

where j_k is the kinetic current and B is the Levich slope given by the Eq. 2:

$$B = 0.2 n F \sqrt[3]{D_{O_2}^2 \frac{C_{O_2}}{\nu}} = 0.0355 \cdot n \quad (2)$$

n is the number of exchanged electrons in the reduction of one O_2 molecule, F is the Faraday constant (96485 C mol^{-1}), C_{O_2} is the concentration of dissolved oxygen ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$), D_{O_2} is the diffusion coefficient of oxygen in water ($1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and ν is the kinematic viscosity of the solution ($0.01 \text{ cm}^2 \text{ s}^{-1}$, for a KOH 0.1M solution).⁸ The constant 0.2 is adopted when the angular rotation speed is expressed in rpm.⁴

The B-, N- and B,N-doped GOQDs were subjected to a chemical reduction treatment in a concentrated solution of $NaBH_4$. 4 mg of pure or doped-GOQDs were dissolved in 1 mL of bi-distilled water; then, 5 mg of $NaBH_4$ (Aldrich) were slowly added (in ~ 30 min) to the solution under vigorous stirring and placed in a thermostated water bath (at 25°C). The solution was left under stirring in the thermostated bath for 12 h. After that, the solution was dialyzed for five days with osmotic membrane (Spectra/Por, Molecular Weight Cut-Off (MWCO) of 1 kD) to remove the excess of $NaBH_4$ and the reduction side products.

The preparation of the films, the XPS analysis and the ORR tests were conducted following the same procedures reported above.

S6. Demonstration of the radical-based mechanism during the electrochemical synthesis of pure and doped-GOQDs

The molecular mechanism involved in the electrochemical preparation of graphene (G) and GOQDs represents still an open question;⁹ nevertheless the most credited explanation is based on a radical-mediated process.¹⁰ In order to prove the central role played by water electrolysis, the potential window during the electrochemical cycling of the GO WE was reduced, so that water dissociation and the consequent gas evolution (oxygen evolution and hydrogen evolution reactions during the anodic and cathodic branch of the CV, respectively) are suppressed, (Figure S4a, b). In this experiment, two different GO WEs were cycled 2000 times at 500 mV/s in PBS electrolyte (solution A, see text) within two different potential windows: the first one was cycled between +3.000 V and -3.000 V vs. $Ag/AgCl/Cl^-_{(sat.)}$ ($-2.803 \text{ V} \div +3.197 \text{ V}$ vs. SHE, as

performed in ref. 3 and 4), while the second one was cycled in the range ± 0.9 V vs. Ag/AgCl/Cl⁻_(sat.) (-0.733 V $\div$ $+1.067$ V vs. SHE). As Figure S4c shows, the solutions produced at low potential are transparent and do not show any photoluminescence, meaning the electrodes were not etched and no GOQDs were then produced. Therefore the mechanism at the basis of the formation of GOQDs must imply the participation of radical species coming from water electrolysis, which can either react with the doping molecules creating other radicals or with the GO electrode surface forming active species that later can react with the molecules bearing the dopants.

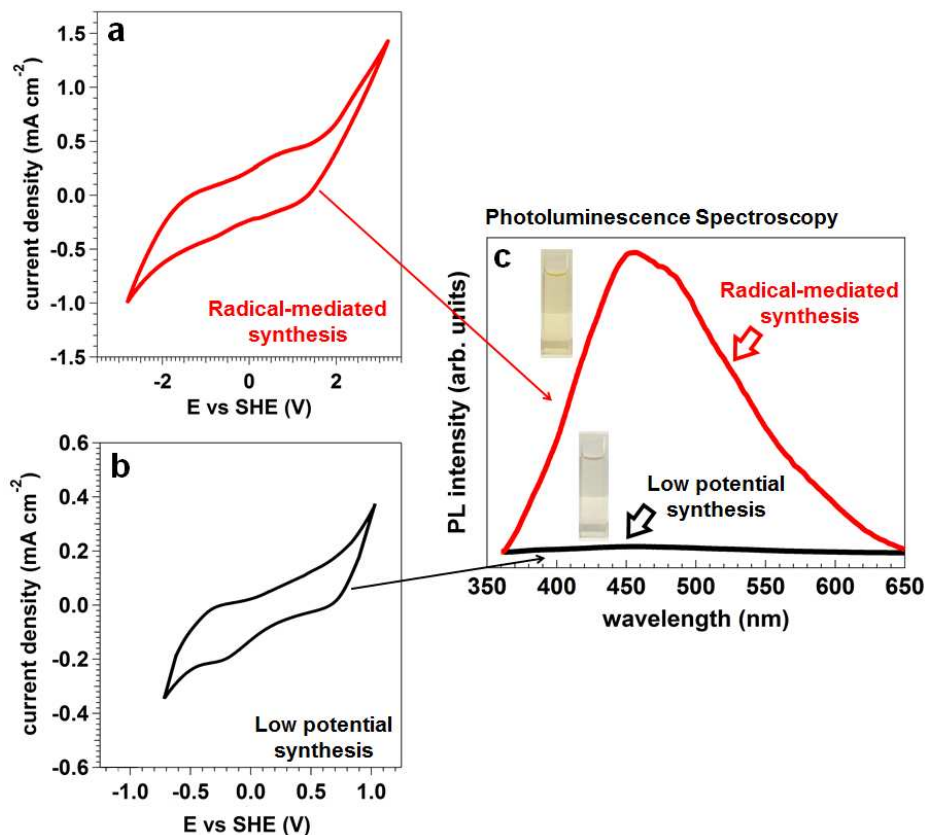


Figure S4. CV curves (recorded at a scan rate of 500 mV/s) during the synthesis of GOQDs within different potential ranges; a: -2.803 V $\div$ $+3.197$ V; b: -0.733 V $\div$ $+1.067$ V; c: photoluminescence spectra of the solutions obtained by the two different methods (the solutions have been purified as described in session S3). The photoluminescence was induced by an excitation wavelength of 340 nm.

S7. XPS survey scans for the prepared systems

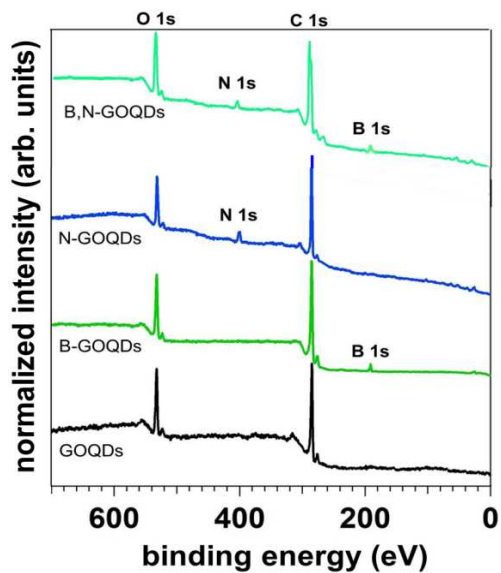


Figure S5. Survey scans for pure and doped-GOQDs.

S8. XPS difference spectra

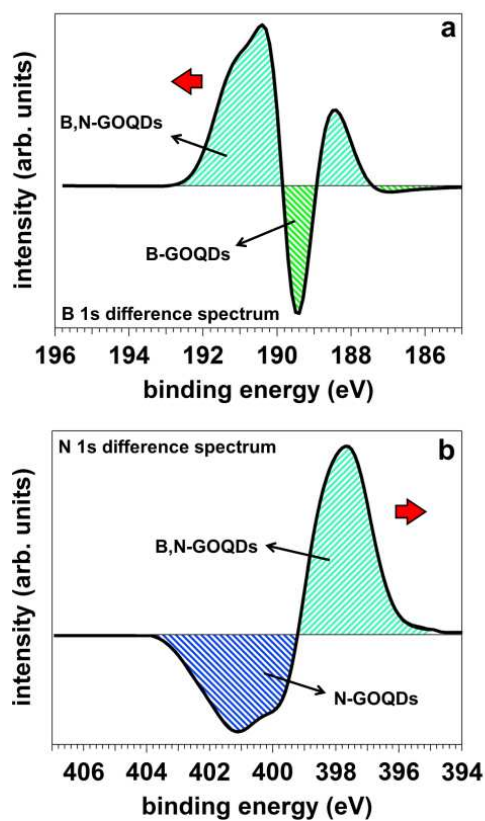


Figure S6. Difference spectra calculated between B (a) and N 1s (b) signals of B- and B,N-GOQDs, after Shirley background subtraction and area normalization.

S9. SEM images of the prepared GOQD film on polished GC

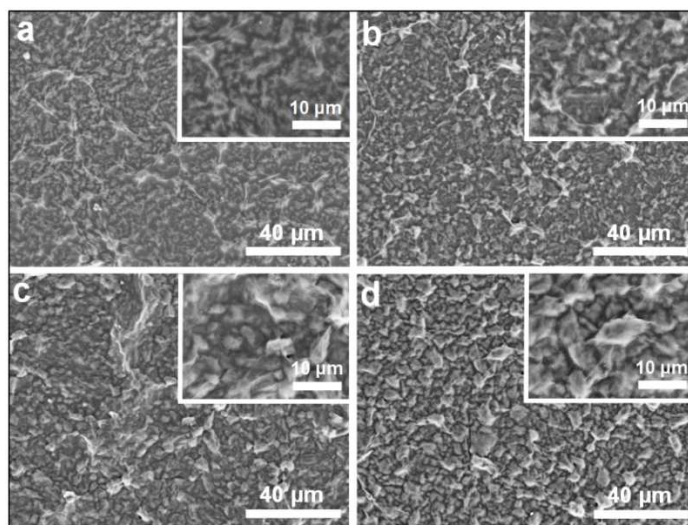


Figure S7. SEM micrographs of pure- (a), B- (b), N- (c) and B,N-GOQD (d) films.

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