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Multiple doping in graphene oxide foams and quantum dots: new switchable systems for oxygen reduction and water remediation

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Experimental Details

2.1 Synthesis of doped-GOQDs

Electrochemical (EC) preparation of GOQDs [1,2] was carried out as reported in our recent work.[3]

In a standard three-electrode EC cell, a Pt ring and a saturated Ag/AgCl/Cl$^-$ were used as Counter (CE) and Reference Electrode[1] (RE), respectively. The electrolytic solutions (constant volume of 50 mL) were kept at 25 °C during the synthesis by a thermostatic water bath. A magnetic stirrer was used to stir the electrolyte during the reactions. All the Cyclic Voltammetries (CVs) were acquired by exposing the same disk area to the electrolytic medium (1.5 cm^2), by enveloping the samples with Teflon tape and contacting them from the back by a copper plate. The electrochemical measurements were carried out using 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 by 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

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[1] The standard electrode potential of Ag/AgCl/Cl$^-_{(sat.)}$, $E^\Theta_{Ag/AgCl\,(sat.)}$, is equal to 0.197 V with respect to the standard hydrogen electrode, SHE. All the potentials reported in this work are referred to the Ag/AgCl/Cl$^-_{(sat.)}$ electrode.

GO in water (15 mg of GO/mL) were drop cast on these GC substrates (GO/GC) and then annealed in a tubular furnace at 150 °C for 30 min under an overpressure flow of N_2 (500 sccm). The EC synthesis of doped-GOQDs were carried out adding to a 0.1 M Phosphate Buffer Solution (PBS) the molecular precursor chosen as dopant source. Table 1 reports the experimental conditions for the different syntheses.

The potential was cycled between ± 3.0 V (vs. $Ag/AgCl/Cl^{-}_{(sat)}$), at a scan rate of 500 mV/s. 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 through osmotic membranes (Spectra/Por, Molecular Weight Cut-Off (MWCO) of 1 kD) to remove the supporting electrolyte and the dopant source. Lastly, the solutions were lyofilized (Edwards, Modulyo) at a pressure of 10^{-1} mbar and at an initial temperature (reached by an acetone/dry ice bath) of -76 °C). Then, the obtained powders of pure and doped-GOQDs were re-dispersed in Milli-Q water (18.2 MΩ cm at 25°C) for further characterization.

Table S1. Experimental conditions for the synthesis of doped-GOQDs.

	Electrolytic Solution	**Dopant Molecule** [1]	**Final pH** [2]
GOQDs	PBS 0.1M (pH 6.86)	-	6.86
B-GOQDs	PBS 0.1M (pH 11.20) [3]	**1.** 1,4-phenylenebis(boronic acid) (**1**)	11.20
N-GOQDs	PBS 0.1M (pH 6.86)	**1.** ethylenediamine (**2**)	11.30
	PBS 0.1M (pH 1.85) [4]	**2.** 1,10-phenantroline (**3**)	1.85
S-GOQDs	PBS 0.1M (pH 12.20) [5]	α-lipoic acid (**4**)	12.20
B,N-GOQDs	PBS 0.1M (pH 6.86)	ethylenediamine + 1,4-phenylenebis(boronic acid)	11.30
S,N-GOQDs	PBS 0.1M (pH 6.86)	L-cysteine (**5**)	6.80

[1] The quantity of the dopant was added in order to obtain a dopant volumetric concentration of 100 mM

[2] The pH was measured after the addition of the dopant to the 0.1 M buffer solution.

[3,5] The pH was increased by adding few drops of a 10 M NaOH solution, in order to allow the solubilisation of the doping molecules.

[4] The pH was decreased by adding a few drops of concentrated H_3PO_4 (85 %), in order to allow the solubilisation of 1,10-phenantroline (by protonation of the pyridinic nitrogens).

2.2 XPS, NEXAFS, optical, Raman and SEM characterizations

The samples for the X-ray photoemission spectroscopy (XPS) and for the near edge X-ray absorption spectroscopy (NEXAFS) measurements were prepared by drop casting pure and doped-GOQD concentrated solution on Cu polycrystalline substrates.

Core level photoemission spectra were taken on a VG ESCALAB MKII spectrometer by using a conventional non-monochromatized X-ray source (Mg Kα=1253.6 eV) and with the analyser 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 by using the Au 4f levels as reference. To characterize the chemical states of carbon and the dopant heteroatoms, the relative photoemission 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 otherwise. The χ^2 minimization was obtained by the use of the nonlinear least squares routines.

The NEXAFS measurements were performed at Bear beamline (Elettra synchrotron facility, Trieste, Italy). The measurements were collected in Total Electron Yield (TEY) with an energy resolution of 50 meV.

The UV-VIS absorption spectroscopy data were recorded by using an Agilent CARY 100 UV-visible spectrophotometer, thermostated at 25 °C. The photoluminescence (PL) spectra in bi-distilled water were measured with a Perkin-Elmer LS 50B spectrophotometer, thermostated at 25 °C. The excitation wavelength starts from 340 nm and is progressively increased to the final value of 540 nm, acquiring a PL spectrum every 20 nm.

For the *Raman characterization* we used a ThermoFisher Raman microscope. All spectra were recorded with an excitation wavelength of 532 nm (1.5 mW), focused on the sample by a 50× objective (Olympus).

The nano- and micro-scale micrographs of the materials here reported were obtained by 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 VP35 system. Micrographs were taken with an acceleration voltage of 5 kV and using in-lens high-resolution detection.

2.3 ORR catalytic tests on pure and doped-GOQDs

The electrochemical activity measurements towards 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/$Cl^-_{(sat.)}$ as RE was used.

For preparing the catalyst ink, 4 mg of dialyzed S- or S,N-co-doped-GOQDs were dissolved in 1 mL of bi-distilled water; after the addition of 20 vol % of perfluorinated Nafion alcoholic solution (5 wt %, Aldrich), the so-obtained solutions were ultra-sonicated for 30 min. Then, the WEs were prepared depositing 15 □L 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 with the angular rotation speed (ω) of the electrode is given by Eq. 1:

$$\frac{1}{j} = \frac{1}{j_{\mathrm{k}}} + \frac{1}{B\sqrt{\omega}} \qquad (1)$$

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

$$B = 0.62\, n\, F \sqrt[3]{D_{\mathrm{O_2}}^{2}}\, \frac{C_{\mathrm{O_2}}}{\sqrt[6]{\nu}} = \ 0.0355 \ \cdot\ n \qquad (2)$$

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_{O2} is the concentration of dissolved oxygen (1.2×10^{-6} mol cm^{-3}), D_{O2} is the diffusion coefficient of oxygen in water (1.4×10^{-5} cm^2 s^{-1}) and ν is the kinematic viscosity of the solution (0.01×cm^2 s^{-1}, for a 0.1 M KOH solution).[4] The constant 0.62 is adopted when the angular rotation speed is expressed in rpm. [4]

The S,N-doped GOQDs were subjected to a chemical reduction treatment in a concentrated solution of $NaBH_4$. 4 mg of S,N-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 through an 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-NEXAFS analysis and the ORR tests were carried out by following the same procedures reported above.

2.4 Water remediation: decomposition of phenol

The activity of pure and S,N-co-doped GOQDs towards the decomposition of phenol was estimated by measuring the decomposition rate of the same chemical in an aqueous solution. 50 mL of a PBS solution (pH = 4.5), saturated with O_2, were used as electrolyte in a standard three-electrode EC cell, using a saturated Ag/AgCl/Cl^- as RE. The WE and CE were prepared by drop-casting 250 μL of pure or S,N-co-doped GOQDs solution (3.0 mg mL^{-1} + 5% $_{\text{vol.}}$ of perfluorinated Nafion alcoholic solution, Aldrich) onto a GC substrate (3.0 cm^2), previously polished as described above. The electrodes were assembled in an EC cell. The cell was enveloped with aluminium foil in order to prevent possible decomposition of phenol by the light. The cell was kept at 25 °C during the electrolysis by a thermostatic water bath. The stirring of the electrolytic medium during the reaction was maintained by a magnetic mixer. The electrochemical measurements were carried out with a EG&G PARC 173 potentiostat/galvanostat. The phenol degradation tests were performed by introducing in the described system 235 mg of phenol (>99.0 %, Aldrich), which corresponds to a concentration of 50 mM. The degradation runs were performed under potentiostatic conditions for about 3.5 h. The phenol degradation was measured by withdrawing small aliquots of the aqueous solution at regular time periods during the reaction (50μL, in order to avoid possible perturbation of the reaction environment).

The withdrawn volumes were diluted in 950μL of Milli-Q water in a quartz cuvette (Aldrich, optical path of 0.5 cm). Phenol concentration was then estimated by colorimetric method using UV–VIS spectrophotometry and the Lambert-Beer equation (Eq. 3):

$$A = \varepsilon_M C \ell \tag{3}$$

where A is the absorbance, ε_M is the molar extinction coefficient and ℓ is the optical path length. ε_M was simulated for phenol dissolved in water in presence of phosphates by PhotoChemCAD package (between 230 and 700 nm), [5] giving a value of 2348.4 cm^{-1}/M (at 270.8 nm).

The spectra were acquired with an Agilent CARY 100 spectrophotometer with a signal averaging time of 0.125 s, a data interval of 1.0 nm and a scan rate of 100.0 nm/min.

Tafel Plots

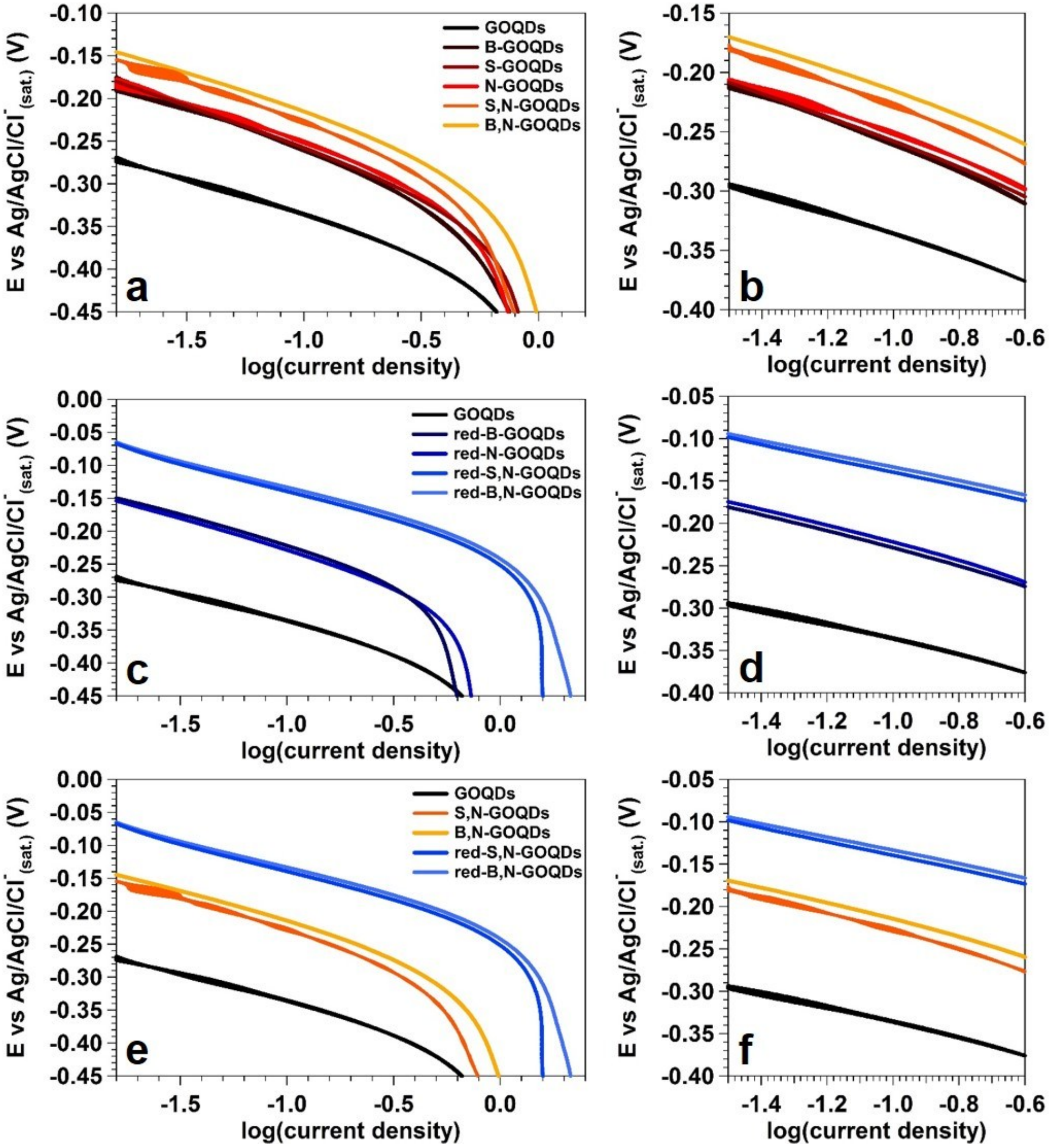

Figure S1: Tafel plots for the different materials deposited on RDE electrode, obtained at a scan rate of 10 mV/s and at a rotation rate of 1500 rpm. Figures b,d and f report a magnification in the linear region of the Tafel plot.

Different active sites on the as-prepared pure, S- and S,N-GOQDs

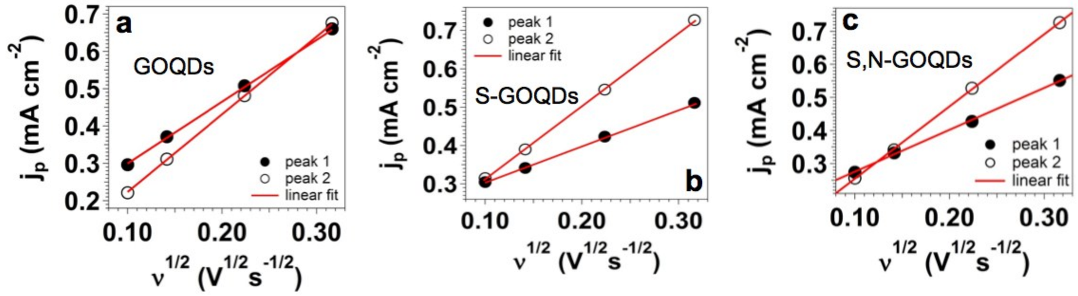

Figure S2. Peak current densities for peaks 1 and 2 for pure (a), S- (b) and S,N-GOQDs (c) as function of the square root of the scan rate. In all the cases the trend is linear, meaning that both the observed voltammetric features are diffusion peaks connected to the irreversible reduction of oxygen on different active sites (see text for the explanation).

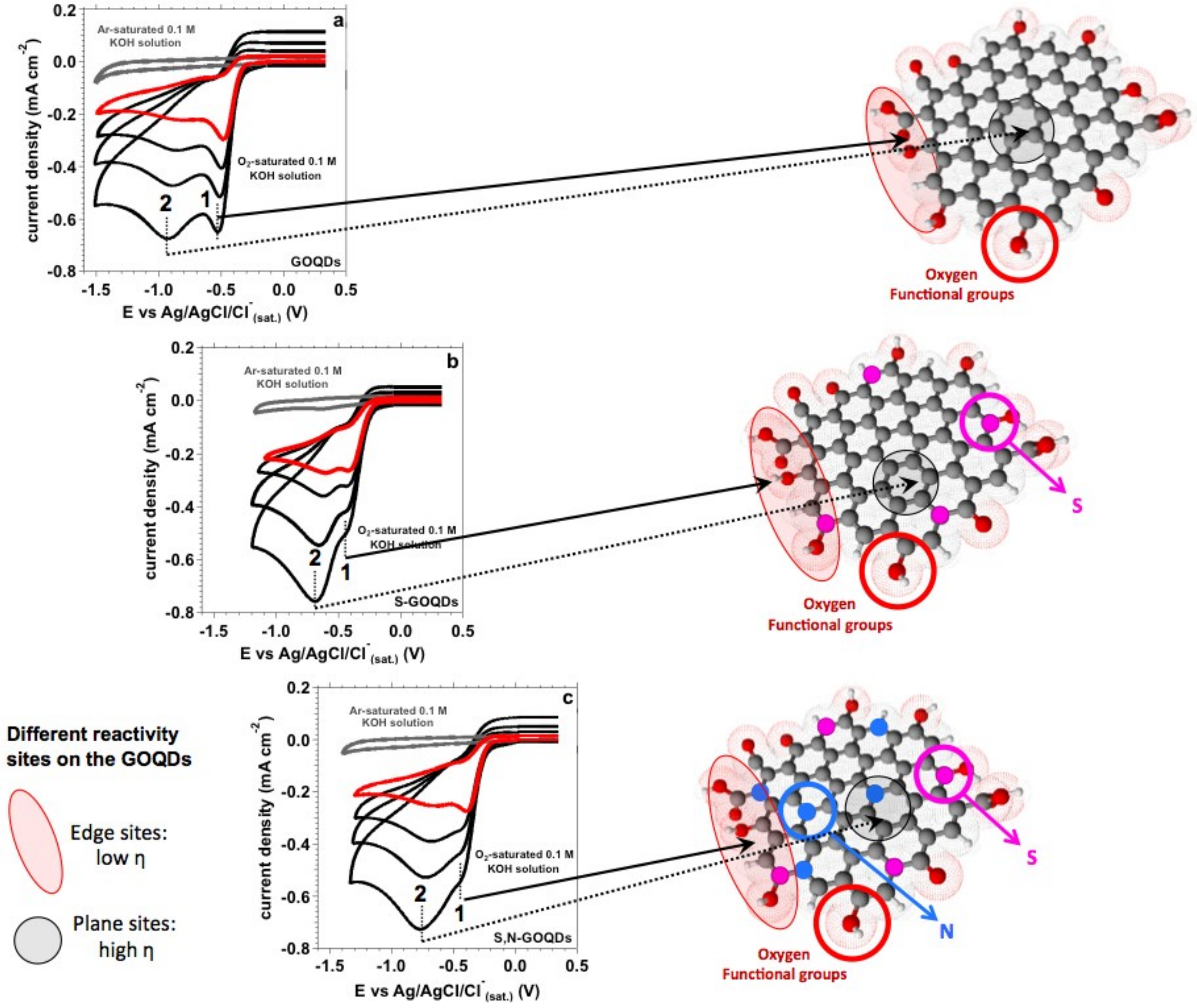

Figure S3. Graphical schematization of the presence of two different active sites on GOQDs (edges vs. basal plane), which are responsible for the presence of the two different diffusion peaks (labelled as 1 and 2, respectively).

Koutecky-Levich analysis on the as-prepared pure, S- and S,N-GOQDs

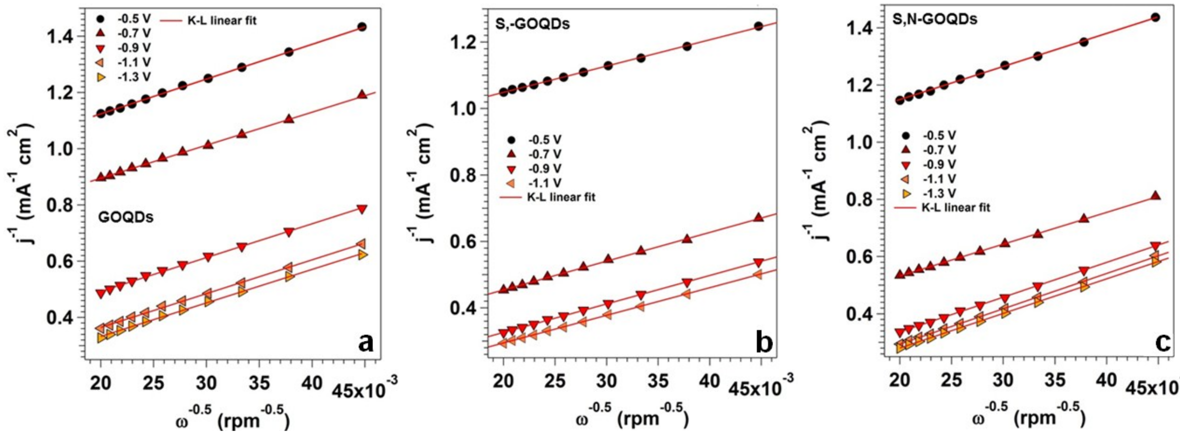

Figure S4. Koutecky-Levich plots for different potentials derived from the RDE measurements, for pure- (a), S- (b) and B,N-GOQDs (c), respectively.

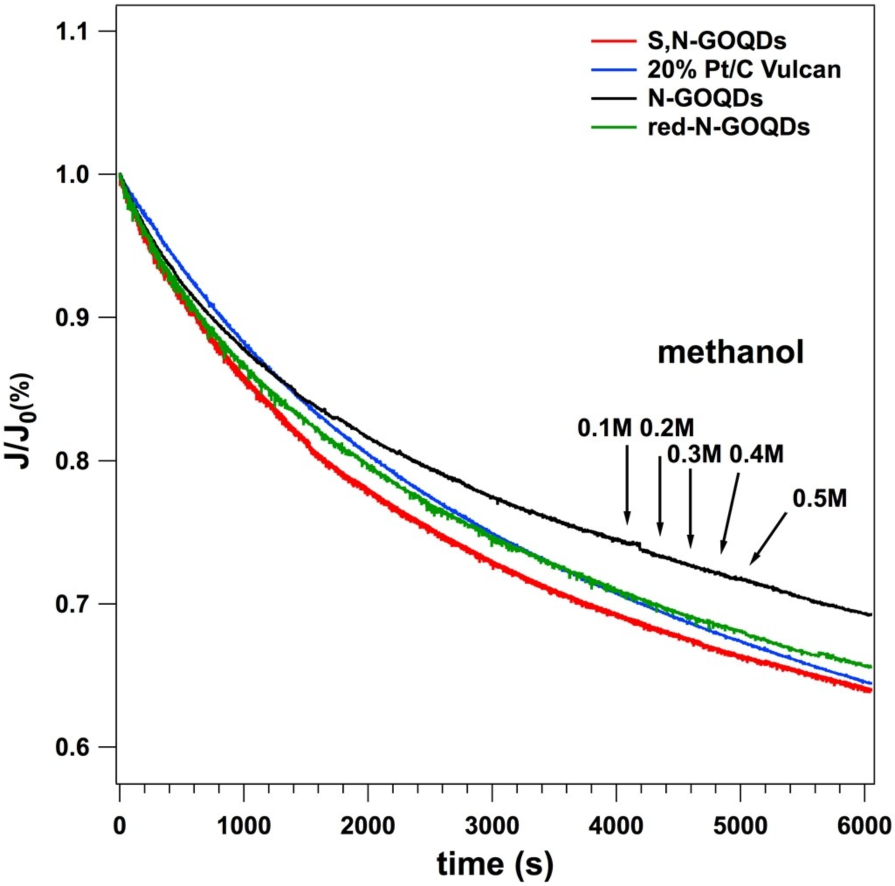

Figure S5: J-t curves for different types of doped GOQDs and commercial 20%Pt on Vulcan XC72. In the case of N-GOQDs small aliquots of methanol (see arrows) have been introduced in reaction ambient to test catalyst tolerance.

XPS analysis of as-prepared pure and doped-GO foams

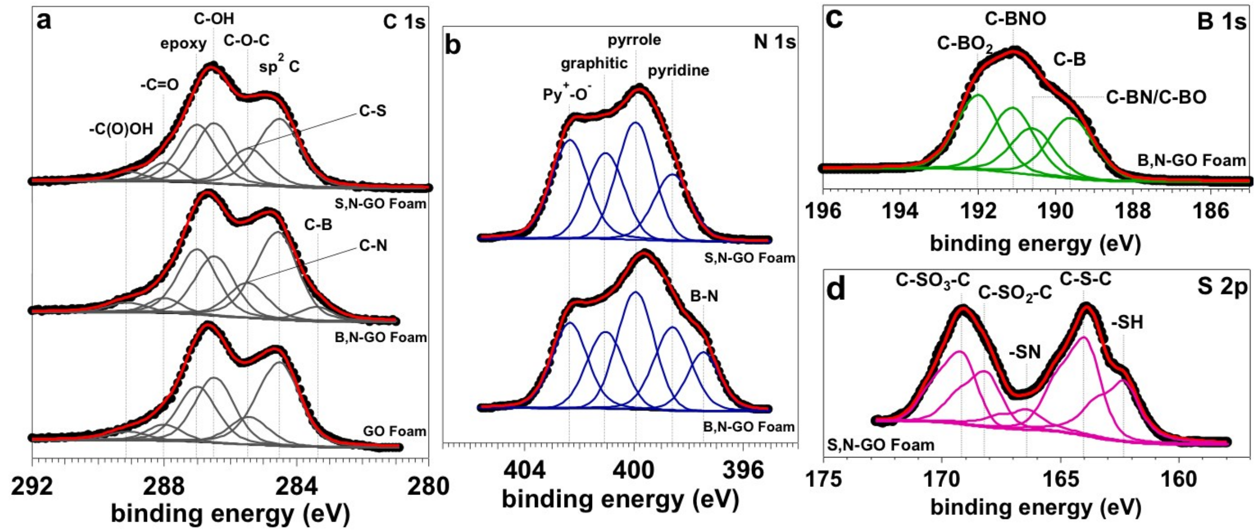

Figure S6. (a) Multicomponent fits of the C 1s photoemission peaks for pure, B,N- and S,N-GO foams; b, c, d: multipeak analysis for N 1s, B 1s and S 2p photoemission lines, respectively.

References

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