Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Nitrogen-Doped Graphene: Effect of Graphite Oxide Precursors and Nitrogen Content on the Electrochemical Sensing Properties

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Experimental section

Apparatus

X-ray photoelectron spectroscopy was performed with a Phoibos 100 spectrometer and a monochromatic Mg X-ray radiation source (SPECS, Germany). Both wide survey and high-resolution spectra for C1s and N 1s were collected. Relative sensitivity factors were used for the evaluation of atomic C/O ratios from XPS wide survey spectra measurements. XPS samples were prepared by coating a carbon tape with a uniform layer of the materials under study. A JEOL-7600F semi-in-lens FE-SEM, operating in SEI mode at 5 kV was used to acquire the SEM images. The solid samples were transferred to a carbon tape held onto a SEM holder for analyses. The analyses of the samples were carried out at an average working distance of 8 mm. Combustible elemental analysis (CHNS-O) was performed using a PE 2400 Series II CHNS/O Analyzer (Perkin Elmer, USA). The instrument was used in CHN operating mode (the most robust and interference-free mode) to convert the sample elements to simple gases (CO_2, H_2O and N_2). The PE 2400 analyzer automatically performed combustion, reduction, homogenization of product gases, separation and detection. An MX5 microbalance (Mettler Toledo) was used for precise weighing of the samples (1.5–2.5 mg per single sample analysis). Using this procedure, the accuracy of CHN determination is better than 0.30% abs. Internal calibration was performed using an N-fenyl urea. Raman spectroscopy was conducted on an inVia Raman microscope (Renishaw, England) with a CCD detector in backscattering geometry. A DPSS laser (532 nm, 50 mW) with a 100x magnification objective was used for the Raman measurements. X-ray powder diffraction data were collected at room temperature on Bruker D8 Discoverer powder diffractometer with parafocusing Bragg–Brentano geometry using CuKα radiation ($\lambda = 0.15418$ nm, $U = 40$ kV, $I = 40$ mA). Data were scanned over the angular range 5–90° (2θ) with a step size of 0.019° (2θ). Data evaluation was performed in the software package EVA. The surface area was measured using a sorption analyzer, Coulter SA

3100 (Backman Coulter). The samples were outgassed for 4 hours at 95 °C under high vacuum (VALUE) prior to the sorption experiments. The reason for such a low temperature is to avoid degradation and further decomposition of oxygen functionalities. A TCD nitrogen cooled (77 K) detector was used for the evaluation of the results using BET (Brunauer, Emmett and Teller) and Kelvin equations. The FT-IR spectroscopy was performed using iS50R spectrometer (Thermo Scientific, USA). A Diamond ATR crystal and DLaTGS detector were used for all measurements, which were carried out in the range 4000–400 cm-1. The samples were diluted with KBr (1:100 by weight) and homogenized in agate mortar before measurement. High resolution transmission electron microscopy (HR-TEM) was performed using EFTEM Jeol 2200 FS microscope (Jeol, Japan). A 200 keV acceleration voltage was used for measurement. Sample preparation was attained by drop casting the suspension (1 mg mL^{-1} in water) on a TEM grid (Cu; 200 mesh; Formvar/carbon) and drying at 60 °C for 12 h.

Procedures

Graphene Oxide Synthesis

Staudenmaier method: Sulphuric acid (98%, 87.5 mL) and fuming nitric acid (>98%, 27 mL) were added to a reaction flask containing a magnetic stir bar. The mixture was cooled to 0°C and graphite (5 g) was added. To avoid agglomeration and to obtain a homogenous dispersion, the mixture was vigorously stirred. While keeping the reaction flask at 0°C, potassium chlorate (55 g) was slowly added. The reaction flask was loosely capped to allow the escape of the gas evolved, upon the complete dissolution of potassium chlorate. The mixture was then continuously stirred for 96 h at room temperature. The mixture was poured into 3 L of deionised water and decanted. Graphite oxide was redispersed again in HCl solution (5%, 3 L) to remove sulphate ions. It was repeatedly centrifuged and re-dispersed in deionized water until a negative reaction on chloride ions was achieved. Graphite oxide slurry was then dried in a vacuum oven.

Hummers method: Graphite (5 g) and sodium nitrate (2.5 g) were stirred with sulphuric acid (98%, 115 mL). The mixture was cooled to 0°C and potassium permanganate (15 g) was then added over a period of 2 h. During the next 4 h, the reaction mixture was allowed to reach to room temperature before being heated to 35°C for 30 min. The reaction mixture was then poured into a flask containing deionized water (250 mL) and heated for 15 min to 70°C. The mixture was subsequently poured into deionized water (1 L). 3% hydrogen peroxide was added to remove unreacted potassium permanganate and manganese dioxide. The reaction mixture was then allowed to settle and decant. The obtained graphite oxide was then purified by repeated centrifugation and re-dispersing in deionized water until a negative reaction on sulphate ions was achieved. Graphite oxide slurry was then dried in a vacuum oven.

Hofmann method: Sulphuric acid (98%, 8.75 mL) and nitric acid (68%, 27 mL) were added to a reaction flask (Pyrex beaker with thermometer) containing magnetic stir bar. The mixture was cooled by immersion in an ice bath for 30 min. With vigorous stirring motion, graphite (5 g) was added to the mixture. While keeping the reaction flask in the ice bath, potassium chlorate (55 g) was slowly added to the mixture. The reaction flask was loosely capped to allow the escape of the gas evolved upon the complete dissolution of potassium chlorate. The mixture was continuously stirred for 96 h at room temperature. The mixture was poured into 3 L of deionised water and decanted. Graphite oxide was redispersed again in HCl solution (5%, 3 L) to remove sulphate ions. It was repeatedly centrifuged and re-dispersed in deionized water until a negative reaction on chloride ions was achieved. Graphite oxide slurry was then dried in a vacuum oven.

Brodie method: Fuming nitric acid (>98%, 62.5 mL) was added to a reaction flask containing a magnetic stir bar. The mixture was subsequently cooled to 0^{o}C and graphite (5 g) was added. The mixture was stirred to obtain a homogenous dispersion. Potassium Chlorate (25 g) was slowly added to the mixture while keeping the reaction flask at 0^{o}C. The reaction flask was loosely capped to allow the escape of the gas evolved upon the complete dissolution of potassium chlorate and the mixture was stirred for 20 h at 40^{o}C. Upon completion of the reaction, the mixture was poured into 3 L of deionized water and decanted. Graphite oxide was redispersed again in HCl solution (5%, 3 L) to remove sulphate ions. It was repeatedly centrifuged and re-dispersed in deionized water until a negative reaction on chloride ions was achieved. Graphite oxide slurry was then dried in a vacuum oven.

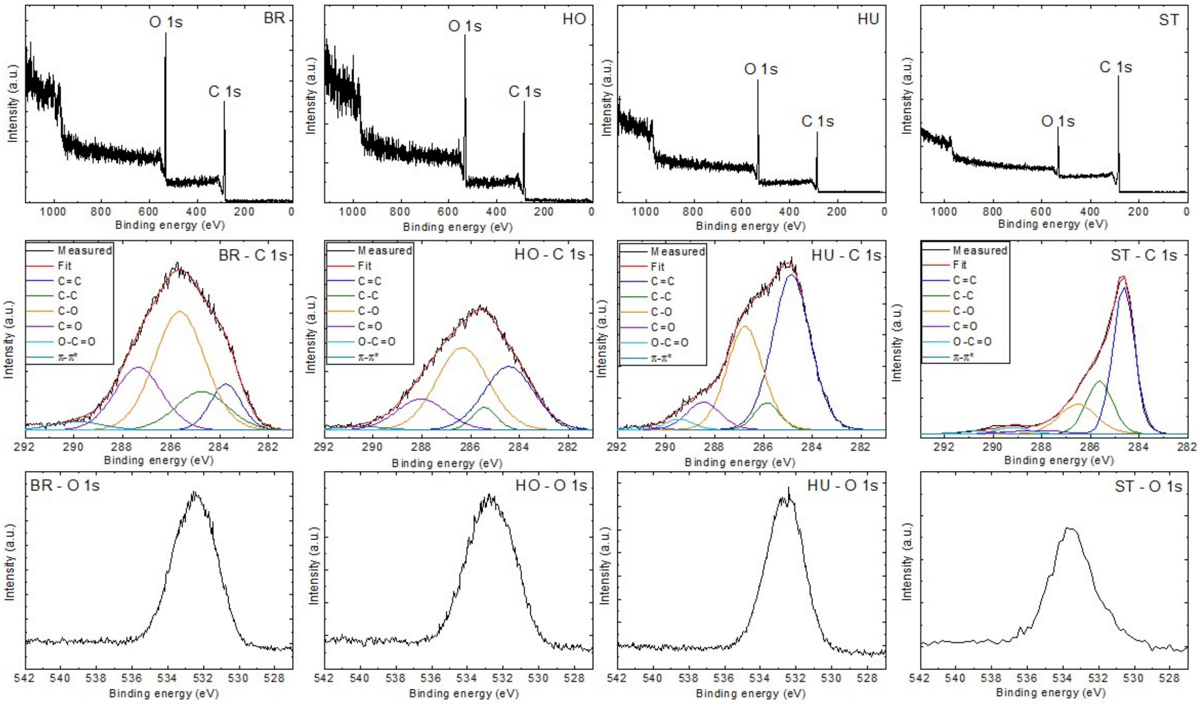
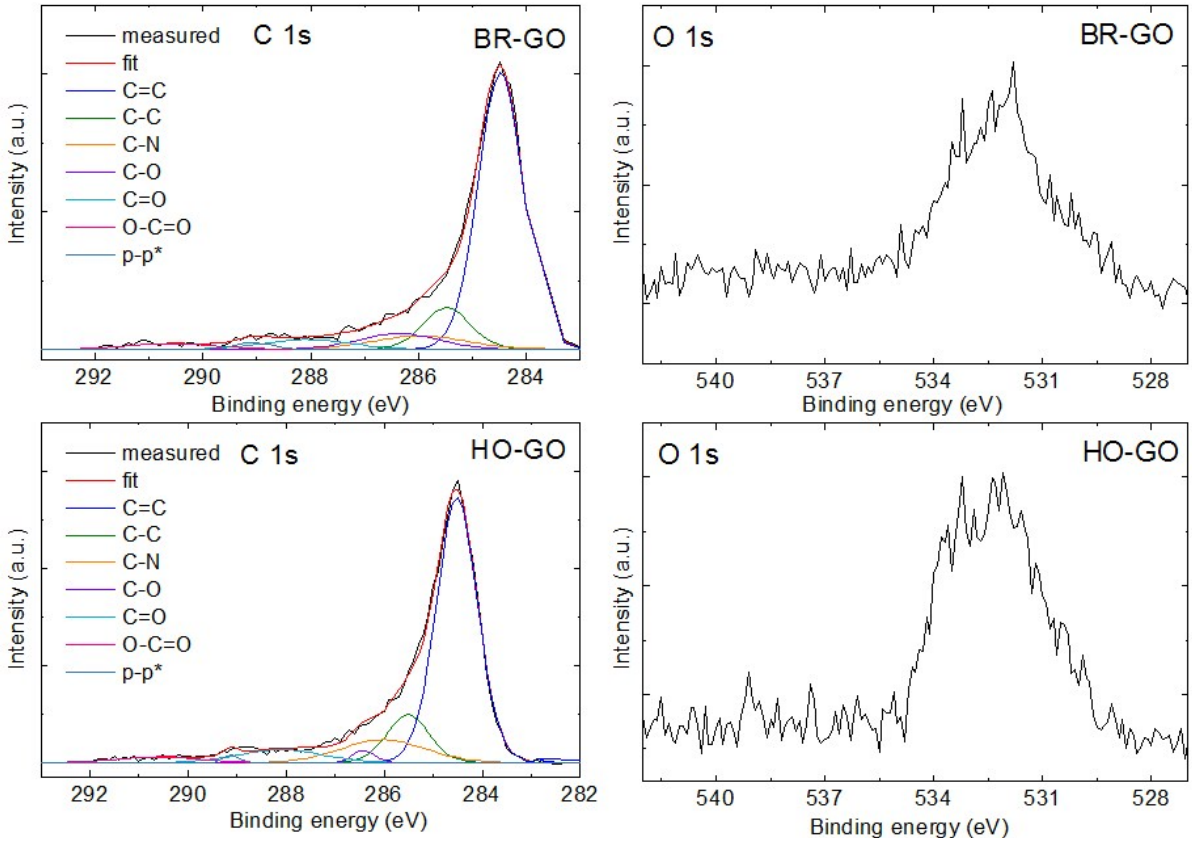


Figure S-1. Detail XPS analysis of starting GO used for synthesis including survey spectra (first line), high resolution C 1s spectra (second line) and high resolution O 1s spectra (third line).



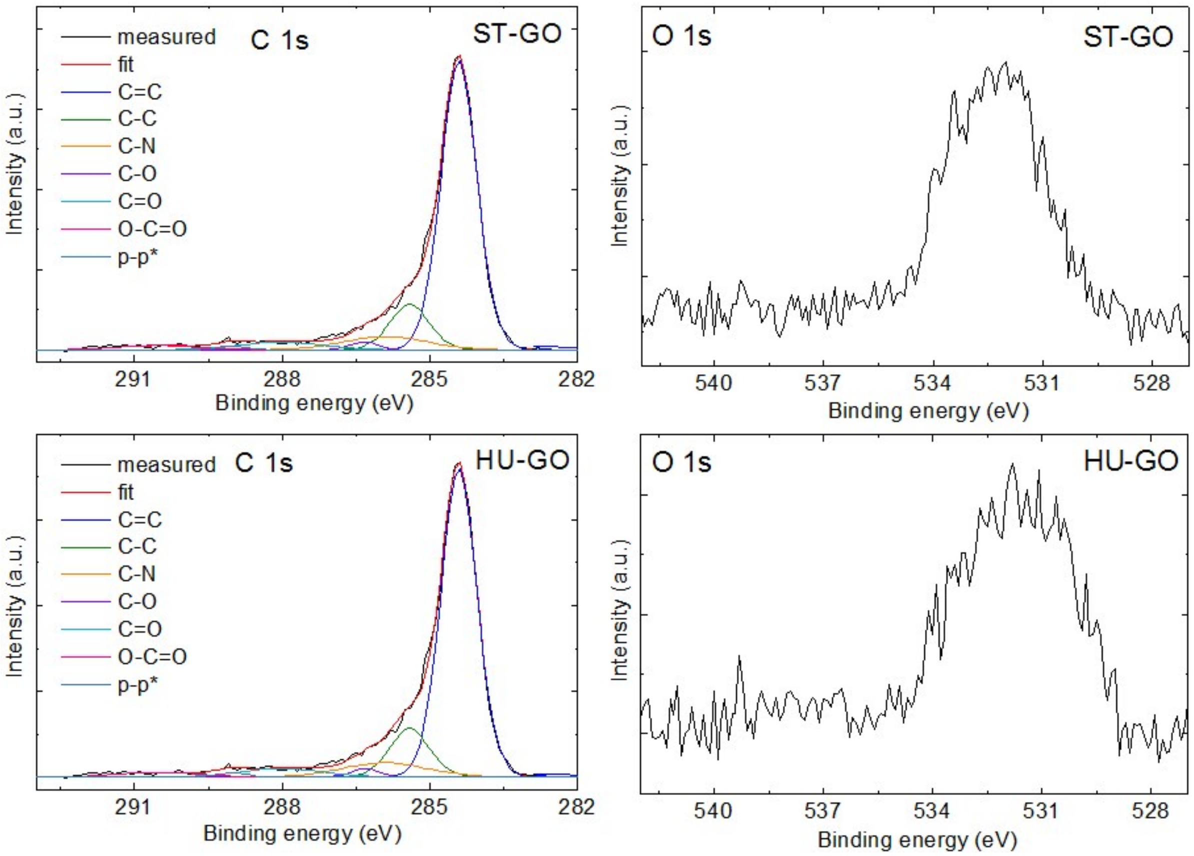


Figure S-2. The high resolution XPS spectra (C 1s and O 1s) of ST-GO, HU-GO, HO-GO and BR-GO samples.

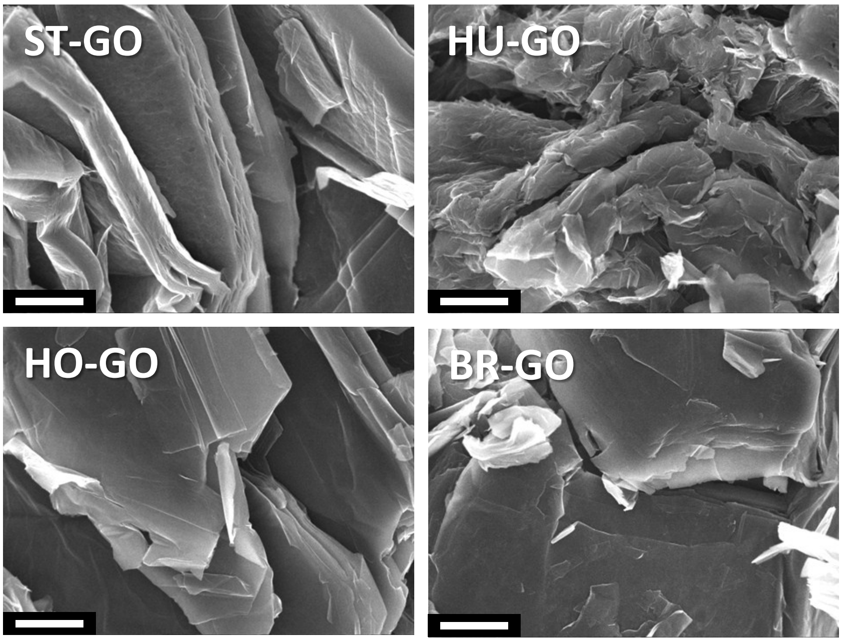


Figure S-3. SEM images of ST-GO, HU-GO, HO-GO and BR-GO at 20000× magnification.

Scale bar indicates 1 μm.

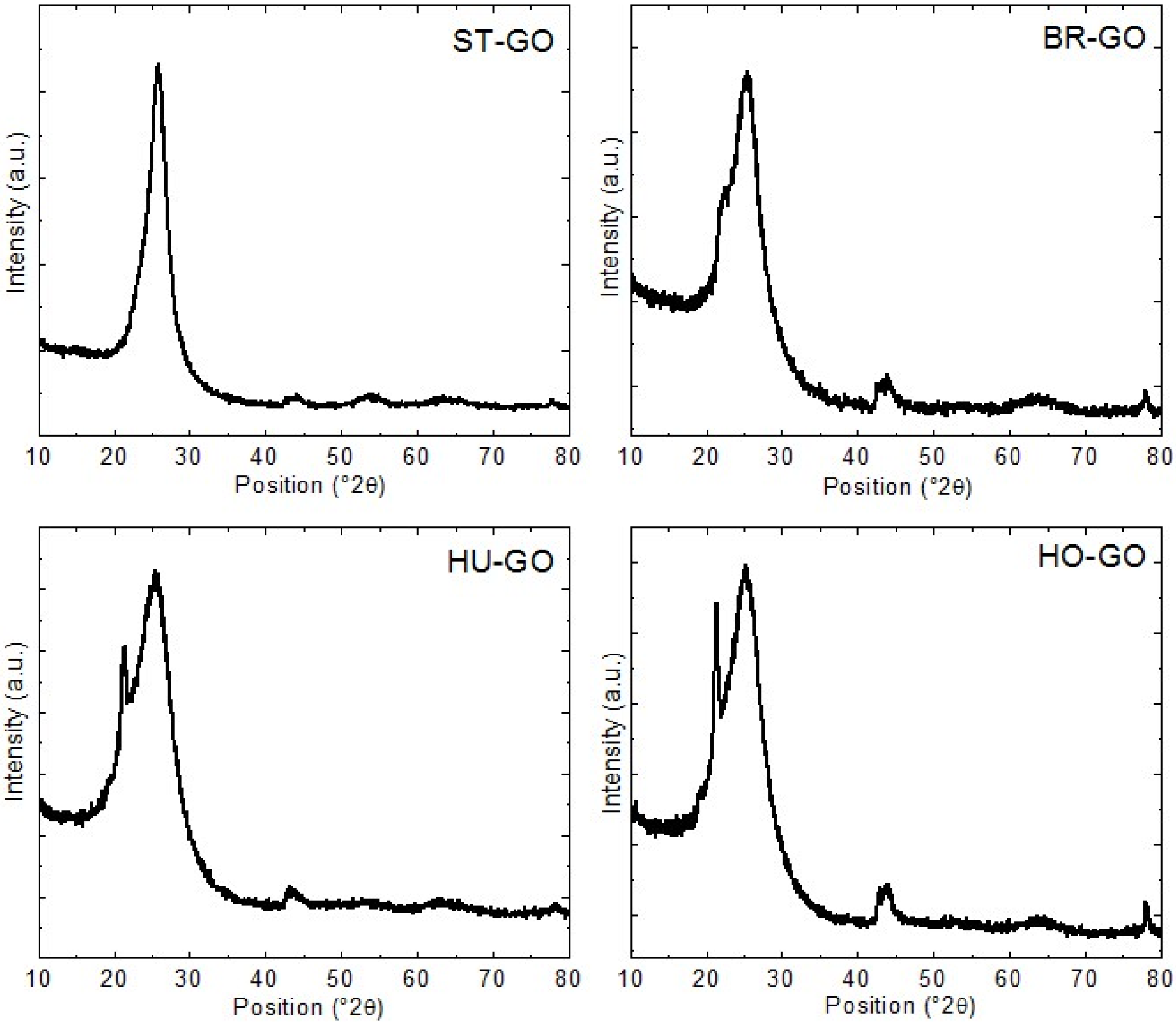


Figure S-4 X-ray diffractograms of ST-GO, HU-GO, HO-GO and BR-GO.

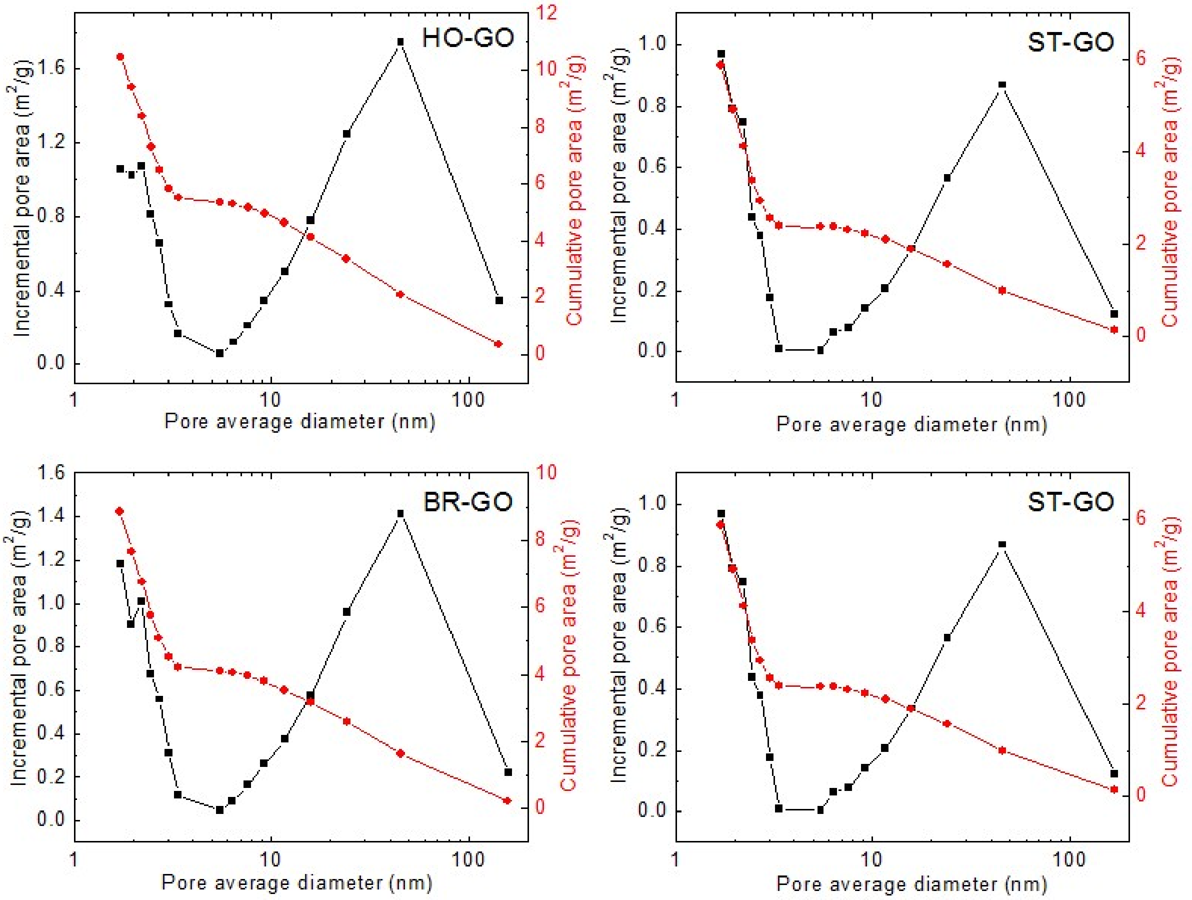


Figure S-5. Pore size distribution of ST-GO, HU-GO, HO-GO and BR-GO.

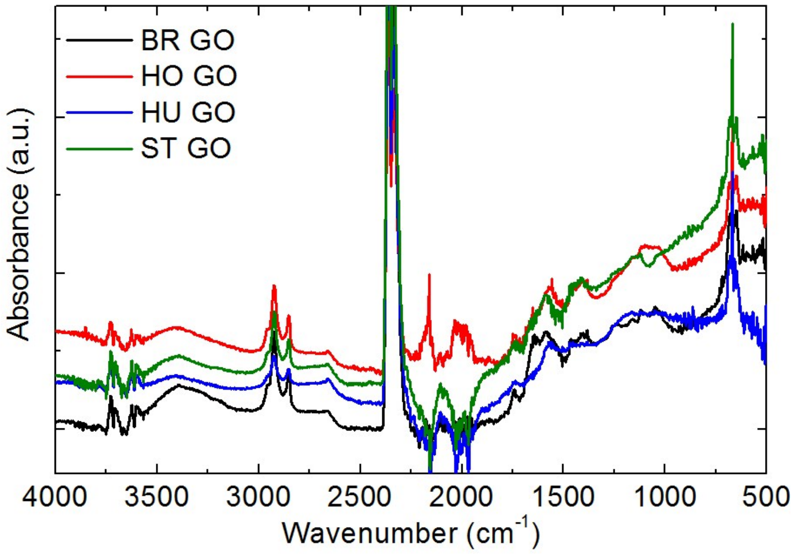


Figure S-6. FT-IR spectra of ST-GO, HU-GO, HO-GO and BR-GO.

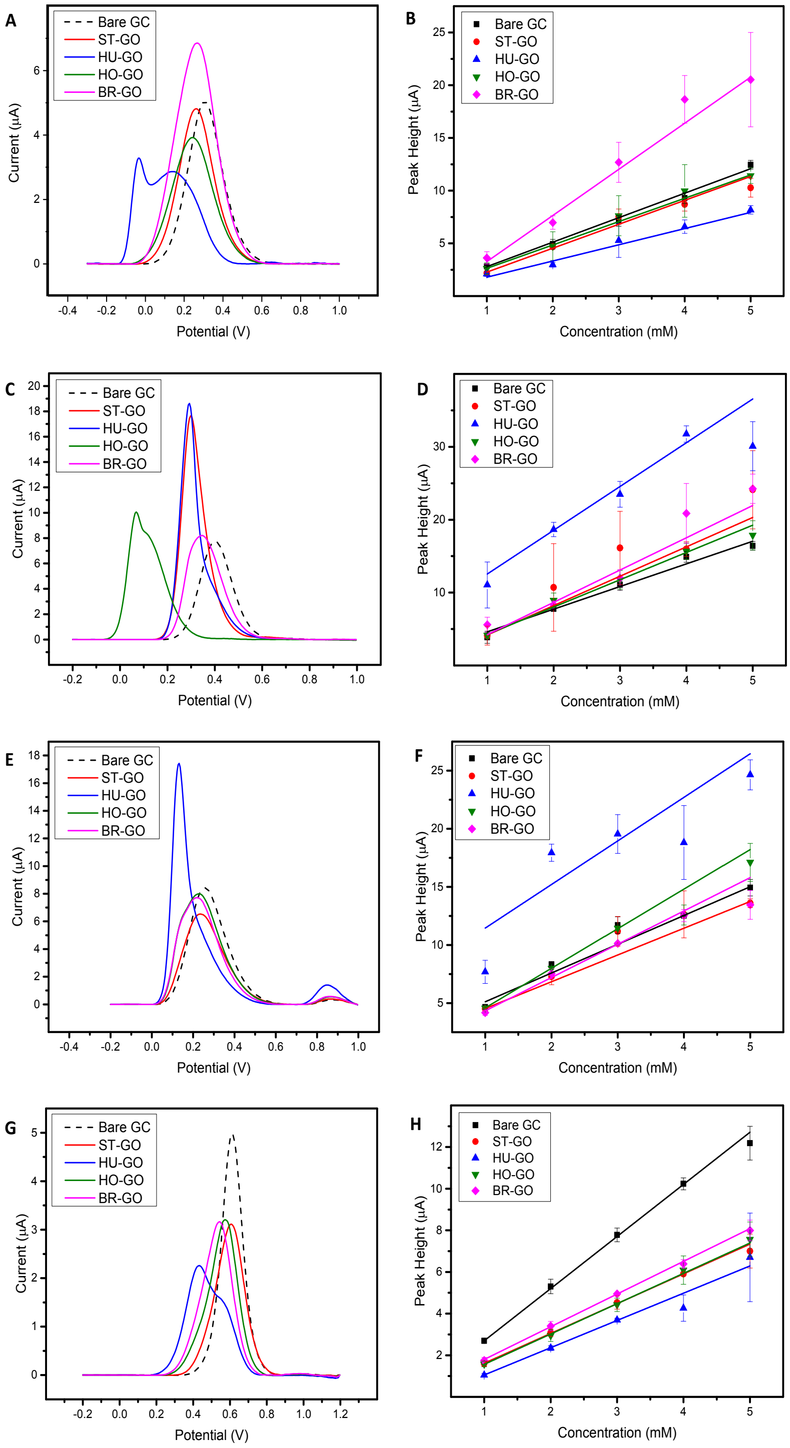


Figure S-7. DPV profiles and calibration plots of (A-B) ascorbic acid, (C-D) uric acid, (E-F) dopamine and (G-H) NADH on bare GC, ST-GO, HU-GO, HO-GO and BR-GO surfaces. Conditions: 50 mM PBS electrolytes, pH 7.2, scan rate 100 mV s^{-1}, amount of material 1 μg. Blank scans did not show any prominent peaks beyond 0.5 μA (data not shown).

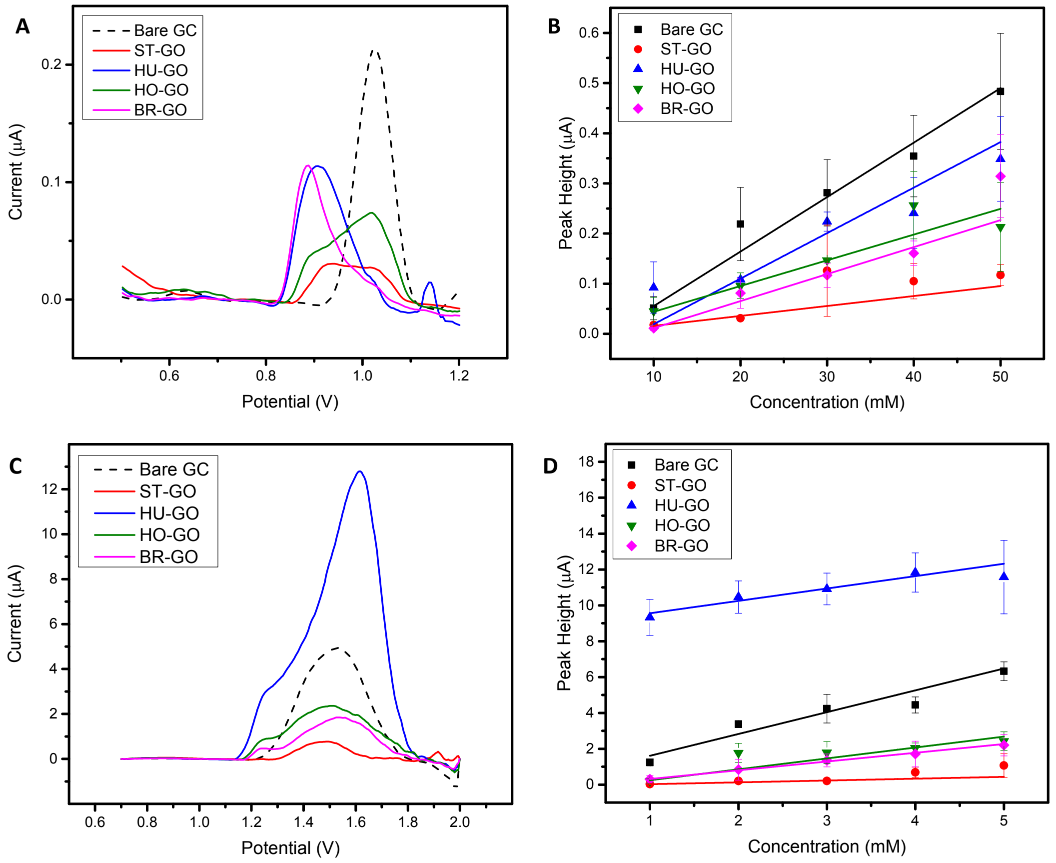


Figure S-8. DPV profiles and calibration plots of (A-B) adenine and (C-D) cytosine on bare GC, ST-GO, HU-GO, HO-GO and BR-GO surfaces. Conditions: 50 mM PBS electrolytes, pH 7.2, scan rate 100 mV s^{-1}, amount of material 1 μg. Blank scans did not show any prominent peaks beyond 0.5 μA (data not shown).

Table S-1. Sensitivity and correlation coefficient of DPV determinations of ascorbic acid, uric acid, dopamine and NADH on bare GC, ST-GO, HU-GO, HO-GO and BR-GO surfaces based on calibration plot from Figure S-2; standard deviations are given in parentheses.

Analyte	**Materials**	**Slope/µA mM^{-1}**	**R-Squared**
Ascorbic Acid	Bare GC	2.323 (0.399)	0.9957
	ST-GO	2.270 (0.509)	0.9823
	HU-GO	1.538 (0.620)	0.9676
	HO-GO	2.216 (1.408)	0.9975
	BR-GO	4.377 (1.973)	0.9525
Uric Acid	Bare GC	2.323 (0.399)	0.9957
	ST-GO	2.270 (0.509)	0.9823
	HU-GO	1.538 (0.620)	0.9676
	HO-GO	2.216 (1.408)	0.9975
	BR-GO	4.377 (1.973)	0.9525
Dopamine	Bare GC	2.475 (0.381)	0.9829
	ST-GO	2.302 (0.903)	0.9916
	HU-GO	3.750 (1.574)	0.6631
	HO-GO	3.404 (0.561)	0.9954
	BR-GO	2.865 (0.516)	0.9873
NADH	Bare GC	2.504 (0.357)	0.9993
	ST-GO	1.431 (0.304)	0.9996
	HU-GO	1.310 (0.608)	0.9964
	HO-GO	1.458 (0.450)	0.9981
	BR-GO	1.571 (0.227)	0.9986

Table S-2. Sensitivity and correlation coefficient of DPV determinations of adenine and cytosine on bare GC, ST-GO, HU-GO, HO-GO and BR-GO based on calibration plots in Figure S-3; standard deviations are given in parentheses.

Analyte	Materials	Slope/µA mM^{-1}	R-Squared
Adenine	Bare GC	10.864 (0.072)	0.9721
	ST-GO	1.984 (0.031)	0.8341
	HU-GO	9.077 (0.046)	0.8733
	HO-GO	5.133 (0.043)	0.9373
	BR-GO	5.382 (0.033)	0.9682
Cytosine	Bare GC	1.217 (0.433)	0.8542
	ST-GO	0.102 (0.224)	0.8035
	HU-GO	0.690 (1.186)	0.8856
	HO-GO	0.608 (0.416)	0.9119
	BR-GO	0.488 (0.495)	0.9950