Characterization of graphene oxide reduced through chemical and biological processes

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Abstract. The study of new materials for transparent electrodes or new heterojunctions made of 2D materials combinations is a very active research topic. Challenges to overcome are the modulation of the optoelectronic properties of such materials to achieve competitive photovoltaic devices. In this work, graphene oxide was reduced into graphene through different chemical (hydrazine, ultraviolet photocatalysis) and biological (microorganisms) processes. We benchmarked the reduction efficiency by probing materials characteristics using various physical characterization techniques. X-ray photoelectron spectroscopy (XPS) analyses were carried out to observe the effectiveness of the reduction processes through the sp²/sp³ content. In addition, the homogeneity of the reduction is investigated on micrometer scale sample with micro Raman mapping and extraction of the ID/IG ratio. Conductive-probe atomic force microscopy (CP-AFM) was employed to investigate the longitudinal conductivity of the different samples. The results show that hydrazine based reduction remains the most efficient. However, the bacterial procedure demonstrated partial reconstruction of the carbon network and reduced the amount of oxygenated functional groups.

1. Introduction
In order to improve the efficiency and reduce manufacturing costs, corporate and academic research groups are striving to develop new alternative technologies for photovoltaic (PV) devices. The emphasis is on both rigid as well as flexible PV devices opening new opportunities for different class of materials and technologies. 2D materials have attracted tremendous attention worldwide for all kind of nanoelectronic applications including PV. Indeed, graphene [1] is seen as a serious candidate to replace Indium Tin Oxide (ITO) as a transparent electrode [2] but manufacturing cost and optoelectronic properties remain difficult to control. In that respect, reduced graphene oxide (rGO) could possibly be an alternative thanks to its potentially low manufacturing cost [3]. Exfoliated graphene exhibits optoelectronic properties that could potentially outperform any alternative to ITO currently investigated. However, there is no technological pathway to exploit exfoliated graphene. On the other hand, reduced graphene oxide (rGO) is a potential alternative under investigation that could be mass produced at low cost [4]. Nevertheless to envision applications the optoelectronic properties of rGO and CVD-graphene still remain to be tailored to become competitive with current rare earth
electrode materials. For that purpose, most of the research work on this topic is devoted to the optimization of the optoelectronic properties through either deposition techniques or reduction for CVD graphene and graphene oxide respectively [5, 6, and 7]. As opposed to pristine exfoliated graphene composed of exclusively sp²-hybridized carbon atoms, a GO sheet is hybrid network of carbon network sp² hybridized with neighboring carbon atoms or with carboxyl and carbonyl groups on the edges as well as sp³ hybridized carbon atoms that form covalent bonds with epoxy and hydroxyl groups [8]. The latter renders the GO soluble in various solvents and allows the development of a low cost wafer-scale technology. However, to achieve an electrically active material, GO must be reduced and different reduction methods have emerged [9, 10, 11]. The reduction process partially restores a sp² network by removing a large fraction of these defects. Therefore, the structural disorder decreases and the carrier transport improves. Nevertheless, electrical properties such as conductivity and mobility are orders of magnitude below the ones attainable with exfoliated graphene [12]. Yet, these values allow the fabrication of low cost electronics that usually don’t require outmost performance. In this work, we investigate the impact of different reduction methods hydrazine, UV-photocatalysis and microorganisms through physical characterization techniques. Micro-Raman spectroscopy has been utilized to investigate the signatures and the structural disorder with the $I_D/I_G$ ratio before and after reduction. X-ray photoelectron spectroscopy monitors the variation of the sp²/sp³ content as well as the oxygen/carbon atomic ratios. At last, conductive CP-AFM set-up was utilized to probe local electrical properties of rGO.

2. Experimental
2.1. General methods
Graphite powder was obtained from SEC Carbon with grade reference SNO-30 [13]. 2D Raman scattering images and Raman spectra were collected at room temperature, using a WiTec alpha 300R confocal Raman microscope with a UHTS300 spectrometer and a DV401A CCD detector. The laser beam spot size was around 900nm. The films were illuminated with 100µW for 2s for each spectrum using a frequency doubled Nd:YAG Laser at 532 nm and Raman signal was collected in a backscattering geometry. A 600 grooves/mm diffraction grating was utilized enabling a spectral resolution of 3cm⁻¹. The mapping was collected with 250 nm between spectra using a piezoelectric stage.

XPS measurements were performed using a VersaProbe PHI5000 spectrometer (Physical Electronics) operating at a base pressure of 1x10⁻⁷ Pa. A monochromatic Al Kα X-ray source (1486.6 eV) was used at 15 kV with take-off angle of 45°. The analysed area of the sample was 50 µm in diameter. High resolution core level spectra were acquired with 23.5 eV pass energy, an energy step of 0.1 eV and a 50 ms dwell time. A dual beam charge neutralisation system consisting of low energy ions and electrons was utilized. The spectrometer was calibrated with Cu 2p₃/₂ and Cu LMM of clean copper at 932.7 eV and 918.7 eV respectively. The binding energy scale was calibrated by positioning the reference peak of Si 2p₃/₂ corresponding to SiO₂ from the substrate to 103.5 eV. Spectroscopic data were processed by the PHI Multipak software, using a peak fitting routine with symmetrical Gaussian-Lorentzian functions. The Shirley background was subtracted from the spectra.

CP-AFM measurements were performed using a Digital Instruments Nanoscope IIIa Multimode AFM associated with the home-made conducting probe extension called “Resiscope” [14]. This setup allows us to apply a stable DC bias voltage (from -10 to +10 V with 0.01 V resolution) to the device and to measure the resulting current flowing through the tip as the sample surface is scanned in contact mode. Local resistance values can be measured in the range of 10²-10¹² Ω, which allows investigations of a variety of materials [15, 16] and devices [17, 18]. Reliable and understandable electrical measurements through CP-AFM setup require a well-characterized conductive tip. Depending on the experimental conditions, the AFM conductive tip should be the most suitable in terms of serial resistance that must be taken into account in the electrical analysis of rGO. PtIr-coated Si cantilever, with a spring constant of about 0.2 N/m, proves to be suitable for our experimental conditions, since
measured resistance values are greater than the intrinsic tip resistance that was estimated around 300 Ω.

In this work, we investigated three different reduction methods: hydrazine, UV photocatalysis and bacterial. All samples were extracted from the initial GO source described in the experimental section. GO and rGOs samples were spin coated, on oxidized (300nm) silicon substrate following the procedure described by [19]. This yields to a dispersion of GO flakes ranging from monolayer to multilayer.

2.2. preparation of graphene oxide
GO was synthesized by the modified Hummer’s method using natural graphite powder (SEC Carbon SNO-30). The powder was cleaned in a K₂S₂O₈ and H₂SO₄ bath and subsequently oxidized in KMnO₄ and H₂SO₄. After centrifuging, the resulting graphite oxide was exfoliated into GO by ultra-sonication (100 W, 30 min, 60 °C). At last, a GO aqueous dispersion was produced by centrifugation and dialysis to neutral pH.

2.3. reduction of graphene oxide by hydrazine
rGOhydrazine was obtained by reduction with hydrazine hydrate [9]. A homogeneous GO aqueous suspension (1 mg.mL⁻¹) was achieved by dispersing GO in distilled water using ultra sonication and 20 mL were loaded in a 50-mL round bottom flask. Hydrazine monohydrate (200 µL) was then added and the solution heated in an oil bath at 100 °C under a water-cooled condenser for 24 h over which the reduced GO gradually precipitated out as a black solid. This product was isolated by filtration on a 0.45 µm PVDF membrane, washed with water and methanol, and dried on the filter in oven (80 °C) during 24 h. The solid was subsequently dissolved in dimethylformamide (DMF) at 1 mg.mL⁻¹.

2.4. reduction of graphene oxide by UV photocatalysis
rGOUV was obtained from a homogeneous GO aqueous suspension (1 mg.mL⁻¹) elaborated by dispersing GO in distilled water using ultra sonication. Aqueous graphene oxide solution (20 mL) in a quartz tube was irradiated for 6 h using a home-made photo reactor (λ = 254 nm) under direct irradiation. The dark insoluble graphene was isolated by filtration over Anodisc 0.22 μm, washed copiously with methanol and dried on the filter in oven (80 °C) during 2 minutes. The solid was dissolved in DMF solvent at 1 mg.mL⁻¹.

2.5. reduction of graphene oxide by microorganisms
rGObacterial was reduced using microorganism extracted from a river in Aichi prefecture (Japan) following multiple iterations of transfer and cultivation of river sediments in a medium containing salts and organic materials in anaerobic conditions. Silicon substrates covered with a suspension of GO flakes were immerged into the microbial culture in serum bottles and incubated in the culture at 28°C for 3 days under dark [19].

3. Results and analysis
Figure 1(a) presents the µ-Raman spectra of the different samples acquired at constant power of 100µW and for 2s per spectrum. All samples exhibit a strong D-band (~1350 cm⁻¹) and G-band (~1580 cm⁻¹) usually assigned to structural disorder and the graphitized structure respectively. GO presents a dominant D peak arising from the attachment of functional groups such as hydroxyl, epoxy on the carbon skeleton. The overtone 2D-band does not vary significantly with respect to the reduction processes indicating that graphitization is rather poor. The D+D’ peak (~2940 cm⁻¹) represents a defect activated combination of phonons with different momenta [20]. The large D-band and the attenuated 2D-band may be attributed to the small sp² domains subsequent to the oxidation process and ultra-sonication [3]. In order to assess the homogeneity of the material, µ-Raman mapping has been carried out on micro scale flakes. The mapping illustrates the variation of the peaks across the sample geometry. The full width half maximum (FWHM) of all samples is large indicating multi-layer
material (not shown). Figure 1(b) represents the μ-Raman two dimensional mapping of D, G and 2D peaks for the GO sample.

![Figure 1](image)

**Figure 1:** (a) Raman spectra of graphene oxide and reduced graphene oxide samples, (b) μ-Raman mapping of GO sample for D, G and 2D bands. The 2D peak mapping is very noisy due to the poor signal to noise ratio given the low intensities of this peak.

The variation observed on the GO is relatively large as well as the D-band intensity for all samples as displayed in figure 1(a), this indicates the poor crystalline quality of the material as-prepared and reduced. In order to evaluate the disorder in the material, we extracted the $I_D/I_G$ ratio for the various samples, table 1.

|          | D (cm$^{-1}$) | G (cm$^{-1}$) | 2D (cm$^{-1}$) | D+D' (cm$^{-1}$) | $<I_D/I_G>$ (%) |
|----------|--------------|--------------|----------------|------------------|-----------------|
| GO       | 1344         | 1593         | 2680           | 2928             | 1.4             |
| Bacteria | 1341         | 1596         | 2645           | 2829             | 1.55            |
| UV-photocatalysis | 1354     | 1603         | 2655           | 2841             | 1.6             |
| Hydrazine| 1351         | 1595         | 2683           | 2932             | 1.9             |

**Table 1:** μ-Raman spectroscopy of GO and reduced GO. $<I_D/I_G>$ represents the average ratio across the mapping.

The $I_D/I_G$ ratios observed present little variation between samples; the slight increase may be related to the removal of the functional groups upon reduction and the subsequent creation of defects [21]. According to [22], this observation implies an inter-defect distance smaller than 3nm and confirms the reduction in size of the sp$^2$ domains. The graphitic structure could not be completed upon the different reduction processes. Figure 2 illustrates the mapping of the $I_D/I_G$ ratio across the different samples.
Figure 2: micro-Raman mapping of GO and rGO showing I_D/I_G ratios. From left to right: GO, rGO_{hydrazine}, rGO_{UV}, rGO_{bacterial}.

To analyse the impact on the carbon content of the different reduction processes, XPS measurements were carried out for all the samples. Figure 3 shows the deconvoluted C1s and O1s peaks after Gaussian-Lorentzian fitting and Shirley background correction [23]. Figure 3 (a) exhibits C1s spectra acquired from all the samples. The GO sample presents a broad tail towards high energies. This tail is constituted of the various carbon bonding configurations i.e. 2 C components, C-C (for sp^3) and C=C (for sp^2) carbon respectively as well as C-OH, C=O and O=C-OH components, figure 3.

Upon reduction, the ratios of the different peaks changed, the sp^2 and sp^3 contents increased whereas the contribution of the oxygenated functional groups is diminished as indicated by the atomic ratio C1s/O1s in table 2. The C/C (O) H atomic ratio indicates that rGO_{hydrazine} presents a better reconstruction of the carbon network. The deconvolution of its C1s spectra for each sample reveals the following components: C=C or sp^2 peak ~284.3 eV, C-C or sp^3 and C-H peaks ~ 284.9 eV, C-O-H ~ 286.2 eV, C=O ~ 287.5 eV and O=C-OH ~ 288.9 eV. As the reduction improves from GO to rGO_{hydrazine}, the sp^2 content increases in intensity and its binding energy shifts to 283.8 eV. The trends are consistent with the decrease in the oxygenated functional groups observed in the O1s spectra for all samples. The bacterial reduction seems to be more efficient in reducing the oxygen content with a
C1s/O1s of 8.1 as opposed to the 3.7 of the UV-photocatalysis but it does not improve the graphitization. However, this interpretation should be confirmed with further experiments as the contribution of the substrates utilized may impact the resulting C1s/O1s ratio. Increasing the contact time with the microorganisms and temperature parameters may improve the process [11]. This latest procedure is of interest as it does not involve any chemical nor radiative process and is fairly simple to implement.

|             | C1s/O1s (atomic ratios) | C/C(O)H (atomic ratios) |
|-------------|-------------------------|-------------------------|
| GO          | 3.24                    | 1.5                     |
| Bacteria    | 8.1                     | 1.94                    |
| UV-photocatalysis | 3.7               | 2.4                     |
| Hydrazine   | 15.9                    | 6.9                     |

Table 2: XPS spectroscopy of GO and reduced GO. Note that the displayed carbon contents do not discriminate between sp² and sp³ configurations.

CP-AFM measurements were performed on the samples in order to observe the lateral conduction within rGO flakes with respect to the initial GO. 1V was applied between the tip and few µm² flakes. The CP-AFM head allows monitoring the change in contact resistance. Note that due to the lack of thickness control during the GO spin coating and subsequent reduction, these measurements only provide qualitative insight on the electrical conductivity of the material. GO sample presents a resistance of 6 GΩ for a monolayer flake estimated from current-voltage measurements exhibiting a linear behaviour in the range -1 to 1 V (not illustrated). This local resistance increases to 170 GΩ for 3 flakes of GO. This is illustrated by the most resistive region on figure 4 (a). Figure 4 (b) represents the mapping for the rGOhydrazine. The distribution is rather homogenous and indicates that the reduction is uniform across the flakes. This sample exhibits the lowest resistance in the order of 10-30 kΩ owing to its relatively large carbon content (sp² and sp³ ~6.9 compared to GO). The same observation holds for rGOUV but with a higher resistance ~1-3 GΩ as expected from the low carbon content (~2.4) compared to rGOhydrazine. Interestingly, the rGO_bacterial on the other hand presents a lower resistance ~1 MΩ on monolayer flake although its carbon content is lower than rGOUV 1.94 versus 2.4%. However, XPS analysis (table 2) showed a more efficient reduction of oxygenated functional groups (8.1 for the rGO_bacterial and 3.7 for rGOUV). As a result, the improvement of the electrical conduction implies both the reduction of functional groups i.e. defects as well as the increase in sp² carbon domain [24].
Figure 4: (top) CP-AFM local resistance mapping. (Bottom) topography mapping of the samples, the arrows indicate the scanning direction. Arrow 1 for GO represents a scan from substrate to a monolayer flake. Arrows 1 for rGO\textsubscript{bacterial} indicates a scan from substrate to a 2 layers flake whereas scan 2 is over a one monolayer flake. RGO\textsubscript{hydrazine} and RGO\textsubscript{UV} topographies show rather thick deposits.

4. Conclusions
Three different reduction processes of graphene oxide have been characterized using $\mu$-Raman spectroscopy, X-ray photoelectron microscopy as well as conductive probe atomic force microscopy. Among the different processes hydrazine remains the most effective to reduce the content of functional groups as well as to increase the $sp^2$ domains. On the other hand, the bacterial reduction is rather poor although more efficient than UV-photocatalysis to reduce the amount of oxygenated functional groups. This must be confirmed by further experiments in order to minimize the substrate contribution. Nevertheless, this bacterial procedure may be substantially improved by increasing contact time between GO and microorganisms. This could yield to a chemical free reduction process more amenable than hydrazine and environmentally safe.

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