

Available at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/carbon

Visualization of defect densities in reduced graphene oxide

Siegfried Eigler^{*}, Christoph Dotzer, Andreas Hirsch

Department of Chemistry and Pharmacy, University Erlangen-Nürnberg, Henkestr. 42, 91054 Erlangen, Germany

Institute of Advanced Materials and Processes (ZMP), University Erlangen-Nürnberg, Dr.-Mack Str. 81, 90762 Fürth, Germany

ARTICLE INFO

Article history:

Received 30 December 2011

Accepted 20 March 2012

Available online 25 March 2012

ABSTRACT

Efficiently reducible graphene oxide (GO) was obtained, even if a high degree of functionalization is present. Graphite with few defects was used as starting material and oxidized according to Hummer's method. An extremely high I_D/I_G ratio for rGO of 2.8 (532 nm) was observed in the Raman spectrum as a consequence of the lower defect density in GO. It was also possible to demonstrate the impact of local defects on the structure in rGO by local laser exposure experiments on single graphene oxide flakes. Raman spectroscopy can visualize the laser impact by I_D/I_G ratio measurements.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Graphene is one of the most exciting materials known due to its exceptional physical properties, as the extremely high charge carrier mobility of 40.000 or even 200.000 $\text{cm}^2/\text{V s}$ that makes new electronic devices reachable [1,2]. Further, transparent electrodes are one desired application for graphene utilizing the transparency and intrinsic conductivity [3]. The main drawback is the poor processibility of graphene, because it is insoluble in most common solvents. This is one reason why graphite is functionalized, either non covalent, or covalent to gain soluble graphene [4–6]. Although this approach is promising, the yield is still poor. Otherwise, graphene oxide (GO) is one promising material for the mass production of graphene. The important advantages are the ease of accessibility from graphite and the processibility in aqueous solution, even at high concentrations of typically 1 mg/ml [7]. After the removal of functional groups (in GO mainly epoxy and hydroxyl groups) reduced graphene oxide (rGO) is obtained and electronic properties are partially restored but e.g. the electrical conductivity of rGO still lacks behind that of pristine graphene and so does the charge carrier mobility. Defects in rGO or inefficient reduction of GO are the two most prominent reasons for poor performance [8].

One possible answer to that problem is to use GO with a low degree of oxidation. Recently, it was shown that it is possible to prepare field effect transistors from that material and charge carrier mobilities up to 10–15 $\text{cm}^2/\text{V s}$ could be determined [9,10]. In another approach, GO was mildly oxidized using less oxidant to yield an increased quality of rGO with fewer defects after reduction what was proved by Raman spectroscopy [11]. Recently, it was demonstrated that the graphite grade used for the preparation can alter the structure of GO [12]. To gain information about defects in graphene based materials, Raman spectroscopy is an adequate method. It provides information for the mean distance between defects in rGO. The ratio between the intensities of the D and G peak correlate with the mean distance of two defects in graphene as it was found by Ar-ion bombardment on graphene [13].

Here, we report a high ratio of about 2.8, the highest value measured for rGO on single layer flakes that originates from GO prepared by Hummer's method. This observation is related to an increased quality of rGO, as discussed later. Further, GO is highly oxidized, as it is proved by TGA-MS and FTIR. This observation is in stark contrast to the latest literature [9,11]. Besides, the GO flakes described here can be structured by laser induced local heat causing defects (CO_2

^{*} Corresponding author at: Department of Chemistry and Pharmacy, University Erlangen-Nürnberg, Henkestr. 42, 91054 Erlangen, Germany. Fax: +49 911 6507865015.

E-mail address: siegfried.eigler@zmp.uni-erlangen.de (S. Eigler).
0008-6223/\$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
<http://dx.doi.org/10.1016/j.carbon.2012.03.039>

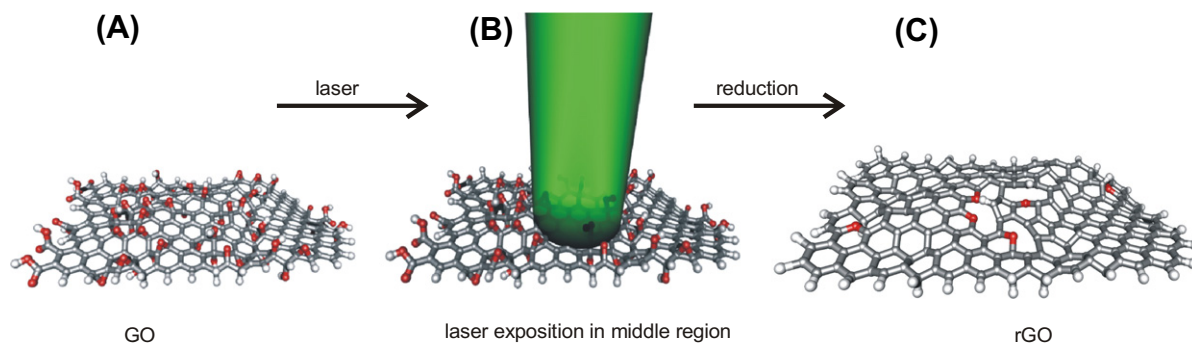


Fig. 1 – Illustration of (A) GO according to the Lerf–Klinowski model; (B) GO during laser exhibition by Raman laser (532 nm); (C) rGO (reduced by hydrazine hydrate), more defects remain (e.g. ethers) in middle region compared to loop region (if no laser exhibition is applied rGO bears fewer defects than illustrated here).

formation) what can be identified by Raman spectroscopy (Fig. 1). This new approach makes it possible to visualize different defect densities in rGO on the same flake for the first time.

2. Experimental procedures

2.1. General methods

Natural flake graphite was obtained from Kropfmuehl AG, Germany. The grade used as reference material was SC-200. The high quality graphite was obtained from Asbury Carbon. The grade used was 3061. Potassium permanganate, sodium nitrate, sulfuric acid were obtained from Sigma-Aldrich®. Thermogravimetric analysis (TGA) equipped with a mass spectrometer (MS) was accomplished on a Netzsch STA 409 CD instrument equipped with a Skimmer QMS 422 mass spectrometer (MS/EI) with the following programmed time dependent temperature profile: RT–800 °C (TGA-MS) with 10 K/min gradient, and cooling to RT. The initial sample weights were about 6–7 mg and the whole experiment was accomplished under inert gas atmosphere with a He gas flow of 80 ml/min. Bruker Tensor FTIR spectrometer equipped with ZnSe was used for the measurements of GO films. Freeze-drying was accomplished on an ALPHA 1–4 LDplus from Martin Christ, Germany. For centrifugation a Sigma 4K15 centrifuge, Sigma Laborzentrifugen GmbH, Germany, was used. Atomic force microscopy (AFM) measurements were performed on in tapping mode using SolverPro from NT-MDT. The samples we prepared by dropping a diluted dispersion of graphene oxide on Si/SiO₂ wafers. The oscillation amplitude was usually chosen to be 5 nm, the setpoint was about 3 nm. Raman spectroscopic studies were done on Horiba Jobin Yvon LabRAM Aramis confocal Raman spectrometer equipped with a microscope and an automated XYZ table, at laser excitation of 532 nm if not mentioned otherwise. Laser energy can be altered by filters (D2: 0.06, D1: 0.38, D0.6: 0.97, D0.3: 1.94 mW). Elemental analysis was performed by combustion and gas chromatographic analysis with an EA 1110 CHNS analyzer from CE Instruments.

The electrical conductivities and the surface resistances of graphite were measured according to the 4-point probe method on graphite pellets (13 mm diameter) pressed with a

typical IR-molding press at 10 t/cm². The resistivity test unit used was RM3000 equipped with a cylindrical 4-point probe head (probe spacing of 0.635 mm) from Jandel Engineering Limited, UK. The thickness of the pellets was determined using a calibrated optical microscope (Axio M1 m Imager, Carl Zeiss, Germany).

2.2. Analysis of starting materials

Grade SC-200. The electrical conductivity of grade SC-200 was determined by 4-point probe method to be 420 S/cm. The ratio of I_D and I_G in the Raman spectra was determined to 0.12 on the flake and 0.16 in average (900 μm²) from the same pellets of the bulk graphite using DuoScan.

Grade 3061. The electrical conductivity of grade 3061 was determined by 4-point probe method to be 1600 S/cm. The ratio of I_D and I_G in the Raman spectra was determined to 0.04 on the flake and 0.10 in average (900 μm²) from the same pellets of the bulk graphite using DuoScan.

2.3. Preparation of GO1 and GO2

Graphene oxide from grade SC-200 (GO1). No pre-treatment of graphite was applied. Graphite (1 g, grade SC-200, Kropfmuehl AG) and sodium nitrate (0.5 g) were dispersed in concentrated sulfuric acid (24 ml). The dispersion was cooled by ice to about 5 °C. After that, within a period of 30 min potassium permanganate (3.0 g) was added in small portions and the dispersion was stirred an additional hour at 20 °C. The reaction mixture was then poured on ice (500 ml) and hydrogen peroxide (10 ml, 3%) was added drop wise until gas evolution was completed. The obtained graphite oxide was purified by repeated centrifugation and dispersion in water until the pH of the supernatant was neutral. Finally, GO1 was yielded by mild sonication using a bath sonicator. The suspension was finally centrifuged three times at 5000 g to remove remaining graphite oxide. Elemental Analysis: C 45.89, H 2.40, N 0.0, S 3.88.

Graphene oxide from grade 3061 (GO2). No pre-treatment of graphite was applied. Graphite (1 g, grade 3061, Asbury Carbon) and sodium nitrate (0.5 g) were dispersed in concentrated sulfuric acid (24 ml). The dispersion was cooled by ice to about 5 °C. After that, within a period of three hours potas-

sium permanganate (3.0 g) was added in small portions and the dispersion was stirred an additional three hours at 20 °C. Due to the lower reactivity of grade 3061 compared to SC-200 a longer reaction time was necessary. The reaction mixture was then poured on ice (500 ml) and hydrogen peroxide (10 ml, 3%) was added drop wise until gas evolution was completed. The obtained graphite oxide was purified by repeated centrifugation and dispersion in water until the pH of the supernatant was neutral. Finally, GO2 was yielded by mild sonication using a bath sonicator. The suspension was finally centrifuged three times at 5000 g to remove remaining graphite oxide. Elemental Analysis: C 43.22, H 2.27, N 0.0, S 6.15.

2.4. GO films on ZnSe

A diluted dispersion of GO was drop-casted on a ZnSe window and the film was formed by evaporation of the solvent at ambient conditions. The thickness of the film was determined using the Z-indicator of the Zeiss microscope. Thereto, the film was scratched and either the top of the film or the substrate was focused. The thickness was about 2–3 μm .

2.5. Structuring GO by Raman laser

GO2 was structured using the Raman laser (532 nm) at low dose using D2 filter and placed a 5s laser pulse (9 μm^2) in the middle of flake (GO2b). A higher dose (5s, D0.3) was used in the case of GO2c.

2.6. Reduction of GO flakes

The flakes were reduced by hydrazine vapor for 1 h at RT and an additional 1 h at 80 °C. Finally, the material was annealed at 120 °C to yield rGO.

3. Results and discussion

3.1. Preparation of GO

In this study we used natural graphite (grade 3061) from Asbury Carbon and prepared GO according to Hummer's method. The purity of that graphite is higher than 99% and the grain size is rather large with about 300 μm (supplier information). Further, Raman spectroscopy proves the low defect density of the graphite by the D peak being almost absent with an I_D/I_G ratio of 0.04 on flakes, neglecting the edges and 0.10 on the surface of 900 μm^2 . The structural integrity is also reflected by the electrical conductivity of 1600 S/cm which was determined by four-point-probe measurements on pellets. As reference material we used grade SC-200 from Kropfmuel AG and here we found an I_D/I_G ratio of 0.12 on flakes and 0.16 on the surface of 900 μm^2 . The electrical conductivity was determined to 420 S/cm, reflecting the higher defect density.

We prepared GO from both materials (SC-200, GO1; 3061, GO2) using Hummer's method [14]. No pre-treatment of graphite was applied and the graphite was oxidized in concentrated sulfuric acid with potassium permanganate as the oxidant and small amounts of sodium nitrate. The work-up

was done using water and hydrogen peroxide. The material was purified by repeated centrifugation and GO was obtained after exfoliation (bath sonicator). In the case of grade SC-200 the oxidation time was 1.5 h compared to 6 h for grade 3061, due to its lower reactivity.

3.2. Characterization of GO by TGA-MS and FTIR

Both grades of GO (GO1, GO2) were analyzed by TGA-MS from freeze dried GO samples and FTIR samples were prepared from aqueous dispersions on ZnSe to verify that both materials were oxidized in the same way. In the recent literature GO with a low degree of oxidation is prepared to minimize defects caused by oxidation [9,11]. We find that a low degree of oxidation is not essential to yield rGO with fewer defects. Here, we find a total weight loss of 53.1% for the reference material GO1 and 50.6% for GO2 obtained from graphite with fewer defects, see Fig. 2A.

The weight loss takes place in three temperature regions. Between RT and about 120 °C the weight loss is mostly attributed to adsorbed water (m/z 18). A further weight loss of 18% is observed for GO1 and GO2 with a maximum at 153 and 169 °C for GO1 and GO2, respectively. GO2 from graphite with fewer defects (grade 3061) appears to be more stable, but 169 °C are still a reasonable value for GO. There are other parameters, e.g. water content, that influences the decomposition temperature of GO in TGA experiments as we demonstrated recently [15]. Mainly m/z 18 (H_2O), m/z 28 (CO) and m/z 44 (CO_2) are detected at this step. An additional weight loss of about 15% and 17% for GO1 and GO2, respectively, was found between 200 and 300 °C. In addition to water, CO and CO_2 , m/z 64 (SO_2) is detected that originates from sulfur species. Even excessive washing with water cannot completely remove these species. Qualitatively the amount of sulfur appears to be constant in GO1 and GO2 with 4 and 6% according to elemental analysis, respectively. At higher temperature up to 800 °C the carbon lattice decomposes and the detected weight loss is 7.5 and 9.6% for GO1 and GO2, respectively. From TGA-MS we conclude that GO1 and GO2 were oxidized in almost the same way. This means that the degree of oxidation is identical with little differences in the stability and the water content. Next, we verified that functional groups are the same in GO1 and GO2. FTIR spectra exhibit the same features as can be seen from Fig. 2B. The origin of the vibrational absorption of functional groups in GO is still discussed [16]. We assign the signals between 3600 and 3200 cm^{-1} to the O–H stretching vibration of free water, associated hydroxyl groups in GO and adsorbed water molecules. In both materials carbonyl signals at about 1735 cm^{-1} and signals that originate from adsorbed water at about 1625 cm^{-1} are found [17]. The signals at about 1415 cm^{-1} correspond to O–H deformation vibrations from carboxylic groups [18]. A shoulder at 1580 cm^{-1} can be assigned to double bonds [17]. Vibrations of C–O of different species mainly epoxy and hydroxyl groups are present in the range of 1300 and 800 cm^{-1} and we find distinct signals at about 1270, 1230, 1050 and 830 cm^{-1} . From FTIR we conclude that both materials are chemically almost identical, with little changes for the intensity of some signals, e.g. the signal at 1050 cm^{-1} that might also originate from skeletal C–C vibrational modes [19].

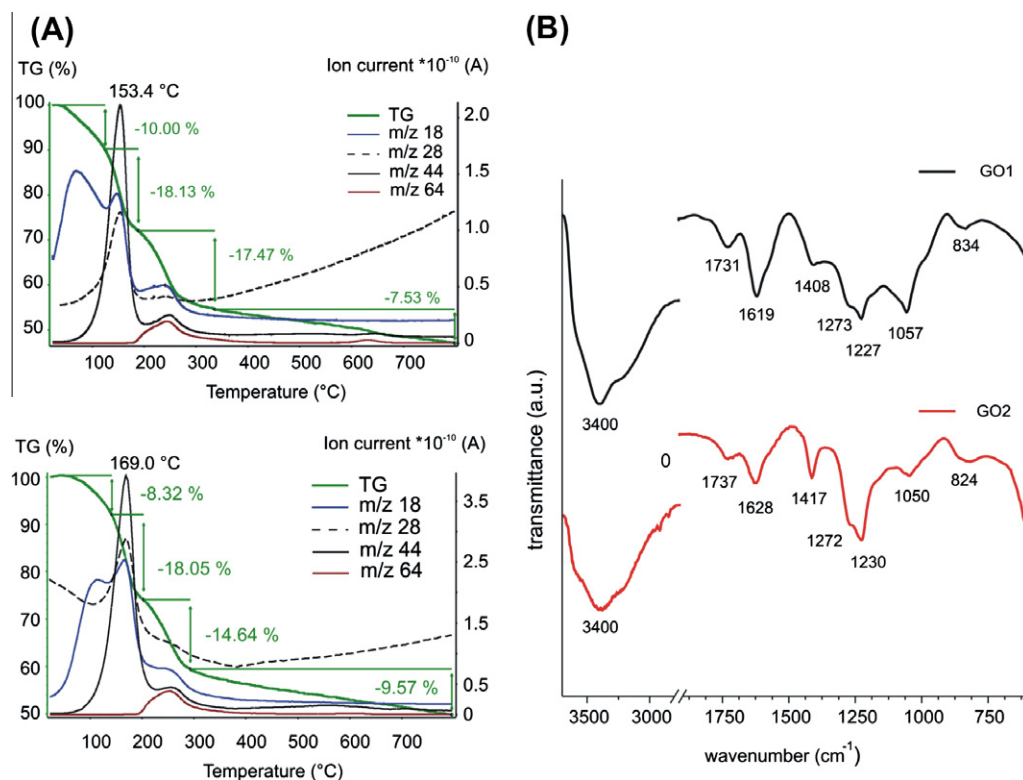


Fig. 2 – (A) TGA-MS of GO1 and GO2 and the corresponding weight loss due to H₂O, CO, CO₂ and SO₂; (B) FTIR spectra of GO1 and GO2.

Finally, two weak signals at 2924 and 2852 cm⁻¹ are found in GO2 only that might be due to methyl groups as it was found in methylated GO before [20].

3.3. Characterization of GO and rGO by AFM and Raman spectroscopy

Furthermore, we analyzed the size of the GO flakes (GO1, GO2) by AFM on Si/SiO₂ wafers. The flakes of GO1 (reference material) are shown in the [Supplementary data](#) and we find small flakes with a diameter of approximately 1 μm. Larger flakes of about 5 μm are found in GO2, as can be seen from Fig. 4A. In addition, we performed a Raman study of GO1 and GO2 in its oxidized and reduced form. To gain homogeneous Raman information as reference data we measured mean spectra of an area of 100 and 400 μm² for GO1 and GO2, respectively (Fig. 3).

Generally, GO exhibits preserved graphene like regions (about 1 nm diameter) and distorted regions (several nm) beneath defects (vacancies or additional atoms) due to the synthesis, known from HRTEM [21]. The I_D/I_G ratio in Raman spectroscopy can be used to evaluate the distance between defects in graphene and for GO it is about 1 (532 nm laser excitation) and increases with increasing mean distance between two defects (L_D) from 1 to about 3 nm (stage 2) followed by a decrease (stage 1, larger than 3 nm) [13,22]. This relation is shown in Fig. 4. We used this relation to characterize GO. In Fig. 3, the main features of the GO Raman spectra are the D, G, 2D and D + D' peak. The D peak at about 1330–1340 cm⁻¹ that

originates from the breathing modes of six-membered rings that are activated by defects and the G peak at 1580–1600 cm⁻¹ that is due to the E_{2g} phonon at the Brillouin zone center. The 2D peak at 2700 cm⁻¹ is the second order of the D peak and the D + D' peak at 2940 cm⁻¹ is due to the defect activated combination of phonons. The I_D/I_G ratio in GO1 (1.14) and GO2 (1.19) are almost the same and the D + D' peak is higher in intensity than the 2D peak, in both spectra (black, Fig. 3A and B). Next, GO1 was reduced by hydrazine hydrate vapor to yield rGO1. The Raman spectrum of rGO1 (red, 100 μm²) is shown in Fig. 3A and only little changes can be observed for the I_D/I_G ratio. It changes from 1.14 to 1.28 that is related to the removal of functional groups and formation of defects. This observation is consistent with the literature [23].

Now we studied single flakes of GO2 and rGO2 and analyzed them by AFM to prove that all subsequent Raman measurements are performed on single layers. The AFM images of GO2a–c are shown in Fig. 5A. The thickness was determined to about 1.2–1.5 nm, neglecting the roughness of the flakes, as it is shown in the corresponding height profiles. The roughness is relatively high and we assume, this is due to adsorbed molecules and salts still present on the surface that could not be removed by the purification method and the processing. The flakes were reduced by hydrazine hydrate vapor as described before. The same flakes were analyzed by AFM and in comparison to GO2a, rGO2a has a mean height of about 0.8 nm. Further, it is interesting to note that some wrinkles present in GO2a disappeared in rGO2a and especially some

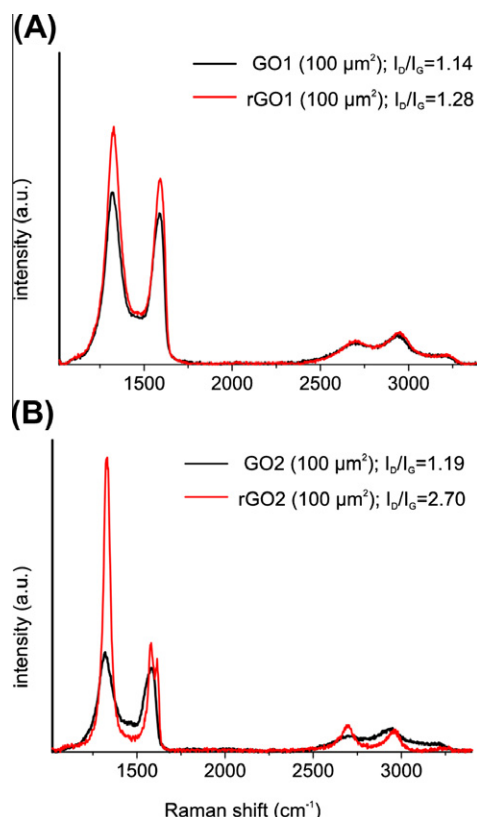


Fig. 3 – (A) Raman spectra of GO1 (black) and rGO1 (red); (B) Raman spectra of GO2 (black) and rGO2 (red). (For interpretation of reference to colors in this figure legend, the reader is referred to the web version of this article.)

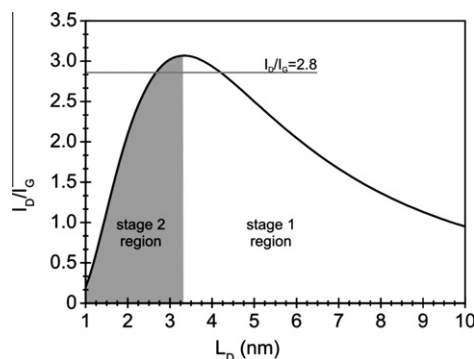


Fig. 4 – I_D/I_G ratio vs. distance between two defects (L_D), for 532 nm laser excitation (maximum I_D/I_G ratio 3.1).

edges folded on the rGO plane. The Raman spectrum of GO2 was already discussed above. Surprisingly, after the reduction of GO2a to rGO2a we find an extremely high I_D/I_G ratio of 2.7–2.8, what means that there is a mean distance of about 2.5–3 nm (compare Fig. 3B, Fig. 5) between two defects instead of about 1 nm as usually obtained for rGO. Besides, next to the G peak the D' peak at 1612 cm^{-1} can be observed caused by a double resonance process. Further, the I_{2D} is higher than the $I_{D+D'}$ in contrast to the pristine GO2 material and rGO1.

To quantify this effect we measured a Raman map of the same flake (rGO2a) after reduction and we find I_D/I_G ratios of

2.5–2.8 in the plane and a ratio of about 1.9 at the edges (Fig. 5C). The ratio of up to 2.8 is an extremely high value compared to other results based on rGO. For example an I_D/I_G ratio of about 1.4 was reported for rGO obtained from GO with a low oxidation degree [11]. In another example GO was reduced at subzero temperatures and an I_D/I_G of about 1.4 was found [24]. A high I_D/I_G ratio of about 1.9 was observed for rGO reduced by HI at 100°C [25]. We note that it is difficult to compare the results in the literature because Raman spectra are often recorded from bulk, few layer or multi-layer rGO, what makes it difficult to quantitatively compare the results.

3.4. Structuring of GO and rGO by Raman laser exhibition

Due to the lower defect density in GO2 it is possible to structure single flakes by light induced local heating, what causes defects mainly due to the loss of carbon (CO_2 formation). This process is illustrated in Fig. 1, starting with GO, followed by laser exhibition and subsequent reduction. That structuring can be visualized by Raman mapping of I_D/I_G ratio. We further analyzed the flakes by AFM. AFM images of the pristine GO2b,c flakes are shown in Fig. 5A with an average height of about 1 nm. We used the Raman laser (532 nm) at low dose using D2 filter and placed a 5s laser pulse ($9\text{ }\mu\text{m}^2$) in the middle of flake GO2b and a higher dose (5s, D0.3) on GO2c. After that the flakes were reduced by hydrazine vapor and AFM images revealed a 0.7–0.8 nm mean height of the flakes (Fig. 5B). Further, in the case of rGO2b a wrinkle was introduced by laser treatment and reduction procedure (Fig. 5B). More striking is the introduction of wrinkles for rGO2c. Radial wrinkles become visible and the position correlates well with that where an I_D/I_G ratio of 1.5 in the Raman map (Fig. 5C) is found. We assume that the laser pulse induces friction by partially decomposing the material. Recently, we found that GO can already decompose at about 50°C to form CO_2 beneath other species [15]. Loss of carbon (CO_2 formation) comes along with the decomposition that can occur also by laser induction. Hence, the flakes were analyzed by Raman mapping and the I_D/I_G ratio map (Fig. 5C) demonstrates the impact of defects on the I_D/I_G ratio. Even for the low dose treatment (rGO2b), the structuring can be observed by the difference in I_D/I_G ratios of 1.8 and 2.3 for the treated middle region and the untreated loop region, respectively (illustrated in Fig. 5B). For rGO2c there are more defects (assumedly vacancies and ether groups) [26] in the middle region and the I_D/I_G ratio is 1.5 with a loop region with fewer defects (I_D/I_G ratio of about 2.2), as can be seen from Fig. 5C. We note, that Raman spectra in Fig. 5D were not normalized and so it is striking that the D peak intensity remains almost the same for GO and rGO, respectively. Since the D peak is due to the defect induced breathing mode of six-membered rings we assume that the intensity remains almost constant, because there remain enough defects after reduction to activate almost the same amount of six-membered rings. These experiments further demonstrate that it is easily possible to tune the mean defect distances in rGO between 1 and about 3 nm.

According to Cançado et al. it is possible to distinguish between stage 2 and stage 1 region by analyzing Raman spectra in terms of the full width at half-maximum (FWHM) [22,27]. This is necessary because an I_D/I_G ratio of 2.8 can correlate

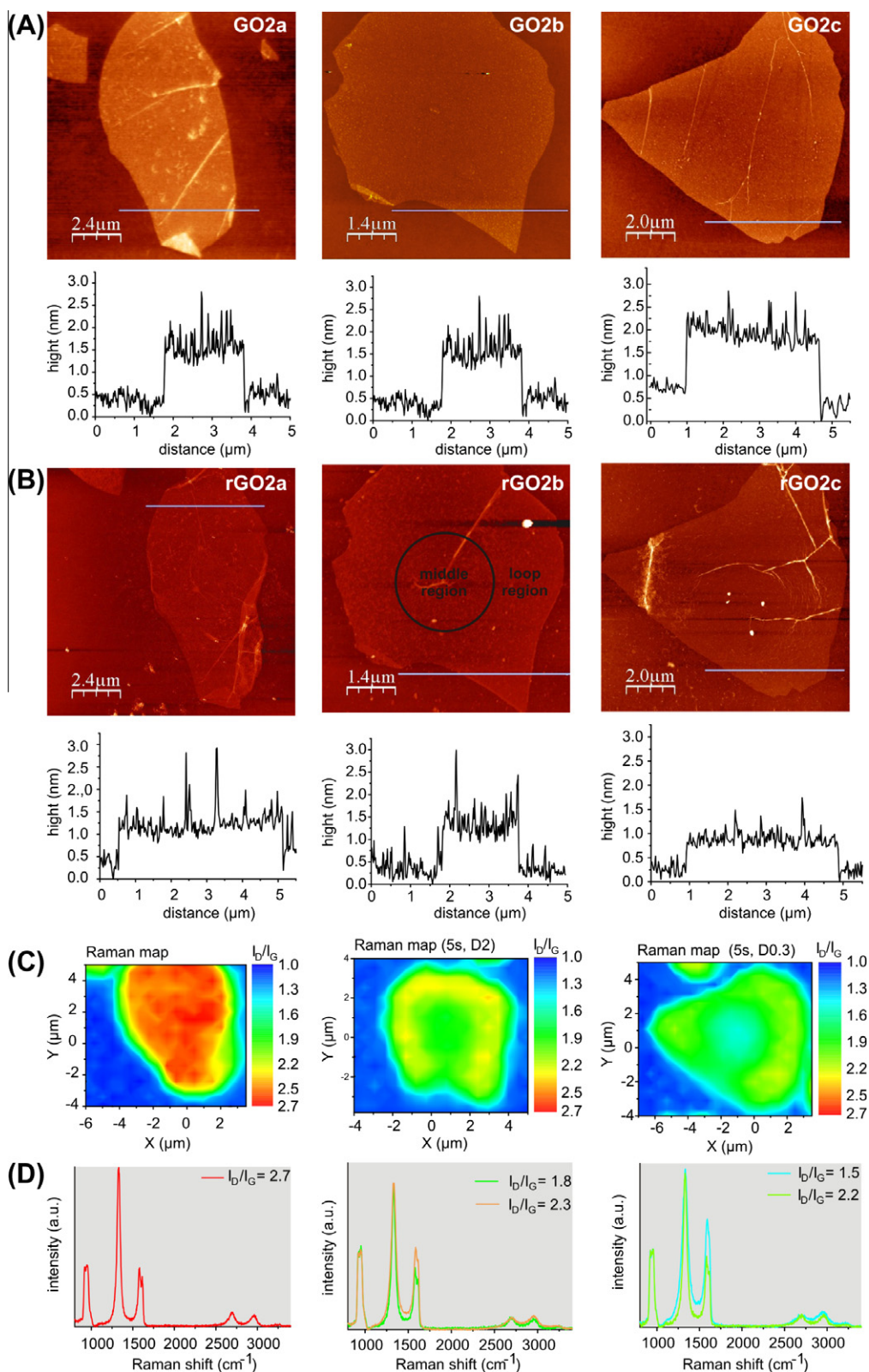


Fig. 5 – (A) AFM images of GO2a-c and height profiles; (B) AFM images of rGO2a-c and height profiles; (C) Raman maps (532 nm), plotted I_D/I_G ratio of rGO2a (pristine rGO2), rGO2b (5s laser pulse with D2 filter at 0.06 mW), rGO2c (5s laser pulse with D0.3 filter at 1.94 mW), from (left to right); (D) corresponding Raman spectra (532 nm) of rGO2a, rGO2b-c (middle and loop region, illustrated in B).

Table 1 – D and G peak position; FWHM of D and G peak; I_D/I_G of rGO2a and rGO2c.

	rGO2a	rGO2c _{middle}	rGO2c _{loop}
D peak (cm^{-1})	1337	1337	1337
D peak FWHM (cm^{-1})	42	81	56
G peak (cm^{-1})	1588	1591	1597
G peak FWHM (cm^{-1})	39	50	44
I_D/I_G	2.8	1.3	1.9

to mean defect distances of about 2.5 or 4 nm whether the material is stage 2 or stage 1 (Fig. 4). Therefore, we performed high accuracy Raman spectroscopy in the region 1000–2000 cm^{-1} checking the calibration (G peak of graphite at 1580 cm^{-1}) before and after each measurement. The results are summarized in Table 1. The I_D/I_G ratio was found to be 2.8 for rGO2a (see Supplementary data). Further, the D peak position is 1337 cm^{-1} (532 nm) and 1327 cm^{-1} (633 nm) that of the G peak is 1588 cm^{-1} and does not shift by altering the laser wavelength (see Supplementary data), typical for defective graphene [22]. We further find that the FWHM of the D peak and G peak are 42 and 39 cm^{-1} , respectively, and thus typical for stage 2 region. For stage 1 region a FWHM of about 20 and 14 cm^{-1} would be expected, respectively [22]. The analysis was also done for the middle region and loop region of rGO2c. In this example it is possible to make accurate Raman analysis on the same flake that exhibits a middle region and loop region and the G peak position shifts from 1597 to 1591 cm^{-1} in the loop region. Besides, the FWHM of the D peak gets sharper from 81 to 56 cm^{-1} (see Supplementary data). All these data support the laser induced defect generation in the middle region of rGO2c and underlines the lower defect density in rGO2a that is close to the transition to stage 1 region.

4. Conclusions

We demonstrated that GO with fewer defects can be obtained from graphite using Hummer's method. Besides large grain size, defects are almost absent in the starting material. Furthermore, we found that Raman spectroscopy cannot distinguish between different GO qualities. FTIR spectroscopy and TGA-MS show little differences also. Thus, the material must be reduced to rGO to determine the distance between defects by Raman spectroscopy utilizing the I_D/I_G ratio. We performed that study on single flakes of GO, rGO and laser structured GO, followed by reduction to visualize the different defect densities in rGO on the same flake for best comparison. In contrast to control experiments on rGO prepared from ordinary graphite we found an I_D/I_G ratio of 2.8 instead of 1.3. We conclude that the graphite grade is mostly responsible for the lower defects generated in GO and rGO, respectively, what can be probed by measuring the electrical bulk conductivity on graphene pellets. Further we found that rGO with an I_D/I_G ratio of 2.8 is still defective and the Raman spectra correspond to stage 2 region. We proved that by analyzing Raman peak positions and FWHMs of the G and D peak. Besides, we found the FWHM of the G peak decreases from 50 to 39 cm^{-1} and the FWHM for the D peak from 81 to 50 cm^{-1} , what clearly demonstrates the increasing quality. Moreover, we conclude that

the model of the I_D/I_G ratio that is derived from Ar-ion bombardment on graphene is generally valid for rGO also. These investigations demonstrate that rGO with tuneable defect densities can be prepared what will make electronic applications feasible. Obviously, rGO with fewer defects will also be a stronger material and improve mechanical properties of composite materials.

Acknowledgments

The authors thank the Deutsche Forschungsgemeinschaft (DFG - SFB 953, Project A1 "Synthetic Carbon Allotropes"), the European Research Council (ERC; grant 246622 - GRAPHE-NOCHEM), and the Cluster of Excellence 'Engineering of Advanced Materials (EAM)' for financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.carbon.2012.03.039](https://doi.org/10.1016/j.carbon.2012.03.039).

REFERENCES

- [1] Bolotin KI, Sikes KJ, Jiang Z, Klima M, Fudenberg G, Hone J, et al. Ultrahigh electron mobility in suspended graphene. *Solid State Commun* 2008;146(9–10):351–5.
- [2] Chen JH, Jang C, Xiao S, Ishigami M, Fuhrer MS. Intrinsic and extrinsic performance limits of graphene devices on SiO_2 . *Nat Nanotech* 2008;3(4):206–9.
- [3] Hecht DS, Hu L, Irvin G. Emerging transparent electrodes based on thin films of carbon nanotubes, graphene, and metallic nanostructures. *Adv Mater* 2011;23(13):1482–513.
- [4] Backes C, Hauke F, Hirsch A. The potential of perylene bisimide derivatives for the solubilization of carbon nanotubes and graphene. *Adv Mater* 2011;23(22–23):2588–601.
- [5] Englert JM, Dotzer C, Yang G, Schmid M, Papp C, Gottfried JM, et al. Covalent bulk functionalization of graphene. *Nat Chem* 2011;3(4):279–86.
- [6] Kozhemyakina NV, Englert JM, Yang G, Spiecker E, Schmidt CD, Hauke F, et al. Non-covalent chemistry of graphene: electronic communication with dendronized perylene bisimides. *Adv Mater* 2010;22(48):5483–7.
- [7] Zhu Y, Cai W, Piner RD, Velamakanni A, Ruoff RS. Transparent self-assembled films of reduced graphene oxide platelets. *Appl Phys Lett* 2009;95(10):103104.
- [8] Bai H, Li C, Shi G. Functional composite materials based on chemically converted graphene. *Adv Mater* 2011;23(9):1089–115.
- [9] Eda G, Ball J, Mattevi C, Acik M, Artiglia L, Granozzi G, et al. Partially oxidized graphene as a precursor to graphene. *J Mater Chem* 2011;21(30):11217–23.

- [10] Yamaguchi H, Eda G, Mattevi C, Kim H, Chhowalla M. Highly uniform 300 mm wafer-scale deposition of single and multilayered chemically derived graphene thin films. *ACS Nano* 2010;4(1):524–8.
- [11] Xu Y, Sheng K, Li C, Shi G. Highly conductive chemically converted graphene prepared from mildly oxidized graphene oxide. *J Mater Chem* 2011;21(20):7376–80.
- [12] Botas C, Álvarez P, Blanco C, Santamaría R, Granda M, Ares P, et al. The effect of the parent graphite on the structure of graphene oxide. *Carbon* 2012;50(1):275–82.
- [13] Lucchese MM, Stavale F, Ferreira EHM, Vilani C, Moutinho MVO, Capaz RB, et al. Quantifying ion-induced defects and Raman relaxation length in graphene. *Carbon* 2010;48:1592–7.
- [14] William S, Hummers J, Offeman RE. Preparation of graphitic oxide. *J Am Chem Soc* 1958;80(6):1339.
- [15] Eigler S, Dotzer C, Hirsch A, Enzelberger M, Müller P. Formation and Decomposition of CO₂ Intercalated Graphene Oxide. *Chem Mater*, <http://dx.doi.org/10.1021/cm203223z>.
- [16] Acik M, Mattevi C, Gong C, Lee G, Cho K, Chhowalla M, et al. The role of intercalated water in multilayered graphene oxide. *ACS Nano* 2010;4(10):5861–8.
- [17] Hontoria-Lucas C, López-Peinando AJ, López-González JDD, Rojas-Cervantes ML, Martín-Aranda RM. Study of oxygen-containing groups in a series of graphite oxides: physical and chemical characterization. *Carbon* 1995;33(11):1585–92.
- [18] Stankovich S, Piner RD, Nguyen ST, Ruoff RS. Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets. *Carbon* 2006;44(15):3342–7.
- [19] Szabó T, Berkesi O, Dékány I. DRIFT study of deuterium-exchanged graphite oxide. *Carbon* 2005;43(15):3186–9.
- [20] Scholz W, Boehm HP. Betrachtungen zur Struktur des graphitoxids. *Z Anorg Allg Chem* 1969;369(3–6):327–40.
- [21] Erickson K, Erni R, Lee Z, Alem N, Gannett W, Zettl A. Determination of the local chemical structure of graphene oxide and reduced graphene oxide. *Adv Mater* 2010;22(40):4467–72.
- [22] Cançado LG, Jorio A, Ferreira EHM, Stavale F, Achete CA, Capaz RB et al. Quantifying defects in graphene via Raman spectroscopy at different excitation energies. *Nano Lett* 2011;11(8):3190–6.
- [23] Moon IK, Lee J, Ruoff RS, Lee H. Reduced graphene oxide by chemical graphitization. *Nat Commun* 2010(6):1:73 <http://dx.doi.org/10.1038/ncomms67>.
- [24] Cui P, Lee J, Hwang E, Lee H. One-pot reduction of graphene oxide at subzero temperatures. *Chem Commun* 2011;47(45):12370–2.
- [25] Pei S, Zhao J, Du J, Ren W, Cheng H-M. Direct reduction of graphene oxide films into highly conductive and flexible graphene films by hydrohalic acids. *Carbon* 2010;48(15):4466–74.
- [26] Gao X, Jang J, Nagase S. Hydrazine and thermal reduction of graphene oxide: reaction mechanisms, product structures, and reaction design. *J Phys Chem C* 2010;114(2):832–42.
- [27] Ferrari AC, Robertson J. Interpretation of Raman spectra of disordered and amorphous carbon. *Phys Rev B* 2000;61(20):14095–107.