

Graphene oxide: efficiency of reducing agents

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The efficiency of reducing agents for the reduction of graphene oxide (GO) could be probed by scanning Raman spectroscopy. A film of graphene flakes derived from GO was probed to be graphene like. We also focus on the surface quality of reduced GO (rGO).

Graphene is a polymer structure made of fused six membered sp²-hybridized carbon atoms and is the building block of graphite.¹ Despite graphite being ubiquitous, graphene is difficult to exfoliate in large quantities. In contrast to graphite, graphite oxide, the oxidation product yielded from graphite, can easily delaminate into graphene oxide (GO). This form of graphene may develop into the cheap precursor of choice to yield processable graphene in large quantities.^{2–4} Another benefit of GO is its high potential to be the most versatile starting material for the preparation of functionalized graphene.⁵ Thereby, possibly even the exciting properties of graphene can be extended to meet the demands for electronic devices,⁶ selective sensors,⁷ functional composite materials,⁸ solar cells,⁹ or energy storage.¹⁰ GO is a single layer of graphite oxide decorated with epoxy and hydroxyl groups. The structure of GO has been studied for more than a century but still needs further clarification, which emerges from the recent discovery of highly reducible GO or organosulfate as part of its structure.^{11,12}

While GO is heterogeneously decorated with functional groups and almost every second carbon atom is sp³-hybridized additional defects are invisible for common spectroscopic methods. After reduction of GO to rGO functional groups are removed and defects dominate the structure that can be probed by Raman spectroscopy.¹³ Nevertheless, the reduction product of conventional GO that was prepared by the protocol introduced by Charpy and later Hummers and Offeman can only provide graphene with numerous defects.^{14,15} The reason for that is the completely destroyed honeycomb lattice by holes, additional atoms or a reorganized carbon lattice, such as five

membered rings.^{2,3} However, there have been tremendous attempts to find a highly efficient reducing agent for GO to yield rGO of enhanced quality.^{2,3} Thus, besides thermal treatment (up to 1100 °C) *in vacuo* or reducing atmospheres, the chemical approach utilizes reducing agents, such as hydrazine, hydrides, hydroxides, metals, redox active sulfur species, reductive acids, or even enzymatic reduction. The reason why these attempts failed are defects already present in GO due to the oxidation process. Therefore, the yielded reduction product was described as Swiss cheese.¹⁶

Recently, we discovered a new method to produce a new GO (GO-n) that exhibits a preserved hexagonal σ -framework of C-atoms and thus is an efficient precursor of graphene with very few defects.¹¹ Because of the limited quality of conventional GO (GO-c) it was impossible to evaluate reducing agents being more or less effective in reducing GO-c. In contrast GO-n provides the ability to be reduced to graphene with a very low defect density and the distance between two defects was found to be up to 10–14 nm.¹¹ The defect distance in GO-c is generally of about 1 nm and thus is graphene that is dominated by defects.

Here we show using GO-n that it is possible to determine the effectiveness of reducing agents. By using scanning Raman spectroscopy we can determine the effectiveness of reducing agents and in addition we focus on the surface quality which is of great importance. Thus, the development of reducing agents should also be focused on being not only effective but also able to yield a clean graphene surface.

Flakes of GO-n with a size of about 3–5 μm were prepared according to the method described before.¹¹ The study presented here is based on single layered films prepared by the Langmuir–Blodgett method.¹¹ The substrates used are Si-wafers/300 nm SiO₂ suitable for making single layers of graphene visible by optical microscopy.^{17–19} The quality of the final graphene was determined by Raman spectroscopy (using laser for excitation at 532 nm), a method that is well established. The method is based on a study where graphene is treated with different doses of Ar-ions and the evolution of peaks in Raman spectra was studied.²⁰ The most important spectral features are the defect induced D-peak, in addition to the G-peak. Further, in graphene the most prominent peak is the 2D peak (second order of the D-peak) and its intensity not only declines

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with increasing defect-density, but also the full width at half maximum (Γ) broadens. Finally, it is possible to translate these spectral properties to determine the distance between distorted regions caused by defects and to define the degree of functionalization.^{20–22}

In this communication we concentrate on the most commonly used reduction methods to prepare rGO. One of the most favored methods for the reduction of GO is thermal annealing.^{23,24} However, even if that method is easily achieved, it comes along with a tremendous weight-loss of about 30% up to 200 °C which is accompanied by formation of CO and CO₂ which results in a highly disordered structure. We heated the samples in air on a hot-plate up to 200 °C.²⁵ Another method is based on the reduction with hydrazine vapor even if hydrazine is toxic. Thus, we used a stream of hydrazine in nitrogen to reduce GO deposited on the surface.²⁶ Due to the toxicity of hydrazine vitamin C was found to be a highly effective reducing agent and it was claimed to be an ideal substitute for hydrazine.²⁷ We deposited a drop of vitamin C (10 mg ml⁻¹) on the rGO-n film at 80 °C for 1 h followed by rinsing with water and methanol. Another reducing agent is hydriodic acid which is often used in combination with other strong acids.^{28,29} We used it in the same way as reported earlier.¹¹ The efficiency of the reduction of GO is often proved by thermogravimetry, X-ray diffraction, photoelectron spectroscopy, Raman spectroscopy or by the C/O ratio. Especially the C/O ratio is not able to identify distorted regions in the carbon lattice. Thus, here we concentrate on Raman spectroscopy (Fig. 1).

Using a statistical approach, we are able to make different reducing agents with comparable reduction efficiency for GO-n because of its intact σ -framework. This is conducted by scanning the surface area of 100 × 100 μm^2 with an increment of 2.5 μm . Finally, 1600 spectra were filtered by the intensity of the G-peak, which varies with the number of layers, to gain information from single rGO-n layers. Subsequently, peak intensities of the D peak and the G peak and the full width at half maximum of the 2D peak (Γ_{2D}) were analyzed. We found that plotting the ratio of the intensity of the D peak and the G peak vs. Γ of the 2D peak makes the differences in yielded quality of rGO-n visible. The Γ_{2D} for graphene is about

32 cm⁻¹ on SiO₂.³⁰ We find that it varies between 32 cm⁻¹ and 200 cm⁻¹ for rGO-n depending on the reduction method. The less efficient method is thermal reduction. After thermal annealing at 200 °C a highly distorted material is obtained with $\Gamma_{2D} = 172 \pm 19 \text{ cm}^{-1}$ and an $I_D/I_G = 1.2 \pm 0.1$. These data demonstrate the highly distorted character of thermally converted GO. If vapor of hydrazine hydrate is used at 80 °C followed by annealing at 160 °C an enhanced quality is obtained with the $\Gamma_{2D} = 78 \pm 18 \text{ cm}^{-1}$ and an $I_D/I_G = 2.7 \pm 0.4$. Using hydrazine the distance between distorted regions is about 2–3 nm and very close to the transition of graphene that is no longer dominated by defects. If vitamin C at 80 °C is used an even more enhanced quality is obtained with the $\Gamma_{2D} = 62 \pm 15 \text{ cm}^{-1}$ and an $I_D/I_G = 2.3 \pm 0.3$. In addition 7.9% of spectra exhibit spectral features of graphene with a $\Gamma_{2D} < 40 \text{ cm}^{-1}$ which is a clear measure of single layers of graphene, while the Γ_{2D} of double layers is larger.^{20,31} If the vapor of hydriodic acid in combination with trifluoro acetic acid (HI-TFA) is used at 80 °C the best performance is found and the $\Gamma_{2D} = 58 \pm 11 \text{ cm}^{-1}$ and $I_D/I_G = 2.6 \pm 0.3$ and 9.5% of spectra exhibit a $\Gamma_{2D} < 40 \text{ cm}^{-1}$ (Table 1). This average quality represents the transition from graphene dominated by defects to graphene that is no longer dominated by defects. With the distance between distorted regions being larger than 3 nm a $\Gamma_{2D} \sim 50 \text{ cm}^{-1}$ is expected (Fig. 1).²⁰

We conclude, neither thermal reduction nor reduction with hydrazine are efficient methods to exploit the full potential of GO-n. Vitamin C and HI-TFA appear to be efficient for yielding graphene. Comparing the maximum of I_D/I_G ratios found it is obvious that the highest I_D/I_G ratios are found for hydrazine ($I_D/I_G \sim 4$) while the $I_D/I_G \sim 3$ for vitamin C rGO-n. One reason for that may be adsorbates on the surface of graphene. Therefore, we had a closer look at the surface of rGO-n utilizing AFM. We note that the rGO-n surfaces were cleaned by immersing rGO in distilled water and methanol for 15 minutes.

After drying AFM reveals the highest surface roughness of 2 nm and an overall thickness of 4 nm for individual flakes of vitamin C rGO-n. These surface adsorbates could not be removed by washing procedures using common organic solvents. The analysis of the surfaces reveals that HI-TFA exhibits the smoothest surface for rGO-n. However, the flake thickness remains larger than that of pristine graphene (Fig. 3).

Finally, we found HI-TFA is an efficient method for the reduction of GO-n and superior to using vitamin C or hydrazine. The limiting factor to yield perfect graphene from GO-n is distorted regions still present in GO-n. Thus, we altered the work-up procedure during graphite oxidation making the hydrolysis of the reduction mixture at 0 °C instead of 10 °C. The finally prepared rGO-n film was analyzed by Raman spectroscopy also. Now we find

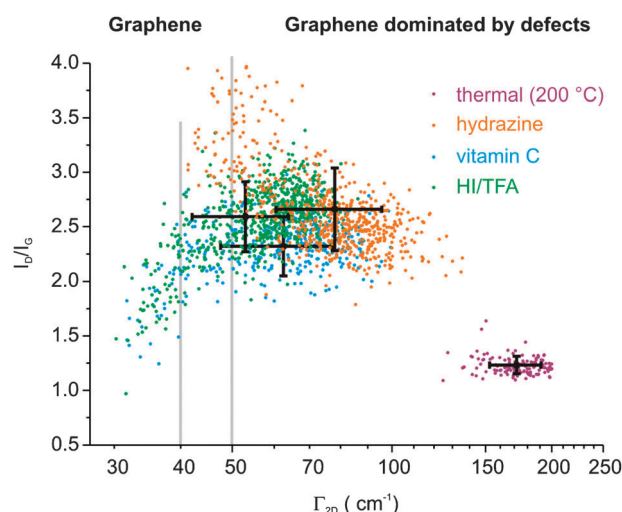


Fig. 1 Raman analysis of the overall quality of rGO-n films prepared by four different reduction techniques.

Table 1 Results of statistical Raman analysis of rGO-n films

| Reduction method for GO-n | Γ_{2D} (cm ⁻¹) | I_D/I_G | % $\Gamma_{2D} < 50 \text{ cm}^{-1}$ | % $\Gamma_{2D} < 40 \text{ cm}^{-1}$ | L_D^b (nm) |
|---------------------------|-----------------------------------|-----------|--------------------------------------|--------------------------------------|--------------|
| Thermal | 172 ± 19 | 1.2 ± 0.1 | 0.0 | 0.0% | ~1 |
| Hydrazine | 78 ± 18 | 2.7 ± 0.4 | 5.5 | 0.0% | 2–3 |
| Vitamin C | 62 ± 15 | 2.3 ± 0.3 | 23.0 | 7.9 | 2–3 |
| HI-TFA | 58 ± 1 | 2.6 ± 0.3 | 25.0 | 9.5 | 3 |
| HI-TFA ^a | 49 ± 9 | 2.8 ± 0.4 | 59.2 | 17.4 | 5 |

^a Optimized GO-n. ^b L_D = average distance between defects.²⁰



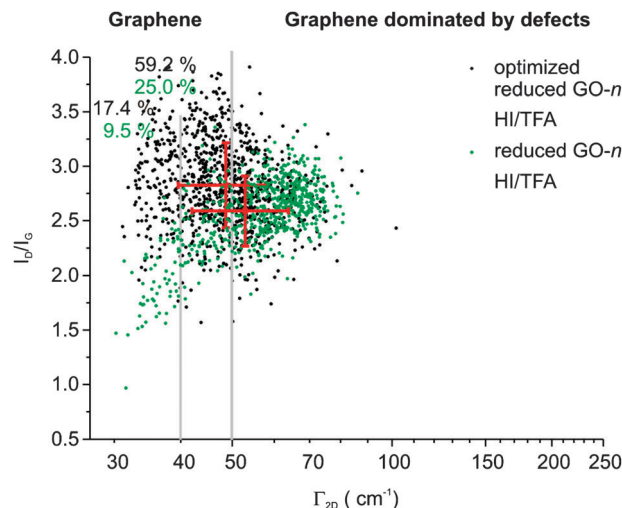


Fig. 2 Raman analysis of an rGO-n film prepared from optimized GO-n and compared to normal GO-n.

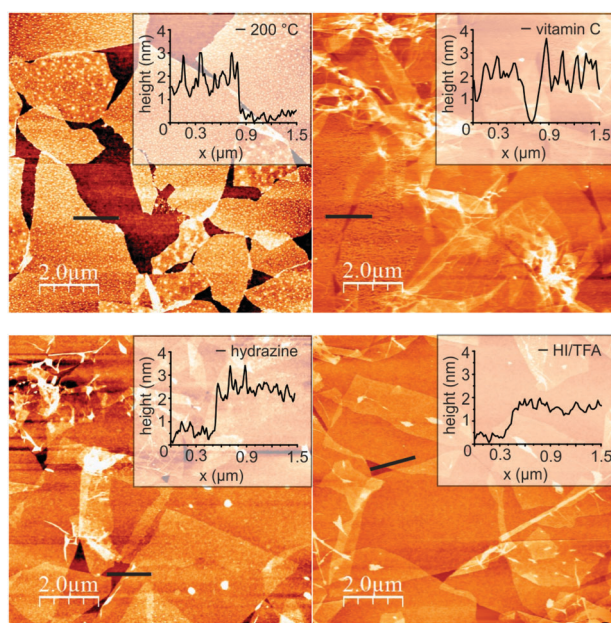


Fig. 3 AFM images of differently prepared rGO-n; inset: height profile along the back line.

that the obtained film can be termed as a film of graphene flakes because the $\Gamma_{2D} = 49 \pm 9 \text{ cm}^{-1}$ and $I_D/I_G = 2.8 \pm 0.4$. Thus, the average distance between defects is about 5 nm (Fig. 2).

Furthermore, 17.4% of spectra are due to a high quality of graphene with $\Gamma_{2D} < 40 \text{ cm}^{-1}$ while 59.2% of spectra belong to a quality that is no longer dominated by distorted regions and thus exhibits a $\Gamma_{2D} < 50 \text{ cm}^{-1}$.

We conclude that for yielding high quality graphene from GO there are two factors that limit the final quality. First, the quality of GO is crucial because intrinsic and permanent structural defects in the σ -framework of C-atoms introduced by the preparation process limit the potential of reduction. Further on, this type of reducing method was identified to be more or less efficient. Reduction that comes along with carbon-loss appears to be worse compared to reducing agents such as hydrazine. Best results were obtained using

a reducing agent in combination with acid. Furthermore, the latter appears to be beneficial in terms of surface quality also. Finally, we show that probing the graphene quality by scanning Raman spectroscopy can result in visible enhancements in the preparation of rGO-n, as shown for an optimized film that could be identified as a film of graphene flakes. Beyond that, we identify surface adsorbates on rGO that limit the purity of graphene. We want to point to that topic that needs to be addressed more in future work to find methods to purify graphene surfaces while the quality of graphene is preserved.

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Notes and references

- 1 A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183–191.
- 2 S. Pei and H.-M. Cheng, *Carbon*, 2012, **50**, 3210–3228.
- 3 S. Mao, H. Pu and J. Chen, *RSC Adv.*, 2012, **2**, 2643–2662.
- 4 Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts and R. S. Ruoff, *Adv. Mater.*, 2010, **22**, 3906–3924.
- 5 T. Kuila, S. Bose, A. K. Mishra, P. Khanra, N. H. Kim and J. H. Lee, *Prog. Mater. Sci.*, 2012, **57**, 1061–1105.
- 6 Q. He, S. Wu, S. Gao, X. Cao, Z. Yin, H. Li, P. Chen and H. Zhang, *ACS Nano*, 2011, **5**, 5038–5044.
- 7 Y. Shao, J. Wang, H. Wu, J. Liu, I. A. Aksay and Y. Lin, *Electroanalysis*, 2010, **22**, 1027–1036.
- 8 X. Huang, X. Qi, F. Boey and H. Zhang, *Chem. Soc. Rev.*, 2012, **41**, 666–686.
- 9 Z. Yin, S. Sun, T. Salim, S. Wu, X. Huang, Q. He, Y. M. Lam and H. Zhang, *ACS Nano*, 2010, **4**, 5263–5268.
- 10 M. Pumera, *Energy Environ. Sci.*, 2011, **4**, 668–674.
- 11 S. Eigler, M. Enzelberger, S. Grimm, P. Hofmann, W. Kroener, A. Geworski, C. Dotzer, M. Röckert, J. Xiao, C. Papp, O. Lytken, H.-P. Steinrück, P. Müller and A. Hirsch, *Adv. Mater.*, 2013, **25**, 3583–3587.
- 12 S. Eigler, C. Dotzer, F. Hof, W. Bauer and A. Hirsch, *Chem.-Eur. J.*, 2013, **19**, 9490–9496.
- 13 S. Eigler, C. Dotzer and A. Hirsch, *Carbon*, 2012, **50**, 3666–3673.
- 14 G. Charpy, *C. R. Hebd. Seances Acad. Sci.*, 1909, **148**, 920–923.
- 15 J. William, S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
- 16 I. Jung, D. A. Dikin, R. D. Piner and R. S. Ruoff, *Nano Lett.*, 2008, **8**, 4283–4287.
- 17 L. J. Cote, F. Kim and J. Huang, *J. Am. Chem. Soc.*, 2009, **131**, 1043–1049.
- 18 S. Roddaro, P. Pingue, V. Piazza, V. Pellegrini and F. Beltram, *Nano Lett.*, 2007, **7**, 2707–2710.
- 19 C. Casiraghi, A. Hartschuh, E. Lidorikis, H. Qian, H. Harutyunyan, T. Gokus, K. S. Novoselov and A. C. Ferrari, *Nano Lett.*, 2007, **7**, 2711–2717.
- 20 L. G. Cançado, A. Jorio, E. H. M. Ferreira, F. Stavale, C. A. Achete, R. B. Capaz, M. V. O. Moutinho, A. Lombardo, T. S. Kulmala and A. C. Ferrari, *Nano Lett.*, 2011, **11**, 3190–3196.
- 21 M. M. Lucchese, F. Stavale, E. H. M. Ferreira, C. Vilani, M. V. O. Moutinho, R. B. Capaz, C. A. Achete and A. Jorio, *Carbon*, 2010, **48**, 1592–1597.
- 22 J. M. Engler, P. Vecera, K. C. Knirsch, R. A. Schäfer, F. Hauke and A. Hirsch, *ACS Nano*, 2013, **7**, 5472–5482.
- 23 H. A. Becerril, J. Mao, Z. Liu, R. M. Stoltenberg, Z. Bao and Y. Chen, *ACS Nano*, 2008, **2**, 463–470.
- 24 A. Bagri, C. Mattevi, M. Acik, Y. J. Chabal, M. Chhowalla and V. B. Shenoy, *Nat. Chem.*, 2010, **2**, 581–587.
- 25 S. Eigler, C. Dotzer, A. Hirsch, M. Enzelberger and P. Müller, *Chem. Mater.*, 2012, **24**, 1276–1282.
- 26 X. Gao, J. Jang and S. Nagase, *J. Phys. Chem. C*, 2010, **114**, 832–842.
- 27 M. J. Fernández-Merino, L. Guardia, J. I. Paredes, S. Villar-Rodil, P. Solís-Fernández, A. Martínez-Alonso and J. M. D. Tascón, *J. Phys. Chem. C*, 2010, **114**, 6426–6432.
- 28 I. K. Moon, J. Lee, R. S. Ruoff and H. Lee, *Nat. Commun.*, 2010, **1**, 73.
- 29 P. Cui, J. Lee, E. Hwang and H. Lee, *Chem. Commun.*, 2011, **47**, 12370–12372.
- 30 Y. Y. Wang, Z. H. Ni, T. Yu, Z. X. Shen, H. M. Wang, Y. H. Wu, W. Chen and A. T. S. Wee, *J. Phys. Chem. C*, 2008, **112**, 10637–10640.
- 31 S. Chen, W. Cai, R. D. Piner, J. W. Suk, Y. Wu, Y. Ren, J. Kang and R. S. Ruoff, *Nano Lett.*, 2011, **11**, 3519–3525.

