

Graphene Oxide: A One- versus Two-Component Material

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S Supporting Information

ABSTRACT: The structure of graphene oxide (GO) is a matter of discussion. While established GO models are based on functional groups attached to the carbon framework, another frequently used model claims that GO consists of two components, a slightly oxidized graphene core and highly oxidized molecular species, oxidative debris (OD), adsorbed on it. Those adsorbents are claimed to be the origin for optical properties of GO. Here, we examine this model by preparing GO with a low degree of functionalization, combining it with OD and studying the optical properties of both components and their combination in an artificial two-component system. The analyses of absorption and emission spectra as well as lifetime measurements reveal that properties of the combined system are distinctly different from those of GO. That confirms structural models of GO as a separate oxygenated hexagonal carbon framework with optical properties governed by its internal structure rather than the presence of OD. Understanding the structure of GO allows further reliable interpretation of its optical and electronic properties and enables controlled processing of GO.

Graphene is a nanomaterial that attracts great interest due to its use in emerging applications such as microelectronics, photonics, or renewable energy systems.^{1–3} Recently, functional derivatives of graphene have evolved as a versatile platform for producing graphene-based materials in bulk quantities at low cost.⁴ Graphene oxide (GO), which is generated directly via oxidation of graphite, stands out among these graphene derivatives.^{5,6} It is not only the simplicity in GO fabrication but also the tunability of its chemical and physical properties provided in part by variation of the synthetic conditions, which renders GO unique.⁷

Notably, GO has been synthesized and isolated long before the discovery of graphene and its outstanding properties. Still a central question remains: What is graphene oxide? As a matter of fact, several structural models have been proposed, most of them based on a two-dimensional sheet of hexagonal

carbons.^{8–13} Some of these models do account for the partial rupture of the carbon lattice due to overoxidation. The most common description of GO involves the coexistence of sp² carbon islands and sp³ carbon regions featuring oxygen-containing functionalities.^{14–17}

The sp² carbon islands may act as confined electronic environments, which causes, on one hand, the band gap opening in GO^{18,19} and, on the other hand, the GO fluorescence in the visible range.^{20,21} In yet another structural model, the optical properties of GO, namely the band gap opening, is ascribed to the localization of electronic environments around specific individual functional groups rather than graphitic islands.^{22,23}

A more recent model implies that GO consists of two different components. One of the two components is graphene with a low degree of oxidation, Figure 1, while the other component is oxidative debris (OD) of graphite covering the graphene surface.²⁴ OD is a polyaromatic oxide material, produced during the oxidative transformation of graphite into GO. During the purification, which involves centrifugation, OD is claimed to be only partially removed with about 30% of the GO weight²⁴ randomly adhered to the surface of GO. It was demonstrated that NaOH reflux enables such surface interactions to be overcome. As a matter of fact, Rourke et al. reported a quantitative separation of these two fractions to yield “true” GO and OD. According to the two-component model, OD dominates in the composite over GO in terms of electroactivity,²⁵ surface adsorption,^{26,27} and fluorescence. To this end, the fluorescence of as-produced GO originates fully from OD.²⁸ Likewise, the presence of OD may also alter the electron transport properties of the GO/OD system²⁵ and affect its solubility in water.^{24,29} Structure reports of GO based on solid state nuclear magnetic resonance spectroscopy^{12,13,15,16} and reports on the optical properties of GOs contradict this two-component model.^{18–23,30} OD, as proposed by Dimiev et al., may be absent in GO initially, but produced during NaOH reflux treatment.³¹ In fact, similar to OD in structure fluorescent GO quantum dots are commonly

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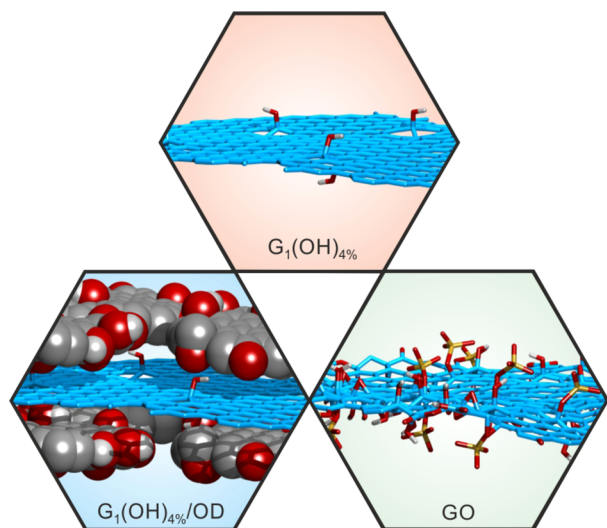


Figure 1. Top: Illustration of $G_1(OH)_{4\%}$. Bottom right: One-component model, GO, highly functionalized graphene (hydroxyl- and epoxy groups and optional organosulfate groups). Bottom left: Two-component model, $G_1(OH)_{4\%}/OD$, graphene with a low degree of functionalization ($G_1(OH)_{4\%}$) and oxidative debris (OD).

produced by reductive treatment of GO.^{32–34} Excessive oxidation of graphite can also yield GO quantum dots,^{32–34} though at conditions markedly different from those for GO synthesis. A definitive answer regarding the role and the origin of OD remains missing, and therefore the model of GO must be revisited. Here, we shed light onto this aspect by examining the function of OD in the GO model by preparing an artificial two-component system consisting of OD and a graphene derivative with a low functionalization degree as a mimic for OD-free GO. In our analyses of the two separate components—OD and OD-free GO—as well as the model system—OD/GO—we have identified the nature of GO as only a single component.

First, we synthesized three different types of GO. GO_{Hummers} was prepared according to the procedure described by Hummers and Offeman.³⁵ While the GO_{Hummers} synthesis is accompanied by overoxidation and, thus, formation of lattice defects, the second synthesized material, oxo-functionalized graphene ($oxo-G_1$), bears an almost intact carbon framework, with only $\sim 0.6\%$ of lattice defects.^{7,36} In addition, the hydroxylated graphene derivative, $G_1(OH)_{4\%}$, was synthesized with a hydroxylation degree of about 4% and 0.05% lattice defects.³⁷

As reported, OD is removed from GO by up to 1 h of NaOH treatment at 70 °C with subsequent centrifugation.^{23,24} We followed this procedure and separated base-treated GO_{Hummers} ($^{base}GO_{\text{Hummers}}$) and oxidative debris (^{base}OD). The fluorescence of $^{base}GO_{\text{Hummers}}$ decreased significantly (Figure 2B) throughout the process. In contrast to earlier reports,²⁸ the fluorescence was not quenched completely but red-shifted instead.

The absorption of $^{base}GO_{\text{Hummers}}$ (Figure 2A) bears great resemblance with the spectra of partially reduced GO. From the latter we deduce a certain degree of defunctionalization. Absorption analyses of just ^{base}OD indicate a strong blue shift in the range below 250 nm (Figure 2C). Similarly, the fluorescence is blue-shifted to ~ 540 nm (Figure 2D).

Next we applied the OD removal protocol to $oxo-G_1$ with an initial lattice defect density of 0.6%. Owing to the fact that

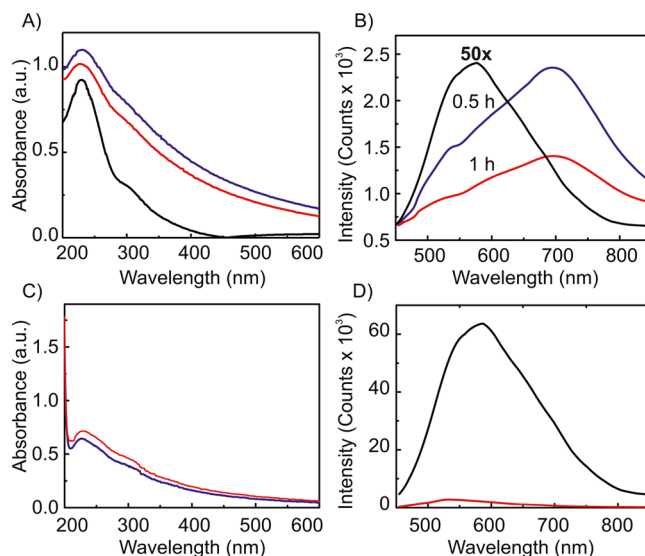


Figure 2. (A) Absorption spectra of GO_{Hummers} (black), treated with NaOH at 70 °C for 30 min (blue) and treated with NaOH at 70 °C for 1 h (red). (B) Fluorescence spectra ($\lambda_{\text{ex}} = 440$ nm) of GO_{Hummers} (black), treated with NaOH at 70 °C for 30 min (blue) and treated with NaOH at 70 °C for 1 h (red). (C) Absorption spectra of ^{base}OD separated from GO_{Hummers} after 30 min (blue) and 1 h (red) of NaOH treatment. (D) Absorption-normalized fluorescence ($\lambda_{\text{ex}} = 440$ nm) of GO_{Hummers} (black) and ^{base}OD (red) separated from GO_{Hummers} after 1 h of NaOH treatment at 70 °C.

preparation of $oxo-G_1$ excludes extensive overoxidation of graphite, low amounts of OD are assumed.⁷ The base treatment of $oxo-G_1$ for up to 3 h led to a decrease in the fluorescence intensity (Figure S1) regardless of the low initial OD content. The aforementioned results alone indicate that GO fluorescence may not be solely ascribed to OD-centered emission. In fact, a quenched fluorescence of base-treated GO could be a result of the post-treatment. A 70 °C reflux, for example, causes an irreversible decrease of fluorescence intensity (Figure S2).

We further studied the optical properties of $oxo-G_1$ and $G_1(OH)_{4\%}$. Common to both is only a slight degree of oxidation³⁷ just like the OD-free component of GO in the two-component model of Rourke et al. As documented in Figure S3, $oxo-G_1$ and $G_1(OH)_{4\%}$ exhibited intense fluorescence when excited at 440 nm. The fluorescence is hardly explainable by OD emission due to the low initial amount of OD. Please note that the presence of OD is linked to overoxidized graphite.

As a complement we looked into a GO/OD two-component material containing larger amounts of OD, as it was proposed in the literature.²⁴ For illustration please see Figure 1. In particular, we combined $oxo-G_1$, which was base-treated for 3 h for complete OD removal, with an equal volume of OD, isolated directly after the preparation of GO_{Hummers} , termed as ^{ox}OD . In this model, base-treated $oxo-G_1$ served as a replacement for the OD-free GO component. ^{ox}OD featured spectral characteristics similar to those of ^{base}OD , with, however, a slightly higher fluorescence quantum yield of $0.49 \pm 0.05\%$ relative to the $0.3 \pm 0.02\%$ found for ^{base}OD . In particular the emission spectra of ^{ox}OD and ^{base}OD are similar, as depicted in Figure S4. Moreover low molecular masses mainly between m/z 100 and m/z 250 are found (Figure S6), similar as described in the literature.²⁴ As depicted in Figure 3A and 3B the absorption and fluorescence spectra, respectively, of the artificial two-component system at an OD content affecting

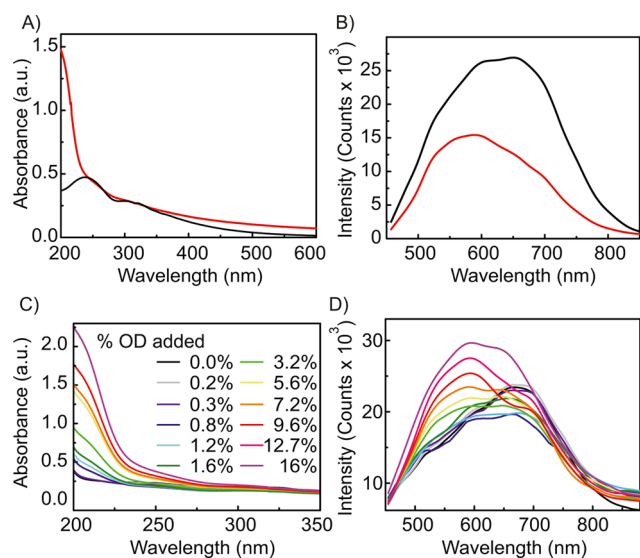


Figure 3. (A) Absorption spectra of as-produced oxo-G_1 (black) and a combination of NaOH-treated oxo-G_1 and oxo-OD (red). (B) Fluorescence spectra of as-produced oxo-G_1 (black) and a combination of NaOH-treated oxo-G_1 and oxo-OD (red). Consecutive addition of oxo-OD to $\text{G}_1(\text{OH})_{4\%}$. (C) Absorption spectra of $\text{G}_1(\text{OH})_{4\%}$ turn to spectra of OD. (D) Emission spectra of $\text{G}_1(\text{OH})_{4\%}$ ($\lambda_{\text{ex}} = 440$ nm); emission maximum at ~ 670 nm gets suppressed by a prevailing feature at ~ 600 nm. Each curve is marked with corresponding weight % of oxo-OD added (legend in C).

absorption and fluorescence did not resemble the optical properties of as-produced oxo-G_1 .

Finally, we prepared a series of two-component systems, featuring variable concentrations of low defect $\text{G}_1(\text{OH})_{4\%}$ and oxo-OD . As suggested, such systems should represent the structure of as-produced GO with substantial OD content and, thus, exhibit similar optical properties.^{24,28,29} Absorption and fluorescence spectra of the mixtures were recorded for each composition (Figure 3C and 3D). In terms of fluorescence, no significant changes are noted at low oxo-OD content of up to 0.3 wt %. In terms of absorption, only a minor gradual increase in intensity evolves between 200 and 250 nm.

At higher oxo-OD , the lower wavelength fluorescence became more prevalent, a trend that is expected when mixing the two components. At the same time, the oxo-OD absorption features dominate the spectra in the range of 200 to 250 nm. None of the recorded spectra resembled the optical properties of as-produced $\text{GO}_{\text{Hummers}}$, $\text{G}_1(\text{OH})_{4\%}$, or oxo-G_1 , rendering OD content over 0.3% unrealistic. Thus, we hypothesize that small amounts of OD as they might be present in as-produced GO should not affect any of the optical properties. Large OD contents resulted in a strongly altered optical response and are unlikely to be present in GO.

Independent support for our hypothesis regarding optical contributions of OD to the two-component model comes from fluorescence lifetime measurements of GO and OD. From the data depicted in Figure 4A lifetimes for $\text{GO}_{\text{Hummers}}$ and $\text{G}_1(\text{OH})_{4\%}$ are calculated as 0.45 and 0.48 ns, respectively, whereas oxo-OD and $\text{base-OD}_{\text{Hummers}}$ exhibit longer lifetimes of 0.76 and 3.6 ns. Note: Taking for example the 0.76 ns oxo-OD sample and fitting it biexponentially afforded lifetimes of 0.45 and 1.9 ns. The extracted values indicate, however, the presence of minor amounts of GO in OD, although absorption and emission spectra represent the shape of OD only.

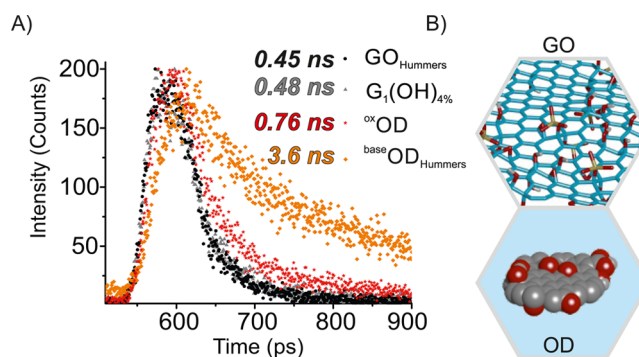


Figure 4. (A) Time resolved fluorescence profiles of $\text{GO}_{\text{Hummers}}$, $\text{G}_1(\text{OH})_{4\%}$, oxo-OD , and $\text{base-OD}_{\text{Hummers}}$. (B) Illustration of GO (top) and OD (bottom) compounds, the structure of GO (top) and OD (bottom).

Considering such significant differences in the time-resolved deactivations, GO and OD should be discernible as two distinctly different processes. No evidence was, however, gathered that would relate to a slower decaying OD component in the overall GO fluorescence (Figure 4A). It is safe to conclude that the optical characteristics of GO are composed of a single component lacking any appreciable contributions, neither in absorption nor in fluorescence, stemming from OD.

In summary, we have studied the optical signatures of GO by examining two-component models including that of OD and oxo-G_1 . The resulting materials appeared to have distinct optical properties, which were monitored and characterized independently from each other. OD separated by base treatment features weak fluorescence, which is not accountable for the optical properties in different types of GO. Interactions of OD and GO cannot be ruled out and may result in blue-shifted fluorescence, as seen when enriching $\text{G}_1(\text{OH})_{4\%}$ with oxo-OD . Concentrations of oxo-OD producing a fluorescence shift also result in the almost complete transformation of the GO absorption spectra into that of oxo-OD . The latter is, however, uncommon for as-produced GO materials. These steady state results are also confirmed by significant differences in fluorescence lifetimes of OD and GO. Thus, we infer that the unique spectroscopic features of GO are independent of the presence of OD. This renders a two-component GO/OD model irrelevant for comprehending the optical properties of GO. Consequently, OD can be considered as a separate compound (Figure 4B). As to the origin of the fluorescence, Frenkel-like excitons in the blue range and charge transfer excitons in the red range stemming from sp^2 carbon domains and localized states involving oxygen and carbon should be considered.³⁸ Notable is the spectral broadening that takes place within a few picoseconds for the charge transfer excitons. In the present case, an unambiguous assignment in terms of spectroscopic and kinetic fingerprints requires, however, additional experiments. To this end, we are currently performing advanced photo-physical characterizations with GOs featuring variable oxygen contents.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05928.

Experimental details; preparation and purification of GOHummers, oxo-G, $G_1(OH)_{4\%}$, artificial system; base and temperature treatment procedures; optical measurements (PDF)

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Notes

The authors declare no competing financial interest.

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