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Photoluminescence and Band Gap Modulation in Graphene Oxide

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Abstract

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Photoluminescence and band gap modulation in graphene oxide

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We report broadband visible photoluminescence from solid graphene oxide, and modifications of the emission spectrum by progressive chemical reduction. The data suggest a gapping of the two-dimensional electronic system by removal of π -electrons. We discuss possible gapping mechanisms, and propose that a Kekule pattern of bond distortions may account for the observed behavior. © 2009 American Institute of Physics. [DOI: 10.1063/1.3098358]

Single layer and bilayer graphene systems can exhibit a remarkable diversity of phenomena, including observations of a room-temperature, unconventional quantum Hall effect,¹⁻³ predictions of the quantum spin Hall effect,⁴ broken spin^{5,6} or pseudospin⁷ symmetries, and finite size effects that can be used to control band structure^{5,6,8,9} and magnetism.^{5,6,9,10} Taken together, these properties suggest that graphene is a promising platform for seamlessly exchanging information between different degrees of freedom. An outstanding challenge in this regard is photonic integration and band gap manipulation. Several theoretical works predict that a direct gap in the visible would occur for sufficiently small graphene nanoribbons,^{5,6,8,9} but no observations of this finite size effect have been reported. Additionally, modifications of the graphene sheet by oxidation can introduce direct gap behavior.¹¹

Here we show that graphene, although intrinsically a zero-gap semimetal, may be oxidized in a manner that produces photoluminescence (PL) for solid, drop-cast samples. We find that despite the high surface area of graphene oxide (GO) and in marked contrast to carbon nanotubes, the strength of PL from GO flakes does not differ significantly between aqueous and drop-cast samples. The resilience of PL for solid GO samples is encouraging for technological applications, implying that GO may be a useful photonic material when incorporated in solid state devices. The large observed gap creates the possibility for spatially modulating the band structure within a single graphene flake by local control of the oxidation profile. Studies of progressive chemical reduction show quenching of PL for both drop-cast and aqueous samples, coordinated with changes in absorption. These studies also find signatures of band gap manipulation, albeit with different character for solid and liquid samples.

Aqueous dispersions of single layer GO with an average area of $\sim 100 \mu\text{m}^2$ were synthesized following a procedure described elsewhere.¹² Solid samples (s-GO) were obtained by drop-casting the concentrated GO solution resulting from this procedure onto polished, low auto-fluorescence, Suprasil-2 substrates and then baking at 95 °C for 30 min. Liquid samples (l-GO) were held in quartz cuvettes, diluted a hundredfold or more as necessary to adjust optical density. PL for both l-GO and s-GO was collected at 90° degrees to

the excitation, and the reflection (transmission) geometry for s-GO corresponded to collection on the same (opposite) side of the film. PL spectra were excited by Xe lamp passed through a monochromator, and additional filters were employed on excitation and collection to reject excitation scatter, second order grating effects, and leakage of Xe lamp spikes. Spectra were spectrally corrected for detector efficiencies, and normalized by excitation power. All PL data shown here (both maps and single spectra) are further normalized to a maximum value of unity and taken at 300 K.

Figure 1(a) compares PL for both l-GO and s-GO samples. Both peaks in the visible with a long infrared emission tail. Differences in measurement geometry make quantitative comparisons of the quantum yield impossible, but generally little difference was seen in PL intensity. An interesting question is whether energy relaxation and spectral diffusion are qualitatively altered by aggregation. For isolated flakes in l-GO, diffusion of free carriers or bound excitons should be confined to the two dimensional GO plane. However, for s-GO, atomic force and optical microscopy, both indicate films of layered GO flakes, which could give rise to additional interflake relaxation pathways. If interlayer coupling is strong enough, the emission spectrum could redshift. s-GO indeed shows more PL spectral weight in the infrared, but the redshift in the PL peak position is not a robust feature of the experiment and was inconsistent from sample to sample perhaps due to variations in the oxidation density. In addition to exciton diffusion, several plausible changes could

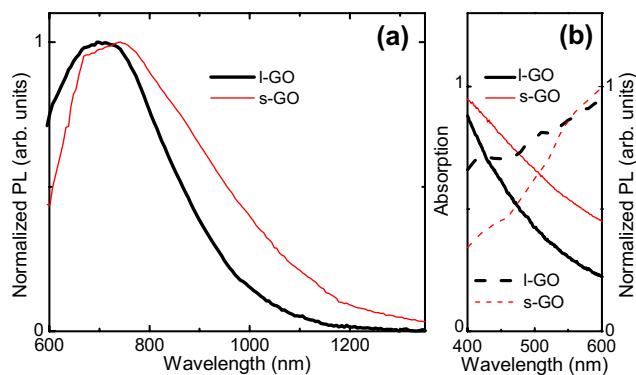


FIG. 1. (Color online) (a) Normalized PL spectra excited at 500 nm (s-GO taken in transmission). (b) Absorption (left axis, solid) and PL intensity detected at 752 nm (right axis, dashed), as a function of excitation wavelength.

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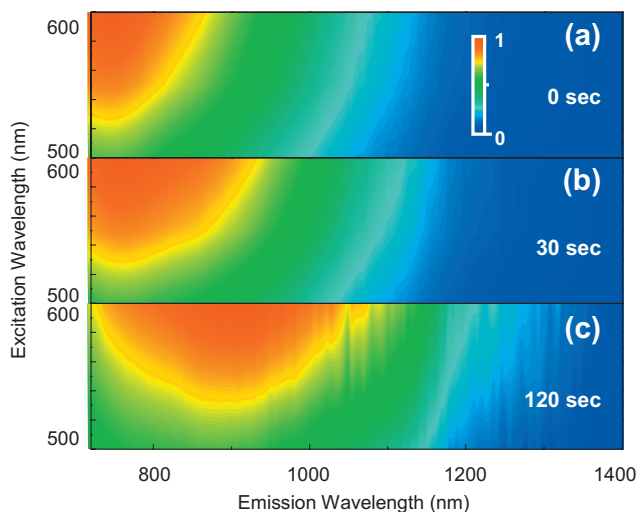


FIG. 2. (Color) Normalized PL excitation-emission maps for s-GO taken in transmission during hydrazine vapor exposure.

also influence the peak position, including modifications of the dielectric environment, spectral reabsorption, and variations in oxidation density.

The GO absorption [Fig. 1(b)] increases with energy from the near infrared to 3.1 eV, and provides an interesting contrast to the nonmonotonic PL spectrum. We further note that PL excitation (PLE) spectra do not mirror the absorbance increases at higher energies. To the contrary, as shown in Fig. 1(b), as the excitation energy increases, PL intensity detected at a fixed wavelength decreases. The latter indicates the presence of nonradiative energy relaxation pathways, but also calls into question the relevance of the absorbance spectrum to the emissive process. With these data in mind, one must consider the possibility that the electronic structure within the flakes is heterogeneous, and that PL emission originates from absorbance into excited states whose total absorptive cross-section is, nevertheless, only a small contributor to the total absorptive spectrum. Absolute values for the emissive quantum yield would help to illuminate this discussion, but accurate measurements of this quantity are problematic for ensembles of heterogeneous nanomaterials and are beyond the scope of this work. Nevertheless we may qualitatively say that the observed quantum yields appear to be far less than unity.

To study the relationship between oxidation density and the optical gap, we performed experiments to vary the oxidation density and while monitoring changes in the PL spectrum. s-GO samples were placed in a covered Petri dish with a container of hydrazine, heated to 50 °C, and their PL maps characterized in the transmission geometry. The process was repeated several times to progressively reduce the sample, resulting in a marked redshift (Fig. 2). Modeling shows that changes in the absorptive spectrum (not shown) could also produce these spectral shifts through reabsorption of the emitted light. To better control these effects, we repeated this study on a different sample in the reflection geometry, while also continually monitoring changes in absorption. Penetration of the exciting and emitting light was then estimated using the relationship $I_{\text{meas}}(1-T_1)\ln(T_1T_2)=I_{\text{PL}}(1-T_1T_2)\ln T_1$, where T_1 (T_2) is the film transmission for the excitation (emission) wavelength, I_{meas} and I_{PL} are the raw and absorbance-corrected intensities, respectively, and mul-

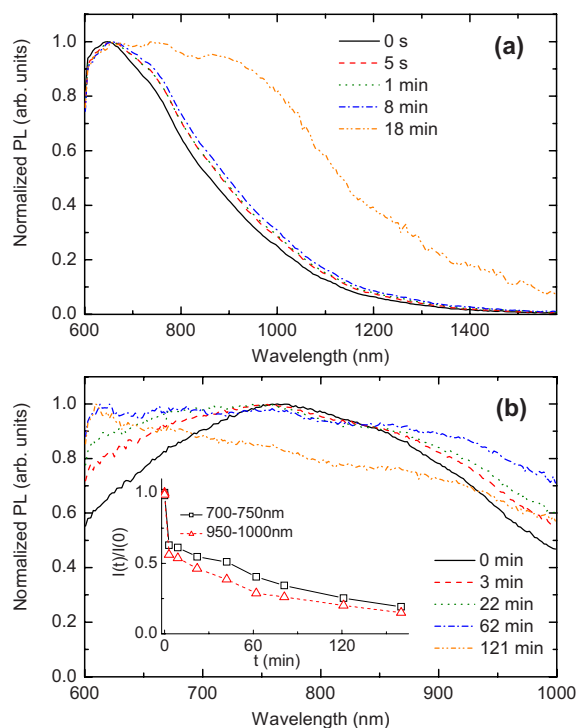


FIG. 3. (Color online) Normalized PL spectra during hydrazine exposure for (a) s-GO in a reflection geometry and (b) l-GO, excited at 488 nm. Data in (a) have been corrected for reabsorption as described in the text, whereas (b) does not require a correction. (Inset) Changes in integrated PL intensity $I(t)$ as a function of cumulative hydrazine exposure t for l-GO. Legend indicates spectral regions over which $I(t)$ was integrated.

tip reflections are ignored. I_{PL} shows a significant redshift in the PL emission for increased exposure times [Fig. 3(a)], consistent with an increase in the disorder length scale upon reduction.

We also studied chemical reduction in l-GO, where reabsorption effects could be brought to a negligible level. l-GO was reduced and held in suspension following the procedure introduced by Li *et al.*,¹³ which may involve electrostatic stabilization. During reduction, l-GO transmission remained >80% relative to water for a 1 cm path length. To further minimize reabsorption, l-GO was excited within 1 mm of the collection window. Figure 3(b) shows the development of a flatter spectral profile as a function of reduction time. Currently, differences between s-GO and l-GO reduction studies are not understood, but the data do hold certain features in common. In all cases, the *relative* intensity of PL in the infrared increases. However, the *absolute* intensity of PL was always seen to decrease with reduction everywhere in the spectrum, including the infrared [Fig. 3(b) inset].

A theoretical framework for interpreting these data is only just emerging. It can be expected that oxidation produces a disruption of the π network and can open a direct electronic band gap for single sheet graphene in one of two ways. The first is a quantum confinement effect whereby the π -electron wave functions occupy a potential landscape with strongly repulsive hard wall barriers at oxidized sites. In the infinite potential limit, a delocalized π -electron wave function will develop nodes at each of these sites. The presence or absence of a gap for a sample with many such oxidized sites then depends on the spatial distribution of these nodes. For example, in graphene ribbons where the edges break the sublattice symmetry, the lateral confinement of the wave

function produces a band gap at its charge neutrality level. Alternatively, for the special edge that preserves sublattice symmetry (a “zig-zag” ribbon) one finds instead a resonant electronic state exactly at zero energy. These results generalize to a disordered potential landscape where the nodes occur in the interior of the sample. Pereira *et al.*¹⁴ modeled the effect of lattice vacancies in a single valley picture, and found that a hard gap opens only in the special situation where there is *complete* sublattice asymmetry in the vacancy distribution. For intermediate asymmetries where unequal fractions of the defects reside on different sublattices, they find a finite, but reduced, density of states (a soft gap) in an energy interval of order $\hbar v_F \sqrt{n}$, where n is the vacancy density and v_F is the Fermi velocity. In the limit of full sublattice symmetry, they find a resonant state at the charge neutrality point. Usually the observation of PL implies a hard gap, since a soft gap permits nonradiative energy relaxation unless a peculiar bottleneck exists. Moreover, despite a lack of consensus as to the structural motif in GO,^{15–17} there is not yet any observation or calculation suggesting a complete sublattice asymmetry in the oxidation profile.

A second gapping mechanism arises when one considers, in addition, the effects of intervalley scattering from the short range potential of the oxidized carbons. Intervalley scattering produces a coherent superposition of Bloch waves near the \bar{K} and \bar{K}' points of the Brillouin zone, giving rise to a $\sqrt{3} \times \sqrt{3}$ modulation of the charge density, which has been imaged by scanning tunnel microscope.¹⁸ For a bond-centered scattering potential, this describes a modulation (alternation) of the bond charge density and a self-consistent potential with this spatial symmetry. The amplitude of this modulation is determined by the scattering strength, direct and exchange electron-electron interactions, and the electron-phonon coupling. The latter is likely to produce some degree of bond alternation in the graphitic regions near an oxidized site, which might even template further oxidation in such a way as to reinforce this pattern of distortions. In this way a “Kekule pattern” emerges naturally in the electronic potential, and provides a spatially modulated intervalley gap parameter of the form envisioned by Hou *et al.*¹⁹ Note that bond alternation in conjugated polymers such as polyphenylene vinylene gives rise to gaps of a similar energy scale.²⁰

Within a context of bond disorder induced energy gaps, one regards the GO plane as a landscape containing a wide range of local band gap minima. This notion is consistent with the very broad range of observed emission energies. If the reduction procedure for l-GO does indeed prevent aggregation, as claimed in Ref. 13, then the observation of PL quenching across the entire spectrum for the liquid sample indicates that interflake or substrate contact is not vital for quenching of PL. Neither theoretical framework discussed above accounts for a loss of quantum yield unless there is significant inhomogeneity of the oxidation profile within the GO plane. If one imagines that chemical reduction results in the nucleation and/or growth of regions where GO is fully reduced to graphene, then migration of nonequilibrium carriers to these zero gap regions could provide an efficient route for nonradiative recombination. In this picture, there is no simple relationship between the oxidation density and the length scale between oxidation sites within gapped, oxidized regions.

In summary, we demonstrate that s-GO emits PL, and that GO PL can be altered by chemical reduction. Broad PL suggests a dispersion of hard gaps, which may arise from bond alternation within the GO plane giving rise to intervalley scattering. The loss of quantum yield during reduction in our experiments suggests that some regions might remain heavily oxidized. In this case, restoration of electrical conductivity resembles a percolation problem and gives very little information about the growth of these regions below the percolation threshold. Future studies might use complementary methods such as Raman scattering,²¹ infrared Landau level spectroscopy,^{22,23} or magnetic anisotropy²⁴ to quantify the emergence of graphenelike regions in reduced GO. Optical anisotropy measurements²⁴ may help to assess the importance of charge transfer transitions, which we have excluded from the discussion here and should have markedly different optical polarization anisotropies when compared to transitions native to the two-dimensional GO plane.

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