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View online: http://dx.doi.org/10.1063/1.4941818

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Synthesis and upconversion luminescence of N-doped graphene quantum dots
Magnetic enhancement of photoluminescence from blue-luminescent graphene quantum dots

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(Received 21 December 2015; accepted 1 February 2016; published online 10 February 2016)

Graphene quantum-dots (GQDs) have been predicted and demonstrated with fascinating optical and magnetic properties. However, the magnetic effect on the optical properties remains experimentally unexplored. Here, we conduct a magneto-photoluminescence study on the blue-luminescence GQDs at cryogenic temperatures with magnetic field up to 10 T. When the magnetic field is applied, a remarkable enhancement of photoluminescence emission has been observed together with an insignificant change in circular polarization. The results have been well explained by the scenario of magnetic-field-controlled singlet-triplet mixing in GQDs owing to the Zeeman splitting of triplet states, which is further verified by temperature-dependent experiments. This work uncovers the pivotal role of intersystem crossing in GQDs, which is instrumental for their potential applications such as light-emitting diodes, photodynamic therapy, and spintronic devices. © 2016 AIP Publishing LLC.

[http://dx.doi.org/10.1063/1.4941818]

By breaking the symmetry of two-dimensional hexagonal lattice of graphene, extraordinary optical and magnetic properties of technical significances can be introduced to a variety of graphene-based nanostructures.1–5 One prototypical example is the material of graphene quantum dots (GQDs) synthesized by cutting one- or few-layer graphene with nanoscale boundaries.2,6–13 In the last few years, GQDs have proven to be efficient fluorophores with a broadband spectral coverage5,12,14–19 that are excitable under electrical20–22 as well as linear/nonlinear optical pumps.6,12,14–16,23,24 A variety of emissive centers relevant to the intrinsic band structures and extrinsic surface/edge states have been found in GQDs, allowing photoluminescence (PL) manipulation with multiple factors including morphology, dopings, surface passivation, excitation wavelength, and synthesis environment.2,24–27 The unique emitters have shown biocompatibility, photostability, and temperature insensitivity, enabling many optoelectronic applications including light-emitting diodes (LEDs).20,22 solar energy conversion,28,29 and biomedical photonics.30

Of equal importance is the unique magnetic property known as a novel type of magnetism with s-p electrons.1–3,31–36 The atom-scale structure imperfections in graphene nanostructures can host unpaired spins31,33 affording the magnetic order in GQDs due to the reduced dimensionality,34 the point defects,31,33 and the important “zigzag” edge structures.32,36 Spin multiplicity is also well defined in GQDs with excitonic levels having singlet and triplet characteristics.2,16 The process of intersystem crossing (ISC) due to the mixing of singlet and triplet states plays a key role to the electronic relaxation dynamics in some GQDs.16,35,37 These spin-relevant features are susceptible to magnetic field, bringing about the exotic magneto-optical properties in GQDs in analogue to other carbon nanomaterials,38,39 which, however, remain experimentally unexplored.

In this work, we conduct a magneto-PL study on blue-luminescence GQD films at cryogenic temperatures with magnetic field (B) up to 10 T. We report an observation of PL enhancement of ~10% for PL emission while the ratio of the two circular polarizations is insignificantly changed at 4 K with B raising up to 10 T. The abnormal magneto-PL properties can be well explained by considering the magnetically controlled ISC in GQDs originating from the variation of singlet-triplet energy levels caused by Zeeman splitting of the triplet excitonic level, which is further verified by additional temperature-dependent experiments. Our work suggests the essential role played by ISC in determining the magneto-optical properties in GQDs, which is instrumental for potential applications of GQDs in areas such as LEDs,20,22 photodynamic therapy,30 and spintronic devices.1,4,31,32,40–42

The samples of GQDs were prepared by the hydrothermal mixing method as reported previously.6,43 The GQDs exhibit uniform thickness of ~1 nm with an average diameter of ~20 nm as characterized by atomic force microscopy (AFM) and transmission electron microscopy (Figures 1(a)–1(d)), respectively. The basic units of sp2-hybridized carbon atomic clusters dictate the energy alignments of the highly occupied molecular orbitals (HOMOs) and the lowly unoccupied molecular orbitals (LUMOs) in GQDs while the carboxyl-bonded sp3 CO matrices are relevant to the surface/
edge states (see supplementary Figure S1\textsuperscript{44}).\textsuperscript{2,45} For magneto-optical measurements, films of GQDs were prepared by drop-casting GQD solution onto glass substrates, which exhibit good optical quality with an average height of \( \lesssim 5 \) nm as shown in the AFM image (see supplementary Figure S1\textsuperscript{44}). Because of the quantum confinement effect, many aspects of the optical properties of such GQDs have been discussed in analogy to semiconductor QDs.\textsuperscript{7,45} Upon excitation at 400 nm, PL from the film sample in this work exhibits a broad emission band centered at 450 nm (Figure 1(e)). The insignificant redshift in the emission wavelength with increasing temperature up to 150 K (Figure 1(e)) is far below that expected for the excitonic emission in conventional semiconductor QDs. Moreover, the correlation between the size and the emission wavelength of GQDs remains highly controversial,\textsuperscript{25,43} which is also divergent from the size and the emission wavelength of GQDs dispersed on a mica substrate. (d) A height profile measured along the solid line labelled on the AFM image (c). (e) Normalized PL spectra of the film of GQDs recorded at different temperatures.

![Figure 1](image1.png)

**FIG. 1.** Sample characterizations. (a) TEM image of GQDs. Inset shows a high resolution TEM image of an individual GQD. The scale bars in the main panel and inset panel are 100 and 5 nm, respectively. (b) Lateral size distributions of GQDs obtained from the TEM image. (c) AFM image of GQDs dispersed on a mica substrate. (d) A height profile measured along the solid line labelled on the AFM image (c). (e) Normalized PL spectra of the film of GQDs recorded at different temperatures.

For both \( \sigma^+ \) and \( \sigma^- \) polarizations (Figures 2(b) and 2(c)), in particular, under high-field condition (\( B > 3 \) T) (Figure 2(d)). No saturation has been observed with field up to 10 T (the maximum value achievable in the system). For comparison, we quantify the PL increment with an enhancement factor defined as

\[
\eta(B) = \left( I_{PL}(B) - I_{PL}(0) \right) / I_{PL}(0),
\]

where \( I_{PL}(B) \) is the field-dependent PL intensity. The field-dependent change in circular polarization has been experimentally observed as the intrinsic emission relevant to the isolated sp\textsuperscript{2} carbon hexagons.\textsuperscript{22,47,48}

To investigate the magneto-optical properties in GQDs, we acquire the PL spectra by placing the film sample under different conditions.\textsuperscript{7} We quantify the magneto-optical effect in semiconductors,\textsuperscript{49–53} which is quantified as

\[
P = \left( I_{PL}^+ - I_{PL}^- \right) / \left( I_{PL}^+ + I_{PL}^- \right),
\]

where \( I_{PL}^+ \) and \( I_{PL}^- \) are the PL intensities of \( \sigma^+ \) and \( \sigma^- \) polarizations, respectively. With increasing magnetic field, the change in \( P \) is insignificant in a scale close to the noise level, suggesting that the theoretically predicted magnetic order is less important for the magneto-optical properties of GQDs studied here. This is consistent with the nearly identical spectra for \( \sigma^+ \) and \( \sigma^- \) polarized PL (Figure 2(e)). The slight difference of PL intensities recorded with \( \sigma^+ \) and \( \sigma^- \) polarizations may be relevant to the magnetic orders at the edge.
of isolated sp² carbon hexagons, which deserves in-depth study in the future. The minor change is due to the possible effect of partially random orientations of GQDs in the film. It has been characterized that the typical energy scale of magnetic orders at the edges of graphene nanostructures is in the order of 10⁰–10² meV,⁴,³² which is much lower than the photon energy of PL emission concerned here. The magnetic orders and emissive centers are likely to be relevant to different domains in GQDs, resulting in the insignificant dependence of P on the magnetic field.

Next, let us try to understand the mechanism of the unexpected enhancement of PL emission at a high-field limit (Figures 2(b)–2(d) and 3(a)). At 10 T, the enhancement factor of η approaches ~10% while the spectral profiles remain unchanged, indicating no detectable modification of the energy distribution of emissive states. In a previous work on carbon nanotubes, the magnetic enhancement of PL emission has been ascribed due to the symmetry-breaking-induced change in excitonic band structures,³⁸ which is unlikely to be the major factor for the results observed here with no spectral shift. In principle, PL increment can be caused by increasing the occupation probability at the emissive states and/or enhancing the radiative efficiency of the emissive states. The radiative efficiency enhancement is always accompanied by a variation in PL decay lifetime since the emissive efficiency enhancement is always accompanied by enhancing the radiative efficiency of the emissive states. The variation in PL decay lifetime since the emissive efficiency enhancement is always accompanied by the increase of radiative efficiency efficiency enhancement can be safely excluded from being the major factor for the observed PL enhancement.

To understand the enhanced probability occupied at the emissive states, we propose a model by considering the effect of magnetic field on the process of ISC to explain the PL enhancement, as illustrated in Figure 4. The spin multiplicity in GQDs results in the singlet and triplet excitonic states.²,¹⁶,³⁷ In the presence of spin-orbital coupling (SOC), the process of ISC with phonon activation can be evidenced by the observation of phosphorescence in GQDs.¹⁶ The rate of ISC is dictated by the energy splitting between the singlet

![Diagram of magnetic field](image)

FIG. 4. Diagram of the scenario of magnetic control of ISC that explains the observed magneto-PL properties of GQDs.

and triplet states (E⁵ = E⁴ − E⁵).¹⁶,³⁷ The value of E⁵, in scaling versus the lateral diameter (d) as E⁵ ∝ d⁻²,²,¹⁶ is estimated to be in the order of 0.1–1.0 meV for the GQDs with relatively large sizes studied here. This small energy gap can be easily compensated by phonons at room temperature. After cooling the sample down to 4 K, the process of phonon activation is inhibited, so that the ISC process favors the relaxation from singlet to triplet states, reducing the population at the singlet states. The population at the excited triplets relaxes to ground states through some nonradiative processes. When the magnetic field is turned on, different Zeeman interactions for the singlet and triplet states can cause a variation of E⁵ that modifies the rate of ISC.⁵⁶ Such a scenario of magnetic-field controlled ISC, as previously established in some biradicals,⁵⁷ is likely to be responsible for the PL enhancement observed in our experiment at the high-field regime.

Qualitatively, let us consider a simplified picture with the lowest singlet (S₁) and triplet (T₁) excitonic states to explain the magnetic enhancement of PL emission in GQDs (Figure 4). The Zeeman interaction splits the triplet level (T₁) into three sub-levels (T₁⁺, T₁⁰, and T₁⁻). To the first order, the energy of T₁⁰ is unchanged with increasing B, while the level of T₁⁺ (T₁⁻) shifts to upper (down) side with an offset of ΔE⁵ = gμBB (≈1.2 meV at 10 T) (Figure 4). Since ΔE⁵ is in the same energy scale as E⁵, the rate of ISC could be significantly modified when the field is applied. Specifically, when increasing B, the ISC from S₁ to T₁⁰ remains unchanged; The ISC from S₁ to T₁⁻ declines with an increased E⁵; However, the ISC rate from S₁ to T₁⁺ state gets more complicated. It increases in the weak-field regime with a decrease in E⁵, but should be suppressed with a further increase in the field since the reverse process from T₁⁺ to S₁ becomes energy favorable in the high-field regime with T₁⁺ higher than S₁. Consequently, the net population occupied at the singlet state S₁ increases with increasing B under the high-field condition, which is responsible for the observed PL enhancement (B > 3 T) (Figure 2(d)). In the low-field regime, the net population at the lowest singlet state is relevant to the tradeoff between the ISC rates relevant to S₁ → T₁⁺ and S₁ → T₁⁻ processes. In principle, a drop in PL emission is anticipated when the levels S₁ and T₁⁺ approach to degeneracy.⁵⁵ Such a resonant effect is not distinct here, which is probably averaged out by the broad size distribution of GQDs (i.e., the broad distribution of E⁵ ∝ d⁻²), resulting in a less significant variation in PL with B < 3 T (Figure 2(d)). The overall probability for transition S₁ → T₁⁺ (i.e., a sum of the probabilities for S₁ → T₁⁺, S₁ → T₁⁻)
→ S\textsubscript{1} → S\textsubscript{1} \textsuperscript{+} and S\textsubscript{1} → S\textsubscript{1} \textsuperscript{−}\) shows different dependences on the magnetic field in the relatively weak and intense regimes, which is plausibly the reason for the observed superlinear dependence of PL enhancement on the magnetic field. From the above discussions, it is safe to ascribe the PL enhancement as due to the magnetically controlled ISC in GQDs. Moreover, it is worth noting here that the simultaneous emergence of two spin sub-levels (T\textsubscript{1} \textsuperscript{+} and T\textsubscript{1} \textsuperscript{−}) when the field is turned on makes the net effect of magnetic field to be independent of the field polarity, which agrees well with the experimental data (Figure 2(d)).

As mentioned above, the PL mechanism is not well determined yet for the blue-luminescent GQDs. The major debate has been on the question of whether the LUMO-HOMO transition (i.e., the singlet and triplet states) or the recombination relevant to other emissive states (i.e., defect and surface states) is the primary radiative channel.\textsuperscript{24,25,27,43,46} The magneto-PL study presented here may shed light on resolving this controversy. We have shown that the scenario of magnetic-field controlled ISC well explains the magneto-PL properties observed in this study and the modified ISC changes the population dynamics of the singlet states. Since the decay dynamics is independent of the field (Figure 3(b)), the radiative recombination from the photo-excited singlet states is unlikely to be the primary origin of PL emission (at least not the origin for the field-dependent PL). The radiative recombination of emissive states (i.e., the defect or surface states) occupied after electron relaxation from the singlet states plays an important role as illustrated in Figure 4, which is consistent with previous spectroscopic experiments on single GQDs or assembly samples.\textsuperscript{25,43} The magnetic field induced changes in emissive states (\sim meV) are orders of magnitude smaller than the broad energy distribution (\sim 0.5 eV) as revealed in PL emission, resulting in the nearly identical spectra for σ\textsuperscript{+} and σ\textsuperscript{−} polarizations (Figure 2(e)).

We note here that the onset of PL kinetics also supports the above explanation (Figure 3(b)), where the maximum of TRPL trace appears at a time delay of \sim 0.5 ns post-excitation. This rising component can be assigned to the buildup process of emissive states due to relaxation from the singlet states. Roughly speaking, the relaxing rate has been quantified by fitting the rising component with an exponential growth function. The estimated lifetime at 10 T (\sim 0.173 ns) becomes slightly longer than that at 0 T (\sim 0.158 ns) (inset, Figure 3(b)), indicating the decay of S\textsubscript{1} state to be slower at 10 T. This change in PL kinetics is consistent with the scenario of magnetically controlled ISC discussed above (Figure 4) where the suppressed ISC at 10 T leads to a relatively slow relaxation of S\textsubscript{1} state. The difference in relaxation rate (\sim 0.54 ns\textsuperscript{−1}) is \sim 9% variation of total decay, which is comparable to the ratio of PL change. Assuming the variation of ISC is the primary origin of the kinetic change, the rate of ISC can be estimated in the scale of ns\textsuperscript{−1} which is comparable to that observed in the organic photovoltaic materials.\textsuperscript{58} Such an efficient ISC is reasonable since the hydrothermally cut GQDs are rich in the bonds and impurities that can dramatically enhance the SOC.\textsuperscript{59,60}

FIG. 5. The factor (\eta) of PL enhancement is plotted as a function of temperature.

We have carried out a temperature-dependent experiment to further confirm the above arguments. In principle, the change in E\textsubscript{ST} in the scale of \sim 1 meV can be cancelled out by thermal effect due to phonon activation with an increased temperature in GQDs.\textsuperscript{2} This effect is manifested in the temperature dependence of \eta, as shown in Figure 5. With increasing temperature, the PL enhancement at 10 T becomes less important and finally vanishes at temperatures above \sim 40 K (Figure 5) except with a slight anomaly at 10 K that may be caused by the interplay between low-energy magnetic orders. The thermal energy at 40 K becomes larger than ΔE\textsubscript{T}, which wipes out the magnetic effect on ISC where the field-induced change in E\textsubscript{ST} is no longer a dominant factor. Such experimental results clearly confirm the key role played by the magnetic control of ISC for PL enhancement at low temperature, which has also been observed in a recent study on the carbon-based nanostructures of nitrogen-vacancy centers in diamond.\textsuperscript{61}

In summary, a remarkable enhancement of PL emission induced by magnetic field is observed in the film of blue-fluorescent GQDs, which is ascribed to the effect of magnetic-field-controlled ISC on the net population of singlet states. The essential role of spin multiplicity suggests the similarity between the magneto-optical behaviors of GQDs and that of organic semiconductors. Considering the diverse forms of GQDs and their colorful optical properties, our work opens a door to search for the fascinating magneto-optical properties in GQDs, which can be very essential for practical applications including LEDs,\textsuperscript{20–22} photodynamic therapy,\textsuperscript{30} and spintronic devices.\textsuperscript{40–42} It is worth noting that the physical process studied here can even play an important role for practical devices working under magnetic-free conditions. For instance, in LEDs, the current-injected carriers are in form with either singlet (25%) or triplet (75%) spin characteristics.\textsuperscript{62,63} The crossover from triplet to singlet states can significantly enhance the LED output as well established in organic LEDs.\textsuperscript{63,64} For photodynamic therapy, the process of ISC is pivotal for generating singlet oxygen in GQDs—the functional chemical curing the tumors.\textsuperscript{30}

This work was supported by the National Basic Research Program of China (2013CB932903 and 2012CB921801, MOST), the National Science Foundation of China (91233103, 11574140, 11227406, and 11321063), and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).