FLUORESCENCE INTERMITTENCY IN GRAPHENE OXIDE: EXPERIMENT VERSUS THEORY

A Dissertation

Submitted to the Graduate School
of the University of Notre Dame
in Partial Fulfillment of the Requirements
for the Degree of

Doctor of Philosophy

by

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April 2018
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Abstract
by
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Despite extensive experimental and theoretical investigations reported over the last three decades, the microscopic mechanism of fluorescence intermittency in nanoscale emitters remains elusive. Most fluorescent nanosystems are zero- and one-dimensional. However, recent experiments show, surprisingly, that despite its two-dimensional structure, graphene oxide also exhibits highly localized emission intensity fluctuations during its photoreduction process. In this thesis, we provide an extensive phenomenological analysis of the spatially resolved fluorescence trajectories in reduced graphene oxide (rGO). We show, for the first time, that the emergence of fluorescence intermittency in this two-dimensional system is accompanied by the appearance of 1/f-like behavior in the local power spectral density of the experimentally measured intensity trajectories. Furthermore, we use the phenomenological multiple recombination center model to show how the spectral evolution of the local trajectories can be related to the change in the number of optically active recombination centers affecting the behavior of a nanoscale region in rGO. We argue that the number density of recombination centers can be linked to the microscopic number of optically active graphene quantum dots generated during the various photoreduction stages of graphene oxide. Finally, we also studied the effect of dimension on the fluorescence in nanostructures via the absorption spectrum 1D-to-0D evolution in CdSe nanowire
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Dedicated to who I love
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D.1 Cartoon of finite cylinder scheme used in electrostatic calculations.
This dissertation is dedicated to the theoretical explanation of fluorescence intermittency, also described as blinking, which is widely observed in nanostructures. We did analysis based on the power spectral density (PSD) and a phenomenological model. We also performed calculations and simulations via multiple approaches including density functional theory (DFT), Monte Carlo (MC) simulation, analytical quantum mechanics calculations. The systems that we focused on are graphene oxide (GO), reduced graphene oxide (rGO) and CdSe nanowires (NWs) and nanorods (NRs). The blinking in GO/rGO is the first time that fluorescence intermittency are observed in the two-dimensional (2-D) systems. The two-dimensional temporal trajectory of emission from laser-irradiated GO/rGO is analyzed within the well-established PSD analysis, from which the dynamical evolution of blinking at different stages of GO sample is studied. The GO sample is reduced by high-intensity laser and the reduction is believed to be due to a photolytic process. The PSD of GO/rGO blinking possesses power law behavior with respect to frequency, which is widely shared in almost all nano-structures that show blinking. The properties studied based on PSD analysis includes the power law exponent $\alpha$, the spatial correlation (SC), the total fluctuating power. The phenomenological multiple recombination centers (MRC) model is utilized in the study of the mechanism behind the blinking. The experimental PSD is fitted within the MRC model. Various parameters, including recombination center (RC) channel numbers and distributions are extracted based on the fitting. Correlations between above-studied properties and the base emission intensity of the blinking trajectory are investigated. Strong and clear spatial corre-
lations between pixels, temporal correlations between the fluctuation and the base emission are observed. At microscopic level, DFT calculations have been performed on the optical properties of polyaromatic hydrocarbons (PAHs) with and without defects. The DFT results are further utilized in the MC method that produces absorption and emission simulation trajectories. The PSD analysis is performed on the MC simulated trajectories to compare with the experiment results. The dimensional crossover of CdSe nanostructure from 1D-to-0D is studied by the modified model we proposed based on the 4-band effective mass model. A critical length at which the 1D-to-0D transition happens is discovered by the experiment. The predicted blueshift of transition contributed from $1\sum_{3/2}1\sum_e$ and $1\sum_{1/2}1\sum_e$ excitons are in excellent agreement of what measured in the experiment. This is the first time that the absorption spectrum transition from 1D-to-0D is studied systematically in semiconductor nanostructures.
ACKNOWLEDGMENTS

I would love to express my sincere appreciation to my mentor, Boldizsár Jankó, for his guidance throughout my journey in studying physics as a graduate student. He not only passed on the knowledge and the insightful way of thinking but also provided patience and support during my graduate years. I would love to thank Professor Masaru Ken Kuno, who has been extremely supportive of me. Via working with him, I gained invaluable access to knowledge in the experiment and excellent experimentalists. His forthrightness and sincerity, his aggressive attitude toward life are the characters I have been and will be pursuing. I would love to thank my other committee members: Professor Zoltán Toroczkai, who has been helping me ever since my application in this program, and Professor Jacek Furdyna. Their experience and expertise in various fields are irreplaceable resources for my research.

I would like to thank Sándor Volkán-Kacsó, who taught me the research tools I utilized in most of this work. I would like to thank Anthony Ruth, Matthew P. McDonald, Yurii Morozov and Felix Vietmeyer. Together we not only collaborated in physics research but also shared great times in our lives.

I would like to thank my best friends: Jie Ma, Sheng Feng and Chao Yin, for their continued support and encouragement during the best and the hardest time in my life. I would also like to express special thanks to Xiaoyu Ma and Shihsin Lin. It’s hard to list all my good friends, but I’m lucky to know them and share the life with them.

We would also like to thank the American Chemical Society Petroleum Research Fund, the Army Research Office (W911NF-12-1-0578), the U. S. Department of En-
ergy, Office of Science, Office of Basic Energy Sciences (W-31-109-Eng-38) for support.
Fluorescence is a phenomenon during which a specimen re-radiates visible light in parallel with the absorption of the excitation light. The radiating light usually has a longer wavelength compared to the excitation light. Together with the phosphorescence phenomenon, which describes the case when the material does not immediately re-radiates light after the excitation of light, fluorescence is one specific case of photoluminescence. The term fluorescence was first introduced by Sir George Gabriel Stokes in his study of mineral fluorite, composed of calcium fluoride, which gave a visible emission when illuminated with invisible UV radiation.

Fluorescence, covering wavelengths of the entire visible range, is found in abundance in the natural world. Creatures like jellyfish and corals show fluorescence as a result of the fluorescent protein in their organs. Many types of calcites and ambers also fluoresce under short wave UV, long wave UV, and visible light.

The shift in visible emissions from the UV range to the visible-light range in the fluorescence of calcium fluoride is not a special case. This phenomenon is called Stokes shift. The reason behind the redshift is that the energy of the absorbed radiation usually does not match the energy difference between the ground electronic state and the lowest excited electronic states. The photons are absorbed and can excite the system into either an excited electronic state with vibronic energy, which can be treated as an excited state plus its corresponding vibrational modes or an electron-hole exciton plus phonons. The relaxation rate of the phonons is usually faster than the decay from the excited state to the ground state of electrons. The
latter corresponds to the re-emission of photons from the system, i.e. the fluorescence process of interest to us. The relaxation from the virtual excited state to the excited state with the 0th order of vibration is introducing the well-known Stokes shift, as shown in Fig. 1.1. This process is also referred as the resonance Raman scattering.  

Fluorescence has wide applications in basic and applied research. One of the most important application is the fluorescence microscopy, which is widely used in biochemistry and biophysics, especially bioimaging. For example, with the help of photoswitchable fluorescent probes, the recent development of sub-diffraction limit, or super-resolution microscopy techniques can obtain images on the nanoscale, which provides us with a very powerful method to probe biological structures at high resolution. Fig. 1.2 shows the great improvement in the resolution of the stochastic optical reconstruction microscopy (STORM) and its use in the study of biosystems.

Fluorescence intermittency, also known as blinking, is a unique and interesting phenomenon shows in quantum scale systems. It was first observed by Nirmal and Brus in 1996. This phenomenon has been widely observed in nanoscale systems, which include quantum dots, nanowires, nanorods and even some organic molecules. As shown in Fig. 1.3 a system showing fluorescence intermittency does not give a stable emission intensity, or quantum yield, while under constant radiation of excitation photons. Instead, the trajectory undergoes large vibrations in intensity with respect to time. Historically, the low-intensity emission durations have been called off state, while the high-intensity emission durations have been called on state. Although there might be ambiguity in the determination of the on and off depending on the choice of threshold emission intensity value, in many nanoscale systems, the distributions of the on and off states have both shown power-law distribution through several ranges of time. The huge range of time scales in the fluorescence intermittency rules out explanations with mechanisms involving a single time constant.

The exact mechanism behind fluorescence intermittency of currently known sys-
tems, and whether they share the same process behind their blinkings process is still not clear. Understanding fluorescence intermittency helps improve the utilization of quantum dots as single-photon sources and biomarkers. What is more important, this leads to a better understanding of quantum optical process in nanoscale systems[50].

In recent experiments, fluorescence intermittency has also been observed during the reduction of graphene oxide. The two-dimensional nature of the graphene oxide has opened a new area of the nanoscale fluorescent systems. Fluorescence and fluorescence intermittency can be studied not only temporally, but also spatially in this system.

Graphene, the two-dimensional material with the thickness of one layer of atoms, is constructed by carbon atoms in a hexagonal lattice structure. Its unique properties in electronic and mechanical aspects, for example, the well-known Dirac point at Fermi level and high intrinsic electron mobility, has drawn a lot of interests in both scientific and industrial domains in both graphene itself and its derivatives.

Graphene oxide can be used as the precursor for the chemical approach in obtaining graphene sheets in large quantities. By oxidizing graphite, one can produce graphene oxide pieces with a small number of atomic layers, which can be then reduced by chemical, thermal or photolytic reduction process to get reduced graphene oxide.
Figure 1.1. The Franck-Condon energy diagram that shows the Franck-Condon principle and the following red shift in the emission photon wavelength compared to excitation photon wavelength.

Figure 1.2. The images of microtubules (green) and clathrin-coated pits (red) in fixed BSC1 cells measured by (A) conventional immunofluorescence and (B) stochastic optical reconstruction microscopy (STORM). (C) a magnified image of the boxed area in image (B).
Figure 1.3. The blinking trajectory observed by Nirmal and Brus during the observation of CdSe nanocrystal emission. [34]
CHAPTER 2

PROPERTIES OF BLINKING

There are several properties shared by nanostructures exhibiting blinking phenomena. One of the most interesting properties is the power law distribution of the ON/OFF duration. The terms ON and OFF were introduced since the fluorescence intensity distribution has in many but not all cases a dichotomous behavior. The intensity distribution of the fluorescence centers around two peak values. For example, in Nirmal’s measurement of the blinking in CdSe QD [34], the intensity centered on zero and another finite value. In the following research, the ON and OFF states are separated by a chosen threshold value $I_{th}$ of fluorescence intensity. In Kuno’s work, $I_{th}$ was defined as 3 times of the standard deviation above the background noise[27]. By doing this, the relatively continuously varying intensity trajectory can be transformed into a two-value temporal series. However, as the study in the fluorescence intermittency of the quantum systems went on, there have been several systems that have been reported not to follow the simple dichotomous behavior. For example, the core-shell CdSe/CdS QD trajectories have shown three peaks in intensity histogram[16].

With ON and OFF states defined, ON and OFF duration are straightforwardly the duration of fluorescence intensity stays above $I_{th}$ until it jumps below $I_{th}$ and vice versa. Masaru Ken Kuno et al. first observed the power law distribution of ON/OFF duration time in their study of CdSe/ZnS dots[26]. This feature for ON duration was later updated as a power-law with an upper truncation time $T_{ON}$, in Shimizu et al.’s study[11], and the distribution was suggested as:
Figure 2.1. The ON (left panel) and OFF (right panel) duration distribution for six different trajectories. The PDFs of different trajectories have been multiplied by the constants labeled in the plot to make them more distinguishable from each other.

\[ P_{ON}(t) \sim t^{-m_{ON}} \exp(-t/T_{ON}). \]  

(2.1)

The left panel of Fig. 2.1 shows the ON time duration distribution of six different trajectories, in which the power law with exponential truncation behavior are clearly shown.

The distribution of OFF time duration also shows clear power law behavior, as shown in the examples in the right panel of Fig. 2.2. However, the truncation time for
the exponential decay, if there is any, goes beyond the length of the whole fluorescence trajectory for many QDs\cite{52}. This is one main reason behind the long OFF time that hinders QDs use as biological tags. That is, the blinking QDs cannot reliably provide stable fluorescence emission and it is difficult to even find a characteristic duration of the OFF states. Nevertheless, the OFF duration time can still be treated in the same way as the ON duration time, i.e.

\[ P_{OFF}(t) \sim t^{-m_{OFF}} \exp(-t/T_{OFF}). \] (2.2)

As shown in the right panel of Fig. 2.1, the lower three trajectories still show an exponential truncation tail, and we can treat the upper three trajectories as cases with truncation times longer than the trajectory lengths.

The power law exponents \( m_{ON} \) and \( m_{OFF} \) are observed to have values larger than \( m_{ON/OFF} = 1 \) for previously studied blinking systems. However, the exact value was found to be strongly dependent on the choice of the threshold value \( I_{th} \) that defines the ON and OFF events\cite{11}. Furthermore, the same study found that there is threshold dependence in both the ON and the OFF truncation times.

In earlier experiments, parameters such as temperature, QD size and excitation light intensity and wavelength have been studied for their influence on the behavior of blinking\cite{41} \cite{24}. The only quantity that showed systematic dependence on these parameters is the ON truncation time, while there have been contradictory results about the effect of excitation intensity. However, as we mentioned above, the dependence might be explained by the fact that the blinking statistics are affected by the choice of the threshold value.

Properties related to second order statistics have also been considered. Stefani et al. found non-zero correlations between the subsequent ON and OFF times\cite{45}. A strong positive correlation was found in the subsequent ON times. There is also
positive but smaller correlations in the subsequent OFF times and small negative correlations in the subsequent ON and OFF times. All these correlation behaviors can be well explained by the multiple recombination centers model. \[52\]

Another property of the blinking trajectory that involves the second order statistics is the power spectral density, which is independent of the threshold value. The power spectral density (PSD) of the time-dependent emission intensity $x(t)$ can be defined as the Fourier transform $S_{xx}(\omega)$ of the auto-covariance function:

$$S_{xx}(\omega) = \int_{-\infty}^{+\infty} \langle x(t)x(t-T) \rangle e^{-i\omega T} dT. \quad (2.3)$$

More details of this function, of fundamental importance, will be discussed in following chapters. The interesting part of the PSD of blinking trajectories from multiple systems is that they all share the power law distribution behavior with respect to the

Figure 2.2. The threshold dependence of the ON (blue) and the OFF (red) duration time distribution power law exponents (a) and truncation times (b). Inset of (b): part of the trajectory (left) and the corresponding intensity histogram (right). \[52\]
frequency. That is, the distribution scales as:

\[ S_{xx}(\omega) \sim \omega^{-\alpha}, \]  

(2.4)

where the exponent \( \alpha \) is close to unity. This is widely known as a 1/f-type fluctuation, which has been encountered in physics, biology, and economics[44]. As shown in Fig. 2.3, the fluorescence trajectories of self-assembled InP QDs, colloidal CdSe/ZnS QDs, colloidal CdSe/CdS QDs, colloidal CdSe/ZnSe NR, CdSe NWs and perylene diimide molecules, all showed the 1/f behavior, with some PSD having their own features, e.g. low-frequency plateau in the trajectories of self-assembled InP QDs[12]. Because of its independence from any arbitrary intensity floor, its universal features but also system-specific characteristics, the PSD will play a central role in the research presented in this thesis.
Figure 2.3. The trajectories (left column), corresponding intensity histograms (middle column) and the PSDs (left column) of self-assembled InP QDs (I), colloidal CdSe/ZnS QDs (II), colloidal CdSe/CdS QDs (III), colloidal CdSe/ZnSe NR (IV), CdSe NWs (V) and perylene diimide molecules. For all the PSD panels (VI). The blue lines are the least square $1/f^\alpha$ fit of experimental PSDs, while red lines are the Lorentzian fits of the PSDs. The error bars are showing the 95% confidence intervals.
CHAPTER 3

THE MULTIPLE RECOMBINATION CENTERS MODEL

The multiple recombination center (MRC) model is based on the concept of the simple stochastic two-level system (TLS). A TLS can be treated as a system with two states |1⟩ and |2⟩. The system can switch between these two states with rates $k_{1\rightarrow 2}$ and $k_{2\rightarrow 1}$. In the model, the switching timescales from one state to the other one are much longer than any other relaxation timescales in the system, so that the temporal sequence of the system state can be treated as a Markov chain. That is, the state at a given time is only related to that of the previous time step:

$$p(s_n, t_n | s_{n-1}, t_{n-1}, s_{n-2}, t_{n-2}, ...) = p(s_n, t_n | s_{n-1}, t_{n-1}). \quad (3.1)$$

Here, $s_n$ indicates the state of the system and $s \in \{0, 1\}$, while $t_1 < t_2 < \cdots < t_n$. Then the equations describe the dynamic state switching of the system can be listed as:

$$\frac{dp_0}{dt} = -\gamma^+ p_0 + \gamma^- p_1 \quad (3.2)$$
$$\frac{dp_1}{dt} = \gamma^+ p_0 - \gamma^- p_1,$$

where $\gamma^+ = k_{1\rightarrow 2}$ and $\gamma^+ = k_{2\rightarrow 1}$.

The autocorrelation function of the TLS system has an exponentially decaying behavior. To prove this, first, we solve the Master equations of this system. As the stochastic matrix is
The eigenvalues of Eq. 3.5 are \( \lambda_{1,2} = \{0, -(\gamma^+ + \gamma^-)\} \). Together with the conservation of probability condition

\[ p_0 + p_1 = 1, \]

the solutions of Eq. 3.2 are in the form of

\[ p_0 = \frac{\gamma^-}{\gamma^+ + \gamma^-} + A \cdot e^{-(\gamma^+ + \gamma^-)t}, \quad (3.4) \]
\[ p_1 = \frac{\gamma^+}{\gamma^+ + \gamma^-} - A \cdot e^{-(\gamma^+ + \gamma^-)t}, \]

where \( A \) is constant that can be determined by the initial conditions.

Now as we know the autocorrelation function is defined as

\[ R(t) = \langle s(t')s(t + t') \rangle, \quad (3.5) \]

and the state \( s(t) \) can only take values of 0 or 1. Since the \( \langle \cdots \rangle \) generates the expectation value of \( s(t)s(t' + t) \). The only surviving terms in Eq. 3.5 are the terms where both \( s(t') \) and \( s(t' + t) \) are both 1. Notice that the choice of \( s \) to be 0 and 1 won’t affect the generosity of our conclusion as a different choice of values will only affect the base value and scale of \( R(t) \), while keeps the form of the function the same:

\[ R(t) = 1 \cdot 1 \cdot p(1, t' + t|1, t')p(1). \quad (3.6) \]

Since the system is in equilibrium, where \( p(1) \) should be the stable form of \( p_1 \) above, which is \( \frac{\gamma^+}{\gamma^+ + \gamma^-} \), and \( p(1, t' + t|1, t') \) is \( p_1 \) under the initial condition of \( s = 1 \) at \( t = 0 \).
\[ p(1, t' + t | 1, t') = \frac{\gamma^+}{\gamma^+ + \gamma^-} + \frac{\gamma^-}{\gamma^+ + \gamma^-} \ast e^{-(\gamma^+ + \gamma^-)t}, \quad (3.7) \]

\[ R(t) = \left( \frac{\gamma^+}{\gamma^+ + \gamma^-} + \frac{\gamma^-}{\gamma^+ + \gamma^-} \ast e^{-(\gamma^+ + \gamma^-)t} \right) \frac{\gamma^+}{\gamma^+ + \gamma^-}. \quad (3.8) \]

One step further, we can have the PSD of the TLS in the form of

\[ S(\omega) = \frac{1}{2\pi} \int_0^\infty R(t)(e^{i\omega t} + e^{-i\omega t})dt \]
\[ = \frac{1}{\pi} \frac{\gamma^+ \gamma^-}{\gamma^+ + \gamma^- + \omega^2 + (\gamma^+ + \gamma^-)^2}. \quad (3.9) \]

In the MRC model\[11\], the blinking system has multiple recombination centers (RCs) and these centers have the behavior of TLSs in their effect on the quantum yield (QY) of the system. The different states of RC lead to different values of non-radiative rates in the energy releasing process after the blinking system is excited by the irradiation of light. Within the steady-state approximation, the emission intensity time dependence can be expressed as\(10, 11\)

\[ I(t) = \frac{k_I k_r}{k_I + k_r + k_n}, \quad (3.10) \]

where \(k_I = \frac{I_0 S}{h\omega}\) is the excitation rate, and \(S\) is the excitation cross section. \(k_I\) is smaller than the radiative decay rate \(k_r\) in real experiments and can be omitted in the denominator. The RC each introduces a non-radiative rate \(k_i\) and the total non-radiative decay rate \(k_n\) can be expressed as

\[ k_n = k_0 + \sum_i k_i \sigma_i, \quad (3.11) \]

with \(\sigma_i = 0\) or \(1\), which indicates the two states of the RC: inactive and active. The
word active here is used to describe the function of the RC in the non-radiative energy releasing process. The active RC is in a state that introduces extra non-radiative decay rate of the excited system, and vice versa. When \( k_i \) is small compared to \( k_r \) and \( k_0 \), we can make the Taylor expansion of \( I(t) \) with respect to \( k_i \),

\[
I(t) = \frac{k_I k_r}{k_I + k_r + k_0} (1 - \sum_i \frac{1}{k_I + k_r + k_0} k_i + o(k_i)).
\]  

(3.12)

This leads to the PSD of the MRC system to be in the form,

\[
S_{xx}(\omega) \sim \sum_{i=1}^{N} \frac{\gamma_i}{\pi \ast (\omega^2 + \gamma_i^2)}.
\]  

(3.13)

when \( \gamma^+ = \gamma^- \) in the Eq. (3.9).

In the general case, for \( Y \) as a function of the state of \( \sigma_i \), the exact form of \( S_{YY}(\omega) \) is more complicated, but the Lorentzian shape is still in the core of \( S_{YY}(\omega) \). More details of the derivation can be found in [12], [11].

Figure 3.1 shows an example of the PSD(blue) as a summation of Lorentzian component(red) generated by RC at different switching frequencies. To generate a power-law PSD, we can choose the \( \gamma_i \) of the RC to be in a geometric sequence[12], that is,

\[
\gamma_i = \gamma_0 \omega_i^{-\beta},
\]  

(3.14)

and the denser the switching rate sequence is, the smoother the PSD will be generated.

The MRC model is capable of capturing the double peak feature of emission intensity distribution shown in many nanostructure blinking processes, by introducing an interaction between TLS in a simple mean-field form. Equation (3.15) describes the switching rates in presence of the interaction.
Figure 3.1. A example shows the sum of multiple Lorentzian shapes (red) reproduces the power law distribution (blue) in certain range of frequency. The plot is in log-log scale.

![Figure 3.1](image1.png)

Figure 3.2. Schematic plot of an MRC system. Each pair of the upper and lower short horizontal bars represents one TLS. The position of the red dot designates the state of the TLS. When the red dot is on the upper position, the TLS is in an active state ($\sigma_i = 1$) and when the red dot is on the lower position the TLS is in an in-active state ($\sigma_i = 0$). In this graph, there are 10 TLSs, 7 of which are in the active states.

![Figure 3.2](image2.png)
\[ \gamma_i^{\pm} = \gamma_i \exp(\pm \alpha \sum_{j=1}^{N} (\sigma_j 1/2) \pm \beta) \]  

(3.15)

In the simple MRC system shown in Fig. 3.2, 7 out of 10 TLSs are in the active \((\sigma_i = 1)\) state. Given a positive \(\alpha\) in Eq. (3.15), the switching frequency from inactive to active state \(\gamma_i^{+}\) will have a higher value than \(\gamma_i^{-}\). This means the system will tend to stay with more active state TLSs when there are more active TLSs. The same logic works when there are more inactive TLSs. The active TLSs leads to non-radiative energy releasing rates, i.e. lower quantum yields. Thus, the introduction of mean-field interaction can reproduce the grouping of ON/Off states seen in experimental trajectories. The term \(\beta\) is a bias parameter that tunes the relative weights of the ON and OFF peaks in emission intensity distribution density, which need to be negative in order to make the ON peak reasonably large.
CHAPTER 4

GRAPHENE AND GRAPHENE OXIDE

Graphene, as an allotrope of diamond, is a single atom layer structure constructed of carbon atoms. Graphite, the more commonly observed allotrope of carbon, can be viewed as layers of graphene stacked over each other and held together by the Van de Waals interaction. The action of writing with a pencil on the papers is a process that produces graphene via mechanical exfoliation. The mechanical exfoliation is a standard way of producing high-quality graphene sheets, and it is the method used to obtain the single layer graphene the first time in 2004 by Novoselov\[36\].

Graphene can be produced in two ways: by exfoliation and by growth on a surface. The exfoliation method is the mechanical exfoliation as we mentioned above. Usually, graphene is detached from a graphite crystal with an adhesive tape. Then the glue can be dissolved into solution, a process that leaves the graphene flakes on a substrates\[36\].

There is another exfoliation method which is similar to mechanical exfoliation. The difference is that the graphite is merged into a solution which has nearly the same surface energy to the graphite. Also, sonication can be used so that the graphene flake will disperse from graphite into the solution\[47\]. When sonicating liquids at high intensities, the sound waves that propagate into the liquid media can create small vacuum bubbles in the liquid. The collapse of the bubbles, or cavitation, can create locally high pressures. With the right choice of solvent, the graphene can be exfoliated from the graphite by sonication.

Both of these exfoliation methods can provide high-quality graphene sheets with
Figure 4.1. (a) A schematic illustration and photo for electrochemical exfoliation of graphite. (b) Photos of the graphite flakes before and after the electrochemical exfoliation. (c) A photo of the dispersed graphene sheets in a dimethyl formamide (DMF) solution.\[17\]

few defects, while the solution dispersion can be more proficient in producing large amounts of graphene flakes compared to the scotch type method. However, due to the limitation that stems from the size of the graphite wafer, both methods can only produce graphene flake in small sizes: nanometers to several tens of micrometers.

The third exfoliation method involves graphene oxide and reduced graphene oxide. First, graphite is oxidized so that several kinds of oxygen-containing functional groups, such as epoxide or hydroxyl, get attached to the graphene layers, which makes this more of a chemical exfoliation compared to those two methods mentioned above. One commonly used oxidization method is introduced by Hummers in 1958 and named after him\[18\]. In this method, potassium permanganate (\(KMnO_4\)) is added into the solution that contains graphite, sodium nitrate (\(NaNO_3\)) and sulfuric acid (\(H_2SO_4\)). The oxygen-containing groups are hydrophilic so that the graphene oxide flakes are easier to dissolve into the solution via sonication or stirring.

After the dispersion, single-layer or multi-layer graphene oxides can be reduced
through several reduction methods, which include thermal, chemical or photolytic processes. We will talk about these in more details later. The final graphene, or reduced graphene oxide flakes usually don't have as good qualities as the mechanical or dispersion exfoliated graphene flakes. An atomic $C/O$ ratio of about 10 remains. This means the reduced graphene oxide still contains oxygen containing function group on the surface, and these function groups play important parts in the optical properties of the reduced graphene oxide. Regardless of the defects in the produced reduced graphene oxide, this method can produce large amounts of reduced graphene oxide flakes easily.

If we are seeking methods that can produce large-scale and layer number controllable graphene sheets, the growth methods will fit our needs much better. There are basically two kinds of growth methods for graphene production: epitaxial growth and chemical vapor deposition (CVD) methods, and they are closely related to each other. Both of the growth methods takes advantage of the good match of lattice structures between two materials. For example, being used in a epitaxial growth method, the lattice constant of $Ni(111)$ surface only has a 1.3% mismatch compared to that of graphene. The carbon atoms come from either diffusion from the other side of the growth surface or decomposition of the vapor molecules that the growth surface is exposed into. The produced graphene don't have a perfect homogeneity without defects or grain boundaries. However, the control we can have in the growth rate and electronic properties, as well as the size of graphene sheet grants this method its own advantages over the exfoliation methods.
Figure 4.2. Schematic shows the process of chemical vapor deposition in graphene synthesis. [23]

Figure 4.3. Schematic of the roll-to-roll method, which is capable of massive production of graphene. [1]
As reported by the Kuno group in 2013, for the first time, the photolytic reduction of graphene oxide into reduced graphene oxide was observed directly, together with its heterogeneous intra-sheet kinetics. In the experiment, the graphene oxide was prepared by a modified Hummers synthesis, which produces the GO sheets in a standard dimension of 5x5 µm, as shown in Fig. 5.1.

When irradiated by 405 nm (3.06 eV) light, there is fluorescence observed from individual GO sheets. The trajectory of the fluorescence from GO sheet can be divided into 3 regions. As shown in Fig. 5.2 in the first region, the emission of the GO sheet decreases in the first tens of seconds after the initial irradiation of light. This is believed to be the phase when the reduction process from GO to rGO occurs. Then the emission moves into the second region and the intensity keeps increasing in the next tens of minutes until it reaches the maximum and starts to decrease again. This marks the beginning of the third region. The decreasing rate in the third region is very slow compared to the first region and intensity fluctuation, or blinking is clearly observed, which we will discuss in details later.

The emission spectrum undergoes a blue shift during region 1, followed by a red shift during region 2. Fig. 5.3 shows an example of the photoluminescence spectrum integrated over an entire sheet, which can be characterized by a center broad peak at 690 nm (1.80 eV) and a shorter wavelength shoulder at 490 nm (2.53 eV). The spectral evolution can be clearly seen in Fig. 5.4 as the spectrum blueshifts during the initial illumination of around 50 seconds (region 1) then redshift back to a spectrum
Figure 5.1. Transmission electron microscopy (TEM) micrographs of individual GO sheets.

Figure 5.2. PL intensity of a single GO sheet under continuous 405 nm laser irradiation ($I_{exc} = 380 W cm^{-2}$) [31].
Figure 5.3. PL spectrum of a single GO sheet (solid green circles) containing both blue and red components. The red dashed line and the blue dashed line are the fitted Gaussian shape centered around $\sim 490\,\text{nm}$ and $\sim 690\,\text{nm}$ respectively. The summation of two Gaussians produce the black dashed line as the fit of the experimental spectrum.[31]

centered at $725\,\text{nm}(1.71\,\text{eV})$. The bottom panel of Fig. 5.4 shows normalized spectra at $t = 0, t = 50$ and $t = 1850\,\text{s}$.

There are clear spatial heterogeneities shown in many properties, including the reduction emission quenching rate, the emission brightening rate and the absorption percentage, during the photolytic reduction of GOs. Fig. 5.5 shows an example of spatial heterogeneity in the initial emission quenching rate during region 1 and the following brightening rate during region 2. Fig. 5.5 (a) shows the zoomed-in initial quenching trajectory at three different positions (marked as $p_1, p_2$ and $p_3$ in the inset of Fig. 5.5 (a), and their corresponding exponential decay fittings. Their respective quenching rates are $0.169\,\text{s}^{-1}, 0.128\,\text{s}^{-1}$ and $0.097\,\text{s}^{-1}$. The variability from position to position is more explicitly shown in Fig. 5.5 (b), as the values on contour map of
Figure 5.4. Waterfall plot of a single layer GO/rGO emission spectrum. This displays the evolution of the spectrum during reduction (region 1 and region 2). The bottom panel shows the emission spectrum at specific time labeled with the same color of the lines (0s, 50s and 1850s).
quenching rates varies from 0.09 to 0.17s$^{-1}$. Similarly, Fig. 5.5 (d) and (e) show the exponential fittings of emission brightening behaviors in region 2 at different positions on the GO/rGO sheet and the dramatic spatial heterogeneity throughout the whole sample.

Fig. 5.6 shows an example of the percentage absorption or absorption coefficients at 405nm, 520nm and 640nm (a, b, c) for single-layer GO. This shows that the GO sheet is spatially heterogeneous before the laser induced reduction process. In the meantime, as shown in Fig. 5.7, the absorption coefficient of the GO/rGO sheet actually increases during the region 1 and decreases during the region 2. Similar to what was done to the emission evolution rates mentioned above, the absorption evolution can be fitted bi-exponentially and the time constants can be extracted for each pixel of the GO/rGO sheets. An example map of weighted (average) rate constants for absorption evolution is shown in Fig. 5.8. Again, spatial heterogeneity is clearly shown in the dynamic process of GO reduction.

The dynamic constants, such as the emission quenching/brightening rates and absorption evolution time constants, not only tell us that the GO reduction is a spatially heterogeneous process but also provides an approach to determine the energy involved in the process via their temperature dependence. The Arrhenius plot of GO/rGO kinetics for temperatures between 298$^K$ and 323$^K$ are shown in Fig. 5.5 (c) and (f). The corresponding $E_a$ values are $E_{a1} \sim 0.13eV - 0.39eV$ and $E_{a2} \sim 0.33eV - 0.71eV$.

At the end of region 2, i.e. when the base fluorescence intensity reaches the maximum value, the fluorescence of rGO starts to show intermittency/blinking. Fig. 5.7 (b) and Fig. 5.9 shows the whole fluorescence trajectory of one pixel on the rGO sheet. In the example of Fig. 5.9, the base fluorescence intensity reaches its maximum around 8000s and strong and sustaining blinking emerges in the following 20000s. The blinking phenomena exist throughout the whole rGO sheet. Similar to what
Figure 5.5. Kinetic analysis of GO reduction (region 1, panel a-c) and rGO brightening (region 2, panel d-f). Panel (a) and (d) shows the emission intensity trajectories at three different spots inside the GO/rGO specimen. p1, p2, and p3 are used to label these three spots, whose specific positions are shown in the inset panel of (a). The dashed lines are the multiple exponential fits of the experimental trajectories with the same color. $k_q$ values are the corresponding extracted exponential constants. Panel (b)/panel (e) shows the contour plots of the constants shown in panel (a)/panel (d). The contour interval is $0.02 \text{s}^{-1}$. Panel (c) shows the Arrhenius plot of GO reduction kinetics for temperatures between 298 and 323K. Error bars indicate the standard deviations of k-values for five individual GO sheets at a given temperature. Panel (f) shows the Arrhenius plot of rGO brightening kinetics under identical conditions as in (c). Scale bars: 5µm. [31]
happens in region 1 and region 2, blinking of each pixel also shows strong spatial heterogeneity. In the following chapters, we will study in details the PSD, spatial and temporal correlation of blinking in rGO, as well as the possible mechanism behind the blinking within and beyond the multiple recombination center (MRC) model.

Figure 5.6. Absorption images of single layer GO acquired at (a) 405 nm (contour interval, 0.2% absorption), (b) 520 nm (contour interval, 0.05% absorption), and (c) 640 nm (contour interval, 0.05% absorption). Scale bar shows the absorption percentage at the corresponding wavelength. The upper panel for each subplot shows the absorption histogram for GO ensemble (grey) and two single GO sheets (blue and green) (d) Single layer and ensemble GO absorption spectra overlaid with measured absorption coefficients. [43]
Figure 5.7. Absorption/emission intensity trajectories of one location on the GO sheet ($\lambda_{abs} = 520$ nm). [43]

Figure 5.8. Absorption ($\lambda_{abs} = 520\,nm$) rate constant maps obtained for region 1 (left) and region 2 (right). [43]
Figure 5.9. The intensity trajectory of one pixel on the CCD camera recording the GO/rGO emission.
CHAPTER 6

THE ORIGIN OF PHOTOLUMINESCENCE FROM GRAPHENE OXIDE

The fluorescence of GO and rGO has also been reported in specimen synthesized and reduced via other methods, and the origin of the fluorescence has been discussed in many previous studies. For example, in the work done by Gokus et al. [15], strong photoluminescence (PL) was observed in single layer GO after being treated by an oxygen plasma treatment. In the experiment, the micro-cleavage of graphite was placed on a silicon substrate covered with 100 nm SiO$_2$, which was then exposed to oxygen/argon (1:2) RF plasma. The oxidization duration changed from 1s to 6s. The PL properties were studied when the GOs were excited by a 473nm laser irradiation. The PL decay dynamics was studied via time-correlated single photon counting (TCSPC) with a time resolution of 3ps. The emission spectrum was measured from 500nm to 850nm. As shown in Fig. 6.1 (a), PL shows up locally on the GO sheet when the specimen is oxidized for 3s, while in (b) for the specimen oxidized for 5s. The PL is present throughout the whole specimen. The dark area around spot 3 was intentionally bleached under laser excitation. Fig. 6.1 (c) shows the spectra of GO PL at position 1 and position 2. The blue shift of the center of PL in position 3 that is photobleached is consistent with the behavior of rGO observed in Kuno’s work mentioned in Chapter 5. However, the TCSPC result mentioned here, showing uniform behavior across the whole GO sheet are inconsistent with the work done by Exarhos, et al. [7] 4 years later. We will discuss this discrepancy in the following part of this chapter.

Raman spectroscopy was also utilized in the work of Gokus et al. As shown in
Fig. 6.2(a), the D and G peak intensity ratio, $I(D)/I(G)$ varies as the oxidation progresses. $I(D)$ can only appear when there are defects in the graphene structure because of symmetry. $I(D)/I(G)$ should be 0 for ideal pristine graphene sheet, as shown in Fig. 6.2(a) and (b). In the meanwhile, $I(D)/I(G)$ can be used as a measure of the size of crystalline graphite $L_a$ in the form of $I(D)/I(G) = C(\lambda)/L_a$, where $C(514.5 \text{nm}) \sim 4.4 \text{nm}$, which is known as the Tuinstra and Koenig relationship.

In the meantime, $I(D)/I(G)$ also has a relationship with $L_a$ as $C(\lambda)L_a^2$, since the presence of D peak requires the presence of six-fold rings. By combining these two relationships together, T. Gokus et al. estimated the $L_a$ evolution based on the Raman spectroscopy, as shown in Fig. 6.2(d).

Combining all the information above, Gokus et al. believe that the spectral properties of PL in GO is caused by the broadening of a single emissive species, uniformly across the GO sheet. This conclusion is based mainly on the lack of diffusion in the TCSPC data and lack of spectral hole burning effect that one would expect for multiple sources of emission candidates at different wavelengths. The single emissive species was speculated to be CO-related localized electronic states at the oxidation sites.

Chih-Tao Chien et al. studied the PL of GO via X-ray photoelectron spectroscopy (XPS), TCSPC and photoluminescence excitation (PLE) spectrum. In the experiment, GO was synthesized using the modified Hummers’ method, as we introduced in Chapter 4. The GO specimen was then reduced via photothermal reduction under a Xenon flash in ambient conditions.

As shown in Fig. 6.3, the XPS spectroscopy of GO and rGO can be decoupled into signals corresponding to $C = C$ bonds in aromatic rings (284.6 eV), $C - O$ bonds (286.1 eV), $C = O$ bonds (287.5 eV) and $C(=O) - OH$ bonds (289.2 eV). The XPS evolution shows the $sp^2$ carbon bonding signal increases as the reduction time increases. In the meantime, the signal of oxygen containing bonds goes from
dominating to a lot weaker compared to the $C = C$ signal. According to their estimation, the fraction of carbon atoms that were $sp^2$ bonded went from 25% in as-synthesized GO to roughly 69% after the irradiation of 3 hours, which is found to be slightly lower than the fraction after chemical or ultra high vacuum (UHV) thermal reduction methods.

The PL spectra measured by Chih-Tao Chien et al., is shown in Fig. 6.4 and it also exhibits blue shift as the reduction goes on. This is consistent with what Gokus et al. observed by photobleaching the fluorescent GO specimen (Fig. 6.1 (c)). The gradual evolution of the PL spectrum is shown more directly in this experiment. The spectrum shows a tendency that the broad PL spectrum of GO is contributed by two peaks $I_{p1}$ and $I_{p2}$ centered in the red and green range, respectively. As shown in Fig. 6.5 instead of a continuous spectrum migration from centering around 600nm to 450nm, the blueshift can be explained by the intensifying of $I_{p2}$ and diminishing of $I_{p1}$ during the reduction of GO.

Furthermore, the PLE spectroscopy and TCSPC data show significant differences in the PL spectrum at 454nm and 605nm. As shown in Fig. 6.6(a), the $I_{p1}$ emission of GO was found over a wide range of excitation wavelength (orange solid), while the $I_{p2}$ emission of rGO shows a narrow 300nm to 350nm excitation band (blue solid), which indicates two different origins of the $I_{p1}$ and $I_{p2}$. The TCSPC result shown in Fig. 6.6 (b) and (c) also indicates different behavior at 454nm and 605nm. According to their fitting, the TCSPC emission decay can be decomposed into multiple exponential components[3]. For the as-synthesized GO sample, the $I_{p1}$ contains 200, 500 and 1400ps components, while the rGO $I_{p1}$ were found to have decreased decay times. In the meantime, the $I_{p2}$ for rGO contains 100ps component, which is approaching the instrumental response function of the setup. The longer decay components were found to increase as the reduction goes on, which is opposite to what happened for $I_{p1}$.
Figure 6.1. Confocal PL image of GO excited at 473 nm (2.62 eV) for 3s (a) and 5s (b). Scale bar 5µm. PL is bleached intentionally by intense laser irradiation at position 3 in (b). (c) Spectra detected at the positions marked in (b) corrected for detector response. (d) TCSPC trace detected at the positions marked in (b).

With these results, Chih-Tao Chien et al. believe that the PL of GO and rGO originates from two mechanisms. They suggested that the electron-hole recombination among the confined aromatic cluster states corresponds to the narrow $I_{p2}$ emission. On the other hand, the broad $I_{p1}$ emission is attributed to optical transitions to localized states caused by disorders, which, based on previous DFT calculations, are the π states that are sensitive to the disorder in the carbon network.
Figure 6.2. (a) Raman spectroscopy of GO with respect to the oxidization time; (b) \( \frac{I(D)}{I(G)} \); (c) FWHM of G band; (d) ratio PL background slope \( m \) to G peak intensity, \( I(G) \)
Figure 6.3. XPS of GO with respect to photothermal reduction time

Figure 6.4. PL spectrum of GO with respect to photothermal reduction time
Figure 6.5. PL spectra of (a) GO, (b) rGO (reduction time=75 min), and (c) rGO (reduction time=180 min) with two deconvoluted Gaussian-like bands of $I_{P1}$ and $I_{P2}$ emission; d) Peak positions and e) the FWHMs of $I_{P1}$ and $I_{P2}$ with respect to photothermal reduction time; (f) Correlation between P2 fractions (circles) and $sp^2$ fractions (triangles; from XPS data) with respect to photothermal reduction time.
Figure 6.6. (a) Measured (dash lines) and normalized (solid lines) PLE spectra of the $I_{P1}$ emission (at 605 nm) from as-synthesized GO and the $I_{P2}$ emission (at 455 nm) from rGO (reduction for 3 h); The TSCPC decay curves of (b) $I_{P1}$ emission and (c) $I_{P2}$ emission with respect to photothermal reduction times.
In this chapter we present our analysis of the PL trajectories for GO. It might be tempting to extract the blinking signal from the fluorescence trajectory while properly defining the temporal base fluorescence intensity, followed by the analysis of the whole blinking session. We actually did extract the base fluorescence intensity by finding out the running median of the trajectory. However, keeping in mind that the photoinduced reduction of GO is a dynamic process, we also sectioned the blinking trajectory into smaller consecutive overlapping sections to study the temporal evolution of the blinking process. Also, we focused our analysis on the PSD analysis, since the analysis itself will not be affected by the base fluorescence trajectory, which contributes to the low frequency spectral weights in the PSD.

The power spectral density (PSD) of the trajectory is calculated based on Welch's method. First, the trajectory of total length $N$ is divided into overlapping segments with a length of $M$. The overlapping rates of the segments are chosen to be 50%, which means there are $K = N \text{mod}(M/2) + 1$ segments. Then the modified periodogram $\hat{S}_m(f)$, as defined below is calculated for each of the segments:

$$\hat{S}_m(f) = \frac{\Delta t_0}{M} \left( \sum_{n=1}^{M} w_n x_{mM-n+1} \exp(i 2\pi f \Delta t_0 (n-1)) \right)^2. \quad (7.1)$$

Here, $\Delta t_0$ is the unit time difference between discrete temporal signals, $w_n$ is the window function that convolves with the signal trajectory, for which we used the Hamming window in our calculation. The periodogram here is proportional to the
Figure 7.1. An example of the Hamming window with a length of 300.

The square of discrete Fourier transform of the signal sequence x modified by the window function $w_n$. For the $m_{th}$ segment of the original signal, the indices of x we are using goes from $(m - 1)M + 1$ to $(m - 1)M + M + 1$. The Hamming window we used in our calculation goes as Eq. (7.2), given the length of the window to be the same as that of the segment.

$$w_n = 0.54 - 0.46 \cos(2\pi \frac{n}{M}), 1 \leq n \leq M$$  \hspace{1cm} (7.2)

Figure 7.2 shows the shape of the Hamming window with a length of 300. As can be seen in Fig. 7.2, the Hamming window reaches 0 at both ends of the segment, which tampers the discontinuity between the values of the signal at both ends and reduces the corruption of the estimated discrete Fourier transform caused by leakage.
Then the periodograms of all segments are averaged to reduce the variance in the periodogram estimator:

\[ \hat{S}_{MAP}(f) = \frac{1}{K} \sum_{m=1}^{K} \hat{S}_m(f). \] (7.3)

The averaged value is used as our estimation of the power spectral density of the blinking trajectory signal.

Before the estimation of the trajectory PSD, the dependence of the window size and frequency for the periodogram estimator is evaluated to find the non-bias region of the estimator, as shown in Fig. 7.3. For a given frequency value, when the window size is large enough, the estimation of PSD has little dependence on the choice of the window size. This is shown by the vertical contour of estimated PSD value when the window size is above the connected circle boundary in Fig. 7.3. We call the regions with little window size dependence non-bias regions of the PSD estimation. The value for the window size of a given frequency is chosen as small as possible in the non-bias regions to maximize the number of estimated windows, so that we can minimize the variance in the periodogram estimator.

Since the trajectory of blinking shows long range self-correlation [53], we utilize an extended version of central limit theorem in the estimation of the variance of the periodogram estimator, in which

\[ \hat{\kappa}_{MAP}(f) = \frac{1}{K} \left( \hat{\kappa}_0(f) + 2 \sum_{m=1}^{m_c} (1 - \frac{m}{K}) \hat{\kappa}_m(f) \right), \] (7.4)

\[ \hat{\kappa}_m(f) = \frac{1}{K - m} \sum_{n=1}^{K-m} \hat{S}_n(f) \ast \hat{S}_{n+m}(f). \] (7.5)

are defined. The variance of the periodogram estimator is determined by the maximum value of \( \hat{\kappa}_{MAP}(f) \) when \( m_c \) goes from 1 to K.

The emission trajectory for each CCD pixel is divided into small sections. These sections are chosen to overlap with each other to obtain a smooth, temporally dynamic
Figure 7.2. An example showing the dependence of PSD on the window size at a given frequency value. The cyan line connecting red circles indicate the chosen relationship between the window size and the frequency value for the PSD analysis.
view of the blinking evolution. The brightening and dimming of the background emission intensity are not contributing in the PSD spectrum when we exclude low-frequency components.

The first five sections have lengths of 300s each, while subsequent sections have lengths of 800s. There are two reasons for choosing shorter lengths in the first five sections. First, there is little blinking in these stages and second as the section number increases, the blinking will start emerging in the tail part of the section. This significantly changes the PSD of that whole section. The first several sections are chosen to be short so that we can study the emergence of blinking with better time resolution.

Fig. 7.3 shows an example of how the whole fluorescence trajectory is sectioned. In this case, the whole trajectory with a total length of 3800s is sectioned into 27 sections as described above. Then the PSD of each of the section is calculated. Fig. 7.4 shows the PSD of multiple selected sections. There is clearly a temporal evolution of the PSD of these consecutive sections. Notice the PSD for section 1 has fewer frequency samples than those of other sections in the graph. This is because we chose shorter section size as we mentioned above, that we have to discard several low-frequency, i.e. long term, sample points compared to the following longer sections.

With the fluorescence PSD of each CCD pixel calculated, we can do more analysis. First we fit the power law exponent, or the slope of the log-log PSD-frequency plot.

Fig. 7.5 shows an example of the linear fitting that is used to estimate the power law exponent \( \alpha \) of the PSD for one section, from which, the exponent was estimated to be 0.79.

By applying the above analysis to all the sections of the whole fluorescence trajectory of one CCD pixel, we can create a picture of the evolution of PSD as the photo-induced reduction of GO continues, through the various stages of rGO blinking. Initially, the PSD has a low amplitude and \( \alpha \) is smaller than 0.2 (Fig. 7.4)
Figure 7.3. The intensity trajectory as a function of time for a single CCD pixel. Fluorescence intermittency is apparent after about 500s. [42]
Figure 7.4. The PSDs at different stages of one pixel, which shows the emission undergoes process from no blinking (section 1) to blinking (sections 6 - 16), and finally, extinction (sections 16 - 21). The log-log scale reveals the power law nature of the PSD. Scale bars: 5µm
Figure 7.5. An example of the calculated experimental PSD (blue) following a power law distribution and the least square linear fitting in the log-log scale plot (red).
section 1). The emission fluctuation in this stage is practically identical to featureless background noise ($\alpha \sim 0.2$). When the background emission grows to a maximum, blinking emerges as the PSD amplitude increases drastically, and $\alpha$ approaches 0.9 across most of the rGO sheet. An overall decrease in QY follows, yet blinking remains intense for minutes. Finally, when blinking diminishes, both the PSD amplitude and $\alpha$ become similar to their pre-blinking values. Due to its parallel evolution with blinking power, $\alpha$ can be used as a quantitative indicator of blinking: when $\alpha < 0.3$, the intensity fluctuation is mainly caused by noise, while $\alpha > 0.3$ correlates with the presence of blinking. Fig. 7.6 shows the evolution of the PSD power law exponent during a total of 27 sections.

We then investigated the spatial heterogeneity of the evolution of the blinking throughout the whole specimen. The spatial range of the GO specimen was determined by a threshold value of the integrated intensity for each pixel. Given that the intensity trajectory of one pixel is $i(t)$, the integrated intensity was defined as

$$\int_{0}^{T_{\text{len}}} i(t) = \sum_{t=0}^{T_{\text{len}}} i(t).$$

(7.6)

where $T_{\text{len}}$ is the length of the trajectory. Pixels having a higher integrated intensity than half of the largest integrated intensity of an individual pixel are analyzed.

As shown in Fig. 7.7 and Fig. 7.8, the power law exponent $\alpha$ exhibits clear spatial heterogeneity in the area of the sample: 1, given a specific section of the trajectory, $\alpha$; 2, the section number, i.e. timing, of $\alpha$ to rise above 0.3 and fall back below 0.3; 3, the duration of $\alpha$ above 0.3, all varies from point to point. As we previously proposed, the power law exponent $\alpha$ can be used as an indicator of the blinking phenomena. These results also show the spatial heterogeneity in the blinking of the rGO.

We continued our studies in the correlations of fluorescence properties in both temporal and spatial respects.
Figure 7.6. An example of the evolution in the power law exponent of the PSDs belong to different section of the emission trajectory of one pixel in CCD movie.
Figure 7.7. Contour plot of the power law exponent throughout the whole sheet for different trajectory sections. Sections 1 and 5 both have a length of 300s for a more precise view of blinking emergence. Sections 10–25 all have 800s length.
Figure 7.8. Contour plot of the blinking duration (in unit of sections), the threshold of determining blinking is chosen to be $\alpha = 0.3$. 
The first property is the spatial correlation between CCD pixels, by defining the spatial correlation with help of the cross power spectral density (CPSD) in the following way:

\[
SC_{x_1x_2}(\omega) = \frac{CPSD_{x_1x_2}(\omega)}{\sqrt{PSD_{x_1}(\omega)PSD_{x_2}(\omega)}},
\]  

\[
CPSD_{x_1x_2}(\omega) = \int dT \langle x_1(t)x_2(t+T) \rangle e^{-i\omega T}.
\]  

The \(CPSD(\omega)\), when \(\omega > 0\), should be 0 for completely independent stable \(x_1(t)\) and \(x_2(t)\), as

\[
\langle x_1(t)x_2(t-T) \rangle = \langle x_1(t) \rangle \langle x_2(t-T) \rangle = constant \langle x_1 \rangle \langle x_2 \rangle,
\]  

which is independent of \(t\). The \(SC(\omega)\) when \(\omega > 0\) should be 1 for completely correlated stable \(x_1(t)\) and \(x_2(t)\), as

\[
\langle x_1(t)x_2(t-T) \rangle = \langle x_1(t) \rangle \langle x_1(t-T) \rangle = \langle x_1(t) \rangle \langle x_1(t-T) \rangle,
\]  

\[
CPSD_{x_1x_2}(\omega) = PSD_{x_1}(\omega) = PSD_{x_2}(\omega).
\]  

The \(SC(\omega)\) for any pair of trajectories from two pixels should fall between the value of above two extreme cases, \(-1 < SC(\omega) < 1\). Ideally, a non-zero \(SC(\omega)\) indicates correlations between trajectories. However, we should also consider the unavoidable 'intrinsic' correlation caused by the diffraction in any optical observation system. The parameters of the optical system in the experiment are as follows: wavelength \(\lambda = 520 nm\), numerical aperture \(NA = 2.8\), magnification \(\beta = 63\). Appendix A shows the detailed derivation of the theoretical spatial correlation introduced by the diffraction only.

Figure 7.9 shows the comparison of the experimental and the theoretical diffraction only spatial correlation. In order to estimate the experimental spatial correlation
Figure 7.9. Comparison of the experimental spatial correlation (blue line) and the theoretical spatial correlation (green line) generated merely by diffraction. The optical system uses an objective with a numeric aperture of 1.4 and with a 100x magnification. The radius of Airy disk of a 520nm light is 22.6\,\mu m. We approximated the Airy pattern with a Gaussian function and calculated the cross power spectral density (CPSD) as a representation of spatial correlation. The length of one pixel distance is 160\,nm.

with respect to pixel distance, we first defined the pixel distance as:

$$D(x_1, x_2) = \text{floor}(\sqrt{(x(x_1) - x(x_2))^2 + (y(x_1) - y(x_2))^2}), \quad (7.12)$$

then we picked pixel pairs inside the area of the rGO specimen. Here the function $\text{floor}(x)$ returns the integer part of the number $x$. $SC(x_1, x_2)$ for every pair is calculated and averaged over the pairs that have the same $D(x_1, x_2)$ as defined above. As can be seen from the plot, the experimental result shows clear spatial correlations above the diffraction effect, which indicates possible interactions between the blinking centers.

We also investigated the temporal correlation between multiple blinking proper-
ties: total power of fluctuation, background fluorescence intensity, PSD power law exponent.

The total power of fluctuation was estimated by the discrete approximation of the integral of PSD with respect to the frequency. In the ideal case that we can calculate the continuous form of PSD $S_{xx}(\omega)$, the total power of fluctuation in a certain range of frequency can be calculated as:

$$P(\omega_1, \omega_2) = \int_{\omega_1}^{\omega_2} S_{xx}(\omega) d\omega.$$  \hspace{1cm} (7.13)

As in our case, PSDs are estimated at multiple discrete frequencies, we use the simple summation form for discrete frequency sequences:

$$P(\omega_1, \omega_2) = \sum_{\omega=\omega_1}^{\omega_2} S_{xx}(\omega).$$  \hspace{1cm} (7.14)

Next, the background fluorescence intensity is calculated using the running median value of the trajectory,

$$I_0(t) = median(i(t), t \in (t, t + T)).$$  \hspace{1cm} (7.15)

Figure 7.10 shows the integrated PSD, i.e. the blinking power, the background intensity and the blinking trajectory of one pixel.

In our work, correlation between two properties is defined in the traditional way of measuring correlation between two variables, $a, b$:

$$Corr(a, b) = \frac{\sum_{i=1}^{N} (a_i - \bar{a})(b_i - \bar{b})}{\sigma_a \sigma_b},$$  \hspace{1cm} (7.16)

where $N$ is the total number of pixels inside the area of rGO specimen.

Figure 7.11 shows the correlation between six pairs of properties of the blinking. It clearly shows strong lagged positive correlations between the PSD total power
Figure 7.10. A comparison of the emission intensity and the integrated fluctuation PSD of one pixel. The median of each section of a 100s length is plotted as a function of the initial time of that section, hence it is shifted to the left. For consistency, the time evolution of integrated PSD is plotted in the same way.
and the background emission, which is also shown in Fig. 7.10 as the behavior of the blinking power lags that of the median trace by around 500s, i.e. 5 sections. This can be explained in more details under the multiple recombination center (MRC) model in the following chapters. Note there is $N_{\text{min}}$, the minimum number of switching channels, which we haven’t introduced so far and we will talk more details about this in the chapters about the MRC model.

We also performed an ordinary least square (OLS) linear regression of $\log(frequency)$ versus $\log(PSD)$ to estimate the power law exponent $\alpha$. The estimation is the slope from the linear fitting and the standard deviation (SD) of $\alpha$ can be easily obtained. Fig. 7.12 shows the contour plot of the SD of $\alpha$. It can be seen that the SD of the power law exponent for any pixel in every section is smaller than 0.09, and those of most pixels are below 0.05.

However, it is worth noticing that the OLS assumes that the PSD estimates at different frequencies are statistically independent. To justify this, we performed a correlation analysis. The PSD estimations were found to be either not correlated or positively correlated for the majority of frequency combinations. From a geometrical perspective, this implies a smaller probability of a line fit that crosses with the OLS fit. Large variations in the slope can only be achieved by a high probability associated with such a crossing fit. In other words, positive correlations favor a smaller confidence interval for the slope. Therefore, by neglecting these positive correlations we are actually providing a more conservative estimation. Hence, the correlation analysis provides strong support in favor of the validity of the OLS error estimation.
Figure 7.11. Pair correlations of intermittency parameters. Contour plots of the correlation between the blinking power (integrated PSD), the PSD slope, the fluorescence intensity median, and the minimum number of switching channels of RC. There is a clear correlation between the intensity median and the integrated PSD, with a shift of 5 sections. There is also a positive correlation between the integrated PSD and the slope of PSD when the sections are close. Thus the shifted positive correlation between intensity median and the integrated PSD is expected and observed. There is hardly any correlation between these variables to the minimum number of switching channels of RC.
Figure 7.12. Contour plots for the standard deviation of the power law exponents at different sections. Scale bar: 5µm
CHAPTER 8

GO FLUORESCENCE INTERMITTENCY ANALYZED WITHIN THE MRC MODEL

To apply the MRC model into the rGO blinking, we generalized the MRC model for the 2D system. In the analysis, the signals from all pixels in the 2D CCD camera recorded trajectory are analyzed individually. Then the spatial and temporal correlations between the properties of these pixels are analyzed, which will be shown in this chapter. We assume that in the resolution limited area of the CCD apparatus there may be several kinds of chemical species or structures acting as RCs. Each kind of RC has a specific structure/chemistry and thus a specific switching rate that shows up as a single Lorentzian component in the PSD. A group of identical RCs has a specific switching frequency between two different non-radiative states. We call the collective contribution of these RCs a switching channel. We propose to extract the minimum number of switching channels by fitting the theoretical PSD with its experimentally estimated counterpart, using available confidence intervals.

First, we calculate the theoretical PSD. It is a sum over the Lorentzian components for all available channels N,

\[ S_{xx}(\omega) \sim \sum_{i=1}^{N} \frac{\gamma_i}{\pi \cdot (\omega^2 + \gamma_i^2)} , \]

where \( S_{xx}(\omega) \) is the theoretical PSD at frequency \( \omega \), \( \gamma_i \) is the rate at which an RC switches between a passive \( (\sigma_i(t) = 0) \) and active \( (\sigma_i(t) = 1) \) state, and \( N \) is the number of channels. In Eq. (8.1) we assume that the number of RCs for each
channel is the same. Furthermore, as we did in our earlier studies of blinking in a wide variety of fluorophores, we choose $\gamma_i$ to have a power law distribution with exponent $\beta$. Also, we fix the highest and lowest frequency of the RCs to be $3Hz$ and $0.001Hz$, respectively.

Next, we can compare the PSD generated by the experiment and that from the MRC model, as shown in Fig. 8.1. Notice that to generate a set of PSD from the MRC, we can have different choices of $\beta$ and number of switching channels $N$ in a certain frequency range. We calculate the quantity

$$\epsilon = \sum_{j=1}^{N} \left( \frac{S_{\text{experimental}}(\omega_j) - S_{\text{theoretical}}(\omega_j)}{\delta_{\text{experimental}}(\omega_j)} \right)^2$$

(8.2)

for all possible combinations of $\gamma_i$ and $N$, to test whether a theoretical PSD fits within the confidence intervals of the experimental PSD. The $\delta_{\text{experimental}}(\omega_j)$ here is the standard deviation of the experimental PSD at $\omega_j$, which is calculated according to Eq. (7.4) and (7.5).

For the study of blinking in rGO, the trial values for $\beta$ in Eq. (3.14) went from 0.1 to 1.5 with a 0.02 increment. In this frequency range, there are 23 values of $\omega_j$ for the PSD estimation from section 6 to section 27, and we choose $\epsilon = 20$ as the upper threshold of $\epsilon$ to decide whether to accept the combination. We will show the statistical meaning of this threshold in this chapter. The minimum acceptable $N_{\min}$ is found for each pixel.

Similar to what we did for the evolution of the PSD power law exponent $\alpha$, we can make the contour map of $N_{\min}$ of each section, as shown in Fig. 8.2. There are white areas inside the specimen map. Those are pixels where the PSD generated by all combination of $\beta$ and $N$ are rejected by our criteria, i.e. the MRC model for blinking cannot generate an acceptable set of PSD to reproduce the experimental counterpart. Notice these white areas appear mainly in sections before 5 and after
Figure 8.1. An example of the calculated experimental PSD (blue) following power law distribution and the best fitted PSD generated from the MRC model in the log-log scale plot (red).
20, while the PSD for most of blinking regions in a section can be reproduced by the MRC model.

Given the PSD values are independent from each other at different frequencies, under the hypothesis that $S_{\text{theoretical}}$ reproduces real value of $S_{\text{rGO}}$ perfectly, Eq. (8.2) corresponds to the summation of $N$ squared normalized standard normal random variables. The summation of the square of $k$ independent standard normal distributed random variables follows a $k$ degree chi-square distribution. [13] That is to say, $\epsilon$ should follow the distribution of chi-squared distribution with the degree of freedom of $N$. We use the chi-square test to statistically determine whether our hypothesis stands. The test is a one-sided test. That is, the larger $\epsilon$ is, the less likely that our hypothesis stands. Since the cumulative distribution function (CDF) of $\chi^2_N$ at 20

$$\chi^2_{23}(20) = \frac{1}{\Gamma\left(\frac{23}{2}\right)\gamma\left(\frac{23}{2}, \frac{20}{2}\right)} = 0.3581,$$

we can say that, statistically, the probability of MRC model under our accepted values can reproduce the real PSD of the rGO system is $1 - 0.3581 = 65\%$. For more details about chi-squared distribution and statistics in Appendix B.

Now we extend the framework to multiple blinkers by summing the contribution of individual fluorescent $sp^2$ domains imaged within each CCD camera pixel. As we show in previous chapters, the fluorescence intensity of the rGO sheet excited by continuous light undergoes an initial photo-brightening and a subsequent dimming phase (regions 2 and 3). This is evident in the evolution of the running median intensity (Fig. 8.3). The blinking power, as defined in Eq. (7.14) over $10^{-2} - 3Hz$, undergoes an almost identical time evolution (see Fig. 8.4). According to what is shown in Fig. 7.10 the blinking lags behind the intensity average by $\sim 500s$. We attributed the evolution of the intensity to the formation and subsequent destruction of fluorescent $sp^2$ clusters. Below, we explain the evolution of blinking and its correlation with the intensity.
Figure 8.2. The evolution of the minimum number of switching channels from MRC modelling. Blank areas are points at which the experimental PSD cannot be well reproduced by the MRC model with exponents in the range mentioned in the main text. Scale bar: 5 µm. [12]
Figure 8.3. Temporal evolution of median intensity. The median is calculated over the temporal sections. Units of intensity: counts 10Hz. Scale bar: 5µm. [42]
Figure 8.4. Temporal evolution of integrated PSD. The PSD of each temporal section is integrated over frequency. According to the Wiener-Khinchin theorem (Appendix III), this quantity equals the expectation value of the square of emission intensity. Units of integrated PSD: \( \text{counts}^2 (10\text{Hz})^2 \). Scale bar: 5\(\mu\text{m} \). [42]
Initially, fluorescent clusters emit steadily but within minutes some of them start blinking. These fluorescent clusters are found in significant numbers within the diffraction limited area projected onto any given pixel of the CCD. The total light intensity that falls on a pixel is the sum of the intensity contributions from all clusters:

$$I_{\text{pixel}}(t) = \sum_m I_m(t) \int_{S_{\text{pixel}}} A(x - x_m, y - y_m) \, dx \, dy,$$

where $I_m(t)$ is the intensity trajectory of cluster $m$, and the integration runs over the pixel area $S_{\text{pixel}}$. The convolution with the aperture function $A(x, y)$ ensures that the effective summation runs over fragments within the first Airy disk from the area imaged by the pixel. More details in diffraction can be found in Appendix A.

We propose that as the rGO specimen breaks up due to photolysis, RCs are created in the proximity of some clusters. This, in turn, initiates their blinking. We assume that typically not more than one RC is created at each cluster. Consequently, the cluster intensity fluctuation can be described as a telegraph process

$$I_m(t) = I_{d,m} + (1 - \delta_m(t))(I_{b,m} - I_{d,m}),$$

where $I_{b,m} = \frac{k_e,m k_r,m}{k_0,m + k_r,m}$, $I_{d,m} = \frac{k_e,m k_r,m}{k_0,m + k_r,m + k_m}$. The rates are defined in a similar way as in Eq. (3.12).

$I_{b,m}$ is the emission intensity of $I_m$ when the system is in the bright, or ON state. $I_{d,m}$ is the emission intensity of $I_m$ when the system is in the dark, or OFF state, which is reflected by the additional non-radiative energy releasing rate $k_m$ in the denominator. $\sigma_m(t) = 1$ when the system is in dark state, $\sigma_m(t) = 0$ when the system is in bright state.

In order to explain the correlation between the evolution of the running average and blinking power, we now look at statistical quantities averaged over time sections along trajectories. We assume that clusters undergo negligible variations of emission
and relaxation rates both in time and space across clusters. Then, the long-term behavior is due to the change in the number of blinking and non-blinking clusters. Empirically, we propose that blinking occurs within an average lag time of \( \tau \) after a cluster has been created. The evolution of the number of blinking clusters can be cast as a function of the total number of clusters,

\[
N_{\text{pix,blink}}(t) = rN_{\text{pix}}(t - \tau), \quad (8.6)
\]

where \( r \) is the fraction of blinking clusters. Thus, the running average is

\[
\langle I_{\text{pixel}} \rangle_T(t) = I_bN_{\text{pix}}(t) - (I_b - I_d)\langle \sigma \rangle_T rN_{\text{pix}}(t - \tau), \quad (8.7)
\]

where the first term is dominant, since in regions 2 and 3 the blinking fluctuation is small compared to the average. Consequently, to a good approximation, the running average of the intensity is

\[
\langle I_{\text{pixel}} \rangle_T(t) \sim I_bN_{\text{pix}}(t). \quad (8.8)
\]

On the other hand, the total power of the blinking fluctuations is identical to the variance integrated over time. Assuming that this identity holds for the sections, we find that

\[
S_{\text{pix,T}}(t) = (I_b - I_d)^2 \text{var}_T(\sigma) rN_{\text{pix}}(t - \tau), \quad (8.9)
\]

which is due to the central limit theorem. This establishes the strong, time-shifted correlation between the running average and the power of fluctuation.[42]
The MRC model is a phenomenological model as an approach to understanding the fluorescence intermittency. In the effort to investigate the microscopic mechanism behind the blinking process in rGO, we used both density functional theory (DFT) calculation and kinetic Monte Carlo (MC) simulation of the photoreduction-induced, structural evolution of GO/rGO.

In my collaborative work with Anthony Ruth, the optical properties of individual graphenic domains were estimated via DFT and time dependent density functional theory (TDDFT) calculations. The minimum transition energies, the absorption cross-sections/emission intensities and the quantum yields (QYs) for graphenic clusters: $C_{24}H_{12}$, $C_{54}H_{18}$, $C_{96}H_{24}$, $C_{150}H_{30}$ and $C_{216}H_{36}$, are calculated, as the results shown in Fig. 9.1.

According to Clar’s work, the optical response of polyaromatic hydrocarbons (PAHs) depends on the number of carbon atoms and the maximum number of possible aromatic sextets. This means that different PAHs that have the same number of carbon atoms and aromatic sextets will have nearly identical optical properties. Therefore, the relationship between the dimension of $sp^2$ carbon clusters and their optical properties can be estimated based on the results from the PAH with a similar dimension, as shown in Fig. 9.2. With the help of Fig. 9.2 we can see the clusters in the range of 50 to 150 carbon atoms contribute significantly to the observed emission in the visible light spectrum range.
Figure 9.1. A table of the optical property results for PAHs from DFT/TDDFT simulation. The top row shows the simulated structure, with big black marbles representing carbon (C) atoms and small grey marbles representing hydrogen (H) atoms.

<table>
<thead>
<tr>
<th></th>
<th>C_{54}H_{12}</th>
<th>C_{52}H_{18}</th>
<th>C_{39}H_{24}</th>
<th>C_{19}H_{20}</th>
<th>C_{16}H_{15}</th>
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<td>Diameter (nm)</td>
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<td>1.23</td>
<td>1.73</td>
<td>2.22</td>
<td>2.71</td>
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<td>7</td>
<td>12</td>
<td>19</td>
<td>27</td>
</tr>
<tr>
<td>Emission Energy (eV)</td>
<td>4.16</td>
<td>2.90</td>
<td>2.18</td>
<td>1.69</td>
<td>1.32</td>
</tr>
<tr>
<td>Radiation Lifetime</td>
<td>2.14 ns</td>
<td>2.95 ns</td>
<td>4.22 ns</td>
<td>6.31 ns</td>
<td>10.2 ns</td>
</tr>
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<td>Internal Conversion</td>
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<td>422 ps</td>
<td>200 ps</td>
<td>80.0 ps</td>
<td>9.44 ps</td>
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<tr>
<td>Lifetime</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quantum Yield (%)</td>
<td>31.8</td>
<td>12.5</td>
<td>4.52</td>
<td>1.25</td>
<td>0.0925</td>
</tr>
<tr>
<td>Emission Intensity</td>
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<td>6.75</td>
<td>4.34</td>
<td>1.88</td>
<td>0.20</td>
</tr>
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<td>(a. u.)</td>
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<td></td>
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</tr>
</tbody>
</table>

Figure 9.2. Calibration curves from DFT results for Monte Carlo simulation: (a) emission energy, (b) quantum yield (c) emission intensity and absorption cross section vs. cluster size. [38]
Next, the dynamical evolution on the scale of carbon atoms and oxygen containing decorating functional groups on the GO/rGO specimen plane is simulated via kinetic MC simulation. In this study, a $20\text{nm} \times 20\text{nm}$ carbon honeycomb lattice is initialized by randomly distributing hydroxide ($-OH$) and epoxide ($C-O-C$) groups throughout the basal plane. Then, three main chemical reaction channels are introduced into the system:

$$C_nOH - > C_n + OH,$$

(9.1)

$$C_nO - > C_{n-1} + CO,$$

(9.2)

$$C_n - > C_{n-1} + C,$$

(9.3)

with corresponding rate constants $k_{OH}$, $k_O$ and $k_C$. Together with the DFT/TDDFT results, the kinetic MC simulation can generate the simulated temporal trajectory of absorption, emission, and quantum yield (QY), which, in turn we are able to compare to the experimental data.

The MC generated results depend on the choice of multiple parameters in the simulation. Fig. 9.3 (a) shows the dependence of the behavior of the absorption and the emission trajectory on the percentage of epoxide in the initialization phase. The percentage of epoxide:carbon (C-O-C:C) was varied from 0 to 25% to find the MC generated trajectory in best agreement with experiment. The optimal percentage of epoxide was found to be 20% as the results best reproduce the experimentally observed trajectories. This value is chosen by comparing absorption maximum and valley-to-peak emission intensity ratio. This is consistent with previous studies showing that the $C : O$ ratios range from 4 : 1 to 2 : 1. As shown in Fig. 9.3 (b), in the simulated emission trajectory, the initial decay and the following low plateau, the second brightening and subsequent decay is caused by the photobleaching and sample
damage were all reproduced.

The two-peak structure in the temporal trajectory of emission during the reduction of graphene oxide is remarkably reproduced by the MC simulation. Furthermore, the optimal epoxide percentage also reproduces the maximum absorption value of the experiment (1.2%). The first peak in the simulated emission trajectory arises from $OH$ removal in Eq. (9.1), the low plateau comes from the $C - O - C$ removal in Eq. (9.2) and the final photobrightening comes from the removal of carbon atoms in Eq. (9.3).

To make the model better describe the reduction process, in which carbon sublimation is expected to constantly happen throughout the whole graphene oxide. The model was then further improved by assigning different carbon removal rates in Eq. (9.3) to carbon atoms in different local molecular environments. Specifically, $k_C$ rates were set as $k_{C1} > k_{Carm} > k_{Czig} > k_{C3}$, where, $k_{C1}$ is for the singly coordinated carbon atoms, and $k_{C3}$ is for the triply coordinated carbon atoms. The doubly coordinated carbons are treated in two cases: the armchair edge atoms with $k_{Carm}$ and the zig-zag edge atoms with $k_{Czig}$. Figure 9.3(c) shows the trend and the fluctuation in the emission can be reproduced by the kinetic MC simulation with right choice of $k_C$ values. As shown in Fig. 9.3(c), with these improvements, the simulation shows superb agreement with experiment. The MC trajectory clearly shows fluorescence intermittency. The magnitude of the intensity fluctuation is also comparable to the experiment. This strongly suggests that by adding the multiple carbon sublimation rates, the MC simulation correctly reproduced the number and size distribution of $sp^2$ domains during the reduction of graphene oxide.

Figure 9.4 shows the specific features of emission and absorption trajectories and associated structure in a $20nm \times 20nm$ area. The MC simulation shows that there are both graphene like carbon network and small isolated $sp^2$ domains exist in the area. Approximately, there is one emissive $sp^2$ domain that corresponds to the emission
Figure 9.3. (a) Evolutions of the theoretical absorption (blue) and emission (red) temporal trajectory based on the MC simulation with respect to the initial epoxide concentration (COC:C); (b) Comparisons between the experimental (dashed lines) and the MC simulated (solid lines) emission (red) and absorption (blue) temporal trajectories; (c) Close-up of the emission profile during the blinking phase. (d) Emission versus absorption correlation plots. [38]
Figure 9.4. Simulated emission, absorption and domain structure during the rGO blinking. Cluster color coding reflects the cluster’s emission photon energy. Black areas show the carbon network that does not emit in the visible light range.
intensity in every \(100nm^2\). The MC simulation suggests the isolation and re-clustering of these domains with respect to the carbon network are corresponding to the emission fluctuation. In the meanwhile, the absorption does not undergo as much fluctuation as the emission because both the inter-connected carbon network and emissive \(sp^2\) domains are contributing to the absorption.

To better understanding the blinking reproduced by the kinetic MC simulation. We first analyzed the simulated trajectory shown in Fig. 9.3(c), which mainly stems from the carbon atom sublimation in Eq. (9.3). The corresponding PSD and the PSD of the experimental trajectory are shown in Fig. 9.5 for comparison. It can be seen that the MC trajectory shows a power-law PSD, although with an exponent \(\alpha\) at 1.9, which is larger than what was observed in the case of rGO blinking (\(\alpha < 0.9\)).

The discrepancy in \(\alpha\) is narrowed by including Poisson noise. There are two sources that can introduce Poisson noise into the simulated MC trajectory. The first one is the counting statistics of the photons counted by the detector. This can be taken into account by generating the intensity from a Poisson distribution that
has the parameter $\lambda_1$ equals the original MC trajectory value before we adding into Poisson noise. Here, $\lambda_1$ is the rate constant of Poisson distribution, which means the average photons counted by the detector is $\lambda_1$ during one binning time. The second source accounts the effect of the reversibility in Eq. (9.1) to Eq. (9.3), that is, the dimension of the $sp^2$ cluster may fluctuate during the evolution. This reversibility should only be important when the timescale of the fluctuation is comparable to the binning time of the detector. If the timescale is too short compared to that of the detector, the binning will average out the effect of reversibility. On the other hand, if the timescale is too long compared to that of the detector, the evolution caused by such reversibility can be observed in the temporal trajectory directly. The Poisson parameter $\lambda_2$ for this case is chosen to be the number of active emitters inside one pixel. Notice these two parameters $\lambda_1$ and $\lambda_2$ can actually be connected by the QY for individual emitters, since the total amount of photons detected in one CCD pixel is the summation of all the photons from the active emitters in the corresponding area on the specimen (not taking into account of the diffraction). Suppose we have $N$ emitters in this area, and the QY for individual emitters are $QY_1, QY_2, \ldots, QY_N$. Then $\lambda_1 \propto \Sigma_{i=1}^{N} QY_i$, while $\lambda_2 \propto N$.

Fig. 9.6 shows that by introducing two kinds of Poisson noise in the trajectory generation, the $\alpha$ of the PSD of the MC trajectory falls into the experimentally observed range $0.3 \sim 0.9$ in both cases. Compared to the $\alpha = 1.68$ for the original MC trajectory shown by the red dots in Fig. 9.6, the PSD of the Poisson noise modified trajectory shows better agreement with the experimental data. Although an accurate estimation of the relevant reverse reaction rates was not established here, we argued above that the Poisson noise should be only important at the timescale of the binning time of the detector, which determines the upper limit of the frequency in the PSD estimation. The introduction of Poisson noise in the modified MC trajectory induces PSD components around the upper limit of the PSD estimation, which decreases the
Figure 9.6. PSDs for trajectories: experimental (cyan square), MC simulation with Poisson noise accounting for stochastic noise from reversibility of carbon sublimation (yellow triangle), MC simulation with Poisson noise accounting for counting statistic of photons (purple diamond), original MC simulation (red circle).
value of the experiment $\alpha$. 
CHAPTER 10

DIMENSIONAL CROSSOVER IN SEMICONDUCTOR NANOSTRUCTURES

To better understand the effect of confinement on fluorescence in nanostructures, we did studies in the dimensional crossover in CdSe nanowires. One may intuitively expect that reducing the length of a nanoscale systems confining potential gradually induces the emergence of quantum confinement ([33] [21] [48]) effects in its spectroscopic response. This crossover is expected to be smooth, without the appearance of a critical length. However, the presence of interactions fundamentally alters this picture of dimensional crossover in many-particle systems. Several low-dimensional systems, in fact, show interaction-induced phases of manner absent in higher dimensions. They include fractional quantum Hall states in two dimensions[46], Tomonaga-Luttinger liquids in one-dimension (1D)[17] and Kondo effects in zero-dimensional (0D) quantum dots (QDs)[22].

In my collaborative work with the Kuno group[32], we demonstrated that analogous many-particle interactions dictate the 1D-to-0D dimensional crossover in low-dimensional semiconductors, as illustrated in Fig. 10.1.

In this study, members of the Kuno group directly probed the 1D-to-0D transition using the single nanowire (NW)/nanorod (NR) absorption spectroscopy to eliminate ambiguities as to the actual evolution of electronic structure across dimensionality. It is discovered by the measurement that, there exists a critical length, where the behavior of the exciton in the nanostructure transforms from 1D to 0D. The critical length discovered in this study is at the order of the bulk exciton Bohr radius, which is much shorter than the predicted values in previous studies.[55]
Figure 10.1. One-dimensional to zero-dimensional crossover of a semiconductor nanowires electronic structure. Top row: structural evolution of a nanowire into a quantum dot. Middle row: corresponding evolution of nanowire and nanorod electron and hole wavefunctions. Bottom row: a plot depicting the interplay between aspect ratio-dependent carrier confinement, $E_k(b)$ and dielectric contrast/dielectric confinement electrostatic energies, $|U|$.\[32\]
In the experiment, they used the spatial modulation microscopy, which entails modulating an NW/NR’s position in and out of a focused laser beam. Subsequent lock-in detection measures the transferred transmitted laser power modulation, which relates to individual nanostructure extinction cross-sections.

Figure 10.2 shows the absorption spectrum of (a) CdSe NW from an ensemble of diameter \(d = 6.8 \pm 1.2 \text{nm}\) with length \(b > 5 \mu\text{m}\), CdSe NR from ensembles of (b) \(d = 6.7 \pm 1.1 \text{nm}\) with \(b = 160 \pm 55 \text{nm}\) and (c) \(d = 6.8 \pm 0.7 \text{nm}\) with \(b = 30.4 \pm 2.6 \text{nm}\).

In all the spectra, three to four transitions are apparent and they are labeled as \(\alpha, \beta, \gamma\) and \(\delta\). These transitions are excitonic in nature as predicted by a model that explicitly accounts for both spatial confinement and enhanced electrostatic interactions in NRs[40], which can be directly related to analogous \(\alpha, \beta, \gamma\) and \(\delta\) transitions in individual CdSe NWs ([14], [51], [30]).

There are notable blueshifts in the \(\alpha\) transitions in the \(b \sim 30\text{nm}\) NRs compared to the longer NRs and NWs: \(\alpha = 1.904 \pm 0.025\text{eV}\) for \(b \sim 30\text{nm}\), while \(\alpha = 1.872 \pm 0.016\text{eV}\) for \(b \sim 160\text{nm}\) and \(\alpha = 1.874 \pm 0.016\text{eV}\) for \(b > \mu\text{m}\). We explained the blueshift via the contribution of both electronic confinement and electrostatic contributions. The confinement contribution has been well established in the previous work ([14], [51], [30]). My work mainly focuses on the electrostatic contributions.

First, the excitonic transition is determined by the interaction between the excited electron and the corresponding hole in the NR/NWs. The electron wavefunction can be simply described as

\[
\psi_{n,\pm, \pm, m} = \frac{u_{n, \pm, 1/2}}{a \sqrt{\frac{\pi b}{2}}} J_m \left( \frac{\alpha_{n,m} a}{b} \rho \right) sin \left( \frac{n_z \pi}{b} z + \frac{m \phi}{b} \right) e^{im\phi},
\]

where \(u_{\pm,1/2}\) is the electron Bloch function, \(a\) is the NW/NR radius, \(b\) is the corresponding length, \(J_m(x)\) are Bessel functions of the first kind and \(\alpha_{n,m}\) is the \(n\)th root of the \(m_{th}\) order Bessel function. Parameters \((n, n_z, m)\) are radial, longitudi-
Figure 10.2. The absorption spectrum of (a) NWs with length \((b > 5\mu m)\), (b) NRs with \(b \sim 160nm\), (c) NRs with \(b \sim 30nm\). Blue open symbols represent measured extinction values plotted as a function of wavelength \((\lambda)\). Spectra are fit to a sum of Gaussians (black dashed line) from where individual transitions (grey dashed lines) are extracted. The insets are each samples sizing histograms.
nal and angular quantum numbers, respectively. The hole wavefunctions are linear combinations of effective heavy-hole $|HH\rangle_{1(2)}$ and light-hole $|LH\rangle_{1(2)}$ states, given by

$$\psi_h^{F_z,n_z} = A|HH\rangle_1 + B|HH\rangle_2 + C|LH\rangle_1 + D|LH\rangle_2,$$  \hspace{1cm} (10.2)

where $A, B, C$ and $D$ are their relative weights; $F_z$ is the angular momentum projection onto the NW/NR z-axis. The confinement contribution in the blueshifts from NWs to NRs comes from the quantum number $n_z$, i.e. longitudinal confinement.

However, for the shortest NRs with $b = 30\text{nm}$, only $\sim 3\text{meV}$ increase is predicted from the mere $z$-axis confinement, which is not enough to explain the blueshift observed. To explain the discrepancy in this predicted blueshift value, we studied the electrostatic contributions. The electrostatic contribution can be further divided into two parts. The first is the dielectric contrast from the dielectric constant $\epsilon$. The differences in $\epsilon$ between the material and its surroundings. The second part is the dielectric confinement, which is because of the repulsive 'mirror' forces at the particle/medium dielectric interface. To explicitly account for how CdSes electronic structure transitions from 1D to 0D, we model these electrostatic effects as a function of NW/NR aspect ratio ($b/d$). Details about the usage of Green’s function and mirror image methods we utilized can be found in Appendix D. The modified electrostatic energy for the electron-hole pair can be described as

$$U(r_e, r_h) = \frac{q^2}{4\pi \epsilon_0 |r_e - r_h|} - qV(r_e, r_h) + \frac{q}{2}V(r_e, r_e) + \frac{q}{2}V(r_h, r_h),$$  \hspace{1cm} (10.3)

where $r_e = (r_e, \phi_e, z_e)$ ($r_h = (r_h, \phi_h, z_h)$) is the electron (hole) position, and $q$ is the elementary charge. The first two terms in Eq. (10.3) represent direct and indirect attractive forces between an electron and a hole in a NR. The last two terms correspond to repulsive forces induced by mirror charges at NR/medium dielectric boundaries. Then Eq. (10.3) is averaged by integrating over the electron and hole.
wavefunctions. This reduces $U(r_e, r_h)$ to a 1-D potential, a function of $|z_e - z_h|$ only. Then the reduced 1-D interaction term $V_{\text{att}}^{e,h}(|z_e - z_h|)$ is used as the potential energy term in the 1D exciton Schrödinger equation.\[14]\]

Figure 10.3 shows the excellent agreement of the predicted transition energy (blue and green) and the measured transition energy (red dots with error bars) of the $\alpha$ exciton. The green dashed line is the $1\sum_{3/2} 1\sum_e$ transition and the blue solid line is the $1\sum_{1/2} 1\sum_e$. Notice that $1\sum_{1/2} 1\sum_e (1\sum_{3/2} 1\sum_e)$ is predicted to be bright under the parallel (perpendicular) polarized light. Consequently, in previous works $\alpha$ in CdSe NWs is assigned to the $1\sum_{1/2} 1\sum_e$ exciton (\[14\], \[51\] and \[30\]). In QDs, $\alpha$ arises from $1\sum_{3/2} 1\sum_e (1S_{3/2}1S_e$ in QD literature) (\[5\], \[35\]). The $\alpha$ assignment therefore shifts from $1\sum_{1/2} 1\sum_e$ to $1\sum_{3/2} 1\sum_e$ with decreasing aspect ratio due to a $b/d$-dependent transition strength. Figure 10.3 denotes this through $1\sum_{1/2} 1\sum_e / 1\sum_{3/2} 1\sum_e$ curve transparencies.

Now, we list out all sources of contributions to the exciton energy in the NW/NR, as shown in Fig. 10.4. The aspect ratio-dependent energies include the longitudinal kinetic confinement ($E_k(b)$) and the electrostatic energy ($U$), while the radical kinetic confinement ($E_k(\rho)$) stays constant given a constant radius, as shown in Fig. 10.4(c) (d). The electrostatic energy contains the dielectric confinement and dielectric contrast terms as defined above. As shown in Fig. 10.4(a) (b), the whole aspect ratio region can be divided into two areas, marked by white and grey in the figure, by the value at which $E_k(b) = |U|$. This is the critical length that the 1D-to-0D transition happens. When the length is over the critical length, the electrostatic energy is in a predominant position compared to the kinetic confinement. When the length is below the critical length, the kinetic confinement contributes more into the blueshift.

In $d \sim 6.8\,\text{nm}$ CdSe, this critical length is $b \sim 8.5\,\text{nm}$, which is just above its bulk exciton Bohr radius ($a_B = 5.6\,\text{nm}$). In $d \sim 4\,\text{nm}$ and $d \sim 10\,\text{nm}$ CdSe, this critical lengths are $b \sim 6\,\text{nm}$ and $b \sim 11\,\text{nm}$ respectively. These findings differ from previous
Figure 10.3. Evolution of CdSe nanoparticle optical properties across dimensionality. Extracted (average) α energies plotted as a function of aspect ratio (b/d) for all three wire/rod samples (solid red circles) as well as tabulated quantum dot literature values (open square) \((d = 6.8\, \text{nm})\)\(^{21}, \, 56\) and \(^{25}\). The open red triangle is the bB30 nm ensemble spectrum α energy. The blue solid line is the theoretical line for the first \((1 \Sigma_{3/2}^1 \Sigma_{e}^1)\) 1-D exciton. The green dashed line is the theoretical line for the second \((1 \Sigma_{1/2}^1 \Sigma_{e}^1)\) 1-D exciton. \(^{40}\). The transparency of the blue line represents the relative transition strength compared to the green line exciton.
studies which suggest the transition length of \( b \geq 30 \text{nm} \) for \( d = 3 - 6 \text{nm} \) CdSe NRs,\cite{ref55} which can be well explained for the evolution of the relative magnitude between \( E_k(b) \) and \( U \) we discussed above.
Figure 10.4. Evolution of different sources of contributions to the exciton energy with respect to the aspect ratio for $d \sim 6.8 \text{nm}$ NW/NR. (a) (b) Evolution of the longitudinal kinetic energy, $E_k(b)$ (dashed black line) and the absolute net electrostatic energy, $|U|$ (solid red line). White and grey areas represent regions of 0D and 1D confinement respectively. (c) (d) Evolution of the radial kinetic confinement $E_k(\rho)$ (dotted green line), the longitudinal kinetic energy, $E_k(b)$ (dashed black line), the dielectric contrast (solid pink line) and the dielectric confinement (dash-dot-dot blue line) contributions.
In this dissertation I first studied and discussed the fluorescence intermittency of GO/rGO. The blinking in GO/rGO is the first time that fluorescence intermittency is observed in a 2-D system. Both blinking and graphene-related systems are of great importance from the point of view of fundamental and applied research. Understanding the mechanism of blinking is essential in the development of a wide variety of fluorophores for applications as biomarkers, single photon sources, optoelectronic circuit elements. Blinking is an intriguing property of fluorophores due to the existence of long off time in the emission trajectory. Many common properties are shared by a wide variety of nanostructures, ranging from self-assembled/colloidal quantum dots and perylene diimide molecules to nanowires, nanorods and even nanoplatelets. These properties as we mentioned are: (1) power law distributions of ON and OFF duration times, (2) exponential truncation at long times in ON duration, (3) no significant temperature and size dependence, (4) strong threshold dependence of the ON and OFF time distributions, (5) correlation between subsequent ON and OFF times, and (6) 1/f-like power spectral density.

Graphene and related materials have received a great amount of interest in the last decades. I presented an overview of the basic properties and the preparation of graphene and graphene oxide. Hummers method is used in the GO specimen in Kunos experiments on the laser induced reduction of GO to rGO[31] [43].

As mentioned above, the traditional analysis based on a definition of ON and OFF states in blinking has major flaws: the ON and OFF duration as well as ON
truncation time have a strong dependence of the choice of the threshold. To analyze the blinking phenomenon in GO/rGO, we utilized the well-established PSD analysis independent on the choice of threshold value. Despite the 2D nature of the GO/rGO system, the PSD also share the 1/f-like behavior with other blinking systems. One feature that makes the GO/rGO blinking special is its dynamical evolution in the power law exponent $\alpha$ of the PSD. We sectioned the trajectories into smaller intervals to investigate this evolution and discovered that $\alpha$ ranges from 0.2 to 0.9 at different stages of the reduction of rGO. We proposed that $\alpha$ can be used as an indicator of the blinking in GO/rGO trajectory.

The 2D characteristics of GO/rGO are nevertheless present, as our data shows multiple blinkers contributing to the signal registered within one pixel. New and unique to GO/rGO blinking is our detection of direct, time-delayed correlations between the changes in the background intensity and the emergence/disappearance of blinking.

The phenomenological MRC model has been proven to be successful in reproducing the key features of the blinking we mentioned above. We utilized this model to obtain the RC switching rates. We propose that functionalized $sp^2$ domains in GO/rGO behave as single molecules and that functional groups act as dynamic RCs.

To investigate the microscopic mechanisms behind the blinking, the kinetic MC method and DFT/TDDFT calculations was utilized to simulate the absorption and emission trajectories[38]. Detaching of $-\text{OH}$, $\text{C}-\text{O}-\text{C}$ and single carbon atoms from the oxygen functionalized carbon network was implemented in the MC simulation. The modeling successfully explains the experimentally observed emission/absorption trajectories with strong temporal variations. The PSD analysis shows that the simulation shares the universal characteristic of power-law PSD as seen in other intermittency emitters. This further strengthens our proposal that the RCs in GO/rGO are related to the functionalized $sp^2$ domains.
Finally, we also pursued a project aimed at understanding the effect of the dimensionality on the fluorescence in nanostructures. The 1D-to-0D transition in the absorption spectrums of CdSe nanowires and nanorods was measured by the Kuno group. The length of the nanostructures ranged from $b > 5\mu m$ to $b = 30nm$ with diameters around 6.8nm. There is a clear blue shift in the exciton energy that cannot be simply explained by the confinement along the longitudinal axis. We proposed a modified 4-band effective mass model that takes into account the electrostatic effect caused by the difference in the dielectric constants of CdSe and its surroundings. The predicted exciton energy excellently matches the experimental value. This study shows that the electrostatic contribution governs the modification of exciton energy in the 1D-to-0D dimension crossover and that there is a critical length where the 1D-to-0D transition occurs.
Let us describe the intensity throughout the surface of the GO specimen as $I(r, t)$, where $r$ is the position of a point on the 2-D surface, and $t$ is the time. Since the dimension of the specimen captured by the CCD camera pixel is $0.16\mu m \times 0.16\mu m$, which is very large compared to the lattice constant $1.42\AA$, we can assume that the intensity distribution can be described as a continuous function of $r$.

When there is no intrinsic spatial correlations in $I(r, t)$, we have

$$\langle I_0(r_1, t)I_0(r_2, t + t') \rangle = constant. \quad (A.1)$$

The $CPSD(r_1, r_2)$ should be 0 under the definition of Eq. (7.8).

Now let us take the account of diffraction into account. Because of the diffraction effect will make the intensity distribution detected by the CCD camera to be

$$I(r, t) = \int d'r' I_0(r', t) F(r - r'), \quad (A.2)$$

where $F(r - r')$ describes the Fraunhofer diffraction pattern. For a circular aperture in our case, it is the Airy disk

$$F(x) = \frac{2J_1(kasin\theta)}{kasin\theta} = \frac{2J_1(x)}{x}, \quad (A.3)$$

where $J_1(x)$ is the Bessel function of the first kind of order one, $k = \frac{2\pi}{\lambda}$ is the wavenumber, $a$ is the radius of the aperture and $\theta$ is the angle of observation. The
diameter of the first dark ring is:

\[ q_1 = 1.22 \ast \beta \ast \frac{\lambda}{NA} = 22.6 \mu m, \quad (A.4) \]

with numerical aperture \((NA = 1.4)\), wavelength \(\lambda = 520 \text{ nm}\), magnification \(\beta = 100\) for our case.

In our calculation, the 2-D Gaussian function was used as an approximation of Eq. \((A.3)\).  

\[
F(q) = \exp(\frac{-q^2}{2\sigma^2}), \quad (A.5)
\]

where \(\sigma = 0.42 \ast \beta \ast \frac{\lambda}{NA} = 7.78 \mu m\).

Now the \(CPSD(r_1, r_2)\) can be calculated as

\[
CPSD_{r_1, r_2}(\omega) = \int dT \langle \int dr' I_0(r', t) F(r_1 - r') \int dr'' I_0(r'', t + T) F(r_2 - r'') \rangle e^{-i\omega T} \\
= \int dT \langle \int dr' I_0(r', t) F(r_1 - r') \int dr'' I_0(r'', t + T) F(r_2 - r'') \rangle e^{-i\omega T} \delta(r' - r'') \\
= \int dT \langle I_0(r', t) \rangle \langle I_0(r', t + T) \rangle e^{-i\omega T} \int dr' dr' F(r_1 - r') F(r_2 - r') \].
\quad (A.6)

Notice that here we used Eq. \((A.1)\), that is, \(\delta(r' - r'')\) is introduced since only when the components in \(I(r_1, t)\) and \(I(r_2, t + T)\) come from the same origin, their product contributes non-trivial components in \(CPSD\).
Similarly the detected PSD of one specific point can be expressed as

\[ PSD_{r_1, r_1}(\omega) = \int dT \int dr' I_0(r', t) F(r_1 - r') \int dr'' I_0(r'', t + T) F(r_1 - r'') e^{-i\omega T} \]

\[ = \int dT \langle I_0(r', t) I_0(r'', t + T) \rangle e^{-i\omega T} \int dr' \int dr'' F(r_1 - r') F(r_1 - r'') \delta(r' - r'') \]

\[ = \int dT \langle I_0(r', t) \rangle \langle I_0(r', t + T) \rangle e^{-i\omega T} \int dr' F(r_1 - r') F(r_1 - r'). \quad (A.7) \]

Notice the common part \( \int dT \langle I_0(r', t) I_0(r', t + T) \rangle e^{-i\omega T} \) in the first line of both Eq. (A.6) and (A.7). Together with the definition of \( SC \) in Eq. (7.7) and the assumption that \( I_0(r', t) \) is homogeneously stable, they will cancel each other in the calculation of the normalized spatial correlation.

Because the CCD camera does not have infinite precise resolution, in order to get the correlation between two pixels, we need to integrate over the range of one pixel for both \( r_1 \) and \( r_2 \) in Eq. (A.6) and (A.7), which leads to the final definition of \( CPSD_{x_1, x_2}(\omega) \) and \( PSD_{x_1, x_1}(\omega) \) as

\[ CPSD_{x_1, x_2}(\omega) = \int dT \int_{x_1} dr_1 \int_{x_2} dr_2 \langle I_0(r', t) \rangle \langle I_0(r', t + T) \rangle e^{-i\omega T} \int dr' dr' F(r_1 - r') F(r_2 - r'). \quad (A.8) \]

\[ PSD_{x_1, x_1}(\omega) = \int dT \int_{x_1} dr_1 \int_{x_2} dr_2 \langle I_0(r', t) \rangle \langle I_0(r', t + T) \rangle e^{-i\omega T} \int dr' F(r_1 - r') F(r_2 - r'). \quad (A.9) \]

With the pixel size of \( x_1 \) and \( x_2 \) set as \( 0.16\mu m \times 0.16\mu m \), by evaluating Eq. (A.8) and Eq. (A.9), \( x_1 \) and \( x_2 \) at areas at different distance, we can calculate the theoretical spatial correlations with from mere diffraction.
APPENDIX B

CHI-SQUARED DISTRIBUTION AND TEST

The chi-squared distribution can be defined as: if $Z_1, Z_2, \ldots, Z_k$ are independent, standard normal random variables, then the sum of their squares

$$Q = \sum_{i=1}^{k} Z_i^2$$

follows the chi-squared distribution with $k$ degrees of freedom, i.e.

$$Q \sim \chi^2_k.$$  \hspace{1cm} (B.1)

This means as under the assumption that the PSD $S(\omega)$ values are independent from each other at different frequency $\omega$, the null hypothesis that 'S\text{theoretical} reproduces the real PSD $S_{\text{real}}$' can be tested by the CDF of the chi-squared distribution with proper degrees of freedom. The experimental PSD $S_{\text{experimental}}$ can be described as

$$S_{\text{experimental}} \sim S_{\text{real}} + N(0, \delta_{\text{real}}),$$

(B.3)

where $N(0, \delta_{\text{real}})$ is the real standard deviation of the $S_{\text{experimental}}$. We are going to use the calculated experimental standard deviation $\delta_{\text{experimental}}$ as the best estimation of $\delta_{\text{real}}$.

And this leads to the hypothesis that the statistic in Eq. (8.2) follows the chi-squared distribution with $N$ degrees of freedom. The one-sided test rejects the null
hypothesis when the statistic goes larger than the value that makes

\[ CDF(\epsilon)_N > \alpha, \]  

(B.4)

where \( \alpha \) is the significance of the test.
APPENDIX C

PROOF OF WIENER-KHINCHIN THEOREM

The power spectral density of the time-dependent emission intensity \( x(t) \) can be defined as the Fourier transform \( S_{xx}(\omega) \) of the auto-covariance function:

\[
S_{xx}(\omega) = \int_{-\infty}^{+\infty} \langle x(t)x(t-T) \rangle e^{-i\omega T} dT. \tag{C.1}
\]

According to the Wiener-Khinchin theorem, this definition is equivalent to the square of Fourier transformation of \( x(t) \). Given the trajectory is stationary,

\[
S_{xx}(\omega) = \int_{-\infty}^{+\infty} dT \langle x(t)x(t-T) \rangle e^{-i\omega T}
= \int_{-\infty}^{+\infty} dT \lim_{T' \to \infty} \frac{1}{2T'} \int_{-T'}^{+T'} dt \ x(t)x(t-T)e^{-i\omega T}
= \int_{-\infty}^{+\infty} dT \lim_{T' \to \infty} \frac{1}{2T'} \int_{-T'}^{+T'} dt \ x(t)x(t-T)e^{+i\omega(t-T)}e^{-i\omega t}
= \int_{-\infty}^{+\infty} d(T-t)x(t-T)e^{+i\omega(t-T)} \lim_{T' \to \infty} \frac{1}{2T'} \int_{-T'}^{+T'} dt \ x(t)e^{-i\omega t}
= \lim_{T' \to \infty} \frac{1}{2T'} F(\omega)^* F(\omega) \tag{C.2}
\]

where \( F(\omega) = \lim_{T' \to \infty} \frac{1}{2T'} \int_{-T'}^{+T'} dt x(t)e^{-i\omega t} = \int_{-\infty}^{+\infty} d(T-t)x(t-T)e^{-i\omega(t-T)} \).
APPENDIX D

ELECTROSTATIC CONTRIBUTIONS

To account for the electrostatic contribution in exciton energy. Ideally, we should solve the Green’s function for the system of the nanorod:

\[
\nabla^2 V(r, r_0) = \frac{q}{\varepsilon \varepsilon_0} \delta(r - r_0) \quad r \text{ inside nanorod}
\]

\[
\nabla^2 V(r, r_0) = 0 \quad r \text{ outside nanorod}
\]

with boundary conditions that:

\[

\left. \frac{\partial V(r, r_0)}{\partial r} \right|_{r=\text{interface}^-} = \left. \frac{\partial V(r, r_0)}{\partial r} \right|_{r=\text{interface}^+} \quad \varepsilon
\]

\[

V(r, r_0)|_{r=\text{interface}^-} = V(r, r_0)|_{r=\text{interface}^+},
\]

where \textit{interface} indicates the interface surface between the nanorod and the surrounding material.

However, direct analytical solution of Eq. (D.1) to Eq. (D.4) is not an easy task. Here we modify the solution for the infinitely long nanowire case to solve the problem. The equations and boundary conditions goes like:

\[
\nabla^2 V(r, r_0) = \frac{q}{\varepsilon \varepsilon_0} \delta(r - r_0) \quad \rho \leq a
\]
\[ \nabla^2 V(r, r_0) = 0 \quad \rho \geq a \tag{D.6} \]

with boundary conditions that:

\[ \varepsilon \frac{\partial V(r, r_0)}{\partial r} \bigg|_{\rho=a_-} = \epsilon_m \frac{\partial V(r, r_0)}{\partial r} \bigg|_{\rho=a_+} \tag{D.7} \]

\[ V(r, r_0)|_{\rho=a_-} = V(r, r_0)|_{\rho=a_+}. \tag{D.8} \]

where \( q \) is the elementary charge, \( a \) is the radius of infinitely long nanowire. \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon \) is the NWs dielectric constant, \( \epsilon_m \) is the surroundings dielectric constant.

The solution of Eq. (D.5) to Eq. (D.8) is

\[ V(r, r_0) = \frac{q}{4\pi \varepsilon \varepsilon_0 |r - r_0|} + \frac{q}{2\pi^2} \sum_{g=-\infty}^{\infty} \int_{0}^{\infty} du e^{ig(\phi - \phi_0)} \cos(u(z - z_0)) \gamma_g I_g(ua) I_g(upa_0), \tag{D.9} \]

where

\[ \gamma_g = \frac{(\varepsilon - \epsilon_m)K_g'(ua)K_g(ua)}{\epsilon_m I_g(ua)K_g'(ua) - \epsilon I_g(ua)K_g(ua)}. \tag{D.10} \]

\( I_g(x) \) and \( K_g(x) \) are modified Bessel functions of the first and second kind, respectively. In Eq. (D.9), integer \( g \) and integration variable \( u \) come about from the Greens function expansion (more information can be found in section 3.10 of Jackson's Classical Electrodynamics\[19\]).

The electrostatic energy of an electron and hole inside the NW is given by\[14\]

\[ U(r_e, r_h) = \frac{1}{2} \int_{-\infty}^{\infty} dr (q\delta(r - r_e) - q\delta(r - r_h))(V(r, r_e) - V(r, r_h)). \tag{D.11} \]
Now in order to modify the solution Eq. \(\text{(D.10)}\) for the nanorod case. We propose the set up shown in Fig. \(\text{D.1}\). First, the infinite cylinder is segmented into three regions along its length, \(z < 0\), \(0 < z < b\), and \(z > b\). These segments are assigned dielectric constants of \(\epsilon_m(z < 0)\), \(\epsilon(0 < z < b)\), and \(\epsilon_m(z > b)\).

Then we utilize the mirror image method to account for the effect of boundary at \(z = 0\) and \(z = b\). Here, mirror image charges (red dots, \(q_{i}^{(n)}\)) are placed at \(r_{i}^{(n)} = (0, \phi_0, z_{i}^{(n)})\) relative to the point charges position (black dot) at \(r_0 = (\rho_0, \phi_0, z_0)\) within the NR. Since there are two planes, two images (indexed by \(i = 1, 2\)) are set for a specific order \(n\). The order indicates the sequence of ’imaging’, i.e. \(q_{i}^{(n)}\) is the image charge of \(q_{i}^{(n-1)}\) with respect to plane \(I (Z = 0 \text{ and } z = b)\). This naturally leads to the magnitude of image charges to be

\[
q_i^{(n)} = \left( -\frac{\epsilon_m - \epsilon}{\epsilon_m + \epsilon} \right)^n q. \tag{D.12}
\]
Now we can combine these altogether and get the modified solution to be:

\[ V_{b<\infty}(r, r_0) = V(r, r_0) + \sum_{n,i} V_i^{(n)}(r, r_i^{(n)}), \quad (D.13) \]

where \( V_i^{(n)}(r, r_i^{(n)}) \) can be gotten simply by putting \( r_i^{(n)} \) and \( q_i^{(n)} \) in to the position of \( r_0 \) and \( q \) in Eq. (D.9). Inserting Eq. (D.13) into Eq. (D.11) gives us the electrostatic energy of a pair of point electron and hole charge inside a finite length nanowire.

\[ U(r_e, r_h) = U_e^{(0)}(r_e, r_h) + U_h^{(0)}(r_e, r_h) + U_{dir}^{(0)}(r_e, r_h) + U_{indir}^{(0)}(r_e, r_h), \quad (D.14) \]

where explicitly

\[ U_e^{(0)}(r_e, r_h) = U_e^{(0)}(r_e) + U_h^{(0)}(r_h) + U_{dir}^{(0)}(r_e, r_h) + U_{indir}^{(0)}(r_e, r_h) \quad (D.15) \]

\[ U_e^{(0)}(r_e) = \frac{q^2}{4\pi^2} \sum_{g=-\infty}^{\infty} du \gamma_g I_g(u\rho_e)^2 \quad (D.16) \]

\[ U_h^{(0)}(r_e) = \frac{q^2}{4\pi^2} \sum_{g=-\infty}^{\infty} du \gamma_g I_g(u\rho_h)^2 \quad (D.17) \]

\[ U_{dir}^{(0)}(r_e, r_h) = -\frac{q^2}{4\pi^2\epsilon\epsilon_0|r_e - r_h|} \quad (D.18) \]

\[ U_{indir}^{(0)}(r_e, r_h) = -\frac{q^2}{4\pi^2} \sum_{g=-\infty}^{\infty} du \cos(u|z_e - z_h|) \gamma_g I_g(u\rho_e) \gamma_g I_g(u\rho_h) \quad (D.19) \]

Similarly,
\[ U_i^{(n)}(r_e, r_h) = U_e^{(n)}(r_e) + U_h^{(n)}(r_h) + U_{dir}^{(n)}(r_e, r_h) + U_{indir}^{(n)}(r_e, r_h). \]  

(D.20)

We can combine the self-energy and interaction terms respectively in Eq. (D.14). That is: (1) the electron self-energy

\[ U_e^{(0)}(r_e) + \sum_{n,i} U_i^{(n)}(r_e) \]  

(D.21)

(2) the hole self-energy

\[ U_h^{(0)}(r_h) + \sum_{n,i} U_i^{(n)}(r_h) \]  

(D.22)

(3) the direct Coulombic attraction

\[ U_{dir}^{(0)}(r_e, r_h) + \sum_{n,i} U_{dir}^{(n)}(r_e, r_h) \]  

(D.23)

(4) the indirect Coulombic attraction

\[ U_{indir}^{(0)}(r_e, r_h) + \sum_{n,i} U_{indir}^{(n)}(r_e, r_h). \]  

(D.24)

Term (3) and (4) represents the attraction interaction between the electron-hole pair. Now if we integrate the summation of term (3) and (4) multiplied the wavefunctions of electron and hole in the semiconductors. We can get a function that only depends
on $|z_e - z_h|$

\[ V_{\text{att}}^{e,h}(|z_e - z_h|) = \int_0^a \rho_e d\rho_e \int_0^a \rho_h d\rho_h \int_0^{2\pi} d\phi_e \int_0^{2\pi} d\phi_h |\psi_{e,z_{1/2}}^{n,n_z,m} |^2 |\psi_{h}^{F_z,n_z}|^2 \]

\[ (U_{\text{dir}}^{(0)}(r_e, r_h) + U_{\text{indir}}^{(0)}(r_e, r_h)) + (U_{\text{dir}}^{(n)}(r_e, r_h) + U_{\text{indir}}^{(n)}(r_e, r_h)). \]

(D.25)

The first two integrands in Eq. (D.25) is further handled in the method in ref. [14], which is used to solve the exciton energy in an infinitely long nanowire system, and last two integrands are treated as a perturbation.


50. F. VIETMEYER, S. VOLKAN-KACSO, P. FRANTSUZOV, M. KUNO, and B. JANKO. Fluorescence imaging: Understanding fluorescence blinking is the first path to an imaging solution.


