Interfacial charge transfer processes between single molecules and nanoparticles

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**INTERFACIAL CHARGE TRANSFER PROCESSES
BETWEEN SINGLE MOLECULES AND
NANOPARTICLES**

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SCHOOL OF PHYSICAL & MATHEMATICAL SCIENCES
NANYANG TECHNOLOGICAL UNIVERSITY
2011**

**Interfacial Charge Transfer Processes between
Single Molecules and Nanoparticles**

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LIST OF ABBRECIATIONS

ADC	analog-to-digital converter
BET	backward electron transfer
BME	β -mercaptoethanol
CB	conduction band
CB7	cucurbit[7]uril
CCD	charge coupled device
CTRW	continuous-time random walk
CTAB	cetyltrimethylammonium bromide
DSSC	dye-sensitized solar cells
FET	forward electron transfer
FHT	forward hole transfer
HBT	Hanbury-Brown-Twiss
ICT	interfacial charge transfer
IRF	instrument response function
ITO	indium tin oxide
NHE	normal hydrogen electrode
NSOM	near-field scanning optical microscopy
PALM	photoactivated localization microscopy
QD	quantum dot
QDSSC	quantum dot-sensitized solar cells
Rh6G	rhodamine 6G
SC	semiconductor
SEF	surface-enhanced fluorescence

SERS	surface-enhanced raman scattering
SMS	single-molecule spectroscopy
SPAD	single-photon avalanche diode
STED	stimulated emission depletion
STORM	stochastic optical reconstruction microscopy
T3R	time-tagged time-resolved
TAC	time-to-amplitude converter
TCSPC	time-correlated single photon counting
TPD	<i>N,N'</i> -diphenyl- <i>N,N'</i> -(<i>m</i> -tolyl)-benzidine
VB	valence band

PUBLICATIONS

1. **Wu, X.**; Yeow, E. K. L. Fluorescence blinking dynamics of silver nanoparticle and silver nanorod films. *Nanotechnology* **2008**, *19*, 035706.
2. **Wu, X.**; Bell, T. D. M.; Yeow, E. K. L. Electron transport in the long-range charge-recombination dynamics of single encapsulated dye molecules on TiO₂ nanoparticle films. *Angewandte Chemie-International Edition* **2009**, *48*, 7379-7382.
3. **Wu, X.**; Yeow, E. K. L. Charge-transfer processes in single CdSe/ZnS quantum dots with p-type NiO nanoparticles. *Chemical Communications* **2010**, *46*, 4390-4392.
4. **Wu, X.**; Yeow, E. K. L. Heterogeneous interfacial hole transfer dynamics from dye molecules to p-type NiO nanoparticles. **2011**, in preparation.

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5. **Wu, X.**; Yeow, E. K. L. (**November 2010, Poster**) Charge-transfer processes in single CdSe/ZnS quantum dots with p-type NiO nanoparticles. The 6th Asian Photochemistry Conference, Victoria University of Wellington, New Zealand.

SUMMARY

This work investigates the dynamics of interfacial charge transfer between single organic dye molecules/quantum dots (QDs) and semiconductors (*e.g.*, metal oxides, organic molecular solids). Our aim is to understand the heterogeneity in interfacial charge transfer dynamics and to design methods to retard charge-recombination. We will characterize the interfacial charge transfer dynamics *via* ensemble-averaged and single-molecule spectroscopy.

In Chapter 1, we briefly introduce the parameters which can crucially influence the interfacial charge transfer process occurring in photovoltaic devices. The recent progress of using single-molecule spectroscopy to examine interfacial charge transfer dynamics will be reviewed. At the end of this chapter, the fluorescence blinking dynamics of noble-metal nanostructures is briefly discussed.

In Chapter 2, heterogeneous interfacial hole transfer (IHT) dynamics in Atto647N sensitized p-type semiconductors (*e.g.*, NiO, *N,N'*-diphenyl-*N,N'*-(*m*-tolyl)-benzidine (TPD)) are investigated using both time-resolved ensemble-averaged and single-molecule spectroscopy techniques. In Atto647N-sensitized p-type NiO nanoparticle (NP), the rate of IHT is dependent on the processing conditions and is enhanced when the oxygen concentration used during annealing of the NiO is increased. This is attributed to an upward shift of the valence band of the semiconductor and an increase in the driving force for IHT. Heterogeneous IHT dynamics of Atto647N on NiO NP possibly originates from an inhomogeneous distribution of (defect) sites on the metal oxide due to the processing conditions. In the study of hole transfer dynamics from Atto647N to TPD molecules, fluorescence quenching in chloroform solution occurs by

diffusion followed by hole transfer. About 60% of collisional events are effective in quenching. Heterogeneous hole transfer dynamics from single Atto647N molecules to TPD doped polystyrene film are observed, indicating that the reactivity of hole transfer temporally fluctuates and varies among different molecules.

In Chapter 3, we have investigated the interplay between radiative relaxation of exciton, ionization and charge-transfer in CdSe/ZnS QDs - sensitized p-type NiO NP using single-molecule fluorescence microscopy. Charge-transfer processes between single QDs and NiO NPs result in fluorescence intensity and lifetime quenching, suppression of blinking behavior and blueing effect, and enhancement of the QD's survival time.

In Chapter 4, the interfacial electron transfer and subsequent charge-recombination between single Atto647N molecules and TiO₂ NP and between single cucurbit[7]uril encapsulated Atto647N molecules and TiO₂ NP are studied. Power-law distributions for the lifetimes of the dark charge-separated states are obtained. This is attributed to the broad time range taken for the injected electron to diffuse between traps on the TiO₂ NP before undergoing back electron transfer (BET) to the oxidized dye. A significantly smaller power-law exponent for the inclusion complex suggests that the spatial separation, created by the macrocyclic host, between the dye molecule and metal oxide results in a slower BET rate and a longer electron transport process. Computational simulations based on the continuous-time random walk are used to model the electron transport process, and the power-law exponent values obtained from the computational simulations are consistent with the experimental observations.

In Chapter 5, fluorescence blinking dynamics of single silver nanoparticles are investigated. The observed power-law off-time distribution is attributed to random surface diffusion and subsequent agglomeration of atomic Ag leading to the formation of photo-active Ag nanoclusters. These nanoclusters can in turn diffuse randomly to form non-emitting Ag clusters after aggregation with another Ag species. This is revealed in the power-law on-time distribution. Silver oxides found on the surfaces of Ag nanostructures are important for photoblinking to take place since silver nanostructures with a protective layer of polymeric citrate or CTAB against atmospheric O₂ do not display the obvious blinking behavior.

CHAPTER 1

GENERAL INTRODUCTION

1.1 Motivation

Single-molecule spectroscopy (SMS) has emerged as a simple and efficient technique to study complicated dynamics in chemical and biological systems at the single-molecule level and offers useful information which cannot be obtained from ensemble-averaged measurements.¹⁻⁶ Recently, SMS has been utilized to investigate interfacial and intra (or inter)-molecular charge transfer processes which play pivotal roles in extensive applications, such as molecular electronics, photocatalysis, and solar/photovoltaic cells.⁶⁻²³ In particular, interfacial charge transfer (ICT) process between photosensitizer (*e.g.*, organic dye molecule and quantum dot (QD)) and metal oxide semiconductor nanoparticle is the fundamental process occurring in dye-sensitized solar cells (DSSC) and quantum dot-sensitized solar cells (QDSSC).²⁴⁻²⁸ In order to design efficient devices for energy conservation and conversion, it is of importance to understand the mechanism and dynamics of ICT. Due to both spatial and temporal heterogeneities at the nanoscale interface, the physical nature of the complex ICT dynamics is still not well understood. SMS provides new insights into the nature of heterogeneous dynamics which complement current mechanisms obtained using ensemble-averaged measurements.

Motivated by designing photovoltaic devices that display higher efficiency, the present study in this thesis is mainly focused on understanding the ICT processes involved in light-driven energy-conversion devices at the single-molecule level. In addition, fluorescence behavior of single Ag nanostructures (*e.g.*, nanoparticles and nanorods) was also investigated to provide information regarding utilizing silver nanostructures to drive

applications in plasmonic photocatalysis, surface-enhanced fluorescence (SEF) and surface-enhanced Raman scattering (SERS).²⁹⁻³²

In the introduction section, ICT in DSSC/QDSSC devices and the various parameters influencing ICT dynamics at both the ensemble-averaged and single-molecule levels are discussed. Then, fluorescence behavior of noble-metal nanostructures at both the ensemble and single-molecule levels will be reviewed.

1.2 ICT dynamics in DSSC/QDSSC

1.2.1 Semiconductors used in DSSC/QDSSC

Semiconductor (SC) plays a pivotal role in energy-conversion devices. n-Type and p-type semiconductors (n-SCs and p-SCs) can serve as photoactive anodes and cathodes.²⁴⁻²⁸ On the other hand, p-SCs can be used to regenerate the photooxidized photosensitizers in solid state DSSC/QDSSC devices. Therefore, p-SCs are regarded as reliable and convenient alternatives to liquid electrolytes found in the original liquid-based Grätzel cells.^{25,33}

n-SCs used in DSSC/QDSSC devices are usually metal oxide semiconductors, such as TiO₂, SnO₂, and ZnO, while p-SCs, also termed as hole transporting materials, can be inorganic solids (*e.g.*, NiO, CuO, CuI, CuSCN), organic molecular solids (*e.g.*, OMeTAD (2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenyl-amine)-9,9' spirobifluorene), TPD (*N,N'*-diphenyl-*N,N'*-(*m*-tolyl)-benzidine)) and polymers (*e.g.*, poly(vinyl carbazole), polythiophene, polypyrrole).

1.2.2 ICT processes involved in DSSC/QDSSC

Figure 1-1. Schematic representation of charge transfer processes in n-type (a) and p-type (b) DSSC devices without involving counter electrode and external circuit. Step 1 is the photoexcitation of a dye molecule (S) adsorbed on the surface of n-/p- SC, step 2 is the electron/hole injection from excited dye molecule (S^*) to the conduction band (CB)/valence band (VB) of n-/p- SC, steps 3 and 4 are the regeneration process of dye molecules and redox mediators (Re), and step 5 is unwanted charge-recombination processes from electron/hole in CB/VB to the oxidized/reduced dye molecule.

Since DSSC devices with high photoconversion efficiency were discovered by Grätzel and co-workers in 1991,²⁴ extensive attention has been dedicated to the design of DSSC devices with higher efficiency in order to replace single crystal silicon or polycrystalline semiconductor based photovoltaic devices. DSSC devices generally consist of the following important components: SCs, organic dye molecules (or QDs), redox mediators, and counter electrodes. The operation principle of DSSC is built on the consecutive charge-injection/charge-recombination processes after photoexcitation (see Fig. 1-1). The major difference between n-type and p-type

DSSC is the role of the SCs. In general, n-SC as photo-anode can accept an electron from the excited dye molecule,²⁴ whereas p-SC as photo-cathode will accept a hole from the excited dye molecule.²⁶ Recently, tandem DSSC, in which n-type and p-type DSSC are combined together, has been developed to give higher energy-conversion efficiency than single-junction DSSCs.³⁴

Figure 1-2. Schematic of charge transfer processes in n-type (a) and p-type (b) QDSSC devices without involving counter electrode and external circuit. Steps 1-5 are the same as those involved in Fig. 1-1. The difference between DSSC and QDSSC is the photoexcitation process, in which an exciton (electron(●)-hole (○) pair) is generated after absorbing a photon.

QD also has been demonstrated to be an effective photosensitizer in energy-conversion devices (*i.e.*, QDSSCs) with the advantages of superior photostability, broad absorption band with high extinction coefficients, and tuneable bandgap which is dependent on the size and shape of the QDs.^{28,29} The operation mechanism is similar to that of DSSC and the charge transfer processes involved in QDSSC are depicted in Fig. 1-2.

The charge transfer processes in n-type DSSC and p-type DSSC devices can be summarized as follows:

	n-type DSSC	p-type DSSC	
photoexcitation	$S + h\nu \rightarrow S^*$	$S + h\nu \rightarrow S^*$	1
charge-injection*	$S^* \rightarrow S^+ + e^- (\text{CB})$	$S^* \rightarrow S^- + h^+ (\text{VB})$	2
regeneration	$\text{Re} + S^+ \rightarrow S + \text{Re}^+$	$\text{Re} + S^- \rightarrow S + \text{Re}^-$	3
	$e^- (\text{CB}) + \text{Re}^+ \rightarrow \text{Re}$	$h^+ (\text{VB}) + \text{Re}^- \rightarrow \text{Re}$	4
charge-recombination*	$e^- (\text{CB}) + S^+ \rightarrow S$	$h^+ (\text{VB}) + S^- \rightarrow S$	5

* Charge-injection can either be the forward electron transfer (n-type DSSC) or forward hole transfer (p-type DSSC), and charge-recombination is due to backward electron transfer.

The focus of this thesis is mainly on the charge injection (step 2) and charge-recombination processes (step 5) occurring at the interface of the photosensitizer and SC since both steps are critical to improve the efficiency of energy-conversion devices. It is therefore of importance to understand which parameters affect ICT dynamics.

1.2.3 Theoretical background for ICT

We will consider the ICT processes in n-type DSSC. The CB of the semiconductor consists of a series of electronic states such that an electron can be injected into any of the unoccupied accepting states. The classical Marcus theory is commonly extended to describe the non-adiabatic forward/backward electron transfer rate (k_{fet} and k_{bet}) occurring at the interface of photosensitizer and n-SC:³⁵⁻³⁷

$$k_{fet/bet} = \frac{2\pi}{\hbar} \int_{-\infty}^{+\infty} \rho(E) (1 - f(E, E_F)) H_{el}(E)^2 dE \frac{1}{\sqrt{4\pi\lambda k_B T}} \times \exp \left[\frac{-(\Delta G_{fet/bet}^0 + \lambda + E)^2}{4\lambda k_B T} \right] \quad (1.1)$$

$$\Delta G_{fet}^0 = E_1 - E_2 - E_{00} \quad (1.2)$$

$$\Delta G_{bet}^0 = -(\Delta G_{fet}^0 + E_{00}) \quad (1.3)$$

$$H_{el}^2 = H_0^2 e^{-\beta R_e} \quad (1.4)$$

where $\rho(E)$ is the density of states near the CB edge, E is the relative energy to the CB edge, $f(E, E_F)$ is the Fermi occupancy factor, $H_{el}(E)$ is the electronic coupling element between photosensitizer and the surface state with the energy E , λ is the reorganization energy, k_B is Boltzmann's constant, T is the temperature, $\Delta G_{fet/bet}^0$ is the free energy of forward electron transfer (ΔG_{fet}^0) or backward electron transfer (ΔG_{bet}^0), E_1 is the first one-electron oxidation potential of dye molecule, E_2 is the energy of conduction band, E_{00} is the energy difference between the lowest vibronic level of the ground and excited electronic states of the photosensitizer, β is the attenuation factor, and R_e is the distance between the electron donating state and accepting state.

Analogous equations 1.1-1.4 can also be used to describe the rates of hole injection and charge recombination occurring in p-type DSSC, but the meanings of some parameters described next are different. In this case, $\rho(E)$ is the density of states near the VB edge, E is the relative energy to the VB edge, $\Delta G_{fet/bet}^0$ is the free energy of forward hole transfer (ΔG_{fht}^0) or backward electron transfer (ΔG_{bet}^0), E_1 is the energy of valence band, and E_2 is the first one-electron reduction potential of photosensitizer.³⁸

Figure 1-3. Plot of $k_{fet/bet}$ against $-(\Delta G_{fet/bet}^0 + E)$ based on the classical Marcus theory.

From equation 1.1, it is noted that $k_{fet/bet}$ reaches a maximum value when $-(\Delta G_{fet/bet}^0 + E)$ equals to λ . Fig. 1-3 displays the dependence of $k_{fet/bet}$ on $-(\Delta G_{fet/bet}^0 + E)$. Two regions, one region termed as “normal region” when $-(\Delta G_{fet/bet}^0 + E)$ is smaller than λ and another region termed as “inverted region” when $-(\Delta G_{fet/bet}^0 + E)$ is larger than λ , are observed. Clearly, $k_{fet/bet}$ increases with an increase of $-(\Delta G_{fet/bet}^0 + E)$ in the “normal region” whereas $k_{fet/bet}$ decreases with an increase of $-(\Delta G_{fet/bet}^0 + E)$ in the “inverted region”.

1.2.4 Factors influencing ICT processes

In order to fabricate practical energy-conversion devices with high efficiencies, it is necessary to reach a compromise between charge injection and charge recombination. Therefore, it is important to investigate which parameters influence the interaction between photosensitizer and semiconductor (see Fig. 1-4) and affect the ICT dynamics.

Figure 1-4. Schematic of parameters that influence ICT dynamics. The solid line in (a) represents different anchoring groups in organic dye molecule used to bind with SC or a linker between dye molecule and anchoring groups.

Factors affecting the rate of charge injection process are first addressed. As shown in equation 1.1, k_{fet} is sensitive to the change in the physical and chemical properties of photosensitizer and SC. As far as the photosensitizer is concerned, if different photosensitizers are used to sensitize SCs, charge injection rate can be altered due to their specific photophysical/photochemical and electrochemical characteristics.³⁹ The rate of forward electron transfer from QD to TiO_2 is closely dependent on QD size because of the larger driving force for forward electron transfer caused by a more negative shift of CB edge with a

decrease in QD size.^{29,40} In addition, it has been demonstrated that different anchoring groups (*e.g.*, -COOH and H₂O₃P-) used to modify organic dye molecules would result in different electron transfer dynamics due to a change in the electronic coupling element, $H_{el}(E)$.³⁶ Introducing a linker (see Fig. 1-4a) of different lengths of alkyl chain (*e.g.*, different lengths of methylene spacer), can also sensitively alter the electronic coupling strength due to the dependence of $H_{el}(E)$ on R_e (see equation 1.4) resulting in a change in the rate of forward electron transfer.^{41,42}

The CB/VB edge of SCs and the density of electron-accepting/donating states in the CB/VB play a pivotal role in determining charge injection rate.⁴³⁻⁴⁸ It is known that the CB edge of n-type SC varies with the pH of the solution used and is approximated using the following equation:

$$E_{CB}(\text{pH}) = E_{CB}(\text{pH} = 0) - 0.059 \times \text{pH} \quad (1.5)$$

where $E_{CB}(\text{pH}=0)$ is the energy of the CB at pH=0. Based on equation 1.5, it is expected that the CB edge is shifted upward with an increase of pH, which will reduce the driving force ($-\Delta G_{fet/bet}^0$) and rate for forward electron transfer. Lian *et al.* and Kamat *et al.* have demonstrated that the rate of forward electron transfer can be modulated this way by changing the solution pH.^{39,44,46} Tuneable CB/VB edges can also be achieved by adding different types and amounts of dopants which can result in different driving force for charge injection. In the case of p-type NiO, CB/VB edges can be tuned by varying the amount of dopants (*e.g.*, Ni³⁺, Al³⁺).^{47,48} Though the CB edge of SnO₂ is lower than that of TiO₂ (*i.e.*, larger driving force for electron transfer to SnO₂), Lian *et al.* reported

that the rate of forward electron transfer from dye molecule to SnO_2 was slower than that from the same dye molecule to TiO_2 .^{36,43} Clearly, the driving force alone cannot account for the difference. They ascribed the difference to the larger density of electron-accepting states in the CB of TiO_2 as compared to SnO_2 and the larger electronic coupling element of TiO_2 than that of SnO_2 . In addition, $H_{el}(E)$ can be tuned by introducing a thin layer of insulator (*e.g.*, Al_2O_3) between photosensitizer and SC (see Fig. 1-4b) where this extra insulator layer plays the same role as the linker (see Fig. 1-4a) by providing extra spatial separation between sensitizer and SC.⁴⁹

In comparison with charge injection process, unwanted charge recombination process is just as crucial in promoting the energy-conversion efficiency. Hence, much effort has been dedicated to investigate ways to retard the charge-recombination process in order to improve the working efficiency of devices. According to equation 1.1, the rates of both charge injection and charge recombination can be tuned simultaneously. Specifically, a thin layer of metal oxide layer acting as a physical barrier can significantly decrease the rate of charge injection and retard charge recombination process. Several groups have demonstrated that a metal oxide layer (*e.g.*, Al_2O_3 ,⁵⁰⁻⁵² SiO_2 ,^{50,52} MgO ,^{50,52} Nb_2O_5 ,⁵³ and ZrO_2 ⁵²) coated on top of a TiO_2 or SnO_2 surface could effectively retard the charge recombination process with the oxidized dye and further improve the energy-conversion efficiency of n-type DSSC. Recently, the same approach has been extended to slow the charge recombination process in p-type DSSC by Mori and co-workers.⁵⁴ In addition, an alternative way (see Fig. 1-4c) to retard charge recombination process is to encapsulate the dye molecules in a macrocyclic host (*e.g.*, cyclodextrin^{55,56}) in order to increase the distance

between the dye molecules and SCs. The strategy shown in Figs. 1-4 d and e effectively increases the spatial distance between the dye molecules and SCs by introducing an electron-donating/accepting group to form an electron/hole transfer cascade. The increase in spatial distance will further retard k_{bet} according to the following equation:

$$k_{bet}(r) = k_0 e^{-\beta r} \quad (1.6)$$

where k_0 is the rate constant at $r = 0$, β is the exponential decay constant, and r is the spatial distance.⁵⁷ Electron-donating groups used in n-type DSSC can be hydrophobic alkyl chain,^{58,59} phenothiazine,⁶⁰ triphenylamine,^{57,59,61} TPD,^{57,58} poly(vinyl-triphenylamine) chain⁵⁷ and *N,N*-(di-*p*-anisylamino)phoxymethyl moiety⁶² while perylenemonoimide³⁴ and naphthalenediimide⁶³ units have been used as electron-accepting groups in p-type DSSC.

1.3 Progress of SMS study in ICT dynamics

1.3.1 Brief introduction of SMS

Near-field scanning optical microscopy (NSOM) and far-field optical microscopy are usually used in single-molecule detection. Compared to NSOM, far-field microscopy has lower spatial resolution due to the diffraction of light. The resolution in the lateral direction of far-field microscopy (d) can be estimated by the following equation:

$$d = \frac{\lambda}{2N.A.} \quad (1.7)$$

where λ and $N.A.$ are the laser wavelength operating in TEM_{00} mode (transverse electromagnetic mode with $p = l = 0$) and the numerical aperture of the objective lens used. When a red laser (*e.g.*, 635 nm) and an oil immersion objective with $N.A. = 1.40$ are used, the lateral resolution is about 230 nm and two fluorescent molecules with a spatial separation that is less than 230 nm cannot be distinguished by far-field microscopy. Super-resolution fluorescence microscopy (*e.g.*, stimulated emission depletion (STED) microscopy, stochastic optical reconstruction microscopy (STORM), and photoactivated localization microscopy (PALM)), have been used to obtain images that are not confined by the diffraction limit.⁶⁴

In this thesis, the fluorescence behavior of single molecules (or particles) was detected by far-field fluorescence microscopy (*e.g.*, time-resolved confocal fluorescence microscopy and wide-field fluorescence microscopy). Compared to wide-field microscopy, confocal microscopy has a smaller detection volume which can be achieved by placing a pinhole before the detector (*e.g.*, single-photon avalanche diode (SPAD)) to remove light that is out of the confocal plane. In addition, the time resolution (*i.e.*, less than ns) of confocal microscopy is higher than that of wide-field microscopy ($\sim$ ms). The setups of time-resolved confocal fluorescence microscopy and wide-field fluorescence microscopy will be described in Chapter 2 and Chapter 5, respectively.

Figure 1-5. Schematic of T3R data acquisition technique including the time-correlated single photon counting (TCSPC) technique. τ_i is obtained using forward start-stop mode.

Time-tagged time-resolved (T3R) technique is used in the time-resolved confocal fluorescence microscope and the principle of T3R is illustrated in Fig. 1-5. As shown in Fig. 1-5, T3R technique can record both macroscopic time (*i.e.*, the arrival time of single photon relative to the beginning of the experiment, T_1 or T_2 shown in Fig. 1-5) and microscopic time (*i.e.*, the arrival time of single photon relative to the laser pulse, τ_1 or τ_2 shown in Fig. 1-5). However, traditional TCSPC method can only be used to obtain the microscopic time. Hence, T3R technique is employed to record the fluorescence dynamics without any loss of useful information from a single photon.

In practice, reverse start-stop mode, where the time when a SPAD detects a fluorescence photon generated by a laser pulse is regarded as “start” and the

time when a SPAD detects the next laser pulse is regarded as “stop”, is used to measure the microscopic time in TCSPC or T3R technique. Since the repetition rate is known, the exact time between the laser pulse and the corresponding photon can easily be converted. The microscopic time can be converted to a voltage by a time-to-amplitude converter (TAC) and then an analog-to-digital converter (ADC) can convert the voltage to a digital timing value which is used to construct the histogram.⁶⁵ After many excitation cycles, the fluorescence lifetime histogram can be constructed.

Figure 1-6. Classic setups of TCSPC (forward start-stop mode, a) and Hanbury-Brown-Twiss (HBT, b). Fluorescence lifetime distribution and interphoton time distribution can be constructed using τ_i measured by TCSPC and HBT setups, respectively. Note that τ_1 and τ_2 shown in the lower panel of a are the microscopic times used to construct the fluorescence decay profile; τ_1 and τ_2 shown in the lower panel of b are the interphoton times of a coincident event and a non-coincident event.

In single-molecule detection, it is important to ensure a single fluorescence emitter excited in the excitation volume. HBT type coincidence setup can be employed to confirm this condition (*i.e.*, the observed fluorescence originates from a single molecule). To better illustrate the setup of HBT, conventional setups of both TCSPC and HBT are shown in Fig. 1-6. In antibunching experiment, the interphoton time between photon pairs, not the time difference between the laser pulse and the corresponding photon, can be measured. Hence, two photons produced by the same laser pulse can be detected using the HBT setup (so-called “coincident events”). Since single emitter with fluorescence lifetime longer than the width of laser pulse cannot emit two or more photons in one excitation cycle, the central peak resulting from coincident events should be zero and the non-zero lateral peaks resulting from non-coincident events are separated by the interval time of pulsed laser. Simply, the relationship between the number of molecules (m) in the excited volume and the ratio of coincident events (N_C) to non-coincident events ($\bar{N}_L$) can be described by the following equation:^{66,67}

$$\frac{N_C}{\bar{N}_L} = 1 - \frac{1}{m} \quad (1.8)$$

If a single emitter is in the excited volume, $N_C/\bar{N}_L$ should be 0. A non-zero central peak, albeit small, is sometimes observed for single photon emitters due to the interaction of background-background and background-signal photon pairs. In general, $N_C/\bar{N}_L$ less than 0.5 can be regarded as an obvious character of single emitter and $0.5 \leq N_C/\bar{N}_L \leq 1$ when two or more independent emitters are found in the detection volume.

1.3.2 Single-molecule fluorescence intermittency

Figure 1-7. Fluorescence intensity time traces of (a) a single Atto647N molecule on TiO_2 nanoparticle film¹⁸ and (b) a single CdSe/ZnS QD on glass substrate.²¹ The bin-time used is 20 ms.

With the advent of SMS, a wealth of information previously obscured by ensemble-averaging measurements has been unravelled.⁶⁸ SMS has been used to investigate complex processes involving single molecules, such as fluorescence resonance energy transfer,³ protein conformation transition,⁶⁹ and electrocatalysis⁴ (or enzyme catalysis⁷⁰), and provides a statistics distribution of behavior rather than an average picture. The most intriguing and at times annoying phenomenon in SMS is fluorescence intermittency (*i.e.*, photoblinking), which refers to the stochastic fluctuation in fluorescence intensity between “on” and “off” states (see Fig. 1-7).^{1-3,5,71-96} Although

valuable static and time-dependent information can be extracted from photoblinking dynamics, photoblinking limits the use of single fluorophores as stable single-photon sources and ideal biolabels.

Figure 1-8. Proposed mechanisms for photo-induced blinking behavior of organic dye molecules (a) and QDs (b). S_0 , S_1 , T , and D are the singlet ground state, the first singlet excited state, the triplet state, and dark state, respectively. In (a), steps 1 to 4 are photoexcitation, photoemission, intersystem crossing, and phosphorescence, respectively. Steps 5 to 7 are the transition process from S_1 to D , from T to D , and from D to S_0 , respectively. In (b), an exciton (*i.e.*, electron (●)-hole (○) pair) is created after photoexcitation. Steps 1 and 2 are radiative recombination (*i.e.*, photoluminescence) and non-radiative Auger recombination process, respectively.

Photoblinking is commonly observed in single emitters including organic dye molecules,^{3,5,72,74-76,78,80,81} QDs,^{19-21,73,77,79,82-89} conjugated polymers,⁷⁵ silver nanostructures,^{31,90-94} silicon nanocrystals,⁹⁵ nanodiamond,⁹⁶ and green fluorescent protein.² In order to suppress fluorescence intermittency behavior, it is necessary to understand the physical nature of photoblinking. The focus of the present section is on the photoblinking behavior of organic dye molecules and QDs.

The following explanations have been proposed to explain fluorescence intermittency of single organic dye molecules:

- (a) Triplet state formed through intersystem crossing process from the S_1 state (see Fig. 1-8a, step 3). Barbara *et al.* ascribed “off” events in fluorescence trajectories to the formation of triplet state in 1,1'-didodecyl-3,3,3',3'-tetramethylindocarbocyanine perchlorate (DiI) under N_2 atmosphere⁷⁵ or embedded in oxygen-depleted polymer film.⁷⁶ They also observed that the rate from T to S_0 is strongly dependent on the concentration of O_2 .
- (b) Cis-trans conformation transition. Millisecond fluorescence fluctuation of Cy5 in solution can be ascribed to cis-trans isomerization because cis conformation is non-fluorescent.⁹⁷ This transition can be suppressed when organic dye molecules are placed in a more rigid environment (*e.g.*, glass surface).⁸⁰
- (c) Spectral diffusion. Lu and Xie investigated the fluorescence behavior of single sulphorhodamine 101 molecules on quartz substrate and ascribed intensity fluctuation to spectral diffusion resulting in the change of absorption cross-section. They also proposed that spectral diffusion originated from the

transition of ground-state between different local or gross energy minima in the nuclear coordinates.⁷⁴

(d) Molecular orientation. Using NSOM, Keller and co-workers ascribed fluorescence intensity fluctuation of Rhodamine 6G (Rh6G) on silica substrate to the change of molecular orientation.⁷² Indeed, fluorescence intermittency induced by the sudden change of molecular dipole can be excluded using a circular polarized light as the excitation source.

(e) Charge-separated states (see Fig. 1-8a). It is well accepted that most oxidized or reduced dye molecules are non-fluorescent or dim emitters. Yeow *et al.* ascribed the long-lived “off”-events to the formation of radical cations for organic dye molecules deposited on glass⁸¹ or embedded in electron-transfer inactive polymer film and to the formation of radical anions when Atto647N is embedded in poly(vinyl-carbazole).⁵ In addition, Orrit *et al.* have previously demonstrated the presence of radical anions in Rh6G/poly(vinyl alcohol) system.⁷⁸ Indeed, charge-separated states were also used to explain the long-lived “off” events in ICT process discussed in Section 1.3.3.⁶⁻²³

Much effort has been devoted to investigating the mechanism of photoblinking behavior of single QD. However, the detailed mechanism is still unknown due to the complicated structure of QD (*i.e.*, a semiconductor core coated by organic ligands or inorganic shell). A consensus so far is that the off-state observed in the emission intensity trajectory of single QDs is attributed to the formation of a charged QD.^{98,99} Specifically, a charge carrier of the QD has a probability to tunnel to a trap state on the surface of the dot or to the surrounding environment of the QD, resulting in the formation of a charged QD. Usually, charged QD stops emitting light or emits very weak light, which

corresponds to the dark “off” states in single QD fluorescence intensity time traces. A photo-generated electron-hole pair (exciton) formed in the charged QD after absorbing another photon can subsequently recombine by non-radiative Auger process with a decay time on the order of 10-100 ps which is faster than radiative recombination with a decay time of a few tens of nanoseconds, and no photon is emitted in the period dominated by the Auger process. QD remains dark until fluorescence is restored when the ejected charge tunnels back to the core.

Photoluminescence blinking dynamics of QD is strongly influenced by the surrounding environment, such as the ligands attached on the surface of QD,^{100,101} the extra shells,^{87,102-104} and different inactive (*e.g.*, non-conductive polymer and glass substrate)^{21,85} or active (*e.g.*, semiconductors and electron/hole transporting materials) matrix,^{19-21,89,105} and excitation wavelength.¹⁰⁶

Photoblinking kinetics can be extracted from on-/off- time duration ($\tau_{on/off}$) histograms of single or a collection of dye molecules or QDs. Due to different origins of on/off events, different functions, such as mono-exponential (equation 1.9),⁷⁵ power-law (equation 1.10),^{5,17-19,21,81} and stretched exponential (equation 1.11) functions⁵, are used to describe the on-/off- time distributions ($P(\tau_{on/off})$):

$$P(\tau_{on/off}) = C + P_0 e^{-(m_{on/off} \times \tau_{on/off})} \quad (1.9)$$

$$P(\tau_{on/off}) = P_0 \tau_{on/off}^{-m_{on/off}} \quad (1.10)$$

$$P(\tau_{on/off}) = P_0 \left[- \left(\frac{\tau_{on/off}}{\tau_{SE}} \right)^n \right] \quad (1.11)$$

where $m_{on/off}$ is the exponential or power-law exponent for the on-/off- time distribution, τ_{SE} is the characteristic time scale of on-/off- time events, n is the stretching exponent, and C and P_0 are constants. Usually, triplet blinking dynamics of organic dye molecules can be described using single-exponential decay function, and more dispersive distributions (*e.g.*, power-law or stretched exponential functions) are used to describe blinking dynamics of organic dye molecules undergoing charge-separation. In addition, photoblinking dynamics of QDs is usually described by the power-law function.

On the basis of the physical nature of fluorescence intermittency, several methods described below have been utilized to suppress photoblinking of dye molecules (or QDs). It is worth noting that photoblinking cannot be completely suppressed.

(a) Anti-blinking reagents were used to reduce blinking behavior. Ha and co-workers first reported non-blinking QDs in the presence of β -mercaptoethanol (BME) and ascribed suppressed blinking behavior to the elimination of surface electron traps by an electron-donating moiety (*i.e.*, thiol moiety in BME).⁷⁹ They also reported that cyanine dye (*e.g.*, Cy5) with suppressed photoblinking behavior and extended survival time could be observed in the presence of Trolox and the enzymatic O_2 -scavenger.³ Other compounds (*e.g.*, dithiothreitol,⁸⁵ mercaptoethylamine¹⁰⁷ and oligophenylene vinylene¹⁰⁸) were also demonstrated to play the same role as BME in reducing blinking behavior of QD. Nesbitt and co-worker observed non-blinking QDs after adding propyl

gallate and attributed non-blinking behavior to the enhancement of radiative rate and the decrease of non-radiative rate.⁸² It is interesting to note that Biju *et al.* reported that blinking behavior of single QDs can be effectively suppressed after adding TiO₂ nanoparticles in aqueous solutions.⁸⁸ In this case, they have proposed that in the presence of TiO₂ nanoparticle in solution, the regeneration rate of neutral QD was enhanced to compete with the Auger recombination process, which is different from QDs on TiO₂ nanoparticle film. In the latter case, the electron injected to the CB of TiO₂ would diffuse in the TiO₂ film so that long off-time events were observed in Lian's work.¹⁹

(b) On the basis of surface plasmon from noble metals (*e.g.*, Ag, Au), metal-enhanced fluorescence technology was applied to suppress the blinking behavior of organic dye molecules or QDs. The enhancement factor is closely dependent upon the shape and size of metallic nanostructures and the distance between fluorophores and metal surfaces. Lakowicz *et al.* observed blinking suppression of single Cy5 molecules³¹ and QDs⁸⁶ when these fluorophores were separated from silver island films with optimized distances. Bawendi *et al.* observed enhanced emission and reduced blinking behavior in CdSe/ZnS QD deposited directly onto a rough gold film, and they proposed that the enhanced emission originated from charged CdSe/ZnS QD.⁷⁷ It is worth noting that non-blinking organic dye molecules with up to 1,340-fold fluorescence enhancement at the single-molecule level was recently obtained by coupling organic dye molecules to gold bowtie nanostructures.¹⁰⁹

(c) An efficient non-radiative channel (*e.g.*, energy transfer, charge transfer) occurring faster than the non-radiative Auger ionization was introduced to suppress the blinking behavior of QDs. Tang and co-workers observed QDs

with suppressed blinking for QDs coupled to Ag nanostructures.⁸⁴ In this case, efficient energy transfer from QD to Ag nanoprism can lead to the simultaneous annihilation of electron and hole in excited QD. Brus and co-workers also attributed blinking suppression of QDs on single-layer graphene to efficient energy transfer from QD to graphene.⁸⁹ We will show that an additional charge transfer process (hole transfer) from excited QDs to NiO results in blinking suppression of single QDs as discussed in Chapter 3.²¹

(d) Blinking suppression of single QDs can be achieved by chemically modifying the structure of QD. Coating a thick shell on nanocrystal core (*e.g.*, CdSe core with CdS shell of 5-8 nm thickness) has been demonstrated to be an effective way to suppress blinking behavior by Hollingsworth *et al.*¹⁰³ and Dubertret *et al.*¹⁰⁴ In their works, the thick shell was capable of preventing the charged carrier from escaping to the surface. Recently, Efros *et al.* synthesized non-blinking and long-lasting QDs with alloyed CdZnSe core and ZnSe shell and ascribed the photophysical behavior to the formation of charged exciton with high fluorescence quantum yield.⁸⁷

1.3.3 SMS of ICT dynamics

Figure 1-9. Schematic presentation of (a) interfacial forward electron (left)/hole (right) transfer (FET/FHT) and backward electron transfer (BET) processes and (b) intermittent interfacial electron transfer reactivity model. S and S* are the ground state and excited state, respectively. $k_{fet/fht}$ and k_r are forward electron/hole transfer rate and radiative rate, respectively.

The scheme shown in Fig. 1-9a illustrates the ICT process at the interface of dyes/QDs and n-/p- SCs. Electron or hole can be transferred from excited photosensitizer to the CB of n-SC or VB of p-SC after photoexcitation and BET process occurs after charge transport in SC. Note that compared to electron transport in n-SCs, hole transport in p-SCs (e.g., NiO) is not significant since

the fast charge recombination process between the reduced photosensitizer and the hole in the VB of p-SCs falls in the ps to ns time range.^{63,110,111} Forward electron/hole transfer acts as an additional non-radiative decay process that can influence the fluorescence intensity and lifetime according to the following equations:

$$\tau = \frac{1}{k_r + k_{nr} + k_{fet/fht}} \quad (1.12)$$

$$\Phi = \frac{k_r}{k_r + k_{nr} + k_{fet/fht}} \quad (1.13)$$

where τ , Φ , k_r , k_{nr} , $k_{fet/fht}$ are the fluorescence lifetime, quantum yield, intrinsic radiative rate, intrinsic non-radiative rate, and forward electron/hole transfer rate, respectively. For dye molecules/QDs on electron-transfer inactive substrates (*e.g.*, glass, ZrO_2), $k_{fet/fht}$ is insignificant. However, τ and Φ will be reduced when dyes/QDs are deposited on active substrates (*e.g.*, TiO_2 , NiO) due to the presence of FET or FHT (*i.e.*, $k_{fet/fht}$ value is non-zero).

Lu and Xie first investigated interfacial electron transfer kinetics of cresyl violet on indium tin oxide (ITO) at the single-molecule level.⁶ They observed that the fluorescence lifetime of individual cresyl violet on ITO was decreased when compared to cresyl violet on glass (*i.e.*, inactive substrate) and attributed this behavior to non-radiative interfacial electron transfer according to equation 1.12. In addition, they proposed that the wide distribution of fluorescence lifetime originates from the inhomogeneity of site-specific interaction between cresyl violet and ITO. It is worth noting that this pioneering work opened new opportunities for other studies involving single-molecule-based ICT processes.

Adams and co-workers investigated the interfacial electron transfer dynamics between single perylene bisimide molecules and ITO.⁷ Compared to the non-blinking behavior for single molecules on quartz, “off” events in the fluorescence intensity time traces of single molecules on ITO were ascribed to forward electron transfer between the two moieties. Photoinduced cations of organic dyes are usually non-fluorescent giving rise to the temporary “off” events. Fluorescence is restored when a charge-recombination process takes place. The k_{fet} and k_{bet} values are extracted from the single-molecule fluorescence trajectories and were found to vary from molecule to molecule.

Since TiO_2 is widely used in DSSC devices, Lu and co-workers investigated the interfacial electron transfer dynamics between single organic molecules, such as cresyl violet, coumarin 343, and zinc-tetra(4-carboxyphenyl) porphyrin, and TiO_2 .^{10,17} Ensemble-averaged k_{fet} measured by bulk techniques generally falls in the ultrafast time domain (*i.e.*, fs to ps) and is much faster than the resolution of the single-molecule experimental set-up.^{36,37} Therefore, it would seem impossible to observe fluorescence from these molecules at the single-molecule level. However, detectable single molecules could still be measured using SMS and they display fluorescence lifetimes ($\sim$ ns) that are longer than the expected value according to equation 1.12 and as measured in the bulk experiment. At the same time, blinking behavior was observed in the single-molecule fluorescence trajectories which were ascribed to off-time events due to interfacial electron transfer from the excited dye molecules to the CB of TiO_2 . In order to explain the longer lifetime decay and fluorescence intermittency behavior, Lu *et al.* proposed the intermittent interfacial electron transfer reactivity model (see Fig. 1-9b) where fluorescence intensity strongly

depends on the difference between k_{fet} and k_r . Based on this model, a high emission intensity of single molecules originates from the low reactivity of forward electron transfer (*i.e.*, when k_{fet} is smaller than the inverse of the intrinsic excited state lifetime) and a low or zero fluorescence intensity occurs when the molecules switch to a high reactivity mode (*i.e.*, when k_{fet} is much larger than the inverse of the intrinsic excited state lifetime). Therefore, fluorescence intensity fluctuation is indicative of the change in interfacial electron transfer reactivity. Recently, they have proposed a two-channel (*i.e.*, strong and weak coupling channels) mechanism to rationalize the ICT dynamics in 9-phenyl-2,3,7-trihydroxy-6-fluorone/TiO₂ system using both femtosecond transient absorption spectroscopy and SMS.¹¹² In the strong-coupling channel, charge separation states are formed in the sub-picosecond range (*i.e.*, high reactivity mode), while forward electron transfer from the excited singlet state to the CB of TiO₂ occurs in the picoseconds or nanoseconds time range in the weak-coupling channel (*i.e.*, low reactivity mode). Factors such as the dynamic change of the energy gap between dye and TiO₂, electronic coupling between the active species and vibrational relaxation energy of the adsorbed dye have been proposed to be responsible for the changing FET reactivities.

Lian *et al.* attributed detectable single Rhodamine B molecules on Sb: SnO₂ to the part of the population with low injection rates because the numbers of molecules on electron-transfer active and inactive substrates are different.¹³ They attempted to retard the rate of electron injection by inserting a linker (*i.e.*, aminosilane) between sulforhodamine B and SnO₂ and observed similar number density of single sulforhodamine B molecules on both electron-transfer active substrate (SnO₂) and inactive substrate (ZrO₂).²² In addition, they also

observed shorter fluorescence lifetimes due to the presence of FET and larger fluctuations of fluorescence lifetime on SnO₂ than those on ZrO₂ which were ascribed to the fluctuation of k_{fet} .

ICT dynamics of single QD/TiO₂ system has been investigated by Lian and co-worker.¹⁹ Compared to glass substrate, QDs deposited on TiO₂ nanoparticle film displayed significantly shorter fluorescence lifetime that undergoes fluctuations with time due to the variation in interfacial electron transfer reactivity and a smaller power-law exponent (m_{off}). They also proposed that “on” events of QDs on TiO₂ are dominated by interfacial electron transfer process and “off” events are controlled by the Auger process. Majima *et al.* investigated ICT dynamics from single QD to an electron acceptor (*i.e.*, pyromellitimide).^{15,113} In their study, smaller m_{off} of QD-pyromellitimide conjugate was also observed compared to that of bare QD due to interfacial electron transfer process, and the ICT kinetics from single QD to pyromellitimide could be modulated by different solvents due to different reorganization energy for the electron transfer process.

Electron transport in n-type SC has been demonstrated to play a pivotal role in practical devices. In general, the electron injected into the CB of n-SCs randomly diffuses between the localized energy states (*i.e.*, the trap sites) near the CB edge and occurs by a series of trapping and de-trapping processes. However, this important process is often neglected when describing the charge-recombination dynamics between injected electrons and TiO₂ at the single-molecule level.^{6,7,10,14,17,114} Durrant *et al.* observed that the dynamics of charge-recombination can be tuned by changing the spatial distance between the photosensitized dye molecules and TiO₂.⁵² In Chapter 4, we investigate the

fluorescence dynamics of the encapsulated dye molecule (*i.e.*, Atto647N-cucurbit[7]uril) to demonstrate the role of electron transport in charge-recombination at the single-molecule level.¹⁸

The above single-molecule studies investigated the interfacial electron transfer dynamics at the interface of dye molecules/QDs and n-SCs. However, the study of p-type semiconductor (*e.g.*, NiO, TPD) at the single-molecule level is still lacking.²¹ Since dye-sensitized p-type semiconductor is used in the fabrication of tandem DSSC devices which have a higher efficiency than single-junction devices, it is necessary to have a clearer understanding of the charge-transfer processes occurring between photoexcited dye molecules (or QDs) and p-type semiconductors.^{26,34} The details will be discussed in Chapters 2 and 3.

1.4 Fluorescence behavior of noble-metal nanostructures

Noble-metal materials from atomic to bulk levels have drawn intense interest because of their unique optical and electric properties. Besides their ability to significantly enhance Raman and fluorescence signal,^{30,31,77,86,109} it has been demonstrated that noble-metal materials could emit fluorescence with superior stability and size-dependent quantum yield from 10^{-10} to 0.7. Noble metal nanostructures are considered as alternatives to organic dye molecules or QDs in bio-imaging.^{90,115-117} However, the blinking behavior of noble metal nanostructure limits its applications in bio-imaging and surface-enhanced fluorescence.³¹ Therefore, it is pertinent to understand the physical nature of photoblinking of noble-metal nanostructures.

In 1969, Mooradian showed that bulk silver, gold and copper exhibited weak photoluminescence with quantum yields on the order of 10^{-10} .¹¹⁵ When the size of noble metal material decreases to nano scale, a relatively strong

fluorescence is observed.^{90-94,118-124} Wilcoxon *et al.* reported a significant increase in the luminescence quantum yield (*ca.* 10^{-4} to 10^{-5}) when gold particles were smaller than 5 nm and ascribed the fluorescence to the radiative recombination of an excited *sp*-band electron and a *d*-band hole.¹¹⁸ In addition, fluorescent noble-metal clusters were generated when Ag colloidal solution^{119,120} and Ag₂O nanoparticle films⁹⁰ were photoilluminated, but the exact nature of the emitting species in these clusters could not be determined. Noble-metal clusters with certain atoms can be obtained using physical and chemical methods. Ertl and co-workers demonstrated that when Ag atoms were evaporated in Ar atmosphere, Ag dimer and trimer which were generated from the coagulation of multi-atomic clusters would emit strong luminescence at the blue and red regions, and larger clusters Ag_{*n*} (*n* ≥ 4) would exhibit a broad emission band observed between 700 nm and 1000 nm.^{121,122} Recently, Dickson *et al.* reported that a series of water-soluble dendrimer encapsulated Au clusters (Au₅, Au₈, Au₁₃, Au₂₃, and Au₃₁) with quantum yields ranging from 0.1 to 0.7 were prepared using a chemical reduction method.¹²³ The group also synthesized Ag clusters encapsulated in single strand DNA with quantum yields ranging from 0.16 to 0.34.¹¹⁷ These Ag or Au clusters exhibited size-specific emission properties with the emission ranging from ultraviolet to near infrared.

The blinking mechanism of silver nanostructures remains controversial. Dickson *et al.* observed obvious photoblinking behavior of Ag₂O nanocrystal films when Ag₂O was photoilluminated by blue excitation and reduced photoblinking behavior when excited by green laser.⁹⁰ They proposed that silver nanocluster's transition from an emissive "on" state to a non-emissive "off" state was due to an emitting cluster breaking up into non-emitting species

or formation of non-fluorescent larger clusters. Wavelength-dependent photoblinking dynamics was ascribed to the overlap between the bandgap of Ag₂O and the green excitation. Jacobson *et al.* demonstrated that O₂ played an important role in the fluorescence intermittency of Ag₂O films due to the absence of photoblinking of Ag₂O films under N₂ atmosphere. They suggested that fluorescent silver clusters formed from the photoreduction of Ag₂O can react with oxygen to re-form non-fluorescent silver oxides.¹²⁵⁻¹²⁷ Pan *et al.* also observed strikingly different dynamics of silver nanowires in air and N₂/polymer film environment and further demonstrated the role of O₂.⁹⁴ On the basis of our controlled experiments described in Chapter 5, silver oxides re-generated by photooxidation could not completely describe the deactivation pathway of silver clusters.⁹³ We also proposed that the origin of the power-law on-/off- time distributions arises from the random diffusion and agglomeration of Ag entities to form either photoactive nanoclusters or non-active ones. The details will be discussed in Chapter 5.

1.5 Outline of this thesis

The outline of this thesis is described as follows:

Chapter 1- General introduction of interfacial charge-transfer dynamics in DSSC/QDSSC devices and fluorescence dynamics of noble metal nanoparticles at both the ensemble and single-molecule levels is provided.

Chapter 2- Heterogeneous hole transfer dynamics from dye molecules to p-type semiconductors (*e.g.*, NiO and TPD) are investigated at both the ensemble and single-molecule levels.

Chapter 3- Charge-transfer processes in single CdSe/ZnS QDs with p-type NiO nanoparticles are investigated and a novel way to suppress the blinking

behavior of QDs is also demonstrated.

Chapter 4- The physical nature of long-lived off-events observed when single dye molecules encapsulated in cucurbit[7]uril (CB7) are deposited on TiO₂ surface is discussed and computational simulations, based on the continuous-time random walk, are performed.

Chapter 5- Fluorescence blinking dynamics of Ag nanostructures are investigated using single-molecule fluorescence microscopy.

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CHAPTER 2

HOLE TRANSFER DYNAMICS FROM DYE

MOLECULES TO P-TYPE

SEMICONDUCTORS

2.1 Introduction

Dye-sensitized solar cells (DSSCs) have been hailed to be important alternatives to conventional solid state devices because of their low costs and ease of fabrication.¹⁻³ DSSCs consisting of n-type semiconductors such as TiO₂ and SnO₂ are commonly used for energy conversion.³⁻⁵ Recently, new photovoltaic devices based on the sensitization of p-type metal oxide semiconductors (*e.g.*, NiO) by excited organic dye molecules have attracted a lot of attention in both the academic and industrial arenas because of their important role in designing efficient tandem DSSCs composing of a photosensitized n-type semiconductor anode and a photosensitized p-type semiconductor cathode.^{3,6-8} In addition, organic hole transporting materials, also termed as p-type semiconductors, are used in solid DSSCs devices to replace the liquid electrolytes found in original liquid-based Grätzel cells.^{2,9}

Nickel oxide is the most common metal oxide semiconductor employed in the fabrication of p-type DSSCs. In particular, non-stoichiometric p-type NiO is chemically stable, possesses a wide band gap and displays low resistivity and high electrical conductivity.¹⁰ The electrical and optical properties of NiO have been shown to be affected by the processing conditions. Chattopadhyay *et al.* have prepared thin films of NiO by utilizing the direct current sputtering technique in different oxygen partial pressures and have demonstrated enhanced electrical conductivity and reduced band gap for NiO synthesized in high oxygen partial pressures.¹¹ Bawendi *et al.* have observed significant quenching of the photoluminescence of quantum dots (QDs) deposited onto highly conductive NiO thin films as compared to QDs on resistive NiO films.¹² Greiner *et al.* have also shown that the work functions and energy-level

alignment of NiO thin films are dependent on the preparation conditions.¹³ In order to develop effective p-type DSSCs using NiO as a photosensitized cathode, it is pertinent to have a better understanding of the interfacial charge transfer processes occurring between dye molecules and NiO films pretreated in different conditions.

On the other hand, organic hole transporting materials (*e.g.*, *N,N'*-diphenyl-*N,N'*-(*m*-tolyl)-benzidine, TPD, see Fig. 2-1) can act as electron donors or acceptors in molecularly doped polymer (MDP) and much effort has been devoted to understanding the mechanism of charge transport in MDP.¹⁴⁻¹⁹ A “trap-free” hopping mechanism, where charge carrier (*e.g.*, hole) hops between adjacent or neighboring identical molecules is well accepted in MDP systems without the introduction of a second dopant.¹⁴⁻¹⁶ In MDP systems where two types of dopants with different ionization energy are present, charge transport can transit from hopping-control to trap-control and is dependent on the relative concentration ratio of the different dopants.^{14,15,17} In addition, the mobility of charge carriers in MDP is strongly dependent on the type and concentration of dopant molecules, temperature, applied external electric field, and the polymer host.¹⁷ The characteristics of MDP systems are different from those of traditional semiconductor (*e.g.*, TiO₂). Hence, it is of great interest to investigate how different types of charge transport in MDP, as compared with metal oxide semiconductors, can affect the single-molecule dynamics.

Interfacial electron transfer dynamics from dye molecules or quantum dots to n-type metal oxide semiconductors has been extensively investigated using ensemble-averaged approaches^{4,5,20} and single-molecule spectroscopy (SMS).²¹⁻²⁴ However, the study of hole transfer dynamics of single dye

in 1-propanol), chloroform (spectrophotometric grade), *N,N'*-diphenyl-*N,N'*-(*m*-tolyl)-benzidine (99%, TPD), and polystyrene ($\overline{M}_w$:290,000, $\overline{M}_n$:130,000, pellets, secondary standard) were obtained from Sigma-Aldrich. The carbodamine dye Atto647N was purchased from ATTO-TEC GmbH. All chemicals were used as received. Glass coverslips used in this thesis were purchased from Menzel-Glaser.

2.2.2 Cleaning process of glass coverslips

The glass coverslips were cleaned by sonication in acetone for 10 min, followed by sonication in aqueous NaOH for 20 min, and then sonication in distilled water for 10 min.

2.2.3 Preparation of NiO nanoparticle films

Nickel hydroxide sol was prepared using a method described elsewhere.^{10,26,27} Basically, 5 mL of 1.0 M NaOH solution was added slowly to 10 mL of 0.2 M Ni(NO₃)₂ solution under vigorous stirring. The solution was allowed to settle overnight, and the Ni(OH)₂ deposit was dialyzed against deionized water for 24 h. Nanostructured NiO films were prepared by spin coating Ni(OH)₂ sol onto cleaned glass coverslips and the Ni(OH)₂ sol was subsequently annealed at 350 °C for 3 h in either air, 5% O₂/95% Ar flow in a tubular furnace (Carbolite) or vacuum created by pumping the tubular furnace to a pressure of $\sim 1 \times 10^{-4}$ mbar.

2.2.4 Preparation of ZrO₂ nanoparticle film

ZrO₂ sol was prepared using a method described as follows.²⁸ A mixture containing 50 μ L of zirconium (IV) propoxide and 2 mL of isopropanol was added slowly to a mixture containing 20 mL of deionized water and 200 μ L of

37% HCl under vigorous stirring. The final solution was stirred at room temperature for 24 h. ZrO₂ sol was concentrated to 6 g/L using a rotary evaporator at 60 °C.

ZrO₂ film was obtained by spin casting 200 µL of 6 g/L ZrO₂ sol onto a cleaned glass coverslip. The as-prepared ZrO₂ film was calcined at 350 °C for 3 h in air.

2.2.5 Sample preparation (Part I)

Fluorescence measurements were performed on samples prepared by spin-coating an aqueous solution of Atto647N (~ 0.17 µM for ensemble-averaged experiments and ~ 0.045 nM for single-molecule experiments) onto either cleaned glass coverslips or thin NiO nanoparticle (NP) films.

2.2.6 Sample preparation (Part II)

Samples for ensemble-averaged experiments: 3.0 mL of Atto647N-TPD mixture solutions were prepared by adding 2.1 mL of TPD chloroform solution with varying concentrations to 0.9 mL of Atto647N chloroform solution. The final concentration of Atto647N was ~0.5 µM and the final concentration of TPD were 1.25, 2.50, 7.50, 10.0, and 20.0 mM.

Samples for single-molecule experiments: TPD/PS chloroform mixtures were first prepared by adding different amounts of TPD to 1% PS chloroform solution and the ratios of TPD to PS were 0, 10%, 20%, and 25% (wt.). Then, 10 µL of 0.16 nM Atto647N chloroform solution and 200 µL TPD/PS chloroform solution were mixed together. Single-molecule samples were prepared by spin casting 200 µL of dye/TPD/PS solution onto cleaned glass

coverslips at 3000 rpm for 5 min and evaporating the residual solvent for 6 h by placing as-prepared samples in a desiccator connected to an oil pump.

2.2.7 Ensemble Measurements

Steady-state absorption and emission spectra were recorded using a Cary 100 UV-vis spectrometer (Varian) and a Cary Eclipse fluorescence spectrometer (Varian), respectively.

Redox potentials of Atto647N and CB7-Atto647N were measured by cyclic voltammetry using a computer-controlled Eco Chemie Autolab PGSTAT 100 with an ADC fast scan generator. A glassy carbon working electrode, a Pt counter electrode, and a Ag/AgCl (3 M KCl) reference electrode were used. The electrochemical experiments were conducted in phosphate buffer solutions (pH = 7) under inert atmosphere.

XPS spectra of NiO films annealed in air and vacuum were recorded on a Thermo Fisher Scientific Thetaprobe XPS spectrometer. A monochromatic Al K α is set as the excitation source and the binding energy reference for the C1s is set at 285 eV.

Time-resolved fluorescence lifetimes were measured using a time-correlated single photon counting (TCSPC) spectrofluorimeter (FluoroCube, Horiba Jobin Yvon). The Atto647N samples were excited at 637 nm using a pulsed diode laser (NanoLED-635L, Horiba Jobin Yvon) and the emission was monitored at 662 nm for Atto647N-related liquid samples and 680 nm for Atto647N-related solid samples. The fluorescence decay profiles were analyzed using the Horiba Jobin Yvon DataStation software for single and double-exponential decays or the Fluofit 4.4 software (PicoQuant) for stretched-exponential decays, and the goodness of fit of the sums of exponentials was

assessed by considering the reduced chi-square (χ^2) value and the randomness of the weighted residuals. All measurements were performed at ambient conditions.

2.2.8 Setup of single-molecule fluorescence microscopy

A schematic representation of the time-resolved confocal fluorescence microscopy (MicroTime 200, PicoQuant) is depicted in Fig. 2-2.

Figure 2-2. Schematic of the time-resolved confocal fluorescence microscopy setup. 1 - laser source, 2 - excitation filter, 3 - optical fiber, 4 - electrical shutter, 5 - half-wave plate, 6 - quarter-wave plate, 7 - dichroic mirror, 8 - oil immersion objective, 9 - scanning stage, 10 - sample, 11 - pinhole, 12 and 14 - 50%/50% non-polarizing beam splitter, 13 - charge coupled device (CCD) camera coupled to a monochromator, 15 and 15' - emission filter, 16 and 16' - SPAD. Note: 4 and 12 are used to obtain single-molecule fluorescence intensity trajectory and emission spectrum simultaneously; 14, 15' and 16' are used to conduct antibunching experiments.

Basically, an inverted microscope (IX 71, Olympus) equipped with a scanning stage (P-733.2CL, Physik Instruments) was used to detect single molecules. A 635 nm pulsed diode laser (LDH-P-C-635B, PicoQuant) was used as the excitation source. The laser beam passed through an excitation filter (Z636/10, Chroma) and was coupled into a polarization maintaining single mode fiber. Circular polarized excitation light was achieved by using half-wave and quarter-wave plates. Circular polarized excitation light was focused through an oil immersion objective lens (100 $\times$, N.A. 1.4, Olympus) which was also used to collect the fluorescence and the fluorescence was then passed through a dichroic mirror (Z638rpc, Chroma), a pinhole and an emission filter (HQ685/70, Chroma) before being detected by a SPAD (SPCM-AQR-15, PerkinElmer). Time-correlated fluorescence decay curves were recorded by the TCSPC technique with the TimeHarp 200 PCI-board (PicoQuant). The data were analyzed using the SymPho Time software (PicoQuant) and the Fluofit 4.4 software (PicoQuant).

The setup of the antibunching experiment was based on the Hanbury-Brown and Twiss (HBT) setup where two SPADs (*i.e.*, one is the start channel and another is the stop channel) and a 50%/50% non-polarizing beam splitter were used.²⁹

2.3 Results and Discussion

PART I: Heterogeneous interfacial hole transfer dynamics from dye molecules to p-type NiO nanoparticles

2.3.1 Ensemble-averaged hole transfer kinetics

Figure 2-3. Time-resolved fluorescence decay profiles of Atto647N deposited on (A) a glass substrate, (B) NiO NP film pre-annealed in vacuum and (C) NiO NP film pre-annealed in air and the instrument response function (IRF). The corresponding theoretical fits based on a single-exponential decay function for curve A and a stretched exponential function for curves B and C are also shown. Standard deviations for dye molecules on glass, NiO NP film pre-annealed in vacuum, and NiO NP film pre-annealed in air, are 0.1, 0.3, and 0.1 ns, respectively.

The time-resolved fluorescence decay profile of Atto647N on a glass substrate (curve A in Fig. 2-3) is well fitted using a single-exponential decay

function with a fluorescence lifetime of 3.8 ns which is close to the unquenched emission lifetime of Atto647N in water. This indicates that the dye coverage on the solid surface is sufficiently low to avoid self quenching between the Atto647N molecules. The fluorescence decay profiles of similar concentrations of Atto647N deposited onto thin NiO NP films pre-treated by annealing in vacuum and in air are also displayed in Fig. 2-3. In both cases, the heterogeneous fluorescence decays cannot be properly described using either a single or double-exponential decay function (*i.e.*, $\chi^2 > 1.8$ were obtained), hence suggesting the presence of a distribution of emission decay times.

In order to satisfactorily analyze the fluorescence decay profiles of Atto647N on NiO NP (*i.e.*, with $1 < \chi^2 < 1.2$), the stretched exponential function is used to fit the experimental data:

$$I(t) = I_0 \exp \left[- \left(\frac{t}{\tau_k} \right)^\beta \right] \quad (2.1)$$

where τ_k is the characteristic time scale of the decay and β is the stretching exponent. The mean lifetime of the distribution is given by $\langle \tau \rangle_{\text{NiO}} = \tau_k \beta^{-1} \Gamma(\beta^{-1})$, where $\Gamma(x)$ is the gamma function. From equation 2.1, the emission decay of Atto647N on a NiO NP film pre-annealed in vacuum (curve B in Fig. 2-3) yields $\tau_k = 1.1$ ns, $\beta = 0.67$ and $\langle \tau \rangle_{\text{NiO}} = 1.5$ ns. For Atto647N on a NiO NP film pre-annealed in air (curve C in Fig. 2-3), the values for τ_k , β and $\langle \tau \rangle_{\text{NiO}}$ are 0.3 ns, 0.66 and 0.5 ns, respectively. It is clear from Fig. 2-3 and the $\langle \tau \rangle_{\text{NiO}}$ values that the fluorescence lifetime of Atto647N molecules is quenched by the NiO

NP with significantly more quenching occurring for the NiO NP pre-annealed in air as compared to NiO NP pre-annealed in vacuum.

Figure 2-4. Time-resolved fluorescence decay profile of Atto647N deposited on a ZrO₂ NP film. The mono-exponential decay function fitting curve (black line) is also given.

The radiative decay constant of an excited state may be perturbed by varying the dielectric constant of the medium.³⁰ The effects of a change in the medium refractive index, from ~ 1.5 for glass to ~ 2 for NiO, are determined by measuring the fluorescence decay of Atto647N deposited on an inactive ZrO₂ NP film whose refractive index is close to that of NiO. The single-exponential fluorescence decay yields a lifetime of 3.5 ± 0.1 ns (Fig. 2-4) which is not significantly different from that obtained for the dye on a glass surface (3.8 ± 0.1 ns). Therefore, the observed fluorescence quenching on NiO cannot be explained by an alteration in radiative decay rate and is, instead, attributed to nonradiative processes. Furthermore, the absorption of light in the visible

region by NiO is weak and energy transfer between the excited dye and NiO NP is not considered to be responsible for the observed quenching (see Fig. 2-5).³¹⁻

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Figure 2-5. Absorption spectra of an aqueous solution of Atto647N (black) and a NiO film annealed in air (grey) and emission spectrum of an aqueous solution of Atto647N (dark grey).

Figure 2-6. The cyclic voltammogram of Atto647N in phosphate buffer solutions (pH = 7) under inert atmosphere.

The cyclic voltammogram (cv) of Atto647N (8.1×10^{-5} M) in phosphate buffer solution (pH = 7) is shown in Fig. 2-6 where the first one-electron reduction potential of Atto647N is measured to be $E_{\text{red}} = -0.89$ V (vs. Ag/AgCl) or $E_{\text{red}} = -0.68$ V (vs. NHE). The first excited singlet state energy of Atto647N is estimated to be 1.889 eV from the absorption and emission spectra of Atto647N.

Figure 2-7: Schematics of charge-transfer processes for an organic dye-sensitized p-type NiO semiconductor. Step 1 is photo-excitation from ground S_0 state to excited S_1 state, step 2 is hole injection and step 3 is electron transfer. The dash lines represent the upward shifted valence band (VB) and downward shifted conduction band (CB) of NiO annealed in a relatively more oxygen rich environment.

The observed reduction in fluorescence lifetime is attributed to interfacial hole transfer from the dye molecules to the p-type NiO semiconductor as illustrated in Fig. 2-7. In this case, the free energy for hole transfer (ΔG_{ht}^0) is calculated using the following equation:⁶

$$\Delta G_{\text{ht}}^0 = E_{\text{vb}} - E_{\text{red}} - E_{00} \quad (2.2)$$

where E_{vb} ($= 0.54$ V vs. NHE) is the valence band (VB) potential of NiO,²⁷ and E_{red} ($= -0.68$ V vs. NHE) and E_{00} ($= 1.889$ eV) are the first one-electron reduction potential of Atto647N and the energy difference between the lowest vibronic level of the ground and excited electronic states of Atto647N,²⁴ respectively. A ΔG_{ht}^0 value of -0.669 eV is obtained from equation 2.2, indicating an energetically favorable IHT process from the Atto647N molecules to the VB of NiO. On the other hand, electron transfer from the dye to the conduction band of NiO is not feasible since the corresponding free energy for electron transfer is positive in value (*i.e.*, $\Delta G_{\text{et}}^0 = 2.017$ eV). The average IHT rates between Atto647N and NiO NP, estimated from $k_{\text{ht}} = \langle \tau \rangle_{\text{NiO}}^{-1} - \langle \tau \rangle^{-1}$ where $\langle \tau \rangle$ ($= 3.81$ ns) is the mean lifetime of the dye on glass, are $k_{\text{ht}} = 4.2 \times 10^8 \text{ s}^{-1}$ and $1.9 \times 10^9 \text{ s}^{-1}$ for NiO NP pre-annealed in vacuum and in air, respectively.

The chemical composition of nickel oxide film is analyzed by fitting the experimentally measured Ni 2p_{3/2} XPS spectrum (peak at binding energy of 855.6 eV) to two overlapping curves with peak positions at 854.6 eV (binding energy for Ni²⁺ from NiO) and 856.1 eV (binding energy for Ni³⁺ from Ni₂O₃) (see Fig. 2-8).³⁵ The integrated peak area ratios of Ni²⁺/Ni³⁺ for NiO annealed in air and in vacuum are determined to be 0.51 and 0.75, respectively, indicating that relatively more Ni³⁺ is formed in the former. During the annealing process in air, oxygen creates extra vacancies in normally Ni²⁺ occupied sites causing some of the surrounding Ni²⁺ to undergo oxidation to form Ni³⁺ in order to preserve charge neutrality. The doping of nickel oxide films with Ni³⁺ and Al³⁺

results in a reduction of bandgap energy and an upward shift of the semiconductor VB.^{11,36} The faster IHT rate observed for NiO annealed in air may be due to an energetically more favorable hole transfer process resulting from a larger energy difference between the HOMO of the dye and the VB of NiO (Fig. 2-7). In addition, the intraband gap states resulting from the formation of Ni³⁺ in O₂ provide extra channels for charge-transfer to take place and hence enhance the IHT rates.

Figure 2-8. Ni 2p_{3/2} XPS spectra of NiO NP films pre-annealed in vacuum (a) and in air (b) at 350 °C for 3 h fitted with curves corresponding to Ni²⁺ (I) and Ni³⁺ (II).

2.3.2 Single-molecule spectroscopy measurements

Figure 2-9. Emission intensity (bin-time used is 5 ms, black) and lifetime (grey) trajectories of single Atto647N molecules deposited on glass (a) and a NiO NP film pre-annealed in air (b and c). The fluorescence lifetime ($\tau_{0.5}$) for every 0.5 s step size is determined from the single-exponential emission decay profile obtained from the photons found in each time interval (0.5 s).

From a number-density analysis, it was found that the average number of detectable single Atto647N molecules deposited onto a NiO NP film pre-annealed in air is about 75% of the single molecules detected on a glass substrate. The rest of the single molecules on NiO ($\sim 25\%$) are significantly quenched by the semiconductor and their emission is too weak to be detected by the current SMS set-up.

Fig. 2-9a shows a typical fluorescence intensity trajectory of a single Atto647N molecule deposited on a glass substrate. The fluorescence lifetime ($\tau_{0.5}$) for every 0.5 s step size is determined from the single-exponential emission decay profile obtained from the photons found in each time interval (0.5 s) and the data is presented in Fig. 2-9a. It is observed that the $\tau_{0.5}$ value does not fluctuate significantly throughout the intensity trajectory and the molecule has a mean $\tau_{0.5}$ value of 4.2 ns. The fluorescence decay profile of the molecule constructed using all the photons detected during its survival time is best fitted using a single-exponential decay function with a lifetime of $\tau_f = 4.2$ ns. The τ_f distribution histogram for 131 single dye molecules is described by a Gaussian function with a mean emission lifetime of 3.9 ns (see Fig. 2-11a) which is in agreement with the lifetime measured from the bulk experiment.

The fluorescence intensity trajectory and $\tau_{0.5}$ distribution of detectable single Atto647N molecules on a NiO NP film pre-annealed in air are classified into two categories as illustrated by two molecules in Figs. 2-9 b and c. The single molecule in Fig. 2-9b exhibits $\tau_{0.5}$ values (from single-exponential decays) that do not fluctuate significantly from the mean value of 0.6 ns. The single-exponential fluorescence decay profile, constructed from all the photons detected before photobleaching, yields $\tau_f = 0.6$ ns.

On the other hand, large fluctuations in both the fluorescence intensity and $\tau_{0.5}$ are seen for the single molecule in Fig. 2-9c. In this case, a positive correlation exists between the fluorescence intensity and $\tau_{0.5}$ such that low $\tau_{0.5}$ values are observed for low emission intensities and *vice-versa*. For an example, at point X in Fig. 2-9c, where the average fluorescence intensity is ~ 3.2 counts/ms, the corresponding $\tau_{0.5} = 0.9$ ns (see the single-exponential decay curve X in Fig. 2-10) whereas at point Y, with a higher average intensity of ~ 11.6 counts/ms, the corresponding $\tau_{0.5}$ is increased to 2.4 ns (see the single-exponential decay curve Y in Fig. 2-10). The fluorescence decay profile of the molecule, constructed by combining all the photons detected before it undergoes an irreversible photobleaching process at ~ 23 s, is given by decay curve Z in Fig. 2-10. Due to the distribution of lifetimes observed throughout the intensity trajectory, the decay curve Z is best described using a stretched exponential function with $\tau_k = 0.7$ ns, $\beta = 0.66$ and $\langle \tau \rangle_{\text{NiO}} = 1.0$ ns. Similar behavior in the fluorescence intensity and lifetime trajectories is observed for single dye molecules deposited on NiO NP film pre-annealed in 5% O₂/95% Ar and in vacuum.

Figure 2-10. The fluorescence decay profiles constructed from photons found in the 0.5 s interval at X and Y of Fig. 2-9c are given by curves X and Y, respectively. Curve Z is constructed from photons emitted during the survival time of the molecule in Fig. 2-9c. A single-exponential decay function is used to fit the decay curves X and Y whereas a stretched exponential is used to fit curve Z.

Figure 2-11. Normalized fluorescence lifetime (τ_f) histogram of single Atto647N molecules on glass fitted to a Gaussian distribution (a). Normalized mean fluorescence lifetime (*i.e.*, τ_f for mono-exponential decays and $\langle\tau\rangle_{\text{NiO}}$ for stretched-exponential decays) histograms of single Atto647N molecules on NiO NP film pre-annealed in vacuum (b), 5% O₂/95% Ar (c), and air (d) and the corresponding Gaussian fits. Standard deviations for (a)-(d) are 0.4, 2.4, 2.0, and 1.5 ns, respectively. Bin-time used is 0.3 ns for (a) and 0.5 ns for (b)-(d).

The normalized distributions of the mean fluorescence lifetime of individual molecules (*i.e.*, τ_f and $\langle\tau\rangle_{\text{NiO}}$) for 154 single dye molecules on NiO NP pre-annealed in vacuum (where 60% of molecules display stretched exponential decay), 134 molecules on NiO NP pre-annealed in 5% O₂/95% Ar (where 58% of molecules display stretched exponential fluorescence decays) and 163 molecules on NiO NP pre-annealed in air (where 51% of molecules

display stretched exponential fluorescence decays) are given in Figs. 2-11 b, c and d, respectively. Molecules that show very low intensity counts give rise to mean lifetimes that are shorter than the time resolution of the experimental set-up (*i.e.*, < 300 ps), and their number of occurrences is represented by the hatch fill column. It is observed that as the concentration of O₂ present in the annealing process increases, the peak of the histogram shifts to shorter mean lifetime (*i.e.*, ~1.9 ns, ~1.1 ns and ~0.5 ns for NiO pre-annealed in vacuum, 5% O₂/95% Ar and air, respectively, as estimated from the Gaussian distribution fit to the histogram), and is accompanied by a decrease in the proportion of molecules displaying relatively long mean lifetime. For an example, 43%, 18% and 6% of the total number of molecules studied have mean lifetimes > 2.0 ns when deposited on NiO NP films pre-annealed in vacuum, 5% O₂/95% Ar and air, respectively.

A similar trend is noted for the distribution of the fluorescence intensity (*I*) of individual molecules, where *I* is defined by $I = (\text{total number of photon counts detected during the survival time})/(\text{survival time})$ (see Fig. 2-12). In this case, the proportion of molecules exhibiting relatively high *I* decrease when the concentration of O₂ utilized during the annealing process increases. For an example, 44%, 24% and 7% of the total number of molecules studied have *I* > 30 counts/ms when deposited on NiO NP films pre-annealed in vacuum, 5% O₂/95% Ar and air, respectively.

Figure 2-12. Normalized fluorescence intensity histograms of single Atto647N molecules on NiO NP film annealed in vacuum (a), 5% O₂/95% Ar (b), and air (c).

Figure 2-13. Typical interphoton time distribution of a single Atto647N molecule on a NiO NP film pre-annealed in air. N_c/N_L histogram for a collection of 45 single Atto647N molecules deposited on a NiO NP film pre-annealed in air.

To ensure that multiple chromophores in the same excitation volume (which can lead to correlated emission intensity and lifetime fluctuations) are not present, antibunching experiment is conducted to confirm that the observed fluorescence originates from a single molecule.^{37,38} A typical interphoton arrival time distribution of a fluorescent spot on a NiO NP film pre-annealed in air (see Fig. 2-13a) displays signature features of a single-photon emitter indicating that only a single dye molecule is emitting in the detection volume. In particular, the ratio of the number of coincident events in the central peak (N_C) to the average number of non-coincident events in the lateral peaks (N_L) is $N_C/N_L \sim 0.15$ which is smaller than 0.5 (note: in the ideal case, $0.5 \leq N_C/N_L \leq 1$ when two or more independent emitters are found in the detection volume). The non-zero, albeit small, coincidence in the central peak for the molecule in Fig. 2-13a can be attributed to background-background and background-signal photon pairs.^{37,38} The histogram of the N_C/N_L ratio for 45 molecules, shown in Fig. 2-13b, clearly demonstrates that close to all of the dye molecules on NiO behave as single-photon emitters.

The emission lifetime quenching for single Atto647N molecules on NiO NP films is due to IHT from the dye to the metal oxide semiconductor (Fig. 2-7). The more efficient overall IHT rate for NiO NP pre-annealed in an environment with a higher oxygen concentration (*e.g.*, in air) is possibly due to an upward shift of the VB of NiO as more Ni_2O_3 are formed. It is shown that the single-molecule and ensemble-averaged spectroscopy results are in agreement with each other. The distribution of IHT rates inferred from the stretched exponential emission decay seen in the bulk experiment for Atto647N on NiO NP film (Fig. 2-3) is rationalized by considering the presence of both

dynamic and static inhomogeneity in the IHT dynamics. The fluctuations in fluorescence lifetime and emission intensity with time within a molecule (Fig. 2-9c) give rise to a dynamic contribution. On the other hand, the lifetime fluctuation behavior of a single molecule varies from molecule to molecule as implied by the broad distribution of mean lifetimes seen in Figs. 2-11 b-d (*i.e.*, static contribution). In addition, ~25% of single molecules deposited onto a NiO NP film pre-annealed in air undergo highly efficient IHT and are not detectable using the current experimental set-up. A change in the microenvironment is capable of perturbing the electronic interaction between the dye molecule and semiconductor, the reorganization energy and the Gibbs free energy for hole transfer. An inhomogeneous distribution in the chemical composition of the metal oxide film, resulting from preparation conditions, may provide (defect) sites for dye molecules that can either promote or inhibit favorable IHT electronic coupling and driving force between the two entities. Individual molecules therefore experience different microenvironments which give rise to the observed heterogeneous IHT dynamics. In addition, other factors such as a time-dependent variation in the spatial separation between dye and semiconductor may influence the electronic coupling. Inhomogeneous distributions of interfacial electron transfer rates between (single) organic dye molecules and n-type semiconductors (*e.g.*, TiO₂) have also been observed and discussed in the past.^{21,23,39-45} However, the exact nature of the mechanism behind the fluctuations in IET rates with time remains unclear.

PART II: Hole transfer dynamics from organic dye to TPD molecules

2.3.3 Ensemble-averaged hole transfer dynamics

Figure 2-14. Fluorescence emission spectra of Atto647N chloroform solution in the absence and presence of varying concentrations of TPD (1.25, 2.50, 7.50, 10.0 and 20.0 mM). Inset is the relative change of fluorescence integration area with varying concentrations of TPD and the theoretical fit (the fitting range: 0 to 20.0 mM) based on the standard Stern-Volmer model is also shown.

The steady-state fluorescence emission spectra of Atto647N dissolved in chloroform in the absence and presence of TPD are given in Fig. 2-14. Clearly, the emission intensity of Atto647N in the presence of TPD is quenched and more quenching is observed with an increase in the concentration of TPD. Furthermore, the dependence of fluorescence quenching efficiency on the concentration of TPD (0 to 20.0 mM) can be described using the standard linear Stern-Volmer equation:

$$\frac{I_0}{I} = 1 + K_{sv}[Q] \quad (2.3)$$

where I_0 and I are the integrated area of the fluorescence spectra in the absence and presence of TPD, respectively, K_{sv} is the Stern-Volmer constant, and $[Q]$ is the concentration of TPD. $K_{sv} = 27.6 \text{ M}^{-1}$ is obtained when $[Q]$ varies in the dynamic quenching range (*i.e.*, from 0 to 20.0 mM). When $[Q]$ is larger than 20.0 mM, the plot of $\frac{I_0}{I}$ vs. $[Q]$ displays a downward curvature. The non-linear relationship observed can be attributed to static quenching and/or multistate emission quenching.⁴⁶⁻⁴⁹

In order to have a better understanding of the quenching mechanism between Atto647N and TPD, time-resolved fluorescence measurements were conducted and the results are shown in Fig. 2-15. The mono-exponential fluorescence decay of Atto647N in chloroform and in the absence of TPD has an emission lifetime of 4.1 ns. Upon the addition of TPD, the fluorescence decay profile of Atto647N, fitted to a single-exponential decay function, yields a progressively shorter emission lifetime as the concentration of TPD (*i.e.*, $[TPD]$) increases to 10.0 mM (see Table 2-1). When $[TPD] = 20.0 \text{ mM}$, the fluorescence decay is best described using a double-exponential decay function with a long lifetime component of $\tau = 3.1 \text{ ns}$ and a short lifetime component of $\tau_2 = 1.5 \text{ ns}$. The latter is due to the emission from a short-lived state and is neglected due to its small contribution ($< 10 \%$) to the fluorescence decay profile.

Figure 2-15. Time-resolved fluorescence decay profiles of Atto647N chloroform solution in the absence and presence of varying concentrations of TPD (1.25, 2.50, 7.50, 10.0, and 20.0 mM). The instrument response function (dot line) is also given. Inset is the relative change of fluorescence lifetime with varying concentrations of TPD and the theoretical fit (the fitting range: 0 to 20.0 mM) based on the standard Stern-Volmer model is also given.

Table 2-1. Fluorescence lifetime(s) of Atto647N in chloroform solution in the presence of various concentrations of TPD ([TPD]).

[TPD]/mM	τ^*/ns	τ_2^*/ns
0	4.1	
1.25	4.0	
2.50	3.9	
7.50	3.5	
10.0	3.4	
20.0	3.1 (92 %)	1.5 (8 %)

*The error is ± 0.1 ns.

It is clear from Fig. 2-15 and Table 2-1 that the lifetime of excited Atto647N is quenched in the presence of TPD, in agreement with the quenched

steady-state emission intensity. The plot of τ_0/τ vs. $[Q]$ is well fitted using the linear Stern-Volmer equation:

$$\tau_0/\tau = 1 + K_{sv}'[Q] \quad (2.4)$$

where $\tau_0 = 4.1$ ns and τ are the fluorescence lifetimes of Atto647N in the absence and presence of TPD, respectively and $K_{sv}' = 18.7 \text{ M}^{-1}$ is the Stern-Volmer constant. The Stern-Volmer constants (K_{sv} and K_{sv}') obtained from both the steady-state and time-resolved experiments are quite similar in value, indicating that the quenching effect originates mainly from dynamic quenching at the low concentrations of quencher used (*i.e.*, $[TPD] \leq 20 \text{ mM}$).

The fraction of effective collision (f_Q) in bimolecular collisions is determined using the following equation:⁵⁰

$$f_Q = \frac{k_q}{k_d} \quad (2.5)$$

where k_q is the bimolecular quenching constant and k_d is the diffusion-controlled rate constant, respectively. The latter is approximated using the Smoluchowski equation:

$$k_d = \frac{4\pi N}{1000}(r_{\text{Atto647N}} + r_{\text{TPD}})(D_{\text{Atto647N}} + D_{\text{TPD}}) \quad (2.6)$$

where N is Avogadro's number, r_{Atto647N} and r_{TPD} are the radii of Atto647N and TPD, respectively, and D_{Atto647N} and D_{TPD} are the diffusion coefficients of Atto647N and TPD, respectively. The diffusion coefficient of Atto647N in

water is assumed to be similar to that of Atto655 whose diffusion coefficient of $4.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ in an aqueous solution at 25 °C has previously been determined using fluorescence correlation spectroscopy.^{51,52} Using the Stokes-Einstein equation, D_{Atto647N} and r_{Atto647N} in chloroform at 25 °C are calculated to be $7.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and 0.58 nm, respectively, and D_{TPD} and r_{TPD} in chloroform at 25 °C are estimated to be $6.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and 0.62 nm (assuming the volume of TPD is 1 nm³).⁵³ From equation 2.6, k_d is calculated to be $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $k_q = 6.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ is calculated by $k_q = K_{\text{sv}}/\tau_0$, where K_{sv} is the steady-state Stern-Volmer constant. $f_Q \sim 0.56$ is obtained suggesting that about 60% of the collisional events are effective in inducing excited state quenching.

Figure 2-16. Absorption spectrum (black line) of 100 mM TPD in chloroform and emission spectrum (grey line) of 0.5 μM Atto647N in chloroform.

The quenched emission intensity and lifetime of Atto647N in the presence of TPD can be attributed to charge (electron or hole) transfer and/or electronic

energy transfer processes. Energy transfer between Atto647N and TPD is excluded due to the insignificant spectral overlap between the absorption spectrum of TPD and the fluorescence spectrum of Atto647N (see Fig. 2-16). The driving force (ΔG^0) for hole transfer from dye molecules to TPD is estimated by the following equation:

$$\Delta G_{\text{ht}}^0 = E_{\text{ox}} - E_{\text{red}} - E_{00} \quad (2.7)$$

where E_{ox} (= 1.092 vs. NHE),⁵⁴ E_{red} (= -0.68 vs. NHE) and E_{00} (= 1.889 eV) represent the oxidation potential of TPD, the first one-electron reduction potential of the dye molecules and the energy difference between the lowest vibronic level of the ground and excited electronic states of Atto647N, respectively.²⁴ A calculated ΔG^0 value of -0.117 eV is obtained indicating an energetically favorable hole transfer process from Atto647N to TPD.

The activated hole transfer rate (k_h) is estimated by the following equation:⁵⁵

$$\frac{1}{k_q} = \frac{1}{k_d} + \frac{1}{Kk_h} \quad (2.8)$$

where the diffusional equilibrium constant of the encounter reactants is given by

$$K = \frac{4\pi NR^2\delta d}{1000} C \quad (2.9)$$

R is the sum of the molecular radii of the two reactants, δd is usually assumed to be 0.2 nm, and C is 1 for neutral molecules diffusing randomly in solution. From equation 2.9, $K = 2.2 \text{ M}^{-1}$ is obtained and the activated hole transfer rate (k_h) is calculated to be $6.9 \times 10^9 \text{ s}^{-1}$.

2.3.4 Single-molecule hole transfer dynamics

Typical fluorescence intensity trajectories of Atto647N in PS film and TPD-doped PS films are shown in Fig. 2-17. Two distinct groups of blinking behavior are observed when dye molecules are embedded in polymer films. More than 80% of the molecules recorded in PS or TPD doped PS films displayed temporary off-events that last from tens of milliseconds to a few seconds (see Fig. 2-17), while the rest of the molecules displayed constant emission intensity before undergoing irreversible photobleaching.

Though the fluorescence intermittency behavior of single Atto647N molecules in the absence and presence of TPD dopants in polymer films is observed, the origins of off-events for both cases are different. When dye molecules are embedded in neat PS film, the off-events can be ascribed to the formation of a dark dye radical ion when a charge is transferred from the excited Atto647N molecule to a localized state found in the polymer matrix.⁵⁶ For dye molecules in TPD-doped PS films, off-events are possibly due to the formation of dark reduced states of Atto647N generated from HT to TPD.⁵⁶⁻⁵⁹ The transition from “off” to “on” occurs when a hole undergoing a series of hopping process in MDP film recombines with the reduced dye molecule.

Figure 2-17. Typical fluorescence intensity (bin-time = 10 ms, black) and lifetime (grey) trajectories of single Atto647N molecules in neat PS film (a) and 25% TPD-doped PS film (b and c). The fluorescence lifetime ($\tau_{0.5}$) for every 0.5 s step size is determined from the single-exponential emission decay profile obtained from photons found in each time interval (0.5 s).

The fluorescence decay profile of the single dye molecule in neat PS film shown in Fig. 2-17a is well fitted using a single-exponential decay function

with a fluorescence lifetime of 3.9 ns (Fig. 2-18), whereas the fluorescence decay profiles of the single molecules in TPD doped PS film (*i.e.*, Figs. 2-17 b and c) cannot be fitted using a mono-exponential decay function. To better describe the fluorescence lifetime, a stretched-exponential function (equation 2.1) is used to fit the decay profiles such that molecules b and c in Fig. 2-17 yield $\langle\tau\rangle = 0.3$ ns with $\beta = 0.58$ and $\langle\tau\rangle = 0.4$ ns with $\beta = 0.57$, respectively. The fluorescence lifetime of Atto647N is quenched in the presence of TPD and is shown to fluctuate with time. This behavior is due to heterogeneous HT dynamics from dye molecules to TPD.

Figure 2-18. Fluorescence lifetime decay profiles of the single dye molecules shown in Fig. 2-17. Black, light grey and grey curves are the corresponding decay profiles of the molecules in Figs. 2-17 a, b, and c, respectively.

The statistics distributions of the mean lifetime $\langle\tau\rangle$ and stretching exponent β for 160 molecules in neat PS film, 145 molecules in 10% TPD doped PS films, 160 molecules in 20% TPD doped PS films, and 131 molecules in 25% TPD doped PS films are displayed in Fig. 2-19. Clearly, compared to dye molecules in neat PS film, the mean lifetimes of dye molecules in TPD

doped films are shorter with higher quenching efficiency observed when the TPD concentration is increased. For an example, about 80% of the molecules in PS film display $\langle\tau\rangle$ longer than 3.0 ns, whereas ~10% of the molecules in 10% TPD doped PS films display $\langle\tau\rangle > 3.0$ ns. When the concentration of TPD is increased to 20% and 25%, only 1 to 2% of the molecules exhibit $\langle\tau\rangle > 3$ ns. The broad $\langle\tau\rangle$ distributions for dye molecules in TPD doped films suggest that the HT reactivity differs from molecule to molecule. In addition, 90% of the molecules in PS film display β larger than 0.9, whereas only 22%, 9% and 5% of the molecules display $\beta > 0.9$ in 10%, 20% and 25% TPD-doped PS films, respectively. The hole transfer rate increases as the concentration of TPD increases since the spatial separation (r) between the two entities decreases and r varies from molecule to molecule giving rise to a distribution of hole transfer rates. The fluctuation of both $\tau_{0.5}$ and emission intensity may also be attributed to a variation in hole-transfer reactivity of dye molecules induced by the dynamic change in the electronic coupling element, reorganization energy and driving force for hole transfer.

Figure 2-19. Histograms of mean fluorescence lifetime and stretching exponent of single Atto647N molecules in neat PS film (A-1 and A-2) and single Atto647N molecules in TPD doped PS films (10%: B-1 and B-2; 20%: C-1 and C-2; 25%: D-1 and D-2).

2.4 Conclusion

In Atto647N sensitized NiO films system, the interfacial hole transfer dynamics of Atto647N on thin films of NiO nanoparticles has been examined using both time-resolved ensemble-averaged and single-molecule spectroscopy techniques. From the bulk experiments, it is observed that the rate of IHT is enhanced for NiO NP pre-annealed in air as compared to NiO NP pre-annealed in vacuum. This is due to the upward shift of the VB of NiO as more Ni_2O_3 are formed in air (O_2) during the processing of the metal oxide. A distribution of IHT rates from dye molecules to NiO is inferred from the stretched-exponential fluorescence decay curve and this observation is in agreement with the results observed in the single-molecule spectroscopy studies. In particular, both static and dynamic fluctuations in the emission intensity and fluorescence lifetime suggest that the microenvironments of individual molecules vary among different molecules and are responsible for the heterogeneous distributions of IHT rates.

In the study of hole transfer from Atto647N to TPD molecules, the linear Stern-Volmer equation is used to describe the relationship between the relative fluorescence quenching efficiency and the concentration of TPD ($[\text{TPD}] \leq 20$ mM). Similar Stern-Volmer quenching constants are obtained from both steady-state fluorescence emission and time-resolved fluorescence lifetime measurements which indicate the presence of dynamic quenching. It is estimated that about 60% of the collisional events are effective in quenching *via* interfacial hole transfer. For dye molecules embedded in TPD-doped PS films, quenched fluorescence intensity and lifetime are also observed as compared to single dye molecules in neat PS films, which can be ascribed to the hole

transfer process from excited dye molecules to TPD. Heterogeneous distribution of lifetime indicates the temporal change of hole-transfer reactivity and the uneven distribution of TPD in PS film.

2.5 Bibliography

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CHAPTER 3

CHARGE-TRANSFER PROCESSES IN SINGLE CdSe/ZnS QUANTUM DOTS WITH P- TYPE NiO NANOPARTICLES

This chapter is adapted from: “Charge-transfer processes in single CdSe/ZnS quantum dots with p-type NiO nanoparticles, Xiangyang Wu and Edwin K. L. Yeow, *Chem. Commun.*, **2010**, 46, 4390-4392.”

3.1 Introduction

Colloidal semiconductor nanocrystal has been hailed to be an important component in the development of next generation solar cells due to its superior photostability and broad absorption band with high extinction coefficients.^{1,2} Charge-separation occurring in QD based solar cells can be judiciously controlled and optimized by varying the size of QD and its corresponding bandgap energy. Several studies have been dedicated to understand the dynamics of electron transfer from QDs to n-type semiconductors (*e.g.*, TiO₂) at both the ensemble^{1,2} and single-molecule³ levels. However, the use of QD-sensitized p-type metal oxide semiconductor (*e.g.*, NiO) in devices is still lacking. Recently, NiO has been shown to be an efficient hole transporting layer and hole collector in QD based light-emitting devices^{4,5} and organic dye-sensitized solar cells.⁶⁻⁸ In order to design efficient QD/NiO based devices for energy conservation and conversion, it is necessary to have a clearer understanding of the charge-transfer processes occurring between QD and NiO.

Fluorescence blinking, commonly seen in QDs, occurs when an excited dot undergoes a transition to a temporary dark state.^{9,10} Several methods including energy transfer to an acceptor (*e.g.*, Ag nanoparticles¹¹ or graphene¹²) and addition of chemicals (*e.g.*, β -mercaptoethanol,¹³ propyl gallate¹⁴ or TiO₂ nanoparticles¹⁵) into QD sample solutions have been designed to reduce this behavior. In addition, suppression of blinking behavior of QDs can be achieved by chemical modification of the structure of QDs. Hollingsworth *et al.*¹⁶ and Dubertret *et al.*¹⁷ reported that a thick CdS shell on CdSe core can reduce the blinking behavior.

In this chapter, we investigated charge-transfer processes in single CdSe/ZnS QDs with p-type NiO nanoparticles and demonstrated a novel pathway to obtain QDs with blinking suppression.

3.2 Experimental Section

3.2.1 Materials

Mercaptoundecanoic acid-functionalized CdSe/ZnS core/shell QD with a CdSe core of ~1.5 nm radius and overcoated with ~4 monolayers of ZnS was obtained from NN-Labs (Batch number: 101309-JS). Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%) and sodium hydroxide (NaOH, pallet, 99.998%) were obtained from Alfa Aesar and Sigma-Aldrich, respectively. All chemicals were used as received.

3.2.2 Preparation of NiO nanoparticle film

Preparation of $\text{Ni}(\text{OH})_2$ sol was described in Chapter 2. Nanostructured NiO film was prepared by spin coating $\text{Ni}(\text{OH})_2$ sol onto cleaned glass coverslips and the $\text{Ni}(\text{OH})_2$ sol was annealed at 350 °C for 3 h in air.

3.2.3 Preparation of single-molecule samples

Single-molecule samples were prepared by spin casting a dilute solution (~ 0.1 - 1 nM) of CdSe/ZnS QD solution onto either cleaned glass coverslips or NiO nanoparticle films.

3.2.4 Setup of single-molecule fluorescence microscopy

The basic setup has been described in Chapter 2. In this work, a 470 nm pulsed laser diode (LDH-P-C-470B, PicoQuant) and HQ 490 LP were used as the excitation source and the emission filter, respectively. The time-dependent

fluorescence spectra and fluorescence intensity time traces were simultaneously recorded using a 50%/50% non-polarizing beam splitter which divided the fluorescence signal into a SPAD and a CCD camera (Pixis 100, Princeton Instruments) coupled to a monochromator (SP2150i, Acton Research) for fluorescence intensity trajectory and fluorescence spectrum measurements, respectively.

3.3 Results and Discussion

Figure 3-1. Absorption spectra of CdSe/ZnS QD (black) and NiO film (grey) and emission spectra of CdSe/ZnS QD (light grey).

Fig. 3-1 shows the absorption spectra of CdSe/ZnS QD and NiO film and the emission spectra of CdSe/ZnS QD. The first absorption and emission peaks of CdSe/ZnS QD are observed at 575 and 606 nm, respectively. The absence of NiO nanoparticle absorption in the range of 400 to 700 nm suggests that electronic energy transfer does not occur between QD and NiO.

The relative energy of the conduction band (CB) and valence band (VB) of QD are dependent on the size of QD due to quantum size effects and can be estimated by the following equations:

$$\Delta E_{\text{CB}} = \Delta E_{\text{BG}} \left(\frac{m_h}{m_h + m_e} \right) \quad (3.1)$$

$$\Delta E_{\text{BG}} = E_{\text{ls}} - E_{\text{g}} \quad (3.2)$$

$$E_{\text{ls}} = \frac{1240}{\lambda} \quad (3.3)$$

where E_{ls} is the bandgap energy of CdSe/ZnS QD and is calculated to be 2.16 eV using the first absorption position (*i.e.*, $\lambda = 575$ nm) and E_{g} is the bandgap energy of bulk CdSe (*i.e.*, $E_{\text{g}} = 1.7$ eV). Therefore, a ΔE_{BG} value of 0.46 eV is obtained from equation 3.2. Given that the hole effective mass $m_h \sim 0.44$ and the electron effective mass $m_e \sim 0.11$, ΔE_{CB} is calculated to be 0.37 eV from equation 3.1. Since ΔE_{CB} is the energy difference of the conduction band between CdSe/ZnS QD and bulk CdSe ($E_{\text{CB}}(\text{CdSe, bulk}) \sim -0.2$ eV *vs.* NHE),¹⁸ a value for E_{CB} of CdSe/ZnS QD is -0.57 eV. The redox potential of the QD VB is 1.59 eV (2.16 – 0.57 eV).

The reported energy of the VB edge of NiO ($E_{\text{VB}}(\text{NiO}) = +0.54$ eV *vs.* NHE) is located between $E_{\text{CB}}(\text{CdSe/ZnS})$ and $E_{\text{VB}}(\text{CdSe/ZnS})$, while the potential of the CB of NiO ($E_{\text{CB}}(\text{NiO}) = -3.06$ eV *vs.* NHE) is above $E_{\text{CB}}(\text{CdSe/ZnS})$,¹⁹ indicating that hole transfer from excited QD to the VB of NiO is thermodynamically favorable and electron transfer from excited QD to the CB of NiO is not favorable (see Fig. 3-2).

Figure 3-2. Schematics of charge-transfer processes in QD-sensitized p-type NiO semiconductor. Step 1 is photo-excitation, step 2 is hole (○) transfer and step 3 is electron (●) transfer.

A typical fluorescence intensity trajectory of a single CdSe/ZnS QD on a glass substrate measured in air is shown in Fig. 3-3a. Rapid intensity fluctuations with long “off” events of duration $\geq$ the bin-time used (*i.e.*, 20 ms) are observed. The off-time distribution for a collection of 125 blinking QDs, obtained using the threshold method,²⁰ follows a power-law distribution:

$$P(\tau_{off}) = P_o \tau_{off}^{-m_{off}} \quad (3.4)$$

with a power-law exponent of 1.7 (Fig. 3-4). The QD temporarily stops emitting photons when a charge carrier (hole or electron) tunnels from the core to a trap state on the surface or surrounding environment of the QD.^{9,10,21} A photo-generated electron-hole pair (exciton) formed in the charged QD can

subsequently recombine by radiationless Auger process and the dot remains dark until fluorescence is restored when the ejected charge tunnels back to the core.

Figure 3-3. Fluorescence intensity time traces of single QDs on (a) a glass substrate and (b and c) a NiO film. The same excitation intensity of $I = 280 \text{ W/cm}^2$ is used for both the glass and NiO substrates and the bin-time used is 20 ms.

Figure 3-4. Off-time distribution for 125 blinking dots on a glass substrate.

A positive correlation exists between the fluctuations in the fluorescence intensity and emission lifetime (τ) of the QD in Fig. 3-3a. The fluorescence decay profile constructed from photons in the maximum intensity range is described using a mono-exponential decay function with $\tau = 24.0$ ns (see Fig. 3-5), in agreement with previously reported lifetimes of CdSe/ZnS QDs.^{22,23} The fluorescence lifetime decreases when a smaller intensity range is used to generate the lifetime decay. Fisher *et al.*²² and Schlegel *et al.*²³ have attributed this behavior to fluctuations in the non-radiative decay pathways of the excited QD to charge traps.

Figure 3-5. Fluorescence decay curves for the QDs in Fig. 3-3a (on glass) and Fig. 3-3b (on NiO). The former is constructed by using photons found in the maximum-intensity range R. The same excitation intensity of $I = 280 \text{ W/cm}^2$ is used for both the glass and NiO substrates.

The effects of NiO on the photophysical properties of CdSe/ZnS QDs measured in air are investigated by studying single dots deposited onto a NiO nanoparticle film. Figs. 3-3 b and c show typical fluorescence trajectories of single QDs on NiO. The QD on NiO film displays reduced fluorescence intermittency behavior for a long period of time before undergoing relatively more blinking at the later stage of the intensity trajectory (at $\sim 70 \text{ s}$ and $\sim 120 \text{ s}$ for the QD in Figs. 3-3 b and c, respectively) followed by irreversible bleaching (at 72 s and 140 s for the QDs in Figs. 3-3 b and c, respectively). Furthermore, the survival time of QDs on NiO is greatly enhanced. The bleaching histograms presented in Fig. 3-6 show that 81% of the QDs on a glass substrate (or 105 out of 130 dots studied) bleached within 20 s after the start of the experiment,

whereas only 30% of the QDs on NiO (or 38 out of 129 dots) did not survive beyond 20 s.

Figure 3-6. Bleaching time histograms for 130 QDs on a glass substrate (black) and 129 QDs on a NiO film (gray). The same excitation intensity of $I = 280 \text{ W/cm}^2$ is used for both the glass and NiO substrates.

The emission intensity of QD on NiO ($< 5,000$ counts/s) is significantly smaller than the maximum intensity of QD on glass substrates (*e.g.*, $\sim 60,000$ counts/s for QD in Fig. 3-3a). This observation complements the fluorescence lifetime quenching of the QD when in contact with NiO. As shown in Fig. 3-5b, the lifetime decay of the QD in Fig. 3-3b is best fitted by a slow decay of 0.9 ns and a fast decay that is shorter than the resolution of the experimental set-up. The exact nature of the short lifetime component is not clear at the present moment.

Figure 3-7. Distributions of the maximum emission intensities (a) and fluorescence lifetimes (b) of single QDs on a glass substrate obtained by fitting the fluorescence decay profiles, constructed from the maximum intensity range, to a single exponential decay function. Distributions of the emission intensities and long lifetime component of the double exponential fit of the fluorescence decay curves of QDs on NiO are also presented in (c) and (d), respectively.

The histograms for averaged emission intensity and lifetime of single QDs on glass and NiO are shown in Fig. 3-7. Averaged emission intensity of single QDs on glass and NiO are 63.6 and 3.3 counts/ms, respectively (Figs. 3-7 a and c). The fluorescence lifetime decay curves of 73 single QDs on a glass substrate, constructed from photons in the maximum intensity range, were fitted to a single exponential decay function and the distribution of the lifetimes is given in Fig. 3-7b. On the other hand, the fluorescence lifetime decay profiles of 87 QDs on NiO were fitted to a double exponential decay function with a short

lifetime component that is shorter than the resolution of the instrument and a long lifetime component whose distribution is presented in Fig. 3-7d. Clearly, the fluorescence intensities and lifetimes of QDs on NiO are quenched as compared to those of QDs on a glass substrate. Both the averaged lifetime and quantum yield of QDs are reduced by a factor of ~ 19 when deposited on NiO.

When a QD is excited, an exciton is created (step 1 in Fig. 3-2). Since the VB of the QD is located at a lower energy than the VB of the p-type NiO, the hole formed is transferred from the VB of the QD to the VB of NiO (step 2 in Fig. 3-2). An averaged hole transfer rate of $1.2 \times 10^9 \text{ s}^{-1}$ is calculated using the averaged lifetimes. Clearly, the nonradiative hole injection process (step 2) is faster than the radiative relaxation of the exciton (averaged value of $6.7 \times 10^7 \text{ s}^{-1}$) and results in significant quenching of the QD's fluorescence intensity and emission lifetime. Subsequently, the excited electron in the CB of the QD can either facilitate non-radiative Auger relaxation or recombine with the injected hole in the VB of NiO via a fast electron transfer process (step 3 in Fig. 3-2). The former gives rise to blinking which is not observed experimentally. We therefore propose that the charged dot is efficiently returned to a neutral state by step 3 resulting in the absence of long-lived "off" states as observed in Figs. 3-3 b and c. This indicates that the rapid electron transfer (step 3) occurs in a time scale shorter than the Auger process which typically takes place within a few hundred ps.²⁴ Hole injection from organic dye molecules (*e.g.*, coumarin 343) to NiO followed by rapid recombination between excited electron in the dye anion with injected hole in the semiconductor have recently been reported.⁶⁻⁸

Recently, Lian *et al.* observed suppressed blinking dynamics and lifetime quenching of single CdSe/CdS_{3ML}ZnCdS_{2ML}ZnS_{2ML} core/multishell QDs on n-

doped ITO.²⁵ In their system, negatively charged QDs are created when electrons in ITO are transferred to the dots to achieve equilibrium between their Fermi levels. The quenched lifetime is attributed to a reduction in the lifetime of negatively charged T^- trions by either Auger relaxation²⁶ or hole transfer to the additional electron in the charged dot or ITO. The authors proposed that blinking is suppressed by removing the VB hole so that dark positively charged dots are not formed. Mulvaney *et al.*²⁷ and Hermier *et al.*²⁸ have shown that positively charged T^+ trions created from CdSe/CdS core/shell QDs exhibit dim states, and the latter group has also demonstrated reduced blinking for the emission from CdSe/CdS T^+ trions.²⁸ On the other hand, charged CdSe/ZnS QDs have been shown to display negligible emission quantum yields and are considered to be non-fluorescent.^{9,10,21,28} Hermier *et al.* suggested that this is due to the more efficient Auger relaxation process in CdSe/ZnS QD as compared to CdSe/CdS QD.²⁸ Indeed, Orrit and co-workers have observed rapid intensity fluctuations for single CdSe/ZnS QDs on ITO.²⁹ Therefore, in our system, the charged CdSe/ZnS dots (created from steps 1 and 2) are probably non-fluorescent and cannot completely describe the suppressed blinking behavior. The rapid electron injection (step 3) is necessary to achieve the non-blinking behavior observed experimentally.

Figure 3-8a

Figure 3-8. Time-dependent fluorescence spectra of single QDs on (a) a glass substrate ($I = 280 \text{ W/cm}^2$) and (b) a NiO film ($I = 560 \text{ W/cm}^2$) in air. The corresponding fluorescence intensity trajectories of each QDs are provided in the top panels (bin-time = 20 ms).

Figure 3-8b

The effects of NiO on the blueing and bleaching behavior of single QDs are investigated next. The time-dependent fluorescence spectra and intensity trajectories of single QDs on a glass substrate in air were simultaneously recorded as given in Fig. 3-8a. It is now generally accepted that the observed unidirectional blue shift of the spectra (*i.e.*, blueing effect) is attributed to photooxidation of the CdSe core by oxygen in air.³⁰⁻³³ Upon light excitation, the excited electron of the QD is ejected to traps found in the shell or core-shell interface. O₂ diffuses through the shell and reacts with the trapped electron to create reactive O₂⁻. In addition, the remaining hole that is trapped at the core surface facilitates the oxidation of the CdSe surface to CdSeO_x (x = 2 or 3) or SeO₂. The erosion of the core leads to a reduction in the core size and an eventual blue shift of the QD emission spectrum.³⁰⁻³³

The blueing effect is also observed as illustrated in Fig. 3-8b for a single QD on NiO whose blue shift rate (0.1 nm/s) is slower than that of the QD on glass substrate (0.6 nm/s for QD in Fig. 3-8a). Note that the blue shift rate of a single QD was calculated using the expression: wavelength-shift/time, where wavelength-shift is the difference in the peak wavelength of the spectrum in the final frame before the dot photo-bleaches and the spectrum in the initial frame, and time is the time between the final and initial frames.³² The fast transfer of charge carriers from QD to NiO lowers the probability for charges to be ejected to the QD surface. This leads to a retardation in the photo-oxidation process and a reduction in the blue shift rate for QD on NiO. The emission spectra for the QDs on NiO (see Fig. 3-8b) were measured using a higher intensity of $I = 560$ W/cm² in order to obtain good signal-to-noise data for both the emission spectra and intensity trajectories collected simultaneously. The intensity of $I = 560$

W/cm² was not used for QDs on glass substrate since the dots photobleached too quickly at this intensity to allow an accurate determination of the blue shift rate. This is possibly due to a greater number of excitation cycles and faster trapping of ejected charges by deep traps. At the higher intensity (560 W/cm²), the QDs on NiO still showed long survival times and slower blue shift rates as compared to QDs on glass substrate ($I = 280 \text{ W/cm}^2$) demonstrating the fast transfer of charge carriers from dots to NiO and a low probability of charges ejected to the QD surface. The average blue-shift rates for QDs (note that QDs that yielded more than 3 frames of spectra were considered in the analysis) on a glass substrate and a NiO film are calculated to be 1.5 nm/s (based on 66 dots) and 0.4 nm/s (based on 77 dots), respectively. Clearly, the spectral shift rate is slower for QD on NiO as compared to that for QD on a glass substrate.

The late onset of fluctuations in the intensity trajectories of QDs on NiO (Figs. 3-3 b and c and Fig. 3-8b) can be rationalized by considering deep traps located at the CdSe/CdSeO_x interface.³⁰ Since the number of these traps increases only after a long period of time due to slow photooxidation,³⁴ there is a greater chance for a charge to be ejected from the core and localized at the CdSe/CdSeO_x interface during the later stage of photo-excitation. The trapped charge is temporarily confined until it transfers itself back to the core or to NiO. An alternative explanation used to understand the increased blinking behavior involves the redistribution of charges around the dot after several cycles of ionization which leads to a lowering of the tunneling barrier height between a charge carrier and a deep trap found in CdSeO_x or the ligand surrounding the dot.³¹ A plausible mechanism based on the above model is used to understand the enhanced survival time of QD on NiO. In ambient conditions, deep traps

located at the CdSe/CdSeO_x interface can act as potential quenching states that permanently trap a charge ejected from the QD (*i.e.*, bleaching).³⁰ Due to slow photooxidation of QD on NiO, these trap states become accessible to QD only after several photo-excitation cycles (*i.e.*, enhanced survival time). It is important to note that the exact nature of the quenching states responsible for bleaching remains unclear.

3.4 Conclusion

We have demonstrated that an additional efficient relaxation pathway for QD (*i.e.*, charge-transfer to NiO) reduces the probability of fluorescence inactivity, suppresses blinking and prolongs the survival time of the nanocrystal. In addition, this additional relaxation pathway complements the strategy of using energy transfer to an acceptor to suppress blinking.

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CHAPTER 4

**ELECTRON TRANSPORT IN THE LONG-
RANGE CHARGE-RECOMBINATION
DYNAMICS OF SINGLE ENCAPSULATED
DYE MOLECULES ON TiO₂ NANOPARTICLE
FILMS**

This chapter is adapted from: “Electron transport in the long-range charge-recombination dynamics of single encapsulated dye molecules on TiO₂ nanoparticle films, Xiangyang Wu, Toby D. M. Bell, Edwin K. L. Yeow, *Angew. Chem. Int. Ed.*, **2009**, 48, 7379-7382.”

4.1 Introduction

Interfacial electron transfer in dye-sensitized semiconductors, such as TiO_2 , has been applied extensively in molecular devices for solar energy conversion.^{1,2} Electron transport in nanocrystalline metal oxide is an important process which is often neglected when describing the charge-recombination dynamics between injected electrons and TiO_2 at the single-molecule level.³⁻⁸ Electron transport is intrinsic to TiO_2 and has been reported to take place on solid-state colloidal TiO_2 films⁹ and TiO_2 films filled with electrolytes.¹⁰ It has been proposed that electron transport occurs by a series of charge trapping and detrapping steps, with the trap sites located predominantly on the metal oxide surface.¹¹ The role of electron transport in determining the charge-recombination dynamics between single dye molecules and TiO_2 is examined.

One of the major drawbacks of molecular devices is the photo-degradation of the dyes used. Supramolecular dyes formed by the encapsulation of dye molecules by macrocyclic hosts such as cucurbituril are known to be highly thermal and photo-stable.¹² Cucurbit[7]uril (CB7, see Fig. 4-1) has been found to effectively complex rhodamine 6G (Rh6G). The significant increase in the photostability of Rh6G upon CB7 encapsulation has been demonstrated at both the bulk and single-molecule levels.^{13,14} Furthermore, retarded charge recombination in the practical devices was observed when macrocyclic hosts (*e.g.*, cyclodextrin) were used to increase the spatial distance between dye molecules and semiconductor surface.^{15,16} Hence, it is advantageous to study the effects of CB7 on the charge-recombination of single dye molecules.

Figure 4-1. Chemical structure of CB7. The depth of the CB7 is 9.1 Å.

4.2 Experimental Section

4.2.1 Materials

Titanium isopropoxide (99.9999%), CB7 (> 90%), and colloidal silica (LUDOX AS-40, 40 wt.% suspension in water) were obtained from Sigma-Aldrich. Isopropanol (HPLC/spectro grade) and hydrochloric acid (37%, HCl) were purchased from Tedia and Panreac, respectively. The carbo-rhodamine dye Atto647N was purchased from ATTO-TEC GmbH. All chemicals were used as received.

4.2.2 Preparation of TiO₂ sol

TiO₂ sol for the ensemble-averaged steady-state fluorescence emission measurements was prepared as follows.¹⁷ A mixture containing 0.4 mL of titanium isopropoxide and 2 mL of isopropanol was added slowly to a mixture containing 20 mL of deionized water and 200 μL of 37% HCl under vigorous stirring. The final solution was stirred until a transparent solution was formed. The transparent TiO₂ sol was concentrated using a rotary evaporator at 60 °C and then dried to yield a white powder. The white powder was re-dispersed in deionized water to obtain 2.5 g/L TiO₂ sol.

TiO₂ nanoparticles for the single-molecule experiments were prepared as follows. A mixture containing 60 μ L of titanium isopropoxide and 2 mL of isopropanol was added slowly to a mixture containing 20 mL of deionized water and 200 μ L of 37% HCl under vigorous stirring. The final solution was refluxed for 8 h to form a concentrated TiO₂ colloidal solution. After cooling, the solution was filtered to remove large TiO₂ particles by using a 0.2 μ m syringe filter.

4.2.3 Preparation of single-molecule samples

Samples used for the study of charge-recombination of single molecules on TiO₂ nanoparticles were prepared by spin coating 100 μ L of *ca.* 9 mM TiO₂ colloidal solution onto cleaned glass coverslips. Subsequently, 0.1 nM of an aqueous solution of either Atto647N, or host-guest complex (*i.e.*, CB7-Atto647N) was spin coated onto the TiO₂ nanoparticles.

Samples containing dye molecules sandwiched between two layers of TiO₂ were prepared by spin coating 100 μ L of *ca.* 9 mM TiO₂ colloidal solution onto cleaned glass coverslips followed by 0.1 nM aqueous solution of either Atto647N or host-guest complex. Subsequently 100 μ L of TiO₂ colloidal solution was spin coated onto the sample to form a top layer of TiO₂.

4.2.4 Setup of single-molecule fluorescence microscopy

The basic setup has been described in Chapter 2. In this work, a 635 nm pulsed laser diode (LDH-P-C-635B, PicoQuant) and HQ685/70 were used as the excitation source and the emission filter, respectively.

4.3 Results and Discussion

4.3.1 Determination of the binding equilibrium constant of the inclusion complex CB7-Atto647N

Figure 4-2. Steady-state normalized absorption spectra (a for [CB7] = 0 mM and b for [CB7] = 2.3 mM) and uncorrected fluorescence spectra (c for [CB7] = 0 mM and d for [CB7] = 2.3 mM) of an aqueous solution of 0.7 μ M Atto647N in the absence and presence of CB7. A_{rel} and I are the normalized absorbance and fluorescence emission intensity.

Both the absorption and emission spectra of Atto647N undergo bathochromic shift upon addition of CB7 as shown in Fig. 4-2. The absorption maximum ($\lambda_{\text{abs,max}}$) of Atto647N undergoes a red shift from 646 nm in the absence of CB7 (*i.e.*, [CB7] = 0 mM) to 651 nm in the presence of 2.3 mM of CB7 (*i.e.*, [CB7] = 2.3 mM). A red-shift in the emission maximum ($\lambda_{\text{em,max}}$) of

Atto647N is also observed when CB7 is added where $\lambda_{\text{em,max}}$ increases from 662 nm in neat water to 668 nm when [CB7] = 2.3 mM.

The observed bathochromic shift in the absorption spectrum of Atto647N when CB7 is added is attributed to the formation of an inclusion complex between Atto647N and CB7. Previous works have shown that for most dyes that form complexes with CB7 (*e.g.*, Rh6G, tetramethylrhodamine, rhodamine 123, cresyl violet), the absorption maxima of the guest molecules are red-shifted with respect to the same molecules in neat water.¹² Several factors such as reduced polarity and polarizability within CB7, and decreased solvation of the encapsulated guest molecules are capable of altering the photophysical properties of the dyes.¹²

Figure 4-3. The time-resolved fluorescence decay profiles of aqueous Atto647N in the absence (**B**) and presence (**C**) of 2.3 mM CB7. The instrument response function (**A**, IRF) is given. **B** and **C** are fitted to a mono-exponential decay function with a fluorescence lifetime of 3.6 and 4.4 ns, respectively.

The formation of CB7-Atto647N complex was also supported by the prolonged lifetime of the inclusion complex. The time-resolved fluorescence decay profiles of aqueous solutions of Atto647N in the absence and presence of 2.3 mM CB7 are given in Fig. 4-3. The fluorescence decays are best fitted to a mono-exponential decay function with a lifetime of 3.6 ns and 4.4 ns when $[CB7] = 0$ mM and $[CB7] = 2.3$ mM, respectively. For the latter, the mono-exponential fluorescence decay indicates that nearly all of the dye molecules formed inclusion complexes with CB7. This is consistent with the high proportion of 1:1 host-guest complex calculated using K_b (see the estimation of binding constant below). The lifetime of 4.4 ns is assigned to the emission from CB7-Atto647N complex. The prolongation of lifetime from 3.6 ns for the free dye to 4.4 ns is due to the lower polarizability experienced by Atto647N when included into CB7.¹² This gives rise to a decrease in the radiative decay rate and an increase in the emission lifetime.

The binding equilibrium constant K_b of the inclusion complex is determined using the Rose-Drago equation for a 1:1 complex:¹⁸

$$[R^0] = \frac{b \Delta A \Delta \varepsilon ([S^0] + K_b^{-1}) - (\Delta A)^2}{b \Delta \varepsilon (b \Delta \varepsilon [S^0] - \Delta A)} \quad (4.1)$$

where $[R^0]$ and $[S^0]$ are the total concentrations of host (R) and guest (S) molecules, respectively, ΔA is the difference between the observed absorbance after each addition of R and the initial absorbance of S , $\Delta \varepsilon$ is the difference between the molar absorptivity of the complex and S , and b ($= 1$ cm) is the pathlength. ΔA is calculated based on the change in the absorbance value at 651 nm. By plotting $[R^0]$ against ΔA for various concentrations of R^0 , the binding

equilibrium constant can be obtained by fitting the resulting curve using equation 4.1. Fig. 4-4 shows the plot of $[R^0]$ against ΔA for the complexation of Atto647N and CB7. K_b ($\sim 2,290 \text{ M}^{-1}$) is obtained from equation 4.1 suggesting that 87% of Atto647N form inclusion complexes with 2.3 mM of CB7.

Figure 4-4. Rose-Draco plot of $[R^0]$ against ΔA for the 1:1 complexation of Atto647N and CB7.

4.3.2 Electron transfer from Atto647N to TiO₂ at the ensemble level

Figure 4-5. The cyclic voltammogram of Atto647N (**A**) and CB7-Atto647N (**B**) in phosphate buffer solutions (pH = 7) under inert atmosphere.

The cyclic voltammogram (cv) of Atto647N (8.1×10^{-5} M) in phosphate buffer solution (pH = 7) is shown in Fig. 4-5A where the first one-electron oxidation potential of Atto647N is measured to be $E_{\text{ox}} = 0.636$ V (vs. Ag/AgCl). The feasibility of electron transfer from Atto647N to TiO₂ is considered by calculating the free energy change, ΔG^0 , involved in the electron transfer process:

$$\Delta G^0 = E_{\text{ox}} - E_{\text{red}} - E_{00} \quad (4.2)$$

The energy difference between the lowest vibronic level of the ground and excited electronic states of, E_{00} , of Atto647N (= 1.889 eV) was calculated by

taking the average value of the absorption maximum and emission maximum. The conduction band edge of TiO_2 at $\text{pH} = 7$ is $E_{\text{red}} = -0.813 \text{ V (vs. SCE)}^{19,20}$ or $-0.794 \text{ V (vs. Ag/AgCl)}$. A ΔG^0 value of -0.46 eV for Atto647N suggests an energetically favorable electron transfer process from the dye to TiO_2 .

The cv of Atto647N ($4.1 \times 10^{-5} \text{ M}$) in the presence of 1.25 mM of CB7 in phosphate buffer solutions ($\text{pH} = 7$) is also given in Fig. 4-5B. About 75% of Atto647N form inclusion complexes with CB7 in our sample solution. The use of higher concentrations of CB7 was avoided due to solubility problems. We note that the cv is not significantly different from that of Atto647N in neat phosphate buffer solution. Furthermore, the first one-electron oxidation potential obtained is $0.629 \text{ V (vs. Ag/AgCl)}$ suggesting that the E_{ox} value of CB7-Atto647N is close to that of Atto647N. Therefore, electron transfer from the inclusion complex to TiO_2 is an energetically favorable process.

The above conclusion is also supported by the quenched fluorescence emission and lifetime of Atto647N in the presence of TiO_2 . Steady-state fluorescence emission spectra of Atto647N in the absence and presence of 2.5 g/L of TiO_2 nanoparticles in water are given in Fig. 4-6. In the presence of the TiO_2 nanoparticles, the dye (R-COO^-) absorbs onto the metal oxide surface by binding onto the hydroxyl groups found on the metal oxide surface. The fluorescence of Atto647N is significantly quenched upon absorbing onto the TiO_2 nanoparticles. The quenching effect increases with time as more dye absorbs onto TiO_2 . Band shift/split was not observed in the absorption spectra of Atto647N in the absence and presence of TiO_2 nanoparticles which suggests that no aggregates were formed.

Figure 4-6. The ensemble-averaged steady-state fluorescence spectra of Atto647N in water (a), Atto647N sensitized TiO₂ nanoparticles in water at 5 min (b) and Atto647N sensitized TiO₂ nanoparticles in water at 4 h (c). The concentrations of Atto647N are the same for all the samples.

Figure 4-7. The time-resolved fluorescence decay profiles of aqueous Atto647N in TiO₂ (**B**) and SiO₂ (**C**) solution. The instrument response function (**A**, IRF) is given.

Compared to Atto647N in silica nanoparticle solution, a short lifetime component faster than the time-resolution of the TCSPC experiment (~ 100 ps) is observed due to the ultrafast electron injection from the excited Atto647N to the conduction band of TiO_2 nanoparticles. The long lifetime component (~ 3.5 ns) arises from the free dye molecules in the solution.

4.3.3 Single-molecule electron transfer dynamics

Figure 4-8. Confocal fluorescence images ($10 \times 10 \mu\text{m}^2$) of single fluorescent Atto647N molecules (bright spots) on glass surface (A) and TiO_2 nanoparticle film (B).

The confocal fluorescence images of single Atto647N molecules on glass surface and TiO_2 nanoparticle film are displayed in Fig. 4-8. The samples were prepared by spin casting the same concentration of Atto647N onto the substrates. It is noted that the number of single Atto647N molecules (bright spots), in an image area of $10 \times 10 \mu\text{m}^2$, is approximately the same for both substrates. Clearly, the majority of Atto647N molecules deposited on TiO_2 nanoparticle film are probed in the single-molecule spectroscopy experiment.

Figure 4-9. Fluorescence intensity time traces (bin time = 20 ms) of single Atto647N (a) and CB7-Atto647N (b and c) molecules on TiO_2 surface in ambient conditions.

Two distinct groups of blinking behavior are observed from the emission intensity time traces of 240 Atto647N molecules on TiO_2 . 197 of them (or 82%) displayed temporary off-events that last from tens of milliseconds to a few seconds (see Fig. 4-9a for a typical trace), while the rest of the molecules

showed constant emission intensity (*i.e.*, absence of blinking) before undergoing irreversible photobleaching. The off-events in Fig. 4-9a are attributed to the dark oxidized states of Atto647N formed as a result of interfacial electron transfer from the dye molecule to TiO₂ nanoparticle. The transition from “off” to “on” states occurs when the electron injected into the conduction band of TiO₂ recombines with the oxidized dye to form the fluorescent molecule.

The fluorescence lifetime (τ_f) distribution of single Atto647N on TiO₂ was fitted to a Gaussian distribution with a mean value of 3.9 ns which is close to the ensemble-averaged emission lifetime of Atto647N in water (see Fig. 4-10).

Figure 4-10. Fluorescence lifetime (τ_f) distribution of single Atto647N molecules on a TiO₂ nanoparticle film. Standard deviation is 0.9 ns.

In general, ensemble-averaged forward electron transfer (FET) rates, measured from bulk techniques, fall in the ultrafast time domain (*i.e.*, fs to ps) and are much faster than the resolution of the single-molecule experimental set-

up.^{21,22} The observation of fluorescence intensity of single dye molecules undergoing rapid electron transfer to metal oxides was explained by Lu *et al.* who reported similar behavior in the interfacial electron transfer dynamics of single dye molecules (*i.e.*, cresyl violet, coumarin and porphyrin) on TiO₂.^{7,8} They proposed that the emission intensity of single molecules, such as that seen in Fig. 4-9a, is determined by the fraction of time that the FET process dominates the fluorescence and is not affected by the rate of the ultrafast FET. In this case, when the reactivity of FET is low (*i.e.*, when FET rate is smaller than the inverse of the intrinsic excited state lifetime), the fluorescence quantum yield and fluorescence intensity are high due to radiative emission from the excited S₁ state of the dye to its ground state (“on” state and unquenched τ_f). The FET then switches to a high reactivity mode (*i.e.*, when FET rate is larger than the inverse of the intrinsic excited state lifetime) which leads to electron transfer to TiO₂ followed by a low or zero fluorescence intensity (“off” state). Factors such as the dynamic change of the energy gap between dye and TiO₂, electronic coupling between the active species and vibrational relaxation energy of the adsorbed dye have been proposed to be responsible for the changing FET reactivities.^{7,8}

Figure 4-11. Off-time distributions for a combination of 197 Atto647N (■) and a combination of 478 CB7-Atto647N (▼) molecules on TiO₂ nanoparticle film. The linear log-log plots yield m_{off} values of 1.4 and 1.0 for Atto647N and CB7-Atto647N, respectively.

The off-time (τ_{off}) duration histogram was constructed using the threshold method.^{23,24} The linear log-log plot for the combination of blinking Atto647N molecules on TiO₂ nanoparticle (see Fig. 4-11) is best described using a power-law distribution:

$$P(\tau_{off}) = P_0 \tau_{off}^{-m_{off}} \quad (4.3)$$

with the power-law exponent $m_{off} = 1.4$.

Figure 4-12. Schematic of electron injection and charge-recombination. Following electron injection into the conduction band (**CB**) and fast relaxation, the injected electron undergoes electron transport (**A**) before back electron transfer (**B**) to the oxidized dye.²⁵

Following electron injection into the CB of TiO₂ and fast relaxation, the injected electron undergoes electron transport by moving from trap to trap on the TiO₂ surface by a series of trapping and thermally activated de-trapping events before arriving at a suitable reactive site where the electron undergoes interfacial back electron transfer (BET) to the oxidized dye (Fig. 4-12).²⁵ The classical Marcus equation is commonly used to describe the BET rate, k_{bet} .²⁶ In Fig. 4-9a, the duration of each off-event (τ_{off}) is equivalent to the total time for electron transport and interfacial BET. Since the dye molecules are in direct contact with the TiO₂ nanoparticles, it is assumed that k_{bet} is much faster than the electron de-trapping rates at the reactive sites.²⁵ In this case, τ_{off} is given by the time taken for the injected electron to visit the traps before arriving at a reactive site (*i.e.*, the first passage time). A power-law distribution for the de-trapping times of an electron at a trap site, $P(t) = Pt^{-1-\alpha}$, where $0 < \alpha < 1$, is

obtained when an exponential distribution of trap energies E_i (depicting the Urbach tail in the conduction band edge) is considered:²⁷⁻²⁹

$$g(E_i) = \frac{1}{k_B T_0} e^{-(E_c - E_i)/k_B T_0} \quad (4.4)$$

where k_B is the Boltzmann's constant and E_c is the conduction band edge energy. The characteristic temperature, T_0 , is related to the temperature T and α by the equation $\alpha = T/T_0$. The duration of each off-event is thus the sum of several power-law variables and follows a power-law distribution with $m_{off} = 1 + \alpha$. α values of *ca.* 0.4 were reported for ruthenium-based dye sensitized TiO₂ using transient absorption spectroscopy, and are in good agreement with the α value obtained from the off-time distribution in Fig. 4-11.²⁷⁻³⁰

The emission intensity time traces of 749 CB7-Atto647N molecules on TiO₂ were recorded and their blinking behavior categorized into two groups. 16% of the molecules (or 120 molecules) did not display any blinking behavior, while the rest of the molecules (629 molecules) showed either long-lived off-events in the fluorescence trajectory (478 molecules, see Figs. 4-9 b and c) or rapid on/off intensity fluctuations with off-states lasting a few ms (151 molecules, see Fig. 4-13a).

Figure 4-13. (a) Fluorescence intensity time trace of a typical CB7-Atto647N molecule on TiO₂ displaying rapid on/off intensity fluctuations (bin-time = 1 ms). (b) The off-time distribution of molecule (a) is fitted to a mono-exponential function with triplet lifetime of 2.3 ms. (c) The histogram of triplet lifetimes for 97 CB7-Atto647N molecules.

The off-time distribution of a typical CB7-Atto647N molecule shown in Fig. 4-13a is fitted to a mono-exponential decay function with a decay constant $k = \tau_{off}^{-1}$ where $\tau_{off} = 2.3$ ms (see Fig. 4-13b). The off-event is probably due to the dark, triplet state of the encapsulated molecule with a lifetime of 2.3 ms. For these molecules, oxygen quenching of the triplet state is reduced when the dye is included into CB7 since the host partially shields Atto647N from atmospheric oxygen.^{31,32} Fig. 4-13c shows the histogram of the triplet lifetime of 97 molecules that possess sufficient off-events. The majority of molecules (78%) display τ_{off} between 1 and 4 ms which is close to the triplet lifetime of Atto647N in the complete absence of oxygen (*ca.* 12 ms).^{33,34}

The intensity time traces of two typical molecules that exhibit long off-events are illustrated in Figs. 4-9 b and c. A power-law distribution for the off-times is observed for the collection of blinking molecules with $m_{off} = 1.0$ (see Fig. 4-11). The small power-law exponent suggests that there is a higher probability of finding long dark periods when Atto647N molecules are included into CB7 as compared to uncomplexed dyes.

The discrepancy in the observed m_{off} values between Atto647N and CB7-Atto647N on TiO₂ is rationalized by considering a reduced k_{bet} when the dye molecule is included into the macrocyclic CB7. In this case, the electronic coupling matrix element (H_{el}) in k_{bet} diminishes exponentially with increasing distance between the electron donating and accepting states (R_e):

$$H_{el}^2 = H_0^2 e^{-\beta R_e} \quad (4.5)$$

where β is the attenuation factor. When Atto647N is included into CB7, the latter increases the spatial separation between the dye molecule and the metal oxide, hence reducing the value of k_{bet} relative to the uncomplexed molecule. In this case, charge recombination is not limited by the first passage time, and the injected electron can visit the reactive sites several times before BET occurs. This results in an decrease in τ_{off} as observed experimentally.

The above argument is supported by studying the blinking behavior of single CB7-Atto647N molecules surrounded by TiO₂ nanoparticles. In this case, the emission intensity time traces of 240 molecules sandwiched between two layers (*i.e.*, top and bottom) of TiO₂ nanoparticle films were recorded. The power-law distribution for the off-time durations, obtained from a combination of 203 blinking molecules, yielded a m_{off} value of 1.4 which is similar to the power-law exponent of uncomplexed Atto647N on TiO₂ nanoparticle. This means that the probability for faster charge-recombination is higher when the oxidized CB7-Atto647N molecule is completely surrounded by TiO₂ nanoparticles as compared to when it is in contact with only a bottom layer of metal oxide. It has been shown, by computational chemistry calculations, that the internal cavity of a CB7 is too small to fully accommodate a Rh6G molecule.¹³ This suggests that the larger Atto647N molecule is partially encapsulated by CB7. For CB7-Atto647N on a bottom layer of TiO₂, the part of the molecule that is not protected by CB7 is separated from the metal oxide. On the other hand, for CB7-Atto647N surrounded by TiO₂ (*i.e.*, top and bottom layers), the unprotected part of the dye is in direct contact with the metal oxide, thus enabling interfacial BET to occur without spatial distance effects.

Long off-events may occur when high FET activity persists for a long time.^{7,8} The greater spatial separation between CB7-Atto647N and TiO₂ may result in either unchanged or shorter periods of high FET activity when compared to the uncomplexed molecule. Clearly, FET activity alone does not completely describe the off-events and electron transport plays an important role in the observed fluorescence intermittency.

Computational simulations, based on the continuous-time random walk (CTRW), were performed to obtain off-time distributions. In order to test the validity of the electron transport model, a computational modeling, based on the CTRW formulation, was performed to obtain off-time distributions. Kopidakis and co-workers have shown that transport-limiting traps are located predominantly at the surface of TiO₂ particles instead of in the bulk of the particles.¹¹ The injected electron is therefore restricted to diffuse only on the surface of TiO₂. For the sake of simplicity, the nanoparticle is modeled as a square lattice of trap sites with periodic boundary conditions. The energy of a trap site i (E_i) is drawn from equation 4.4. So the corresponding waiting time of an electron with energy E_i is $t_i = \nu_o^{-1} e^{-E_i/kT}$, where ν_o is the attempt-to-escape frequency and E_c is taken to be 0.²⁷ The waiting time of a trap site i is computed from the expression $t_i = \nu_o^{-1} [\text{Rand}(0,1)]^{-1/\alpha}$, where $\text{Rand}(0,1)$ is a random number between 0 and 1.²⁷ The density of trap sites on the surface of TiO₂ has been reported to be about a few hundred traps per 10 nm radius nanoparticle.³⁵ In order to model a reasonable number of traps per nanoparticle, a square lattice of dimensions 20×20 units is used in the simulations.

At low dye concentrations ($\sim$ nM), the number of dye molecules adsorbed onto a TiO₂ nanoparticle is at most 1. Therefore, only the photogenerated

electron from the dye is responsible for the charge-recombination reaction. Dark electrons are ignored since their number density is small at zero bias (*e.g.*, ~ 0.1 for a 10 nm radius nanoparticle).^{27,28} The location of the photogenerated electron on the surface of TiO₂ is randomly selected, and the electron moves randomly from site to site while adopting the waiting time t_i of the site i at which it is trapped. It is assumed that the reactive sites are adjacent to the dye and that the injected electron can only diffuse between neighboring trap sites. For the uncomplexed dye, the simulation ends when the injected electron reaches a reactive site. This scenario does not apply when $1/k_{bet}$ exceeds the time taken for the electron to hop to a neighboring trap.²⁵ For CB7-Atto647N, there exists the possibility that an electron at a reactive site does not undergo recombination but releases itself from the trap and continues to diffuse randomly on the metal oxide surface.²⁵ A probability P_{bet} ($= k_{bet}/(v_o + k_{bet})$) is introduced to decide if the electron at a reactive site recombines or hops to a neighboring trap with rate v_o . In this case, $P_{bet} = 1$ when fast BET is present (*i.e.*, $k_{bet} \gg v_o$) and P_{bet} tends to 0 when $v_o \gg k_{bet}$ (*i.e.*, slow BET). The attempt-to-escape frequency (v_o) of a trapped electron is often treated as a fitting parameter and values ranging from 10^9 to 10^{15} s⁻¹ have been reported depending on the physical model used.^{10,27,28} A value of v_o ($= 1 \times 10^{10}$ s⁻¹) smaller than the atomic frequency ($\sim 10^{12}$ s⁻¹) is utilized in the simulation. The effects of Coulomb interaction between the trapped electron and the dye cation are neglected since the high dielectric constant of the metal oxide (*i.e.*, 86 for anatase TiO₂)³⁶ may render the electrostatic interaction to be small.

Figure 4-14. Normalized off-time distributions based on the Monte-Carlo simulations. The linear log-log plots yielded m_{off} values of 1.4, 1.3, 1.1 and 1.0 for $P_{bet} = 1$ (∇), 0.01 ($\blacktriangle$), 0.001 ($\bullet$) and 0.0005 ($\blacksquare$), respectively.

Fig. 4-14 shows the (normalized) off-time distributions for various P_{bet} obtained from the computational simulations. The off-times follow a power-law distribution with $m_{off} = 1.4$ ($\alpha = 0.4$), 1.3 ($\alpha = 0.3$), 1.1 ($\alpha = 0.1$) and 1.0 ($\alpha = 0$) for $P_{bet} = 1$, 0.01, 0.001 and 0.0005, respectively. When an electron at a reactive site has an increased probability of hopping to a trap, the charge-recombination dynamics is no longer limited by the first-passage time. The electron continues to diffuse on the metal oxide surface, and undergoes several encounters with the reactive site before BET occurs. This results in an increase in the probability of finding long off-times, and a concomitant decrease in the α value in accordance with experimental observation. Similar trends are observed when different ν_o is employed in the simulations.

The configuration with the empty portal of CB7 sitting on the nanoparticle will result in a maximum separation between the unprotected portion of the dye

and TiO_2 and gives rise to long off-events. In this case, the separation between the unprotected dye and the metal oxide is at least the depth of the macrocyclic CB7 ($\sim 9 \text{ \AA}$).³⁷ The latter is the most important configuration for the long off-events. When $m_{\text{off}} = 1.0$, $\nu_0 = 1 \times 10^{10} \text{ s}^{-1}$ and $P_{\text{bet}} = 0.0005$, a value of $k_{\text{bet}} \approx 5 \times 10^6 \text{ s}^{-1}$ is obtained for the back electron transfer reaction between the inclusion complex and TiO_2 . The exact separation between Atto647N and TiO_2 (R_e) is not known, and by assuming an R_e value of $9 \text{ \AA}$ (*i.e.*, depth of CB7) and an attenuation factor of $\beta = 1 \text{ \AA}^{-1}$,²⁵ a value of $k_{\text{bet}} \approx 4 \times 10^{10} \text{ s}^{-1}$ is obtained for the uncomplexed dye. The latter is reasonable since several studies have shown that interfacial BET occurs within a few ps to ns.^{38,39}

4.4 Conclusion

We have detected the presence of long-lived dye cations in the majority of dye molecules on TiO_2 , especially for the encapsulated Atto647N and have demonstrated that electron transport might play a pivotal role in charge-recombination at the single-molecule level as it adequately describes the power-law dispersion of τ_{off} .

4.5 Bibliography

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CHAPTER 5

FLUORESCENCE BLINKING DYNAMICS OF SILVER NANOPARTICLE AND SILVER NANOROD FILMS

This chapter is adapted from: “Fluorescence blinking dynamics of silver nanoparticle and silver nanorod films, Xiangyang Wu and Edwin K. L. Yeow, *Nanotechnology*, **2008**, *19*, 035706.”

5.1 Introduction

Noble metals (*e.g.*, silver, gold, and copper) have attracted considerable interests because of their unique optical properties, such as surface plasmon absorption. Noble metal nanostructures are routinely used in surface-enhanced Raman scattering (SERS) and surface-enhanced fluorescence (SEF) spectroscopy to achieve large signal enhancements at both the ensemble and single-molecule levels.¹⁻³ It has been demonstrated that the enhancement factor is strongly dependent on the size⁴ and morphology⁵ of the noble metal nanomaterials.

Strong fluorescence signal from noble metal can interfere with the analyte's emission leading to ambiguity when interpreting single-molecule fluorescence data.³ In addition, intermittent fluorescence behavior of single noble metal nanoparticles hinders their practical application in SERS and SEF. However, the blinking mechanism of silver nanostructures is still a debate. Dickson *et al.* proposed that silver nanoparticle's transition from an emissive "on" state to a non-emissive "off" state is due to an emitting cluster breaking up into non-emitting species, or that the cluster has grown too large to fluoresce.^{6,7} Recently, Jacobson *et al.* suggested that silver clusters formed from the photoreduction of Ag₂O can react with oxygen to re-form silver oxides indicating the important role of O₂ in the blinking mechanism.⁸⁻¹⁰

Hence, it is pertinent to understand the blinking mechanism, and the effects of the surrounding environment on the blinking behavior. In this chapter, we intend to investigate the effect of protective layer and the surrounding environment on the blinking behavior of Ag nanostructures.

5.2 Experimental Section

5.2.1 Materials

Cetyltrimethylammonium bromide (98%, CTAB) and ascorbic acid (99+%) were obtained from Alfa Aesar. Silver nitrate (99.9999%, AgNO_3), 3-(aminopropyl)-triethoxysilane (99%, APS), sodium borohydride (99%, NaBH_4), trisodium citrate ($\geq 99.0\%$), catalyse, D-(+)-glucose, carbohydrazide (98%) and 2-mercaptoethanol (99%) were purchased from Sigma-Adrich. Glucose oxidase was obtained from Fluka. All chemicals were used as received.

5.2.2 Preparation of APS-modified glass coverslips

For preparation of APS-modified glass coverslips, the cleaned coverslips were further treated with warm HCl aqueous solution for 60 min, and then rinsed with plenty of distilled water. HCl removes organic surface contaminants and ensures a uniform deposition of APS on the glass surface.¹¹ The cleaned coverslips were incubated at room temperature in a 2% APS in chloroform solution for 24 h. The functionalized coverslips were then rinsed repeatedly with chloroform and distilled water before treatment in a UV ozone system (PSD_UV, Novascan) for 10 min.

5.2.3 Preparation of silver nanoparticle film

Two methods (*i.e.*, Method I and Method II) were used to prepare the silver nanoparticle films. The first method (Method I) involved the chemical reduction of AgNO_3 (40 mL of 0.25 mM) by NaBH_4 (1.2 mL of 10 mM) under vigorous stirring. The color of the solution turned quickly from yellow to brown and then to white. Silver nanoparticles were also prepared using the procedure

described by Jana and co-workers (Method II).¹² 1.2 mL of 10 mM NaBH₄ solution was added slowly into a 40 mL mixture containing 0.25 mM of AgNO₃ and 0.25 mM of trisodium citrate under vigorous stirring.

Then, cleaned APS-coverslips were immersed in the as-prepared silver nanoparticle solution for 4 h followed by thorough rinsing with methanol and distilled water and drying under Ar flow.

5.2.4 Preparation of silver nanorod film

Silver nanorods were prepared following the rapid deposition method described by Aslan and co-workers (Method III).¹³ Deposition of silver seeds onto the APS-coverslips were performed by immersing the coverslips into a silver seed solution for 30 min. After washing with water, the coverslips were put into a beaker containing 10 mL of 80 mM CTAB solution for 30 min. Then, 0.25 mL of 10 mM AgNO₃, 0.50 mL of 100 mM ascorbic acid and 0.10 mL of 1.0 M NaOH were added into the beaker. After 4 h, the coverslips were removed, washed and dried under Ar flow.

5.2.5 Setup of single-molecule fluorescence microscopy

The setup of time-resolved confocal microscopy has been described in Chapter 2. In this work, a 635 nm pulsed laser diode (LDH-P-C-635B, PicoQuant) and HQ685/70 were used as the excitation source and the emission filter, respectively.

The schematic of the setup of the wide-field fluorescence microscope is shown in Fig. 5-1. Basically, the wide-field microscope consists of an inverted microscope (IX 71, Olympus) and a 633 nm HeNe laser source (35 mW, Melles Griot). The excitation light was tuned to be circular polarized using $\lambda/4$ and $\lambda/2$

waveplates and expanded *via* a beam expander (ThorLabs) before being focused onto the back-focal plane of an oil immersion objective lens (100 $\times$, N.A. 1.3, Olympus). An excitation filter (Z633/10, Chroma) was used to filter the excitation light. The fluorescence was passed through a dichroic mirror (Z633rdc, Chroma) and an emission filter (HQ645LP, Chroma) and subsequently detected by a highly sensitive CCD camera (CascadeII 512B, Photometrics) after magnification with a 3.3 $\times$ camera lens.

Figure 5-1. Schematic representation of wide-field fluorescence microscope. 1 - 633 nm HeNe laser source, 2 - half wave plate, 3 - quarter wave plate, 4 - beam expander, 5 - excitation filter, 6 - dichroic mirror, 7 - oil immersion objective, 8 - stage, 9 - sample, 10 - emission filter, 11 - CCD camera.

5.3 Results and Discussion

5.3.1 On- and off-time distributions of single silver nanostructures

Two distinct groups of blinking behavior are observed for silver nanoparticles prepared using Method I. Out of the 140 nanoparticles recorded, 124 of them (or 89%) displayed frequent fluorescence blinking (see Fig. 5-2a for a typical trace), while the rest do not show any on-and-off blinking behavior

(see Fig. 5-2b). In the latter case, emission intensities of *ca.* 10 to 50 counts per ms are observed for excitation intensity $I = 1.0 \mu\text{W}$ ($\sim 415 \text{ W/cm}^2$). Similar intensities were also observed for the background emission from blinking nanoparticles (off-events). This is probably due to a combination of relatively weak emission^{3,14,15} and inelastic scattering¹⁶ from the nanoparticle. Fig. 5-2a shows that the photon bursts result in significantly higher emission intensities (on-events) compared with the background level with some bursts achieving photon counts as high as 3000 counts per ms.

Figure 5-2. Typical fluorescence intensity time traces of a Ag nanoparticle prepared *via* Method I recorded at ambient conditions showing rapid intensity fluctuations (a), and no blinking behavior (b). The excitation light intensity is $I = 1.0 \mu\text{W}$ ($\sim 415 \text{ W/cm}^2$).

Figure 5-3. Typical fluorescence intensity time trace of a Ag nanoparticle prepared *via* Method II showing rare occurrences of blinking at ambient condition and with $I = 1.0 \mu\text{W}$ ($\sim 415 \text{ W/cm}^2$).

Silver nanoparticles and nanorods prepared using Method II and Method III, respectively, also showed two types of blinking behavior, namely, (i) infrequent fluorescence blinking as shown in Fig. 5-3 for the case of silver nanoparticles, and (ii) no on-and-off blinking behavior. The majority of nanoparticles and nanorods do not undergo fluorescence intermittency as indicated by the absence of blinking events for 130 nanoparticles out of 150 (or 87%) and 99 nanorods out of 120 (or 83%).

The fluorescence intermittency of single nanoparticles prepared using Method I was characterized by constructing the on- and off-time duration histograms from the emission time traces with 1 ms bin time. A suitable threshold value was chosen such that fluorescence intensity above the value was considered an on-event.^{17,18} Fig. 5-4 shows the combined on-time (Fig. 5-4a) and off-time (Fig. 5-4b) duration histograms for a collection of 174 nanoparticles, and the on-time (Fig. 5-4c) and off-time (Fig. 5-4d) distributions for a single nanoparticle whose emission intensity time trace is given in Fig. 5-

4a. It is obvious from the linear log-log plots that the on- and off-times for $I = 1.0 \mu\text{W}$ cover a large time range and are described using a power-law distribution:

$$P(\tau_{on/off}) = P_o \tau_{on/off}^{-m_{on/off}} \quad (5.1)$$

where $m_{on/off}$ is the power-law exponent for the on/off-time distribution. A m_{on} value of 2.1 and m_{off} value of 1.4 were obtained for the combined nanoparticles. For the single nanoparticle, $m_{on} = 2.1$ and $m_{off} = 1.3$, which are similar to the values obtained for the combined nanoparticles within experimental error (± 0.1). The τ_{on} distribution for a collection of 50-60 nanoparticles excited using different excitation intensities $I = 0.5 \mu\text{W}$ ($\sim 207 \text{ W/cm}^2$), $1.5 \mu\text{W}$ ($\sim 623 \text{ W/cm}^2$) and $2.5 \mu\text{W}$ ($\sim 1038 \text{ W/cm}^2$) obeys power-law function with m_{on} ranging between 1.9 and 2.1 (see Fig. 5-5).

Figure 5-4. Power-law on-time (a) and off-time (b) distributions for a collection of 174 silver particles, and power-law on-time (c) and off-time (d) distributions for a single Ag nanoparticle prepared *via* Method I at ambient condition and with $I = 1.0 \mu\text{W}$ ($\sim 415 \text{ W/cm}^2$).

Figure 5-5. Power-law on-time distributions for a collection (50 to 60) of silver particles for $I = 0.5 \mu\text{W}$ ($\sim 207 \text{ W/cm}^2$, $\square$), $I = 1.5 \mu\text{W}$ ($\sim 623 \text{ W/cm}^2$, Δ), and $I = 2.5 \mu\text{W}$ ($\sim 1038 \text{ W/cm}^2$, $\circ$) obtained at ambient conditions.

Power-law on- and off-time distributions for silver nanoparticles are observed for the first time here. Other systems that exhibit power-law blinking behavior include organic dye molecules^{17,18} and semiconductor nanocrystals.^{19,20} For dye molecules, the power-law distribution arises from a charge tunneling model whereby a charge is transferred between individual molecules and localized states found in the surrounding matrix (*e.g.*, polymer films, glass surfaces). This creates a dark charge-separated state that subsequently returns to an emitting state *via* back charge tunneling. A similar model has also been proposed to explain the blinking behavior of quantum dots where off- and on-events are due to electron tunneling to, and returning from traps located in the vicinity of the quantum dots.²⁰ In addition, a model based on the random walk of either an electron or hole before charge recombination has

been proposed to rationalize power-law behaviors in organic molecules and quantum dots.^{18,21}

5.3.2 Blinking dynamics

The photon bursts observed in Fig. 5-2a arise from emitting Ag nanoclusters generated from silver oxides found on the surfaces of Ag nanoparticles.^{6,7,22,23} Ag₂O and AgO absorb light at the excitation wavelength,²⁴ and are subsequently reduced to atomic Ag according to the following reactions:

Since only ‘magic number’ nanoclusters consisting of 3 Ag atoms or more (*i.e.*, Ag_x, *x* is a magic number ≥ 3) fluoresce in the red,²⁵ diffusion and aggregation of Ag atoms are necessary in order to produce active clusters Ag_x as illustrated in step 1:

where Ag_n and Ag_m are either Ag or small, multi-atomic clusters formed after agglomeration. The nanocluster creation process in step 1 determines the “off” time dynamics.

An on-event arises when a nanocluster created in step 1 undergoes repeated cycles of light-induced excitation (step 2) and radiative emission (step 3):

Previous studies have shown that Ag nanoclusters can absorb red light and fluoresce at longer wavelengths.²⁶ Transition from an emitting “on” state to a dark state takes place when the nanocluster Ag_x converts to a species that does not fluoresce in the red. In step 4, the photo-active nanocluster diffuses on the surface of the nanoparticle before combining with another silver species Ag_y ($y \geq 1$) to form a non-active cluster Ag_z . Another deactivation pathway is given in step 5 where Ag_x reacts with O_2 to re-form AgO or Ag_2O that can be further reduced to an emitting nanocluster *via* step 1.

The intensity fluctuation observed in Fig. 5-2a suggests a continuous nanocluster creation-and-destruction process. The majority of Ag nanoparticles prepared using Method I shows fluorescence intermittency since adsorbed borohydride does not protect metallic surfaces from atmospheric oxygen. Therefore, silver nanoparticles prepared using this method can undergo oxidation in air to form silver oxides. On the other hand, polymeric citrate (Method II) and CTAB (Method III) layers bound to the particle surface prevent oxidation of neutral silver in solution.^{27,28} This leads to a significant reduction in the number of blinking events for the nanostructures prepared *via* Methods II and III as observed experimentally.

The effects of oxygen on the on-time dynamics (step 5) is investigated using wide-field fluorescence microscopy. Fig. 5-6 shows sequential wide-field fluorescence images of individual Ag particles, prepared *via* Method I, at ambient condition (Fig. 5-6A), and in the presence of an O_2 scavenger (Fig. 5-6B). The latter was recorded 8 min after the addition of the O_2 scavenger. This O_2 scavenger is efficient and will drastically reduce the oxygen content in water/buffer solutions by more than 94 % within a few minutes.²⁹ In the event

that step 5 is the only deactivation pathway for Ag_x , the removal of O_2 will lead to a constant emission intensity after silver oxides have been converted to the photostable Ag_x (*i.e.*, no blinking). Fig. 5-6, however, shows persistent blinking behavior at long times and in the absence of O_2 . In both environments, the fluorescence images from individual nanoparticles alternate between the background level and a significantly brighter spot indicating that fluorescence intermittency is not significantly suppressed when O_2 is removed. Similar observation was also noted when 0.1 M of carbohydrazide was used as the O_2 scavenger. This clearly demonstrates that step 5 does not completely describe the deactivation pathway of Ag_x .

Figure 5-6. Successive wide-field fluorescence images of silver particles excited at 633 nm recorded at (A) ambient conditions, and (B) 8 min after the addition of an O₂ scavenger (240 µg/ml glucose oxidase, 50 µg/ml catalase, 25 mM glucose, 1% β-mercaptoethanol). The integration time of each frame is 34.3 ms, and the dimension of the frame is 24.5 × 24.5 µm². The arrows indicate particles that showed blinking behavior in the time window of interest.

Spectral blinking in single-molecule SERS has been attributed to surface diffusion of adsorbate molecules.³⁰ The slow diffusion of organic molecules into and out of active SERS sites on silver nanoparticle surfaces is a low-energy process and occurs within the diffraction-limited area of the excitation beam. It is therefore feasible for silver nanoclusters to undergo random diffusion on the particle surface. Power-law function emerges for the off- and on-time

distributions as a result of the random diffusion of silver species in step 1 and step 4, respectively. This is not unexpected since many properties of random walks are known to be distributed according to power law.³¹ It is interesting to note that the observed m_{off} value (~ 1.4) is much smaller than the m_{on} value, suggesting that there is a higher probability to find long dark periods. This is rationalized in terms of the significantly fewer number of photo-active clusters (*i.e.*, magic number clusters) compared with the non-active ones. The probability to form a non-emissive cluster after each association reaction in step 4 is high due to the fact that most of the Ag clusters are not luminescent in the red. On the other hand, it would take a much longer time for the Ag species to aggregate into an emissive Ag_x cluster in step 1. If the diffusion of Ag nanoclusters is thermally activated, then the on-time distribution should be dependent on the excitation light intensity I . However, Fig. 5-5 shows that m_{on} is not significantly affected by varying I . A possible explanation is the narrow range of I used that does not allow an obvious change in the diffusion kinetics of the nanocluster.

The emission lifetimes of the Ag nanoclusters are of the order of the time-correlated photon counting technique used in this work (~ 100 ps), and were therefore not obtainable with the current experimental set-up. Previous studies reported fluorescence lifetimes of DNA-encapsulated Ag nanoclusters²⁶ and Ag_3 in a Ne matrix³² to be in the range of 2 to 10 ns. The ultrafast lifetimes seen here are due to the stabilization effects of the interaction between the nanoclusters and the plasmon resonance of the nanoparticle. This is in agreement with the ensemble lifetimes reported by Treguer and co-workers.²²

5.4 Conclusion

In summary, the origin of the power-law off- and on-time distributions in Ag nanoparticle films arises from the random diffusion and agglomeration of Ag entities to form either photoactive nanoclusters or non-active ones. In order for this to take place, silver oxides should be present on the nanoparticles as seen by the reduction in the fluorescence intermittency when the oxidation of colloidal Ag nanostructures is suppressed by a protective layer of either polymeric citrate or CTAB.

5.5 Bibliography

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