Origin of Size-Dependent Energy Transfer from Photoexcited CdSe Quantum Dots and Fluorescent Dyes to Gold Nanoparticles

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ORIGIN OF SIZE-DEPENDENT ENERGY TRANSFER FROM PHOTOEXCITED CdSe QUANTUM DOTS AND FLUORESCENT DYES TO GOLD NANOPARTICLES

by

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The photoluminescence quenching of CdSe quantum dots (QD) and fluorescent dyes by hexanethiolate Monolayer Protected Clusters (MPCs) with core diameters of 1.1-4.9 nm is described.

The CdSe QD investigated had the following core diameters of 2.0, 2.6, 3.4 and 6.9 nm. The fluorescent dyes used were: Coumarin 440 (CM440), Fluorescein 548 (F548), Rhodamine 6G (R6G), Pyromethene 597 (PM597) and Lyssamine Dye (LD700). Experimental evidence suggests that the photoluminescence quenching of both CdSe QD and the fluorescent dyes occurs through energy transfer and that the AuMPCs are efficient quenchers in both cases. The larger MPCs are more efficient quenchers.

There is a remarkable linear correlation found between the quenching efficiency determined by Stern-Volmer plot and the MPC core volume which suggests that the quenching efficiency is governed by the MPC core-size dependent extinction cross-section that determines the spectral overlap between the emission of the donor (QD and fluorescent dyes) and the absorption of the MPC.
# TABLE OF CONTENTS

**ACKNOWLEDGMENTS** ......................................................................................................................... ii

**LIST OF TABLES** ................................................................................................................................. v

**LIST OF FIGURES** ................................................................................................................................... vi

## CHAPTER

### I. INTRODUCTION ........................................................................................................................................ 1

1.1. Fluorescence and Deactivation Pathways of Excited Molecules ......................................................... 2

1.2. Monolayer Protected Cluster Au Nanoparticles ......................................................................................... 6

1.2.1. Surface Plasmon Resonance .............................................................................................................. 6

1.2.2. Concentric Sphere Capacitance Model .............................................................................................. 8

1.2.3. Double Layer Charging and Single Electron Transport in MPCs ....................................................... 9

1.3. Quantum Dots and Quantum Size Effect .................................................................................................. 13

1.3.1. Positronium Model and Excitons ..................................................................................................... 14

1.3.2. Synthesis of CdE (E=S, Se, Te) ........................................................................................................ 16

1.4. Fluorescence Quenching and Stern-Volmer Equation ............................................................................ 18

### II. SYNTHESIS, CHARACTERIZATION AND EXPERIMENTAL DETAILS .................................. 23

2.1 Synthesis and Characterization of Monolayer Protected Au Clusters (MPC) ........................................ 23

2.1.1. Brust- Schiffrin Synthesis of MPC .................................................................................................... 23

2.1.2. Characterization of Au Monolayer Protected Clusters MPC ........................................................... 25

2.1.2a. UV-Vis Absorbance ....................................................................................................................... 25

2.1.2b. Transmission Electron Microscopy TEM ....................................................................................... 26

2.1.2c. Electrochemical Analysis ............................................................................................................... 26

2.2. Characterization of CdSe QDs .............................................................................................................. 27

2.2.1. UV-Vis Absorbance and Photoluminescence Spectra (PL) ........................................................... 27

2.2.2. Transmission Electron Microscopy TEM ........................................................................................ 28
### Table of Contents – continued

#### CHAPTER

2.3. Details of Quenching Experiments ...................................................... 28

2.3.1. QD-Au MPC System Experimental Details ............................. 28
2.3.2. Dyes-Au MPC System Experimental Section ..................... 31

III. ORIGIN OF SIZE-DEPENDENT ENERGY TRANSFER FROM PHOTOEXCITED CdSe QUANTUM DOTS TO GOLD NANOPARTICLES 34

IV. PHOTOLUMINESCENCE QUENCHING IN FLUORESCENT DYES-Au MONOLAYER PROTECTED CLUSTERS SYSTEM ...................................... 51

V. CONCLUSIONS AND FUTURE WORK .............................................. 62

REFERENCES ......................................................................................... 64
LIST OF TABLES

2.1 Sizes of Au MPC used in the CdSe QDs-MPC experiment ................................ 28
2.2 Concentration, emission and excitation wavelengths of CdSe QDs .................. 30
2.3 Sizes of Au MPC used in the Dyes-MPC experiment ................................... 31
2.4 Concentration, emission and excitation wavelengths of fluorescent dyes ........ 33
3.1 The quenching constants $K_Q$ in the case of 2.0, 2.6, 3.4 and 6.9 nm CdSe QDs by Au$_{25}$, Au$_{140}$, Au$_{309}$, Au$_{807}$, and Au$_{4033}$ MPCs ................................................................. 40
4.1 The quenching constants $K_Q$ in the case of fluorescent dyes by Au$_{25}$, Au$_{140}$, Au$_{309}$, Au$_{976}$, and Au$_{2406}$ MPCs ................................................................. 55
# LIST OF FIGURES

1.1 Jablonski diagram. Processes by which photoexcited molecules return to the ground state ........................................................................................................................................... 3

1.2 Illustration of the excitation of the dipole surface plasmon in the case of spherical nanoparticles ........................................................................................................................................... 7

1.3 Description of I-V curve of ideal single electron transport Coulomb Staircase ............................................................................................................................................... 9

1.4 Single-electron transfer mechanism in Monolayer Protected Clusters MPC ........................................................................................................................................... 11

1.5 Formation of electron-hole pair or exciton .............................................................................................................................................................................................. 14

1.6 Synthesis of CdSe Quantum Dots ............................................................................................................................................................................................. 18

1.7 Illustration of dynamic quenching process .................................................................................................................................................................................. 19

1.8 Static quenching description ............................................................................................................................................................................................. 21

1.9 Static quenching simplified diagram .................................................................................................................................................................................. 21

1.10 Illustration of combined static and dynamic quenching .................................................................................................................................................. 22

2.1 Structures of Coumarin 440 (CM440), Fluorescein 548(F548), Rhodamine 6G Perchlorate (Rh6G), Pyromethene 597(PM597) and LD700 Perchlorate (LD700) ........................................................................................................................................... 32

3.1 TEM images of CdSe QD’s with the corresponding histograms of 2.0 nm, 2.6 nm, 3.4 nm and 6.9 nm ........................................................................................................................................... 34

3.2 TEM images of Au MPC with the corresponding histograms of Au$_{25}$, Au$_{140}$, Au$_{309}$, Au$_{807}$ and Au$_{4033}$ ........................................................................................................................................... 35

3.3 a) Absorption spectra of hexanethiolate-coated Au$_{25}$, Au$_{140}$, Au$_{309}$, Au$_{807}$, and Au$_{4033}$ MPCs in toluene. b) Absorption and PL spectra of 3.4 nm diameter CdSe QD in toluene ........................................................................................................................................... 36

3.4 Photoluminescence quenching of a photoexcited CdSe QD by a Au MPC ........................................................................................................................................... 37
3.5 PL spectral change of a 0.6 µM 3.4 nm CdSe QD colloidal solution upon addition of a Au$_{140}$ MPC solution ................................................................. 38

3.6 Decrease in the PL intensity upon addition of Au$_{25}$, Au$_{140}$, Au$_{309}$, Au$_{807}$ and Au$_{4033}$ MPC solutions in the case of 2.0, 2.6, 3.4 and 6.9 nm CdSe QDs ............... 39

3.7 Corresponding Stern-Volmer plots and best fit lines in the case of 2.0, 2.6, 3.4 and 6.9 nm CdSe for Au$_{25}$, Au$_{140}$, Au$_{309}$, Au$_{807}$, and Au$_{4033}$, respectively ....... 40

3.8 Absorption comparison of the QD to the QD-MPC mixture and QD-MPC mixture after the subtracting the absorption profile of MPC ........................................ 41

3.9 Lifetime measurement of 3.4 nm CdSe ............................................................... 42

3.10 Emission and absorbance spectra of 2.6 and 6.9 nm CdSe QDs ......................... 44

3.11 PL spectra of 2.6 nm ($\lambda_{\text{peak}} = 533$ nm) and 6.9 nm ($\lambda_{\text{peak}} = 645$ nm) CdSe QDs in toluene before (dashed line) and after (solid line) mixing ........................................ 45

3.12 Relationship between $K_Q$ and the MPC core volume for excited-state quenching of the 3.4 nm diameter CdSe QD by Au$_{25}$, Au$_{140}$, Au$_{309}$, Au$_{807}$, and Au$_{4033}$ MPCs. ................................................................. 49

4.1 Quenching efficiency of Au MPCs in the case of the fluorescent dyes: a) CM440, b) F548, c) Rh6G, d) PM597 and e) LD700 ................................................ 52

4.2 Emission spectra of CM440, F548, Rh6G, PM597 and LD700 and absorption spectra of Au MPCs ................................................................. 57

4.3 Absorbance correction in the case of PM597 and Au$_{309}$ .................................. 58

4.4 Comparison between quenching efficiencies in QD-MPC and Dyes-MPC systems ............................................................................................................. 59

4.5 Relationship between $K_Q$ and the core volume of MPC for excited fluorophore dyes ............................................................................................................. 60

4.6 Relationship between $K_Q$ and MPC extinction coefficient in the case of CM440, F548, R6G, PM597 and LD700 .................................................. 61
CHAPTER I
INTRODUCTION

In recent years, semiconductor-metal nanocomposites have drawn much attention because of their potential applications in photocatalysis and solar energy conversion. Semiconductor quantum dots (QDs) with tunable band gaps and excellent photostability in particular offer new opportunities for such applications in the visible and infrared regions of solar light. Earlier investigations have revealed that deposition of noble metal nanostructures on semiconductors greatly enhances the photoinduced charge carrier separation in light harvesting systems. Metal surfaces and nanoparticles are also quenchers of photoexcited states along a directed energy or charge transfer mechanism. While there is growing interest in the utilization of such nanoparticle composites in many applications, experimental evidence that reveals factors controlling the excited-state interactions is still limited. We report here quantitative results delineating the origin of the size-dependence in photoluminescence (PL) quenching of a CdSe QD by small gold nanoparticles that encompass the transition between bulk and molecular regimes.

Monolayer Protected Metal clusters (MPCs) are stable, structurally well-defined nanoparticles even in the dried state, which has allowed detailed characterizations of their structures, compositions and properties. The size-dependent optical and electrochemical charging properties of MPCs have been described. In a previous study, Cheng et al. described the fluorescence quenching of small dye molecules by Au MPCs in which they showed the essentiality of the donor-acceptor spectral overlap and the associated nanoparticle core density of electronic states in energy transfer (ET).
quenching. More recently, it was demonstrated that the quantized electronic charging properties of Au MPCs can be used to control the transfer of photogenerated electrons from the conduction-band of a large band-gap semiconductor (TiO$_2$) nanoparticle to Au MPCs$^{32}$. The excited-state quenching occurred via charge transfer (CT) and the quenching efficiency was remarkably dependent on the core size of Au MPCs. The origin of the size-dependence was interpreted by the size-dependent capacitance of Au MPCs.

1.1. Fluorescence and Deactivation Pathways of Excited Molecules

Upon illumination with ultraviolet or visible light, molecules can be promoted by absorption of photons from ground state to electronically excited states. Once excited, the molecules return to the ground state via a series of deactivation pathways like fluorescence emission, phosphorescence emission, vibrational relaxation, internal conversion, external conversion and intersystem crossing$^{33}$.

The heavy line labeled $S_0$ in Figure 1.1, shown below, represents the electronic energy of the molecule in the ground singlet state which represents the state with the lowest electronic state, and $S_1$ is the energy of the excited electronic state. The rest of the lines represent several vibrational energy levels associated with each of the levels $S_0$ and $S_1$. 

2
Figure 1.1 Jablonski diagram. Processes by which photoexcited molecules return to the ground state, where

- I represents absorption $S + h\nu_a \rightarrow S^*$
- II represents vibrational deactivation in singlet state
- III represents singlet state quenching $k_{cc} \quad S^* + Q \rightarrow S + Q$
- IV represents fluorescence emission $k_f \quad S^* \rightarrow S + h\nu_f$
- V represents intersystem crossing ISC from $S_1$ to $T_1 \quad S^* \rightarrow T^*$
- VI represents vibrational deactivation in triplet state
- VII represents triplet state quenching $T^* + Q \rightarrow T + Q$
- VIII represents phosphorescence emission $T^* \rightarrow S + h\nu_p$
- IX represents internal conversion IC $k_{ic} \quad S^* \rightarrow S$

The intensity of fluorescence can be decreased by a variety of processes. This decrease in intensity is called quenching and occurs by different mechanisms. The most preferred path to the ground state is the path which minimizes the lifetime of the excited state. Nonradiative pathways include internal and external conversion. Internal conversion describes the process by which the molecule passes to a lower energy
electronic state without emission of radiation and without change in the multiplicity of the levels involved in the transition. The energy of the electronically excited state is given off to vibrational modes of the molecule and the excitation energy transformed into heat. The smaller the difference in the energy of levels involved the better the efficiency of the internal conversion.

Internal conversion is a very efficient process in the case of overlap of two electronic energy levels. Internal conversion is a more probable mechanism than fluorescence deactivation from a higher excited state.

External conversion represents the nonradiative deactivation through collisions with solvent molecules or between excited molecules. This process is also called collisional quenching. Intersystem crossing represents another nonradiative deactivation pathway and occurs when the molecule deactivates from a singlet to a triplet state. The spin of the excited state is reversed and change in the multiplicity of molecule results. The two vibrational levels with different multiplicities involved in intersystem crossing have the same energy.

Fluorescence and phosphorescence are two deactivation processes which occur when an excited molecule returns to the ground state emitting radiation. Fluorescence occurs between two singlet states, the deactivation from a singlet excited state to a singlet ground state, while phosphorescence involves a change in the electron spin, between a singlet and a triplet state. A singlet-singlet transition is more probable than a triplet-singlet, and as a consequence, phosphorescence (lifetime $10^{-4}$ to $10^{0}$ seconds) lasts longer than the fluorescence (lifetime $10^{-5}$ to $10^{8}$ seconds).
Fluorescence always occurs from the lowest vibrational level of excited state $S_1$ to any of the vibrational levels of the ground state from where it could further deactivate to the lowest level of the ground state by vibrational relaxations. If the emitted radiation has the same frequency as the incident radiation, the fluorescence is called resonance fluorescence. On the other hand, non-resonance fluorescence initiates with a vibrational deactivation followed by the emission of a photon with a smaller frequency. The maximum in the fluorescence spectrum occurs at a longer wavelength than the maximum in the absorption spectrum because of energy loss in the excited state due to vibrational relaxation. The difference between the absorption and the emission wavelengths is called Stokes shift. Possible deactivation processes are shown in Figure 1.1.

Collisional quenching occurs when the excited-state fluorophore is deactivated upon contact with some other molecule in solution, which is called the quencher. The fluorophore is returned to the ground state during a diffusive encounter with the quencher. The molecules are not chemically altered in the process.

For collisional quenching the decrease in intensity is described by the Stern-Volmer equation:

\[
\frac{F_0}{F} = 1 + k_q \tau_0 [Q] = 1 + K_D [Q]
\]  

(1.1)

where $F_0$ and $F$ are the fluorescence intensity of the fluorophore in the ground and excited state, $K_D$ is Stern-Volmer quenching constant which indicates the sensitivity of fluorophore to a quencher, $k_q$ is the bimolecular quenching constant, $\tau_0$ is the unquenched lifetime and $[Q]$ is the concentration of quencher.
Aside from collisional quenching, fluorescence quenching can occur by a variety of other processes. Fluorophores can form nonfluorescent complexes with quenchers. This process is referred to as static quenching since it occurs in the ground state and does not rely on diffusion or molecular collision. Quenching can also occur by non-molecular mechanisms, such as attenuation of incident light by the fluorophore itself or other absorbing species.

1.2. Monolayer Protected Cluster Au Nanoparticles

There is ongoing intensive research interest in nanoscale particle materials because of their technological potential in optical, electronic and magnetic applications. Great scientific interest rests with nanoparticles, because they have unusual size-dependent properties and they represent a bridge between bulk and atomic structures.

1.2.1. Surface Plasmon Resonance

The optical properties of the metal nanoparticles are intriguing. Unusual colors are displayed by metal nanoparticles\textsuperscript{24,35,36}. Changes in size, shape and composition lead to significant changes in their properties and variations in color. The metal nanoparticles owe their color to the coherent excitation of the conduction-band electrons (so called surface plasmon absorption). The surface plasmon resonance is caused by the collective interaction of conduction band electrons which interact with the incoming electromagnetic field as shown in Figure 1.2.
The electrons are polarized with respect to the much heavier ionic core due to the electric field of the incoming light wave. There is a net charge difference at the nanoparticle surface which acts as a restoring force.

The color from the absorption of the nanoparticle is observed when the frequency of the incoming electromagnetic field is in resonance with the coherent motion of the electrons.

Mie’s theoretical model\textsuperscript{37} studied Maxwell’s equations and applied then the interaction of spherical nanoparticles with the electromagnetic field at the boundary with a dielectric. When the size of the nanoparticle is much smaller than the wavelength of the incoming electromagnetic filed (<20 nm), the extinction cross section $\sigma_{\text{ext}}$ is expressed only by the dipole oscillation\textsuperscript{35}.

Mie’s theory can be expressed by:

$$
\sigma_{\text{ext}} = \frac{9V\varepsilon_m^{3/2}}{c} \frac{\omega \varepsilon_2(\omega)}{[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + \varepsilon_2(\omega)^2} \tag{1.2}
$$

where $V$ is the particle volume, $\omega$ is the angular frequency of the exciting light, $c$ is the speed of light, $\varepsilon_m$ is the frequency independents dielectric constant of the surrounding medium and $\varepsilon(\omega) = \varepsilon_1(\omega) + ie_2(\omega)$ is the dielectric constant of the metal.
The peak intensity and position of the surface plasmon absorption band is dependent on the size and shape of the metal nanoparticles as well as the dielectric constant of the medium surrounding the particles\textsuperscript{38}. As the size increases, the absorption maximum is slightly red shifted.

### 1.2.2. Concentric Sphere Capacitance Model

The thin monolayer dielectric layer surrounding the Au core influences the ability to store electronic charge (capacitance)\textsuperscript{24, 39}. Theoretical models have been developed for Au MPCs in order to explain the existence of the current peaks observed in differential potential voltammetry (DPV). The models developed were based on electrostatic interaction\textsuperscript{40}. The models assumed that the MPC core was spherical and is surrounded by a nonpenetrable dielectric with fully extended chains. The metal-like core of MPC and the hydrocarbon-like dielectric coating led to the concentric sphere capacitance model.

The capacitance of a spherical nanoparticle coated with a uniform monolayer and immersed in an electrolyte solution was approximated to be\textsuperscript{41}:

\[
C_{\text{cluster}} = 4\pi\varepsilon_0\varepsilon \left( \frac{r}{d} \right)(r + d) \tag{1.3}
\]

where \(C_{\text{cluster}}\) is the MPC capacitance, \(r\) is the radius of the metal core, \(d\) is the thickness of the protecting dielectric monolayer, \(\varepsilon_0\) is permittivity of free space and \(\varepsilon\) is the static dielectric constant of the monolayer medium around the metal core. The MPC capacitance was assumed to be spherical even though the actual geometry of the MPCs is a truncated octahedron or decahedron and independent of its state of charge. The effects of HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) gaps were neglected.
1.2.3. Double Layer Charging and Single Electron Transport in MPCs

The phenomenon of single-electron transfer (SET) has been identified and studied in nanoparticles for quite some time\textsuperscript{41,42}. The single-electron transfer (SET) or Coulomb staircase, shown in Figure 1.3, is performed on single particles at reduced temperature\textsuperscript{43} usually through scanning tunneling microscopy (STM).

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{fig1.3.png}
\caption{Description of I-V curve of ideal single electron transport Coulomb Staircase.}
\end{figure}

If an electron is transferred to the MPC nanoparticle, its Coulomb energy increases by:

\[ E_c = \frac{e^2}{2C} \]  \hspace{1cm} (1.4)

where \( e \) is the charge of electron and \( C \) capacitance of the particle.

The thermal motion of the atoms has effect on the charge of particle and the Coulomb energy, the result being the tunneling process of electrons. To control single electron tunneling processes, the thermal energy of the particle must be much smaller than the Coulomb energy:
\[ kT \ll \frac{e^2}{2C} \quad (1.5) \]

where \( k \) is Boltzmann's constant and \( T \) is temperature.

Another condition for single-electron tunneling refers to the magnitude of the tunneling resistance relative to the quantum Hall resistance. With additional charge transferred to the nanoparticle, a voltage \( U = \frac{e}{C} \) is produced leading to the following tunneling current:

\[ I = \frac{U}{R_T} = \frac{e}{R_T C} \quad (1.6) \]

where \( R_T \) is the tunneling resistance.

The second condition for single-electron tunneling\(^{35}\) is then:

\[ R_{QH} \ll R_T \quad (1.7) \]

where \( R_{QH} \) is quantum Hall resistance and \( R_T \) is the tunneling resistance.

The monolayer-protected clusters MPCs meet both conditions for single-electron tunneling.

In the case of freely diffusing MPCs in solution and connected to a working electrode/electrolyte interface, the MPCs are diffusonally transported to the electrode and the electron transfers occur to equilibrate the Fermi level of the MPC metallic core with that of the working electrode\(^{43}\). The gain and loss of electrons of the MPC cores lead to the formation of an electrochemical double-layer around the MPC, as shown in Figure 1.4 below.
For sufficiently small MPCs the associated electrical capacitance $C_{clu}$ is very small, of the order of subattofarads (aF). Because of this fact, the single-electron transfer (SET) causes a significant change in the potential of MPC and sequential SET processes between the working electrode and MPCs diffusing towards it can be monitored.

The associated electrical capacitance $C_{clu}$ is given by

$$\Delta V = \frac{e}{C_{clu}} \text{ and } \Delta V > k_B T \tag{1.8}$$

where $e$ is the electronic charge.

The sequential single-electron transfer (SET) between the working electrode and MPCs occur at well separated and evenly spaced potential intervals $\Delta V$ which depend on the size of the MPC. Due to the fact that the potential intervals depend on the size of the MPCs, the dispersity of the sample investigated plays a crucial role. In the case of a polydisperse sample of MPCs the peaks are unresolved and featureless, and no information can be drawn from the electrochemistry of the solution.

For MPCs with a large core size, the separation of the SET peaks might not be possible even in the case of a monodisperse sample. The fact that the current peaks are
evenly spaced reflects the electrostatic nature of the MPC double-layer charging process and it is consistent with metal-like behavior\textsuperscript{41}.

If the MPC core is small there is a large separation between the peaks, between the initial oxidation and reduction, and an electrochemical band gap develops. The electrochemical band gap represents the HOMO-LUMO gap and molecule-like behavior becomes obvious. Alkanethiolate Au MPCs freely diffusing in electrolyte solutions are small enough to exhibit Coulomb staircase-like properties and it was proven that they have well-defined electrical double-layer capacitance\textsuperscript{44,45}.

Electron transfer has been reported in the case of hexanethiolate Au nanoparticles (Au\textsubscript{146} 1.64 nm) with a core mass of 28 kDa adsorbed on gold-mica substrate under ultrahigh vacuum at 83 K. Using a STM tip, with access at only individual clusters, the I-V experimental curve collected proved to display Coulomb staircase behavior. Scanning tunneling microscopy assured the monodispersity of the sample investigated\textsuperscript{45}. The I-V curve was reversible and repeatable with regularly spaced charging steps of 0.34 V increments between ±1 V bias.

The constant spacing in the experimental I-V curve between the staircase steps was consistent with $\Delta V = \frac{e}{C}$ where $e$ is the electron charge and $C$ is the combined capacitances of the tip-monomer-Au core and Au core-monomer-substrate junctions.

Cyclic (CV) and differential pulse voltammetry (DPV) of ensembles of the same clusters at a metal/solution interface was performed and there was a noticeable correspondence between the tip-based spectroscopy of a single Au cluster molecule and the cyclic and differential pulse voltammetry of ensembles of the same clusters. There
was a remarkable similarity between the tunneling capacitance and the electrochemical capacitance.

Further research was performed investigating the transition to molecule-like charging for Au nanoparticles of varied sizes using the same STM method and DPV. The Au nanoparticles investigated had 8 to 38 kDa core mass with size of 1.1 to 1.9 nm. It was discovered that the large Au nanoparticles (22, 28 and 38 kDa) exhibited Coulomb staircase behavior consistent with double-layer charging of metal-electrolyte interface while the small Au nanoparticles (8 and 14 kDa) displayed redox chemical character with large central gap, i.e. molecular redox-like behavior.

DPV showed also a difference in peak spacing depending on the size of the Au nanoparticle. The DPV peak spacing for the larger Au nanoparticles (22, 28 and 38 kDa) was less than the DPV spacing in the case of smaller Au nanoparticles (8 and 14 kDa). The peak spacing decreased as the size of Au nanoparticles increased. A correlation between the energy gap and the electronic structure was established; the DPVs displayed an evident transition from the metal to nonmetal structure.

1.3. Quantum Dots and Quantum Size Effect

Quantum dots or nanocrystals represent an interesting class of semiconductors with novel quantum properties and wide applications. Unlike the traditional semiconductors, quantum dots have a tremendous versatility. The nanometer-size materials have size-tunable properties arising from quantum confinement in the nanometer scale. The more traditional semiconductors have fixed bandgaps while the nanocrystal semiconductors have size tunable bandgaps which are proportional to the
particle size. As the size of the quantum dots (QDs) decreases, the size of the bandgap increases. This unique ability of the quantum dots for tuning the emission covers a wide range of the spectrum using the same material and by controlling the size of the semiconductor nanocrystal. The quantum size effect can be understood using the quantum treatment of a particle in a box or infinite potential well. For a free electron, the allowed energy levels can have a continuous range of values while for the electron in a box the energies become quantized as a result of confinement.

1.3.1. Positronium Model and Excitons

Upon incident radiation a photon, enters a semiconductor and the excited electron leaves the valence band, being promoted to the conduction band. The electron is placed in the conduction band and the hole in the valence band, as shown in Figure 1.5 below.

![Figure 1.5 Formation of electron-hole pair or exciton.](image)

After leaving the valence band, the electron leaves a hole behind, of opposite electric charge, to which it is attracted by the Coulomb force. The electron-hole pair represents an exciton and results from the binding of the electron with its hole.

In an unconfined (bulk) semiconductor, the electron-hole pair, called an exciton, is bound within a specific length, called the Bohr exciton radius. In the case of quantum dots, the exciton is constrained to a confinement in all three directions.
The excited electronic states of semiconductor nanocrystals can be studied using the analogy of the Bohr positronium model. In the Bohr model, the electron can orbit around the small, positively charged nucleus only at quantified distances from the nucleus, depending on their energy. A single electron revolves around the nucleus and the smallest possible orbit for the electron is given by the Bohr radius $a_0$. In the positronium model the electron-nucleus system may be approximated with the bound electron-hole system. The energy levels in the positronium model are given by:

$$E_n = \frac{-e^2}{8\pi\varepsilon_0 a_0 n^2} = \frac{-6.8eV}{n^2}$$ (1.9)

where the Bohr radius $a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m_0 e^2} = 0.0529nm$ (1.10)

and $\varepsilon_0$ represents permittivity of free space, $\hbar$ reduced Planck constant, $m_0$ electron rest mass, $n$ the quantum number and $e$ electron charge. When the size of the nanocrystal becomes comparable with the natural length scale of the exciton, the quantum size effect occurs. Bohr radius is used as convenient length scale. The Bohr radius of the exciton dictates the level of confinement of the quantum dots.

There are three levels of confinement: weak, intermediate and strong. Weak confinement requires the condition:

$$R \gg a_{\text{eff}}$$ (1.11)

where $R$ represents the radius of nanocrystal and $a_{\text{eff}}$ is the effective radius, while intermediate confinement requires for $R \sim a_{\text{eff}}$ and strong confinement requires $R \ll a_{\text{eff}}$.

The effective radius is defined by:
\[ a_{\text{eff}} = \frac{\varepsilon/\varepsilon_0}{m^*/m_0} a_0 = \frac{0.0529}{m^*/m_0} \text{nm} \]  
(1.12)

where \( \varepsilon \) is the dielectric constant of the material, \( m^* \) is mass of the particle, \( m_0 \) is rest mass of the electron and \( a_0 \) is Bohr radius.

The confinement regime depends on the nanocrystal material and size. In the case of InAs the exciton Bohr radius is 36 nm, for CuCl the exciton Bohr radius is 0.7 nm\(^5\). The energy of the electron-hole pair is defined by:

\[ E_{\text{ex}} = \frac{m^*/m_0}{(\varepsilon/\varepsilon_0)^2} e^2 = \frac{13.6}{4\pi\varepsilon_0 a_0 n^2} eV \]  
(1.13)

and the energy gap for a nanocrystal is:

\[ E_g (QD) = E_g (\text{bulk}) + \left( \frac{\hbar^2}{8R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{4\pi\varepsilon_0 \varepsilon R} \right) \]  
(1.14)

**1.3.2. Synthesis of CdE (E=S, Se, Te)**

An important factor in the study of semiconductor nanoparticles was the ability of obtaining reproducible monodisperse samples with the same structure and surface derivatization\(^{51-53}\). The most popular and successful methods were Murray’s and Peng’s\(^5\). Murray’s method is based on pyrolysis of organometallic reagents, namely dimethylcadmium. \( \text{Me}_2\text{Cd} \) is extremely toxic, unstable at room temperature and requires very restrictive conditions.

Peng made a major contribution in the synthesis of semiconductor nanoparticles by replacing dimethylcadmium and using CdO as a precursor instead.
The organometallic route\textsuperscript{55} of Murray consists of a rapid injection of organometallic reagents into a hot coordinating solvent. The rapid injection leads to homogenous nucleation. This method can be used to obtain CdS, CdSe and CdTe. For synthesis of TOP/TOPO capped CdSe the following steps were used. The tri-n-octylphosphine oxide TOPO was purified using distillation and the transferred fraction between 260 and 300°C at pressure $P = 1$ torr retained. Dimethylcadmium was purified by filtration under vacuum using a filter of 0.250 $\mu$m. A certain mass of Cd was dissolved in enough tri-n-octylphosphine TOP to obtain a 1.0 M stock solution of trioctylphosphine selenide TOPSe. In a reaction vessel, a mass of 50 g TOPO was dried and degassed by heating at approximately 200°C flushing periodically with Argon for twenty minutes. The pressure was $P_{Ar} = 1$ atm. After 20 min, the temperature is stabilized at 300°C under $P_{Ar} = 1$ atm. Independently two reagent solutions A and B are prepared in a dry box.

The solution A was prepared by mixing 1.00 ml of 13.35 mmol Me\textsubscript{2}Cd with 25.0 ml TOP. The second solution B was prepared by adding 10.0 ml of 1.0 M TOPSe stock solution to 15.0 ml TOP. Then solutions A and B were mixed together and loaded into a syringe in the drybox. The reaction vessel, containing the dried TOPO, and previously at 300°C, is removed from heat. The reagent solution A+B is introduced quickly into the reaction vessel using a syringe through a rubber septum in a single injection with vigorous stirring. Upon addition of the reagents at room temperature, the temperature of the mixture drops to about 180°C. The depletion of reagents as well as the temperature drop impedes any further nucleation. As a consequence, the temperature is restored by reheating and is gradually increased to 230-260°C. The gradual reheating allows the
slow growth of the crystallites. The result is a yellow/orange solution which presents an absorbance peak at 440-460 nm. The growth of the crystallites is monitored over time with absorption spectra. Size distribution may be roughly estimated from the absorption line widths. When the desired absorption spectrum is observed, the portion having the desired size may be extracted. The average size of the crystallites and the sample monodispersity are modulated by the growth temperature.

A schematic of the CdSe synthesis is shown in Figure 1.6 below.

![Figure 1.6 Synthesis of CdSe Quantum Dots.](image)

1.4. Fluorescence Quenching and Stern-Volmer Equation

The Stern-Volmer equation is the most widely used method of studying the efficiency of quenching of fluorescence for dynamic quenching, static quenching or combination of the two. In the case of a fluorophore $F$ under external perturbation by a light pulse $f(t)$, deactivation of the excited state $F^*$ back to the ground state, includes intrinsic pathways and competing with the intrinsic de-excitation, intermolecular processes, which occur in the presence of another molecule $Q$, called the quencher.

Due to these competing intermolecular processes there is a loss in fluorescence
called fluorescence quenching. In Figure 1.7 below, the case of dynamic collision is illustrated along with the decay rates. Dynamic quenching is a diffusive encounter between the fluorophore and quencher during the lifetime of the fluorophore.

![Diagram of dynamic quenching process](image)

Figure 1.7 Illustration of dynamic quenching process.

The Stern-Volmer equation can be derived by considering the fluorescence intensities in the absence and presence of quencher. The fluorescence intensity observed for a fluorophore $F$ is proportional to its concentration in the excited state $[F^*]$.

Under continuous illumination, a constant population of excited states $F^*$ is established and therefore $\frac{d[F^*]}{dt} = 0$ \hspace{1cm} (1.15)

In the absence of quencher, the decay rate of the populated state $F^*$ is $\gamma = \tau_0^{-1}$ where $\tau$ represents the lifetime of the excited state, and is composed of radiative and nonradiative deactivations. In the presence of a quencher there is an additional decay rate $k_q$ which represents the bimolecular rate constant.

In the absence of quencher the differential equation describing $[F^*]$ is

$$\frac{d[F^*]}{dt} = f(t) - \gamma[F^*]_0 = 0$$ \hspace{1cm} (1.16)

In the presence of quencher the differential equation describing $[F^*]$ is
\[
\frac{d[F^*]}{dt} = f(t) - (\gamma + k_q [Q])[F^*] = 0
\]  

(1.17)

where \( f(t) \) is the external excitation source, \( \gamma = \tau_0^{-1} \) is the decay rate of the fluorophore in the absence of quencher and \( k_q \) is the bimolecular quenching constant.

If the external perturbation is a constant pulsed light, the population of excited molecules is constant also, so the derivatives can be set to 0. Dividing the differential equations in absence and presence of quencher, the following equation is obtained:

\[
\frac{F_0}{F} = \frac{\gamma + k_q [Q]}{\gamma} = 1 + k_q \tau_0 [Q]
\]  

(1.18)

which represents the Stern-Volmer equation.

The product \( k_q \tau_0 = K_{sv} \) is also known as Stern-Volmer quenching coefficient so Stern-Volmer equation can also be written as:

\[
\frac{F_0}{F} = 1 + K_{sv} [Q]
\]  

(1.19)

In general the \( \frac{F_0}{F} \) ratio is plotted against \([Q]\), the concentration of quencher. The plot \( F / F_0 \) versus \([Q]\) yields a linear dependence with a y-intercept of 1 and slope equal with \( K_{sv} \).

While the collisional quenching occurs through diffusive interactions between fluorophore \( F \) and quencher \( Q \) during the lifetime of the fluorophore, in static quenching, the fluorophore interacts with the quencher and forms a non-fluorescent complex or interacts through a sphere of effective quenching. The quencher can interact with the ground state fluorophore \( F \) or with the excited fluorophore \( F^* \). The non-fluorescent \( FQ \) complex is a ground state complex and in the case of absorption of light the deactivation
back to the ground state is nonradiative. When the fluorophore is in the excited state and interacts with the quencher, the distance between fluorophore and quencher, or the sphere of effective quenching, becomes of great importance. In rigid media, the quenching of a fluorophore is complete if the fluorophore is located inside of a sphere of volume $V_q$ surrounding the fluorophore $F$. The sphere is called sphere of effective quenching, or active sphere of quenching, as illustrated in Figure 1.8.

![Static Quenching](image)

Figure 1.8 Static quenching description.

In the static quenching, the decay of the fluorophore quencher complex is a nonradiative process and the rate of decay is $K_s$, which is the association constant for the complex formation. The static quenching is illustrated below in Figure 1.9.

![Static quenching simplified diagram](image)

Figure 1.9 Static quenching simplified diagram.
In the case of static quenching the Stern-Volmer equation is:

\[ \frac{F_0}{F} = 1 + K_s [Q] \]  \hspace{1cm} (1.20)

To differentiate between dynamic and static quenching, lifetime measurements can be a useful tool. In the diffusive encounter of the fluorophore with quencher in the dynamic case, the lifetime of the excited fluorophore changes because of the additional nonradiative depopulation processes of the excited state. In the static quenching there is no change in the lifetime because only the uncomplexed fluorophores are observed, the ground state fluorophore-quencher being nonfluorescent. In the dynamic quenching there is an equivalent decrease in both fluorescence intensity and lifetime.

In some instances both static and dynamic quenching occurs as seen below in Figure 1.10.

![Figure 1.10 Illustration of combined static and dynamic quenching.](image)

The Stern-Volmer equation can be written in this case as:

\[ \frac{F_0}{F} = 1 + K_{\text{app}} [Q] \]  \hspace{1cm} (1.21)

where \( K_{\text{app}} = (K_D + K_S) + K_D K_S [Q] \)  \hspace{1cm} (1.22)

\( K_D \) is the dynamic quenching constant and \( K_S \) is the static quenching constant.
CHAPTER II

SYNTHESIS, CHARACTERIZATION AND EXPERIMENTAL DETAILS

2.1 Synthesis and Characterization of Monolayer Protected Au Clusters (MPC)

2.1.1. Brust-Schiffrin Synthesis of MPC

All chemicals used in the synthesis of AuMPC were purchased from Sigma-Aldrich: Gold (III) chloride trihydrate ≥99.9%; Tetraoctylammonium bromide 98%; Sodium borohydride 99.0%, Sodium Sulfate 99.9% ACS Reagent, anhydrous; 1-Hexanethiol 98.0%, Toluene 99.5 %, ACS Reagent; Ethanol anhydrous denatured, Dichloromethane 99.9%, ACS HPLC grade; Acetone 99.5% ACS HPLC grade, Acetonitrile 99.5% ACS Reagent; Dimethyl Sulfoxide 99.7% ACS Reagent, Hexane 95.0% ACS Reagent, MilliPore Water (18.2 MΩ·cm).

A modified two-phase procedure by Brust and Schiffrin\textsuperscript{32,56-58} was followed for the synthesis of alkanethiolate gold monolayer protected clusters (AuMPCs). The MPCs core size was controlled by employing a varied thiol:gold molar ratio and solvent fractionated to reduce size dispersity. Briefly, the water-soluble Au, in the form of chloroaaurate salt was extracted into toluene with tetraoctylammonium bromide. Hexanethiol was added to the toluene solution, the result being formation of gold polymer (\((-\text{Au}^1\text{SC}_6\text{H}_{13}\cdots)^n\)). This was followed by further gold reduction with sodium borohydride. The final result is neutral Au\textsuperscript{0}MPCs with a 1-5 nm range in core diameters.

The equations involved in the Au MPC synthesis are:

\[
\text{Au}^{III}\text{Cl}_4^- (\text{aq}) + \text{N}(\text{C}_8\text{H}_{17})_4 + (\text{C}_6\text{H}_5\text{Me}) \rightarrow \text{N}(\text{C}_8\text{H}_{17})_4^+\text{Au}^{III}\text{Cl}_4^- (\text{C}_6\text{H}_5\text{Me})
\] (1.23)
\[
\text{Au}^{III}\text{Cl}_4^- (C_6H_5Me) + C_6H_{13}SH \rightarrow (-\text{Au}^1\text{SC}_6\text{H}_{13}^-)\text{n} + \text{BH}_4^- \rightarrow \text{Au}^{0}_x(\text{SC}_6\text{H}_{13})_y \quad (1.24)
\]

For example, for a 1:3 gold-thiol ratio, which leads to the formation of small AuMPCs (1.1 and 1.7 nm), the procedure consists of the following steps. A quantity of 0.5 g (1.27 mmol) \(\text{HAuCl}_3\cdot3\text{H}_2\text{O}\) in 30 ml Milli-Q water is added to 1.04 g (1.9 mmol) \(\text{TOABr}\) in 125 ml of toluene and the mixture is stirred vigorously for 20 minute or until two layers are present. The organic phase is separated from the aqueous phase and 0.536 ml (3.8 mmol) of hexanethiol is added under continuous stirring for another 10-20 minutes or until the mixture is completely colorless. When the mixture becomes colorless it is placed in an ice bath for approximately 1 hour or until the temperature reaches 0 °C. While stirring, a quantity of 0.480 g (12.7 mmol) \(\text{NaBH}_4\) in 30 ml of Milli-Q water is added to the already cold organic phase and placed in an ice bath under continuous stirring for another 30 minutes. The organic phase obtained is separated and washed repeatedly with approximately 1 L of Milli-Q water in small portions of approximately 300 mL. The aqueous layer is discarded each time. After washing, the mixture is dried with a qualitative amount of sodium sulfate and poured through filter paper in a funnel. More toluene is added to the sodium sulfate and poured through the filter again. The step is repeated until the remaining sodium sulfate has no color left. Using a rotary evaporator the toluene is evaporated from the synthesized nanoparticles. When the toluene is completely evaporated, 50 mL of ethanol is added and allowed to soak overnight. Using a glass filter, the solution is filtered the next day into a solid and liquid part. The liquid portion contains \(\text{Au}_{25}\) particles and excess remaining thiol and the solid part contains \(\text{Au}_{140}\) particles and bigger sizes of AuMPCs.
The ethanol is evaporated from the liquid portion using a rotary evaporator. When the ethanol is evaporated completely, 50 mL acetonitrile is added (it removes excess thiol) and allowed to soak overnight. The next day, the acetonitrile is filtered and discarded and the remaining solid (Au$_{25}$) dissolved in dichloromethane. After evaporation of dichloromethane, the solid part which represents Au$_{25}$ MPCs can be stored in a vial in the freezer.

To the solid portion containing Au$_{140}$ particles and bigger sizes of AuMPCs, 50 mL acetone is added (it dissolves Au$_{140}$ nanoparticles) and allowed to gravimetric filtrate overnight into a flask. This step of the procedure allows collecting Au$_{140}$ nanoparticles. The acetone is evaporated using a rotary evaporator and the Au$_{140}$ nanoparticles stored in the freezer.

The nucleation-growth-passivation process is a vital step of the Au synthesis which dictates the size of Au MPC along with the Au:thiol ratio. MPCs core sizes depend on gold-thiol mole ratio, speed of the reductant addition and the reduction temperature. Low temperature and high concentration of thiol lead to relatively monodisperse AuMPCs$^{59}$. Size-selective precipitation is frequently used to obtain monodisperse samples based on size-dependent solubility of the nanoparticle.

2.1.2. Characterization of Au Monolayer Protected Clusters MPC

2.1.2a. UV-Vis Absorbance. The Au Monolayer-Protected Clusters MPC samples were investigated using UV-vis absorbance spectroscopy, tunneling electron microscopy TEM and electrochemistry. The UV-vis absorbance spectra were collected with a Perkin-Elmer Lambda 40 spectrometer over a range of 300 to 1100 nm and
normalized to unity at 300 nm. All the MPC solutions were freshly prepared in toluene and concentrations chosen so that solution absorbance was <0.2 to avoid self-absorbance effects.

2.1.2b. Transmission Electron Microscopy TEM. TEM is one of the tools with which the size of the AuMPCs is determined. TEM images of Au MPC were obtained using Ted Pella Formvar/carbon coated films on copper grids (400 mesh) and dried in air using the dipping technique in a solution of 1 mg/mL MPC in CH$_2$Cl$_2$. The images were obtained with JEOL-JEM 1230 transmission electron microscope at 80 keV. Samples were investigated at 600K magnification and the size distribution of the gold cores was measured using at least 300 individual cluster core images using Scion Software (www.scioncorp.com).

2.1.2c. Electrochemical Analysis. The electrical and optical properties of nanoparticles depend strongly on their size, a small change in the size leading to a huge change in their properties. Thus, determining the core size of the nanoparticle becomes imperative in obtaining insightful conclusions. Differential pulse voltammetry is one of tools used to characterize the size of Au MPCs using the quantized double layer charging properties of MPCs.$^{45,60}$

Electrochemical Measurements were performed with 0.1 M Bu$_4$NClO$_4$ in CH$_2$Cl$_2$ using 660B Electrochemical Workstation, CH instruments. A 3-electrode probe was used, polished with 0.05 µm Al$_2$O$_3$ slurry and cleaned electrochemically by potential cycling in 0.1 M H$_2$SO$_4$ solution. The reference electrode was a 0.5 mm diameter Ag wire, the counter electrode a 2 mm diameter Pt wire, and the working disk electrode a 0.4
mm diameter Pt wire. The solution was purged with high-purity Ar to remove air in a well sealed vial. Potentials are reported versus Ag QRE or Fe/Fc+. The voltammograms were performed on freshly prepared solutions and positive and negative potential scans were recorded and values of peak potentials averaged. The scan rate for cyclic voltammetry (CV) was 50 mV/s. Differential pulse voltammetry (DPV) was performed with potential steps of 4 mV, square wave amplitude of 25 mV, square wave frequency of 15s⁻¹, and quiet time of 10 s. Square wave voltammetry (SWV) was done with potential steps of 4 mV, square wave amplitude of 25 mV, square wave frequency of 15s⁻¹, and quiet time of 10 s. Sublimed ferrocene (Fc) was added as an internal reference for AgQRE⁶¹.

2.2. Characterization of CdSe QDs

The CdSe QDs used were coated with octadecylamine and purchased from NN-Labs (Fayetteville, AR). The CdSe QDs were examined using UV-Vis absorbance and Photoluminescence Spectra (PL) and Transmission Electron Microscopy TEM.

2.2.1. UV-Vis Absorbance And Photoluminescence Spectra (PL)

The UV-vis absorbance spectra were collected with a Perkin-Elmer Lambda 40. The fluorescence measurements were taken at standard right angle configuration using a Perkin-Elmer Luminescence Spectrometer LS50B, with Xenon discharge lamp and gated photomultiplier with S5 response for operation up to around 650 nm. All samples were freshly prepared in toluene with concentrations that gave solution absorbance less than 0.2.
2.2.2. Transmission Electron Microscopy TEM

The core sizes of QD’s were determined by transmission electron microscopy TEM and determined to be 2.0 ± 0.2 nm, 2.6 ± 0.2 nm, 3.4 ± 0.2 nm and 6.9 ± 0.2 nm. The TEM images were obtained by using a JEOL transmission electron microscope JEM-1230 and samples prepared using dipping technique on Formvar/carbon coated copper grid 01814F from Ted Pella, Inc (Redding, CA). All the solutions prepared for TEM used toluene as solvent with the following concentrations: 30 µM (2.0 nm CdSe), 13 µM (2.6 nm CdSe), 9.6 µM (3.4 nm CdSe) and 0.7 µM (6.9 nm CdSe).

2.3. Details of Quenching Experiments

2.3.1. QD-Au MPC System Experimental Details

The organic soluble hexanethiolate Au MPC sizes used in the QD-MPC experiment are specified in Table 2.1, shown below.

<table>
<thead>
<tr>
<th>Au MPC</th>
<th>$\text{Au}_{25}(\text{SC}<em>6)</em>{18}$</th>
<th>$\text{Au}_{140}(\text{SC}<em>6)</em>{53}$</th>
<th>$\text{Au}_{309}(\text{SC}<em>6)</em>{92}$</th>
<th>$\text{Au}_{807}(\text{SC}<em>6)</em>{163}$</th>
<th>$\text{Au}_{4033}(\text{SC}<em>6)</em>{453}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abbreviation</td>
<td>$\text{Au}_{25}$</td>
<td>$\text{Au}_{140}$</td>
<td>$\text{Au}_{309}$</td>
<td>$\text{Au}_{807}$</td>
<td>$\text{Au}_{4033}$</td>
</tr>
<tr>
<td>Core diameter (nm)</td>
<td>1.1±0.2</td>
<td>1.7±0.2</td>
<td>2.2±0.2</td>
<td>2.9±0.2</td>
<td>4.9±0.3</td>
</tr>
</tbody>
</table>

Table 2.1 Sizes of Au MPC used in the CdSe QDs-MPC experiment.

Due to solubility constraints, the quenching was studied in toluene solution and the procedure consisted of adding several 1-50 5-µL increments of MPC solution to 3 mL of CdSe solution with photoluminescence PL spectra taken after each addition. The volume of MPC added to the QDs solution varied from size to size of the Au MPC. The
photoluminescence spectra were taken using a Perkin-Elmer LS-50B fluorimeter with a 390 nm cut-off filter. Prior to the addition of the Au MPC, the QDs solution was purged with high-purity Ar gas for 30-40 min to remove oxygen from the solution. The Au MPC solution was also purged before being added to the QDs solution. Concentration of the QDs solution was chosen in such a way that the absorbance was < 0.2 to avoid self-absorbance effects.

The optical absorption spectra were taken with a Lambda 40 Perkin-Elmer spectrophotometer. Due to the colloidal nature of the QDs solution, the solution containing both QDs and the MPC was mixed on a Corning Stir plate for a period of 2 minutes to allow proper mixing.

All sizes of QDs were excited with a wavelength of 400 nm and the exact details are illustrated in the following Table 2.2. The efficiency of quenching was determined with the Stern-Volmer plot and the quenching coefficients obtained will be presented in Chapter III.

Lifetime measurements of the 3.4 nm QD (0.60 µM) were performed using a fluorescence lifetime spectrometer (FL920, Edinburgh Instruments). Decay curves were collected at 573 nm with excitation at 380 nm using a pulsed diode laser (PLS 370, PicoQuant) operating at 10 MHz. Decay curves were fitted with FAST software (v 1.9.1, Edinburgh Instruments) using reconvolution fit with instrumental response.
<table>
<thead>
<tr>
<th>Core size of CdSe QDs</th>
<th>2.0 nm CdSe</th>
<th>2.6 nm CdSe</th>
<th>3.4 nm CdSe</th>
<th>6.9 nm CdSe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{absorption}}$ (nm)</td>
<td>469</td>
<td>521</td>
<td>561</td>
<td>634</td>
</tr>
<tr>
<td>$\lambda_{\text{emission}}$ (nm)</td>
<td>489</td>
<td>533</td>
<td>573</td>
<td>645</td>
</tr>
<tr>
<td>$\lambda_{\text{excitation}}$ (nm)</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Stock solution concentration ($\times 10^{-5}$ M)</td>
<td>9.25</td>
<td>8.3</td>
<td>6.01</td>
<td>2.95</td>
</tr>
<tr>
<td>Solution concentration (µM) in 3 mL solvent</td>
<td>2.77</td>
<td>1.10</td>
<td>0.81</td>
<td>0.049</td>
</tr>
<tr>
<td>Solvent stock solution</td>
<td>toluene</td>
<td>toluene</td>
<td>toluene</td>
<td>toluene</td>
</tr>
<tr>
<td>Solvent solution</td>
<td>toluene</td>
<td>toluene</td>
<td>toluene</td>
<td>toluene</td>
</tr>
</tbody>
</table>

Table 2.2 Concentration, emission and excitation wavelengths of CdSe QDs.
2.3.2. Dyes-Au MPC System Experimental Section

Besides the CdSe QDs, a series of fluorescent laser dyes were used. The quenching of the fluorophore dyes by the AuMPCs was studied in 1:1 (v/v) CH₃CN/toluene and 1:1 (v/v) MeOH/toluene mixtures depending on the dye. These certain mixtures were chosen for solubility purposes.

The typical procedure consisted in adding 1-50 5-µL increments of purged MPC solution to a 3 mL of dye solution. The dye solution was purged before adding the MPC solution for 20-30 minutes. The MPC solution is added until a quenching of 40-50% of the initial fluorescence intensity is achieved. After each addition of MPC the UV-Vis and fluorescence spectra were taken. The concentration of each dye was chosen so that absorbance was less than 0.2. The efficiency of quenching was studied with Stern-Volmer plot and quenching coefficients determined. Quenching coefficients will be presented in Chapter III.

The AuMPC sizes used in the Dyes-MPC system are presented in Table 2.3 below.

<table>
<thead>
<tr>
<th>Au MPC</th>
<th>Au₂⁵(SC₆)₁₈</th>
<th>Au₁₄₀(SC₆)₅₃</th>
<th>Au₃₀₉(SC₆)₉₂</th>
<th>Au₉₇₆(SC₆)₁₈₇</th>
<th>Au₂₄₀₆(SC₆)₃₂₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abbreviation</td>
<td>Au₂₅</td>
<td>Au₁₄₀</td>
<td>Au₃₀₉</td>
<td>Au₉₇₆</td>
<td>Au₂₄₀₆</td>
</tr>
<tr>
<td>Core diameter (nm)</td>
<td>1.1 ± 0.2</td>
<td>1.7 ± 0.2</td>
<td>2.2±0.2</td>
<td>3.1±0.3</td>
<td>4.0±0.1</td>
</tr>
</tbody>
</table>

Table 2.3  Sizes of Au MPC used in the Dyes-MPC experiment.

The structure of the dyes used is illustrated in Figure 2.1 and their characteristics given in Table 2.4, both shown below.
Figure 2.1 Structures of Coumarin 440 (CM440), Fluorescein 548 (F548), Rhodamine 6G Perchlorate (Rh6G), Pyromethene 597 (PM597) and LD700 Perchlorate (LD700).
<table>
<thead>
<tr>
<th>Dye</th>
<th>CM440</th>
<th>F548</th>
<th>Rh6G</th>
<th>PM597</th>
<th>LD700</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{excitation}}$ (nm)</td>
<td>340</td>
<td>515</td>
<td>529</td>
<td>525</td>
<td>650</td>
</tr>
<tr>
<td>$\lambda_{\text{emission}}$ (nm)</td>
<td>410</td>
<td>529</td>
<td>549</td>
<td>560</td>
<td>672</td>
</tr>
<tr>
<td>Stock solution concentration (mM)</td>
<td>1.00</td>
<td>0.25</td>
<td>0.25</td>
<td>1.00</td>
<td>0.90</td>
</tr>
<tr>
<td>Solution concentration (µM) in 3mL solvent</td>
<td>0.70</td>
<td>0.65</td>
<td>0.38</td>
<td>2.00</td>
<td>2.10</td>
</tr>
<tr>
<td>Solvent stock solution (v/v)</td>
<td>MeOH</td>
<td>MeOH</td>
<td>9:4</td>
<td>CH$_3$CN/toluene</td>
<td>1:9</td>
</tr>
<tr>
<td>Solvent solution (v/v)</td>
<td>1:1</td>
<td>CH$_3$CN/toluene</td>
<td>1:1</td>
<td>MeOH/toluene</td>
<td>1:1</td>
</tr>
</tbody>
</table>

Table 2.4 Concentration, emission and excitation wavelengths of fluorescent dyes.
CHAPTER III

ORIGIN OF SIZE-DEPENDENT ENERGY TRANSFER FROM PHOTOEXCITED CdSe QUANTUM DOTS TO GOLD NANOPARTICLES

In the present work, the photoluminescence (PL) quenching of CdSe QDs by Au MPCs is described. The QD is octadecylamine-stabilized CdSe nanoparticle described in Chapter II, Table 2.2 and Au MPCs include a series of hexanethiolate-coated gold nanoparticles described in Chapter II, Table 2.1. The CdSe QDs had core diameters ranging from 2.0 to 6.9 nm as seen from TEM images in Figure 3.1 below.

![TEM images of CdSe QD's with corresponding histograms](image)

Figure 3.1 TEM images of CdSe QD’s with the corresponding histograms of 2.0 nm, 2.6 nm, 3.4 nm and 6.9 nm. The scale bar is 50 nm.

The Au MPCs had core diameters ranging from 1.1 to 4.9 nm as seen from TEM images in Figure 3.2 below.
Figure 3.2 TEM images of Au MPC with the corresponding histograms of Au$_{25}$, Au$_{140}$, Au$_{309}$, Au$_{807}$ and Au$_{4033}$. The scale bar is 50 nm.

The PL quenching efficiencies of Au MPCs of different sizes are compared by Stern-Volmer plots$^{34}$. The results show a great increase in quenching efficiency with MPC core size. A remarkable correlation is observed between quenching efficiency and
MPC core volume, which provides insights into the origin of the size effect in energy transfer (ET) quenching in these nanoparticle assemblies.

Figure 3.3a below shows absorption spectra of Au MPCs with core diameters of 1.1, 1.7, 2.2, 2.9, and 4.9 nm, corresponding to, respectively, Au\textsubscript{25}, Au\textsubscript{140}, Au\textsubscript{309}, Au\textsubscript{807}, and Au\textsubscript{4033}\textsuperscript{32, 57, 58}.

![Absorption spectra](image)

Figure 3.3 a) Absorption spectra of hexanethiolate-coated Au\textsubscript{25}, Au\textsubscript{140}, Au\textsubscript{309}, Au\textsubscript{807}, and Au\textsubscript{4033} MPCs in toluene. The absorptions have been normalized at 300 nm for comparison. b) Absorption and PL spectra of 3.4 nm diameter CdSe QD in toluene.

As evident from the Figure 3.3a, the surface plasmon band at ~520 nm becomes weaker with decreasing core size, highlighting the size-dependent optical properties. When core size is further decreased to Au\textsubscript{25}, distinct step-like structures emerge, indicative of molecule-like properties and transitions to discrete energy levels. These spectra, in effect, represent the pure absorption of MPCs as the scattering contribution to the extinction is negligible in this size region\textsuperscript{62}. Absorption and PL spectra of the 3.4 nm diameter CdSe QD in Figure 3.3b exhibit a small Stokes shift of the PL band (573 nm)
with respect to the lowest-energy absorption peak (561 nm), indicating that the PL band corresponds to the band-edge emission as expected for QDs with well-passivated surfaces.

Figure 3.4 illustrates the PL quenching process between a CdSe QD and a Au MPC in a colloidal solution.

![Figure 3.4 Photoluminescence quenching of a photoexcited CdSe QD by a Au MPC.](image)

Band-gap illumination of CdSe colloids excites electrons to the conduction-band while holes are generated in the valence-band. The excited electron-hole pair then undergoes a radiative recombination process. When Au MPC is brought into contact with the excited QD, the quenching process competes with the radiative decay process, resulting in decrease in the PL intensity. The PL quenching process can be quantified by the Stern-Volmer equation derived for describing the relationship between excited states quenching and quencher concentration as shown in chapter I, Equations 1.18 and 1.19.

\[
\frac{I_0}{I} = 1 + K_Q[MPC]
\]
where $I_0$ and $I$ are the PL intensity in the absence and presence of quencher (MPC), respectively, and $K_Q$ is the Stern-Volmer quenching constant for collisional quenching.

Figure 3.5 shows the resulting spectra recorded following successive addition of a MPC (Au$_{140}$) solution, displaying a gradual decrease in the PL intensity.

![Normalized PL Intensity vs Wavelength](image)

**Figure 3.5** PL spectral change of a 0.6 μM 3.4 nm CdSe QD colloidal solution upon addition of a Au$_{140}$ MPC solution.

The effect of the MPC size on the PL quenching of 3.4 nm CdSe QD was investigated with Au$_{25}$, Au$_{140}$, Au$_{309}$, Au$_{807}$, and Au$_{4033}$ MPCs. It is apparent from Figure 3.6, shown below, that the excited-state quenching occurs with all MPCs and the quenching efficiency increases with the MPC core size.
Figure 3.6 Decrease in the PL intensity upon addition of Au$_{25}$, Au$_{140}$, Au$_{309}$, Au$_{807}$, and Au$_{4033}$ MPC solutions in the case of 2.0, 2.6, 3.4 and 6.9 nm CdSe QDs.

The corresponding Stern-Volmer plots in the following Figure 3.7 show that the quenching efficiency is remarkably size-dependent. The quenching constant ($K_Q$) taken from the slopes in Figure 3.7 increases vastly with increasing MPC core size. For example in the case of 3.4 nm CdSe, $K_Q$ increases from $3.6 \times 10^5$ to $2.3 \times 10^8$ by more than 600-fold as core size increases from Au$_{25}$ to Au$_{4033}$. The $K_Q$ values were averaged from at least three measurements and presented in Table 3.1 immediately after Figure 3.7.
Figure 3.7 Corresponding Stern-Volmer plots and best fit lines in the case of 2.0, 2.6, 3.4 and 6.9 nm CdSe for Au$_{25}$, Au$_{140}$, Au$_{309}$, Au$_{807}$, and Au$_{4033}$, respectively.

<table>
<thead>
<tr>
<th>$K_Q$ (M$^{-1}$)</th>
<th>2.0 nm CdSe</th>
<th>2.6 nm CdSe</th>
<th>3.4 nm CdSe</th>
<th>6.9 nm CdSe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_{25}$</td>
<td>6.39 ± 1.69 x 10$^5$</td>
<td>5.50 ± 1.54 x 10$^5$</td>
<td>3.58 ± 0.41 x 10$^5$</td>
<td>4.01 ± 0.63 x 10$^5$</td>
</tr>
<tr>
<td>Au$_{140}$</td>
<td>2.22 ± 0.11 x 10$^6$</td>
<td>1.43 ± 0.20 x 10$^6$</td>
<td>1.76 ± 0.32 x 10$^6$</td>
<td>1.14 ± 0.11 x 10$^6$</td>
</tr>
<tr>
<td>Au$_{309}$</td>
<td>3.09 ± 0.62 x 10$^6$</td>
<td>2.44 ± 0.06 x 10$^6$</td>
<td>4.61 ± 0.08 x 10$^6$</td>
<td>3.96 ± 0.61 x 10$^6$</td>
</tr>
<tr>
<td>Au$_{807}$</td>
<td>1.56 ± 0.14 x 10$^7$</td>
<td>1.01 ± 0.15 x 10$^7$</td>
<td>1.28 ± 0.18 x 10$^7$</td>
<td>0.93 ± 0.13 x 10$^7$</td>
</tr>
<tr>
<td>Au$_{4033}$</td>
<td>1.30 ± 0.62 x 10$^8$</td>
<td>1.25 ± 0.42 x 10$^8$</td>
<td>2.06 ± 0.29 x 10$^8$</td>
<td>1.01 ± 0.25 x 10$^8$</td>
</tr>
</tbody>
</table>

Table 3.1 The quenching constants $K_Q$ in the case of 2.0, 2.6, 3.4 and 6.9 nm CdSe QDs by Au$_{25}$, Au$_{140}$, Au$_{309}$, Au$_{807}$, and Au$_{4033}$ MPCs.

The absorption of the excitation light by the MPC must be taken into account in the analysis of the quenching results since it could result in a decrease in the PL intensity. This can be estimated by subtracting the MPC absorption profile from the absorption
spectrum of the QD and MPC mixture, which yields the fraction of light absorbed only by the QD at the wavelength of excitation. Figure 3.8 presented below, shows representative absorption spectra for the QD, QD + MPC mixture, and QD + MPC mixture after subtraction of the absorption profile of MPC. In the case shown in Figure 3.8, the PL intensity drop was 45% in the presence of Au$_{309}$ (0.2 µM). As can be seen from the same Figure 3.8, the absorption profiles of the QD were virtually identical in the absence and presence of the MPC, and therefore, no correction for the MPC absorption was needed.

![Absorption comparison](image)

Figure 3.8  Absorption comparison of the QD to the QD-MPC mixture and QD-MPC mixture after the subtracting the absorption profile of MPC. The PL intensity drop of the 3.4nm QD (0.6 µM) was 45 % at the presence of Au$_{309}$ (0.2 µM). The absorption profiles of the QD are identical in the absence and presence of MPC.

The PL quenching may occur via dynamic (collisional) as well as static quenching pathways$^{34}$. When the quenching process is dictated by the dynamic quenching pathway, the Stern-Volmer quenching constant ($K_Q$) reflects diffusive encounters between the fluorophore and quencher during the fluorescence lifetime. Thus, the dynamic quenching
constant \((K_D)\) can be expressed by the product of the bimolecular quenching constant \(k_q\) and the lifetime of the fluorophore in the absence of quencher \(\tau_0\)^{34}:

\[
K_D = k_q \tau_0
\] (2.2)

The bimolecular quenching constant \(k_q\) may be calculated using the Smoluchowski equation^{34}:

\[
k_q = \frac{4\pi N_A (R_f + R_q)(D_f + D_q) \cdot 1000}{1000^\cdot\cdot}
\] (2.3)

where \(N_A\) is Avogadro's number, \(R_f\) and \(R_q\) are the molecular radii of the fluorophore and quencher, and \(D_f\) and \(D_q\) are the diffusion coefficients of the fluorophore and quencher, respectively. The calculated \(k_q\) values for the 3.4 nm QD-MPC system using the hydrodynamic radii (core and ligand) of QD and MPCs and the reported diffusion coefficients^{64} are in the range \(1.3\times10^{10}\) to \(1.7\times10^{10}\ \text{M}^{-1}\text{s}^{-1}\) for QD-Au_{25} to QD-Au_{4033} pairs. These values and \(\tau_0\) (20.8 \pm 0.4 \text{ ns}) obtained from lifetime measurements described in Chapter II and shown in Figure 3.9 below, predict \(K_D\) to be only 354 \text{ M}^{-1} at most, which is much smaller than the observed quenching constants.

![Figure 3.9 Lifetime measurement of 3.4 nm CdSe. Lifetime obtained was 20.8 ns.](image)
This result suggests that the dynamic portion of the observed quenching is negligible and therefore the quenching must occur via the static pathway through the formation of fluorophore-quencher conjugates or via a noncontact pathway. Considering the fact that the QD and MPCs have no obvious functional binding sites, it is likely that the QD-MPC conjugate assemblies are formed via interdigitation of the ligand chains of QD and MPC or some type of interparticle binding interactions. Recent cryogenic TEM studies have shown that anisotropic aggregates of semiconductor nanocrystals are formed in the colloidal solutions through dipolar coupling. Further studies are required to unravel the nature of the QD-MPC assemblies.

Both charge transfer (CT) and energy transfer (ET) can be considered as the major deactivation mechanisms of photoexcited states in the QD-MPC system. In a CdSe QD-Gold nanoparticle system, it was suggested that the PL quenching occurred via CT through a relatively short mercaptopropionic acid link between CdSe QDs and gold nanoparticles. In the present system, however, both QD and MPC particles are well-passivated and the thicknesses of capping layers are estimated to be 2.5 nm and 0.8 nm for QD and MPCs, respectively. The presence of these thick layers would thus impose a high barrier for CT, the electron tunneling probability exponentially decays with distance, making the CT quenching mechanism improbable. On the other hand, ET can occur at a relatively longer donor-acceptor distance. In fact, the Förster radius for resonance energy transfer between oppositely charged QD and Au nanoparticles was found to be 7.4 nm, suggesting that the long-range ET is a viable quenching mechanism in the present QD-MPC system.
Because alkanethiolate MPCs exhibit very weak PL intensity, it is not straightforward to monitor the ET event in the QD-MPC system. To test the long-range ET as an effective mode of quenching, we have carried out PL quenching of a large band-gap QD (2.6 nm CdSe) by a small band-gap QD (6.9 nm CdSe). Note that both QDs have the same capping layer (octadecylamine). There is sufficient donor-acceptor spectral overlap as seen in Figure 3.10 for efficient ET between these QDs that would result in concurrent PL quenching of the donor and enhancement of the acceptor. 

![Figure 3.10. Emission and absorbance spectra of 2.6 and 6.9 nm CdSe QDs.](image)

Figure 3.10. Emission and absorbance spectra of 2.6 and 6.9 nm CdSe QDs.
Figure 3.11 below shows that efficient ET indeed occurs in the mixture of their colloidal solutions.

Figure 3.11 PL spectra of 2.6 nm (λ_{peak} = 533 nm) and 6.9 nm (λ_{peak} = 645 nm) CdSe QDs in toluene before (dashed line) and after (solid line) mixing. Concentrations of 2.6 nm and 6.9 nm QD solutions are 550 nM and 25 nM, respectively. Inset: Stern-Volmer plot for PL quenching of 2.6 nm QD by 6.9 nm QD in toluene. Slope = 1.1×10^8 M⁻¹.

The PL spectrum of the mixture of 2.6 nm and 6.9 nm QDs displays concurrent ca. 6-fold decrease at 533 nm and ca. 4-fold increase at 645 nm in the PL intensity, compared to those of unmixed solutions (at the same QD concentrations), indicating efficient ET from 2.6 nm QD to 6.9 nm QD. The ET quenching constant taken from the Stern-Volmer plot (Figure 3.11 inset) is 1.1×10^8 M⁻¹, which is comparable to that of Au_{4033}. These results strongly suggest that the long-range ET is the most likely dominant mode of excited-state quenching in the present QD-MPC system.
Energy from donor molecules in the excited state can transfer to neighboring acceptor molecules in the ground state by a variety of mechanisms. When the donor-acceptor separation, $d$, is very small ($<1$ nm), a direct energy exchange resulting from wave function overlap can occur\textsuperscript{71}. At larger distances when wave function overlap is negligible, energy transfer through resonant dipole-dipole interaction between the donor and acceptor becomes dominant. This resonant ET mechanism also depends on the donor-acceptor separation\textsuperscript{72,73}. When the donor and acceptor are far apart ($d > \lambda/10$), the dominant process is radiative transfer, in which a photon is emitted by the donor and is subsequently absorbed by the acceptor. In contrast, when the donor and acceptor are close, transfer is nonradiative, being mediated by a virtual photon. The latter, a process known as Forster resonance energy transfer, generally exhibits the well-known $1/d^6$ distance dependence of the decay rate\textsuperscript{34}. Recently, Strouse and co-workers have reported that a relaxed $1/d^4$ distance dependence is observed when a fluorophore is attached to a gold nanoparticle\textsuperscript{74-76}. The distance dependence of the radiative decay rate is chiefly dominated by a $1/d^3$ dependence\textsuperscript{73}. Lidzey and co-workers\textsuperscript{77} have demonstrated control over the photon-mediated radiative transfer process between two exciton states separated by ca. 140 nm. More recently, Dulkeith et al. have found that perturbation of the radiative rate is responsible for the observed quenching for a molecular dye placed in the vicinity of a metal nanoparticle\textsuperscript{18,78}. Both resonant ET mechanisms require an overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor\textsuperscript{72}. 

46
In addition to these resonant ET pathways, nonspecific absorption of the emitted light by the MPC (the inner filter effect\textsuperscript{79}) may also contribute to the observed PL quenching. We have estimated this effect by\textsuperscript{79}:

\[
\eta = \frac{A_0 (1 - 10^{-A})}{A_i (1 - 10^{-A})}
\]  

(2.4)

where \(\eta\) is the correction factor for the inner filter effect, \(A_0\) and \(A_i\) are the solution absorbencies of the QD and QD-MPC mixture, respectively, at the emission wavelength. For example, the correction factor for the case shown in Figure 3.8 (45\% PL quenching) is calculated to be 0.96, which accounts for only 4\% of the total quenching, suggesting that the PL quenching is dominantly due to the resonant ET presumably induced by the specific dipolar interaction between the QD and MPC and not due to the inner filter effect. The absorbencies \(A_0\) and \(A_i\) were 0.0757 and 0.1105 at 573 nm.

It is yet to be determined which ET mechanism plays the dominant role in the observed PL quenching. While nonradiative ET is expected to dominate at short distances probably through the formation of the QD-MPC conjugate, radiative ET may operate at long distances in a noncontact mode. Further comparative studies with various QD-MPC assemblies differing in binding interaction would be useful to distinguish these mechanisms.

To understand the origin of the size effect in Figure 3.7, one can briefly trace a theoretical rationale for a connection between ET quenching efficiency and MPC size. Since ET is the most likely dominant quenching mode in the present QD-MPC system, we assume that the observed quenching constant \((K_Q)\) is proportional to the ET rate from
the photoexcited QD to the MPC. In the resonant ET theory\textsuperscript{34} the ET rate is directly related to the overlap integral that expresses the degree of spectral overlap:

\[
J(\lambda) = \int f_D(\lambda) e_A(\lambda) \lambda^4 d\lambda
\]  

(2.5)

where \(J(\lambda)\) is the overlap integral (M\(^{-1}\) cm\(^{-1}\) nm\(^4\)), \(f_D(\lambda)\) is the normalized emission spectrum of the donor, \(e_A(\lambda)\) is the extinction coefficient (M\(^{-1}\) cm\(^{-1}\)) of the acceptor at wavelength \(\lambda\), and \(\lambda\) is in nanometers. For a dilute colloidal solution, the absorbance is given by Beer's law, \(A = e_A(\lambda) bc\), where \(b\) is the path length (cm) and \(c\) is the particle concentration (M). The extinction coefficient and extinction cross-section (\(\sigma_{ext}, \text{cm}^2\)) of a single particle are interrelated through\textsuperscript{62}:

\[
e_A(\lambda) = \frac{N_A \sigma_{ext}}{2.303(1000)}
\]  

(2.6)

where \(N_A\) is Avogadro's number.

When the size of the particle is much smaller than the wavelength of the interacting light, phase retardation and effects of higher multipoles are neglected and \(\sigma_{ext}\) can be presented by the simplified Mie formula\textsuperscript{35,80}:

\[
\sigma_{ext} = \frac{9V \varepsilon_m^{3/2}}{c} \frac{\omega \varepsilon_2(\omega)}{\left[\varepsilon_1(\omega) + 2\varepsilon_m\right]^2 + \varepsilon_2(\omega)^2}
\]  

(2.7)

where \(V\) is the particle volume, \(\omega\) is the angular frequency of the exciting light, and \(c\) is the speed of light. \(\varepsilon_m\) and \(\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)\) are the dielectric functions of the surrounding medium and the metal core, respectively. The dielectric function is complex and depends on the frequency. This extinction cross-section is due to dipolar absorption only. Both the scattering cross-section and higher multipolar contributions are strongly
suppressed in this size region\textsuperscript{80}. Accordingly, Equation 3.7 can be used to present the absorption cross-sections of small MPCs.

The combination of Equations 3.5-3.7 forms the basis for expecting a linear correlation between the ET quenching efficiency and the MPC core volume. The size-dependent scaling law examined by a log-log plot in Figure 3.12 shown below, indeed shows a remarkable linear correlation between $K_Q$ and the MPC core volume, suggesting that the ET quenching efficiency is governed by the absorption cross-section of the MPC quencher that scales as its core volume.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure312}
\caption{Relationship between $K_Q$ and the MPC core volume for excited-state quenching of the 3.4 nm diameter CdSe QD by Au\textsubscript{25}, Au\textsubscript{140}, Au\textsubscript{309}, Au\textsubscript{807}, and Au\textsubscript{4033} MPCs. The slope of the linear fit line is 1.4.}
\end{figure}
This correlation clearly explains the size dependence observed previously. That is, the ET efficiency increases with the MPC core volume such that the larger MPCs are progressively more efficient ET quenchers.

In a previous study of a TiO₂-MPC system, it has been observed that the CT quenching efficiency of photoexcited TiO₂ is significantly decreased for Au₂₅ due to its molecule-like properties with a wide HOMO-LUMO (the highest occupied and lowest unoccupied molecular orbitals) gap. That is, the charge transfer to the elevated LUMO of Au₂₅ would be energetically less favorable, resulting in a low quenching efficiency. Interestingly, it does not appear to greatly matter that Au₂₅ is molecule-like in the present CdSe QD-MPC system, where the ET quenching efficiency linearly scales as the MPC core volume, contrasting the size-dependent CT and ET quenching mechanisms.

In conclusion, we have shown that PL quenching of a CdSe QD by well-defined, small MPCs occurs via a resonant ET mechanism. The ET quenching efficiency increases greatly with increasing MPC size. The remarkable correlation observed between the ET quenching efficiency and the MPC core volume suggests that the quenching efficiency is governed by the absorption cross-section of the MPC quencher that scales with core volume. These results could aid in understanding the photoexcited-state interactions and their controlling factors in nanoparticle assemblies. Further, these could pave the connection between excited-state energy transfer events and optical properties of metal nanoparticles, which has practical implications in sensor and phototherapeutic applications.
CHAPTER IV
PHOTOLUMINESCENCE QUENCHING IN FLUORESCENT DYES-Au MONOLAYER PROTECTED CLUSTERS SYSTEM

In the previous chapter we studied the deactivation pathways of photoexcited CdSe QDs by Au MPCs and we determined that the most likely deactivation mechanism is energy transfer governed by the extinction cross-section of the Au MPC that scales as its core volume.

With the purpose of examining the generality of these findings and evaluate the efficiency of Au MPCs as quenchers, as well as the dependence of quenching coefficients on the emission wavelength of the donor, we pursued the study of photoluminescence quenching in a different system. Fluorescent dyes were employed instead the CdSe QDs as donors and the same MPCs as acceptors. The fluorescent laser dyes used are listed in Chapter II, Table 2.4.

In the case of a different donor, i.e. fluorescent dyes, but with the same Au MPCs as acceptor, the quenching efficiency increases as the size of the Au MPC increases. The quenching constant $K_Q$ values were averaged from at least three measurements and they are reported in Table 4.1 after Figure 4.1. It became evident that the larger MPCs were more effective quenchers, as seen in Figure 4.1 below. The only anomaly was observed for CM440 in the case of Au976 and Au2406. Possible causes could be polydispersity of the sample or stability in time.
Figure 4.1 Quenching efficiency of Au MPCs in the case of the fluorescent dyes: a) CM440, b) F548, c) Rh6G, d) PM597 and e) LD700.
<table>
<thead>
<tr>
<th>$K_Q$($M^1$)</th>
<th>CM440</th>
<th>F548</th>
<th>Rh6G</th>
<th>PM597</th>
<th>LD700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_{25}$</td>
<td>$4.1 \pm 0.33 \times 10^5$</td>
<td>$3.29 \pm 0.70 \times 10^5$</td>
<td>$1.63 \pm 0.42 \times 10^5$</td>
<td>$1.67 \pm 0.25 \times 10^5$</td>
<td>$1.66 \pm 0.165 \times 10^5$</td>
</tr>
<tr>
<td>Au$_{140}$</td>
<td>$2.05 \pm 0.09 \times 10^6$</td>
<td>$8.46 \pm 1.16 \times 10^5$</td>
<td>$7.09 \pm 0.44 \times 10^5$</td>
<td>$6.58 \pm 0.55 \times 10^5$</td>
<td>$6.08 \pm 1.54 \times 10^5$</td>
</tr>
<tr>
<td>Au$_{309}$</td>
<td>$7.47 \pm 0.88 \times 10^6$</td>
<td>$2.87 \pm 0.28 \times 10^6$</td>
<td>$2.36 \pm 0.17 \times 10^6$</td>
<td>$2.22 \pm 0.35 \times 10^6$</td>
<td>$7.56 \pm 2.1 \times 10^5$</td>
</tr>
<tr>
<td>Au$_{976}$</td>
<td>$6.67 \pm 0.44 \times 10^7$</td>
<td>$6.16 \pm 1.31 \times 10^6$</td>
<td>$7.17 \pm 0.39 \times 10^6$</td>
<td>$6.51 \pm 1.32 \times 10^6$</td>
<td>$3.56 \pm 0.21 \times 10^6$</td>
</tr>
<tr>
<td>Au$_{2406}$</td>
<td>$2.80 \pm 0.81 \times 10^7$</td>
<td>$2.56 \pm 0.47 \times 10^7$</td>
<td>$2.75 \pm 0.13 \times 10^7$</td>
<td>$2.19 \pm 0.08 \times 10^7$</td>
<td>$1.46 \pm 0.13 \times 10^7$</td>
</tr>
</tbody>
</table>

Table 4.1 The quenching constants $K_Q$ in the case of fluorescent dyes by Au$_{25}$, Au$_{140}$, Au$_{309}$, Au$_{976}$, and Au$_{2406}$ MPCS.
The goal was to understand the deactivation mechanisms in the second donor-acceptor system, namely fluorescent dyes-Au MPCs. Charge transfer and energy transfer\textsuperscript{67, 68} were investigated as potential deactivation mechanisms in the fluorescent dyes-Au MPCs system. In the case of QD-MPC system, both donor and acceptor were well passivated, leading to a highly improbable charge transfer due to a large donor-acceptor separation. Unlike the QD-MPC system, in the fluorescent dyes-MPC system only the MPC is passivated and the donor-acceptor separation determined by the thickness of MPC capping layer (0.8 nm). Due to the shorter separation, charge transfer may represent a potential deactivation pathway of photoexcited fluorescent dyes. Cheng et al\textsuperscript{17} found that electron transfer quenching is unlikely in the case of quenching of fluorescent dyes by small Au MPCs (1.1-2.0 nm core radius) due to the lack of similarity in redox behavior of the fluorescent dyes and the lack of large differences in quenching constants\textsuperscript{27, 28, 84}. The energy transfer seems the most likely deactivation pathway of the excited fluorophore-excited fluorescent dyes by the Au MPC quenchers.

The energy transfer depends on the extent of spectral overlap of donor’s emission spectrum and acceptor’s absorption spectrum, distance between acceptor and donor and relative orientation of the donor and of the acceptor transition dipoles\textsuperscript{34}. In the case of fluorescent dyes-MPC solution, there is no control over the orientation of donor and acceptor transition dipoles.

To test the spectral overlap between the donor (fluorescent dyes) and the acceptor (Au MPCs), the fluorescent dyes were chosen as to match the emission wavelength of donors with absorption spectra of acceptors. The fluorescent laser dyes F548, Rh6G, PM597 emit in the range of 529-560 nm very close to the surface plasmon of the larger
MPC sizes (520 nm) leading to surface plasmon (SP) excitation. The other two fluorescent dyes CM440 and LD700 were chosen to test the low and high energy end of spectrum. The emission spectra of CM440, F548, Rh6G, PM597 and LD700 and absorption spectra of Au MPCs are illustrated in the following Figure 4.2.

Upon addition of Au MPCs the intensity of the emission spectrum of dyes decreases. Since Au MPCs absorb light, the absorption correction is necessary since it could result in additional decrease in intensity. As in the case of the QD-MPCs, the absorption profile of the dyes were almost identical in the presence and absence of the Au MPCs and no absorption corrections were necessary as shown in Figure 4.3 in the case of PM597 and Au309.
To find insight into the origin of the size dependence of the quenching coefficients observed in Figure 4.1, we used the same rationale as in the QD-MPC system. Combining Equations 3.5-3.7 from previous chapter, one may conclude that there is a linear dependence between energy transfer ET quenching efficiency and the MPC core volume in the fluorescent dye-MPC system.

The most probable factor, which greatly influences the energy transfer, is the spectral overlap of fluorophore emission and quencher absorption spectrum, which translates to molar absorbances.

To test if the same energy transfer mechanism applies in the fluorescent dye-Au MPC systems, we used the size-dependent law expressed by the log-log plot in the following Figure 4.4. The comparison was performed in the case of 3.4 nm CdSe and PM597 dye with Au MPCs. The emission of 3.4 nm CdSe and PM597 dye is 573 nm and respectively 560 nm. The slopes in the two cases were comparable and it showed
linear correlation between $K_Q$ and MPC core volume which lead to the conclusion that the deactivation mechanism in both cases is energy transfer and it is volume-controlled.

![Figure 4.4 Comparison between quenching efficiencies in QD-MPC and Dyes-MPC systems.](image)

In fact, the same correlation was found in all the fluorescent dyes-Au MPCs systems as seen in Figure 4.5 below. The slopes of the linear fit in all the cases are very similar. As seen in the Figure 4.5, the photoluminescence quenching is controlled mainly by the MPC core volume.
Figure 4.5 Relationship between $K_Q$ and the core volume of MPC for excited fluorophore dyes.

The spectral overlap of the fluorophore emission (fluorescent dyes) and quencher absorption (MPC) can be determined by comparing quenching coefficients to the molar absorbances $\varepsilon$. The molar absorbances of the MPCs are dictated by their size. The spectral overlap being closely related to the extinction coefficient of the absorber-quencher Au MPCs, the next step was to follow the correlation between the quenching efficiency and the extinction coefficient. The assumption proved to be right as seen in the Figure 4.6 below, given the linear correlation between $K_Q$ and $\varepsilon$. The quenching coefficients $K_Q$ scale with the extinction coefficients $\varepsilon$. 

60
Figure 4.6 Relationship between $K_Q$ and MPC extinction coefficient in the case of CM440, F548, R6G, PM597, LD700.

The linear correlation between $K_Q$ and $\varepsilon$ suggests that the quenching coefficients scale not only with the core volume or the cross-section of the nanoparticle but it also depends on how the optical absorbances changes with size of nanoparticle. The extinction coefficients of the Au MPCs increase with the core size, the larger Au MPCs being more efficient quenchers.

In conclusion, the energy transfer efficiency in the case of fluorescent dyes-MPC system is governed by the absorbance coefficient of the acceptor Au MPC. The quenching coefficients scale with the absorbance coefficients $\varepsilon$, which are determined by the size of MPC.
CHAPTER V
CONCLUSIONS AND FUTURE WORK

The goal of present work was to evaluate the efficiency of Au MPC as quenchers and to study the origin of the size-dependent energy transfer from photoexcited CdSe quantum dots and fluorescent dyes to Au MPCs.

In summary, we have performed photoluminescence quenching measurements of photoexcited CdSe quantum dots and fluorescent dyes by hexanethiolate-coated monolayer-protected Au clusters (MPC) with core diameters of 1.1-4.9 nm. The CdSe quantum dots were octadecylamine coated with core diameters of 2.0, 2.6, 3.4 and 6.9 nm. The investigated dyes were the following: Coumarin 440, Fluorescein 548, Rhodamine 6G Perchlorate, Pyromethene 597 and LD700 Perchlorate.

The efficiency of quenching was examined using Stern-Volmer plots. A remarkable correlation between the quenching efficiency and the Au MPC volume was observed, the quenching coefficients obtained displaying an increase by nearly 1000-fold as the core size of Au MPC increases from 1.1 to 4.9 nm.

Deactivation mechanisms of the photoexcited donors (CdSe quantum dots and fluorescent dyes) by the Au MPC quenchers were investigated and dynamic quenching as deactivation mechanism ruled out. The experimental data showed that the major deactivation mechanism in photoluminescence quenching of photoexcited CdSe quantum dots and fluorescent dyes by Au MPC is energy transfer governed by the absorption cross-section of the MPC quencher that scales as its core volume. The efficiency of the Au MPCs as quenchers has been proved, the larger MPCs being more efficient quenchers.
Further research is needed to gain insight into the deactivation mechanisms of excited state interactions, and factors controlling them. The photoluminescence quenching may occur through dynamic (collisional) pathway or static quenching pathway. In the present work we concluded that the dynamic quenching is negligible and that the quenching must occur through static pathway through formation of fluorophore-quencher conjugates or interdigitation.

Future work will include investigations into static quenching pathways by using photoexcited fluorophores and Au MPC quenchers which interact through electrostatic binding. Water-soluble Au clusters protected by monolayers of tiopronin (N-2-mercaptopropionylglycine) as quenchers and fluorescent dyes, such as Rhodamine B, in water with pH control, could be used to further study the static nature of the deactivation mechanisms of excited state. Also, the solvent effect on the photoexcited states would be another direction to follow in the future.
REFERENCES

(26) Yang, Y.; Chen, S. *Nano Lett.* 2003, 3, 75-79.
(61) Kim, J. Ph.D. Thesis **2008**.
(70) The ligand thicknesses were calculated by Gaussian03 software.


