

# 單一膠體半導體及金屬奈米結構的光學性質

研究生：院繼祖

指導教授：周武清博士

國立交通大學電子物理研究所

## 中文摘要

在此論文中，我們利用單分子檢測技術來研究奈米材料的螢光性質，包括膠體硒化鎘相關的量子點及金奈米團簇。對於硒化鎘／硫化鋅量子點而言，在表面加上 HDA 分子後，其螢光閃爍行為會有明顯的改變，亮暗期比例及亮期內所輻射出的光子數分別增加 2.8 和 13 倍。此外螢光衰減呈現出接近單一指數衰減的曲線並且有著較長的生命期。這些實驗結果顯示 HAD 分子提供了更高程度的表面鈍化。另外，我們也研究了在不同高壓下硒化鎘／硫化鋅量子點的振動與電子態。在 PL 及 Raman 光譜中，壓力引起晶格常數呈現二次方的變化可以明顯的觀察到，直到約 7Gpa。這樣二次方的關係和理論預期是相符合的。

對於碲硒化鎘／硫化鋅量子點而言，我們利用群體及單一量子點螢光量測來研究光引起的螢光增強現象。群體量子點在空氣和真空中都可以發現到螢光增強的現象，但有著不同的增加因子。從單一量子點來看，在光照之後有一些單一量子點螢光會增強。對於這些光照螢光增加的單一量子點而言，在其螢光閃爍行為中發現存在較長的亮期及亮期中有著較高的量子效率，且其亮期的螢光強度呈現著不同強度的分佈。根據群體與單一量子點的螢光量測，我們假設螢光增強的來源為光照引起的表面鈍化以及形成了中性核／帶電表面層的量子點兩者的貢獻。

最後我們也研究了金奈米團簇的螢光性質，尤其是針對單一金奈米團簇，我們發現在溶液中的群體金奈米團簇會有光引起螢光增加現象，但在空氣中則呈現著

光漂白現象。從單一金奈米團簇來看，螢光閃爍的行為可以被觀察到，且其亮暗期的分佈也呈現著和硒化鎘量子點類似的 Power-law 行為，此外單一金奈米團簇的螢光衰減呈現以~7 ns 生命期的單一指數衰減曲線。



# Optical Properties of Single Colloidal Semiconductor and Metal Nanostructures

Student: Chi-Tsu Yuan

Advisor: Dr. Wu-Ching Chou

**Institute of Electrophysics**

**National Chiao Tung University**

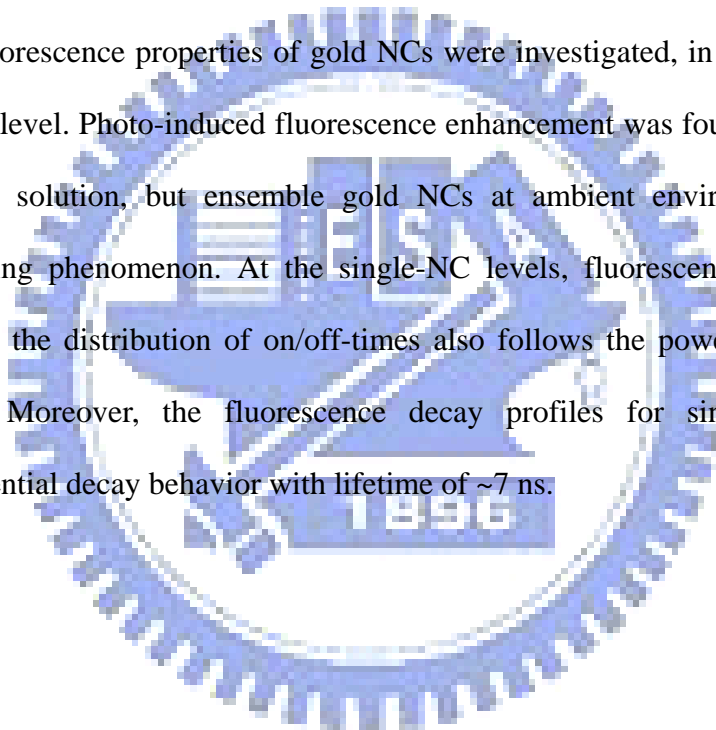
## Abstract

In this thesis, fluorescence properties of nanometer-sized materials, including colloidal CdSe related quantum dots (QDs) and gold nanoclusters (NCs) were investigated based on single-molecule detection techniques. For CdSe/ZnS QDs, the blinking behavior can be dramatically modified by additional hexadecylamine (HDA) ligands. The on/off time ratio and the total number of emitted photons within the on-time duration can be enhanced up to 2.8 and 13-fold, respectively. Further, fluorescence decay exhibits more close to single exponential decay profiles and has longer measured lifetime. These results suggested that HDA ligands can provide the higher degree of surface passivation. Moreover, we also studied the vibrational and electronic states of CdSe/ZnS QDs under various high pressures. Pressure-induced quadratic lattice variations can be observed explicitly from both the PL and Raman spectra up to  $\sim 7$  GPa. This quadratic relationship is consistent with the theoretical prediction.

For CdSeTe/ZnS QDs, Photoinduced fluorescence enhancement (PFE) was studied by means of both ensemble and single-QD fluorescence measurements. Ensemble

fluorescence intensity can be increased either in air or in vacuum, but with different enhanced factors. At the single-QD levels, fluorescence intensity was increased for some of individual QDs upon illumination. For these PFE individual QDs, relatively long on-times, high quantum yields within the on-times, and multi-levels on-states was found in fluorescence blinking time traces. According to ensemble and single-QD fluorescence measurements, we proposed that the origin of PFE phenomenon is attributed to the both contributions of surface passivation by photo-induced charged carriers and formation of the neutral core/charged shell QD states.

Finally, fluorescence properties of gold NCs were investigated, in particular, down to single-NC level. Photo-induced fluorescence enhancement was found for ensemble gold NCs in solution, but ensemble gold NCs at ambient environment exhibits photo-bleaching phenomenon. At the single-NC levels, fluorescence blinking was observed and the distribution of on/off-times also follows the power-law similar to CdSe QDs. Moreover, the fluorescence decay profiles for single NCs show mono-exponential decay behavior with lifetime of  $\sim 7$  ns.



## 致 謝

回想五年前和我的指導教授周武清老師一起進入交大電物所，五年後和我的共同指導教授褚德三老師一起畢業，很幸運剛好參與到這兩位教授在一起的五年時間，共同指導著我做研究。最要感謝的是我的指導教授周武清博士，記得剛進交大電物所時，因老師也剛到交大因此我們並沒有實驗室，但老師並沒有忘記我，帶著我跟褚老師 meeting，用褚老師的儀器，帶著我去中原跟張恆雄老師 meeting，引領我進入膠體量子點的領域。此外每當 meeting 時老師會以客觀的立場所給予我寶貴的意見，常常會讓身陷在問題中的我找到方向。

再來就要感謝我的師公褚德三老師，雖然我的名字並沒有掛在褚老師底下，但老師從沒把我當成外人，記得去年褚老師在 meeting 時談到要找大家去美國物理年會一起畢業旅行，大家在底下講得非常高興，只有我安靜的在想這個“大家”有包括我這個“外人”嗎？原來只有我自己認為我是外人，也因此去年是我第一次去國外用英文發表演講。

謝謝我的口試委員中研院應科中心湯朝暉老師，也是我未來博士後的老師，在我還沒有跟他時就已經對我非常照顧了，謝謝中原生醫系張恆雄老師在樣品的提供及研究上的討論，謝謝中原物理系沈志霖老師在我資格考及博士班口試都能夠給我一些寶貴的意見，謝謝彰師物理系石豫臺老師亦師亦友的給予研究上的幫助，也謝謝兩位從我的學長變成口試委員；成大物理系岳男學長及交大電物的志偉學長，都能很親切的給予學弟在研究及論文上的意見。

也要謝謝褚老師理論室及周老師實驗室的學長高進、英彥、祝壽、振豪等給予很多在理論上及實驗上的指導，謝謝我的同學瑞雯、英瓚一起在博士班期間的努力，謝謝實驗室學弟文忠、彥丞、瑞泰、崑峰、復凱、鏡學、威智、俊榮等在生活中及實驗上的幫忙，謝謝中原生醫所的政鞍學長在樣品及研究上的幫忙。

最後謝謝我的家人，謝謝我父母親給了我一個很好的家庭，很健康的身體，來完成我的博士學位，一路上受到很多人的幫忙，謝謝你們。

## Contents

中文摘要.....	i
英文摘要.....	iii
致謝.....	v
Contents.....	vi
Figure captions.....	vii
<b>Chapter 1 Overview of Nanometer-sized Materials.....</b>	<b>1</b>
1.1 General introduction.....	1
<b>Chapter 2 Introduction to Colloidal Quantum Dots.....</b>	<b>5</b>
2.1 Fluorescence properties of ensemble colloidal CdSe QDs.....	5
2.2 Band edge exciton fine structures in colloidal CdSe QDs.....	7
2.3 Single-molecule detection.....	8
2.4 Single-QD fluorescence blinking.....	10
2.5 Fluorescence dynamics of single QDs.....	18
<b>Chapter 3 Experiments and Techniques.....</b>	<b>27</b>
3.1 Laser scanning confocal microscopy.....	27
3.2 Single-QD measurements.....	28
3.3 TCSPC techniques and TTTR acquisition modes.....	30
3.4 High pressure Raman measurements.....	32
<b>Chapter 4 Fluorescence Enhancement by Surface Modifications.....</b>	<b>37</b>
<b>Chapter 5 Fluorescence Enhancement by Phototreatment.....</b>	<b>52</b>
<b>Chapter 6 Electronic and Vibrational States under High Pressures.....</b>	<b>65</b>
<b>Chapter 7 Fluorescent Properties of Single Gold Nano-clusters.....</b>	<b>78</b>
<b>Chapter 8 Conclusions.....</b>	<b>92</b>
<b>Publication lists.....</b>	<b>94</b>

## Figure captions

Figure 2.1: Emission color under UV illumination for colloidal CdSe/ZnS QDs with various sizes.....	20
Figure 2.2: Emission spectra of R 6G (red line) and colloidal QDs (black line).....	20
Figure 2.3: Band edge exciton fine structures in colloidal CdSe QDs.....	21
Figure 2.4: Figure 2.4 Fluorescence images with $4 \times 4 \mu\text{m}^2$ for single CdSeTe/ZnS QDs onto a glass coverslips.....	21
Figure 2.5: Fluorescence time traces of single colloidal CdSe/ZnS QDs.....	22
Figure 2.6: Histogram of normalized events of on-time length by log-log plot.....	22
Figure 2.7: Schematic illustration of photoinduced ionization by Auger process.....	23
Figure 2.8: (a) Fluorescence time traces for a single bare CdSe QDs and (b) core/shell CdSe/ZnS QDs.....	23
Figure 2.9: (a) Fluorescence time traces for a single CdSe/ZnS QDs accompanied with time-resolved fluorescence spectra (b), and (c) decay profiles with various intensity regimes.....	24
Figure 3.1: Fluorescence intensity images of $6 \times 6 \mu\text{m}^2$ for colloidal CdSe/ZnS QDs onto the glass coverslip.....	33
Figure 3.2: Laser pattern with diffraction limited spot size of $\sim 300$ nm.....	33
Figure 3.3: Experimental setups for single-QD fluorescence measurements.....	34
Figure 3.4: Schematic illustrations of TCSPC techniques and TTTR acquisition modes.....	35
Figure 3.5: Instrument response function of experimental setup.....	35
Figure 4.1: Fluorescence spectra of ensemble colloidal CdSe QDs with TOPO, ZnS shell, and ZnS/HDA surfaces.....	44
Figure 4.2: Fluorescence intensity images of $6 \times 6 \mu\text{m}^2$ area from single colloidal CdSe/ZnS QDs.....	45

Figure 4.3: Fluorescence intensity time traces for CdSe QDs with (a) original TOPO, (b) ZnS shell, and (c) ZnS/HDA.....	46
Figure 4.4: Histograms of on-time duration for CdSe QDs with (a) original TOPO, (b) ZnS shell, and (c) ZnS/HDA.....	47
Figure 4.5: Histograms of burst sizes for CdSe QDs with (a) original TOPO, (b) ZnS shell, and (c) ZnS/HDA.....	48
Figure 4.6: Fluorescence decay profiles for CdSe QDs with (a) original TOPO, (b) ZnS shell, and (c) ZnS/HDA.....	49
Figure 4.7: Distribution of fluorescence lifetime for CdSe QDs with original TOPO, ZnS shell, and ZnS/HDA.....	50
Figure 5.1: Fluorescence spectra of colloidal CdSeTe/ZnS QDs with various illumination times in air (a) and in vacuum (b).....	59
Figure 5.2: Fluorescence images without (a) and with 20 min illumination (b).....	60
Figure 5.3: (a) Representative fluorescence time traces for single PFE QDs and unilluminated single QDs in the inset, (b) the distributions of events of fluorescence intensity for unilluminated QDs, (c) for PFE QDs.....	61
Figure 5.4: Schematic illustration for PFE origin from single-QD viewpoints.....	62
Figure 6.1: Pressure dependent PL spectra of colloidal CdSe/ZnS QDs at room temperature.....	72
Figure 6.2: PL peak energy as a function of applied pressures.....	73
Figure 6.3: Raman spectrum of colloidal CdSe/ZnS QDs at 1.43 GPa at room temperature.....	74
Figure 6.4: Pressure dependent Raman spectra of colloidal CdSe/ZnS QDs at room temperature.....	75
Figure 6.5: Raman peak shifts of (a) LO and (b) 2 LO phonon as a function of applied pressure.....	76



Figure 7.1: Absorption (a) and emission spectra (b) for ensemble gold NCs in solution. ....84

Figure 7.2: Fluorescence intensity variations with time in solution (a) and at ambient environments (b).....85

Figure 7.3: Fluorescence intensity images with  $4 \times 4 \mu m^2$  for single NCs.....86

Figure 7.4: Fluorescence time traces for single NCs for total measured time (a) and initial 5 s time window (b).....87

Figure 7.5: A plot of histograms of on-time duration (a) and off-time duration (b)...88

Figure 7.6: Fluorescence decay profiles of ensemble aggregated NCs (a) and single NCs (b).....89

