# DEDICATION ACKNOWLEDGEMENTS

#### CONTENTS

#### LIST OF FIGURES

#### LIST OF TABLES

#### LIST OF ACRONYMS

#### <u>CHAPTER I</u>

# Introduction

1.1 Major issues of the study on CdSe nanocrystals	1
1.2 Wurtzite and zinc-blende structure	3
1.3 Electronic structure of CdSe nanocrystals	7
1.4 Framework of the thesis.	.12
1.5 References	.14
RII	

#### CHAPTER II

## **Experimental Principles and Approaches**

2.1 Preparation of CdSe nanocrystals by colloidal method18
2.2 TEM and optical characterization
2.3 X-ray diffraction
2.4 X-ray absorption spectroscopy
2.5 Photoemission spectroscopy
2.6 References

#### CHAPTER III

# **Size Dependence of Structural Characteristics**

## in CdSe Nanocrystals

3.1 Introduction
3.2 Simulation of X-ray diffraction patterns
3.3 Diffraction patterns fitted with a simple model
3.4 EXAFS studies on bond lengths
3.5 Discussion
3.6 Summary
3.7 References

#### CHAPTER IV

#### **Photoemission Final-State Effect**

# on Electronic Properties of CdSe Nanocrystals

4.1 Introduction	83
4.2 Size dependence of photoemission spectra	84
4.3 Photoemission final-state effect	91
4.4 Discussion.	92
4.5 Summary	04
4.6 References	04

#### CHAPTER V

#### **Relation between Surface Properties**

# and Photoluminescence Efficiency in CdSe Nanocrystals

5.2 Growth rate
5.3 Absorption and photoluminescence measurements 109
5.4 Photoemission studies
5.5 Discussion
5.6 Summary
5.7 References

# CHAPTER VI



## LIST OF FIGURES

## Figure

<b>1.1:</b> The scheme of a unit cell of wurzite structure
<b>1.2:</b> Crystal structure of zinc-blende structure and atomic positions
<b>1.3:</b> Three views of the wurtzite and zinc-blende crystal structures
<b>1.4:</b> Absorption spectrum of CdSe nanoparticles with size of 33 Å
<b>1.5:</b> Lowest transition energy of CdSe nanoparticles as a function of size9
2.1: The schematic representation of the organometallic preparation of CdSe NCs
using TOPO, HDA, and TOP
2.2: TEM images of CdSe nanocrystals passivated with TOPO/HDA and treated by
pyridine
2.3: Size histograms of CdSe NCs
2.4: Optical spectra of CdSe nanocrystals
2.5: Color photograph for different size samples of CdSe nanocrystals
<b>2.6:</b> Relations involved in letting the $r_{mn}$ vector take all orientations in space
2.7: Schematic representation of X-ray diffraction apparatus used in conventional
mode
<b>2.8:</b> The brilliance of X-ray sources as a function of time
2.9: Schematic representation of the accelerator and experimental facilities at the
NSRRC, the Taiwan Light Source
2.10: The bright spectra from NSRRC light sources, compared to traditional light

sources	31
2.11: X-ray absorption measurements.	.33
<b>2.12:</b> The absorption cross-section $\mu/\rho$ for Cd and Se over the x-ray energy range of	f 1
to 100 keV	34
2.13: Schematic representation of the set-up for EXAFS measurements usi	ng
synchrotron radiation.	36
2.14: Se <i>K</i> -edge EXAFS spectrum of bulk CdSe	.37
2.15: Schemes of scattering processes.	38
<b>2.16:</b> Se <i>K</i> -edge EXAFS <i>k</i> - and $k^3$ -weighted spectra of bulk CdSe	.39
2.17: Energy diagram of the photoemission process.	43

2.18:	Synchrotron	photoemission	spectrum	of	CdSe	nanocrystals	passivated	with
ТОРС	)/HDA							44
2.19:	Schematic dia	agram of photoe	mission ex	peri	iment.			46

<b>3.1:</b> Powder X-ray diffraction spectra of bulk CdSe and CdSe NC
3.2: Powder diffraction pattern of TOPO/HDA-passivated CdSe NCs and the
calculated patterns for wurtzite and zinc-blende NCs with size of 31 Å
<b>3.3:</b> Experimental diffraction spectra of bulk CdSe and three CdSe NCs as well as the
corresponding simulations by Debye formula
<b>3.4:</b> The wurtzite stacking fraction as a function of the NC mean diameter
<b>3.5:</b> Powder X-ray diffraction patterns of CdSe NCs and the corresponding fits59
3.6: Size-dependent lattice parameters of CdSe NCs determined by fit of powder
XRD data
<b>3.7:</b> $k^3$ -weighted Cd and Se <i>K</i> -edge EXAFS spectra of bulk CdSe and NCs 61
3.8: Fourier tranforms of Cd and Se K-edge EXAFS spectra for bulk CdSe and
three-sized nanocrystals
<b>3.9:</b> Fourier filtered EXAFS spectra and the best fits of CdSe NCs
<b>3.10:</b> Fourier tranforms of Se K-edge EXAFS spectra, measured at $\sim 10$ K, for CdSe
NCs with mean diameter 31 Å
3.11: The measured first-shell coordination numbers of five NCs are plotted with the
calculated values by the ball-and-stick model
<b>3.12:</b> Mean length of the Cd–Se and Cd–O/N bonds for CdSe nanocrystals68
<b>3.13:</b> The scheme of a tetrahedral structure
<b>3.14:</b> Single-shell filtered Se K-edge data measured at the temperature of $\sim 10$ K and
the corresponding fits
<b>3.15:</b> Size dependence of normalized bond lengths, $R^{(1)}$ and $R^{(2)}$ , for CdSe NCs
passivated with TOPO/HDA is plotted together with the normalized lattice parameters,
<i>c</i> and <i>a</i>
<b>3.16:</b> The structural parameters <i>u</i> of CdSe nanocrystals
<b>3.17:</b> Relative structure parameters of CdSe NCs dependent on particle size74
<b>3.18:</b> Surface energy of TOPO/HDA-passivated CdSe NCs as a function of size76
<b>3.19:</b> Schematic diagram of the size-dependent phase transition of CdSe

4.1: Size-dependent Cd  $3d_{5/2}$  and Se 3d photoemission spectra of bulk CdSe and

A.1:	An ellipsoidal particle represents in real and reciprocal space.	127
<b>B.1:</b>	The representation of a charge q inside a dielectric sphere.	130

# LIST OF TABLES

# Table

<b>1.1</b> Structural parapeters of CdSe and ideal wurtzite.	.4
<b>3.1</b> Structural parameters derived from EXAFS spectra of CdSe nanocrystals	65



# LIST OF ACRONYMS

DW factor	Debye-Waller factor
ESCA	electron spectroscopy for chemical analysis
EXAFS	extended X-ray absorption fine structure
HDA	hexadecylamine
IMFP	inelastic mean free path
КТ	Koopman's theorem
NCs	nanocrystals
OA	oleic acid
ОРА	octadecylphosphonic acid
PES	photoemission/photoelectron spectroscopy
PL	photoluminescence
QDs	quantum dots
ТЕМ	transmission electron microscope
ТОР	trioctylphosphine
ТОРО	trioctylphosphine oxide
UV	ultraviolet
WZ	wurtzite
XANES	X-ray absorption near-edge spectroscopy
XRD	
ZB	zinc blende