CHARGE MANIPULATION IN II-VI SEMICONDUCTOR NANO-HETEROSTRUCTURES

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by

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Submitted

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Dedicated to
My Parents

CERTIFICATE

This is to certify that the thesis entitled, "**Charge Manipulation in II-VI Semiconductor Nano-heterostructures**" being submitted by **Ms. SUSHMA YADAV** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by her. Ms. SUSHMA YADAV has worked under my guidance and supervision. She has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

Date

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ABSTRACT

Semiconductor nanocrystals have attracted considerable attention because of their unique chemical and physical properties that can be tuned with size, shape and surface functionality. These nanomaterials have important applications in cell labeling, medical imaging, and sensing in biomedical technology, light-emitting diodes (LEDs) for lighting and displays, as well as solar cells and other photovoltaic devices. These potential applications have encouraged research into nanostructure design and wavefunction engineering. The modification of nanocrystal surfaces and deposition of other semiconductor materials also modifies the optical and structural properties; the main focus of work in the present thesis. The present thesis is mainly focused on designing of hetero-nanocrystals (core/shell, core/crown and nanoparticle-decorated nanostructures) and tailoring their optical and electronic properties by surface engineering.

The first two chapters (Chapter 1 and 2) are dedicated to the extensive literature survey of research work related to semiconductor nanomaterials, synthetic methodologies to synthesize the high-quality semiconductor nanoparticles and their heterostructures along with brief accounts of various techniques employed for the characterization of as-synthesized materials are also provided. In Chapter 3, we have synthesized dual emitting CdSe/ZnSe/CdS heterostructures composed of Type-I and Type-II band alignments, where ZnSe acts as a barrier for charge carriers between the CdSe core and the CdS shell. We investigated the effect of the thickness of the barrier i.e. ZnSe and the shell i.e. CdS, on the charge carrier dynamics by using UV-Visible absorption, photoluminescence (PL), and time-resolved fluorescence techniques.

Chapter 4 and 5 describe the role of the surface modification of two dimensional CdSe nanoplatelets onto the photophysics of the CdSe NPLs. Chapter 4, deals with CdSe/ZnSe dots-on-plate (DoP) heterostructure with quasi-Type-II band alignment such that hole delocalizes on both whereas electron remains confined to CdSe portion. A selective charge extraction is demonstrated from CdSe nanoplatelets (NPLs) as well as those decorated with ZnSe nanoparticles. In Chapter 5, we have investigated the effect of thickness of shell as well as the surface terminating layer – anionic and cationic – on the optical properties in CdSe/CdS which is a quasi-Type-II system and CdSe/ZnS, a Type-I heterostructured core/shell nanoplatelets (NPLs). The photoluminescence, PL lifetime, and PL linewidth oscillates between low and high state depending upon whether the terminating surface is composed of anions or cations. In Chapter 6, we have presented synthesis and study of photophysical properties of Type-II CdS/ZnSe core/crown nanoplatelets, where electron will be confined to CdS and hole will reside in ZnSe. Thus by changing the lateral dimensions with another band gap materials, the optical properties can be modified without changing their thickness. Chapter 7 summarizes the results presented in the thesis highlighting the role of surface modifications for engineering the functionality and the properties of nanomaterials.

सार

अर्धचालक नैनोक्रिस्टल्स ने उनके अद्‌वितीय रासायनिक और भौतिक गुणों की वजह से काफी ध्यान आकर्षित किया है जो आकार, आकृति और सतह की कार्यक्षमता के साथ ट्‌यून किए जा सकते हैं। इन नैनोमटेरिअल्स का सेल लेबलिंग, मेडिकल इमेजिंग और बायोमेडिकल टेक्नोलॉजी में संवेदन, प्रकाश और डिस्प्ले के लिए प्रकाश उत्सर्जक डायोड (एलईड), साथ ही सौर सेल्स और अन्य फोटोवोल्टिक उपकरणों में महत्वपूर्ण अनुप्रयोग हैं। इन संभावित अनुप्रयोगों ने नैनोस्ट्रक्चर्स डिजाइन और वेवफंक्शन इंजीनियरिंग में अनुसंधान को प्रोत्साहित किया है। वर्तमान थीसिस में काम का मुख्य लक्ष्य नैनोक्रिस्टल सतहों के संशोधन और अन्य अर्धचालक पदार्थों की जमावट द्‌वारा ऑप्टिकल और संरचनात्मक गुणों को संशोधित करना है। वर्तमान थीसिस मुख्य रूप से हेटरो-नैनोक्रिस्टल (कोर/शेल, कोर/क्राउन और नैनोपार्टिकल द्‌वारा सजाए गए नैनोस्ट्रक्चर्स) को डिजाइन करने और सतह इंजीनियरिंग द्‌वारा ऑप्टिकल और इलेक्ट्रॉनिक गुणों को संशोधित करने पर केंद्रित है।

पहले दो अध्याय (अध्याय 1 और 2) अर्धचालक नैनोमटेरियल्स, उच्च गुणवत्ता वाले अर्धचालक नैनोपार्टिकल्स और उनके हेटरोस्ट्रक्चर्स को संश्लेषित करने के लिए सिंथेटिक पद्‌धतियां से संबंधित अनुसंधान कार्य के व्यापक साहित्य सर्वेक्षण के लिए समर्पित हैं, तथा इसके लक्षण वर्णन के लिए नियोजित विभिन्न तकनीकों के संक्षिप्त खातों की सामग्री भी प्रदान की जाती हैं। अध्याय 3 में, हमने टाइप-1 और टाइप-2 बैंड संरेखण से बना दोहरी उत्सर्जित CdSe/ZnSe/CdS हेटरोस्ट्रक्चर्स को संश्लेषित किया है, जहां ZnSe, CdSe कोर और CdS शेल के बीच चार्ज वाहक के लिए एक बाधा के रूप में कार्य करता है। हमने पराबैगनी/दृश्यप्रकाश अवशोषण, प्रकाशसंदीप्ति (पीएल), और

समय-समाधानित प्रतिदीप्ति तकनीकों का उपयोग करके चार्ज वाहक गतिशीलता पर बाधा की मोटाई के परिणाम, अर्थात ZnSe और शेल, CdS, की जांच की है। अध्याय 4 और 5 CdSe नैनोप्लेटलेट्स के फोटॉफिज़िक्स पर, दो आयामी CdSe नैनोप्लेटलेट्स के सतह संशोधन की भूमिका का वर्णन करते हैं। अध्याय 4, CdSe/ZnSe डॉट-ऑन-प्लेट हेटरोस्ट्रक्चर्स से अर्ध-टाइप-2 बैंड संरेखण के साथ काम करता है, जैसे कि होल दोनों भागों पर विस्थानित है जबकि इलेक्ट्रॉन CdSe भाग तक ही सीमित रहता है। CdSe नैनोप्लेटलेट्स और ZnSe नैनोपार्टिकल्स से सजाए गए CdSe नैनोप्लेटलेट्स द्वारा एक चयनात्मक चार्ज निकासी का प्रदर्शन किया जाता है। अध्याय 5 में, हमने CdSe/CdS जो कि अर्ध-टाइप-II प्रणाली और CdSe/ZnS, एक टाइप-I कोर/शेल नैनोप्लेटलेट्स (एनपीएल) के ऑप्टिकल गुणों पर शेल की मोटाई के साथ-साथ सतह की समाप्ति की परत - अनिओनिक और कतिओनिक - के प्रभाव की जांच की है। प्रकाशसंदीप्ति, पीएल लाइफटाइम, और पीएल लाइनविड्थ में कम और उच्च अवस्था के बीच दोलन होता है, जो कि इस बात पर निर्भर करता है कि क्या समाप्त सतह anions या cations से बना है। अध्याय 6 में, हमने टाइप-2 CdS/ZnSe कोर/ क्राउन नैनोप्लेटलेट्स के संश्लेषण और फोटॉफिजिकल गुणों का अध्ययन किया है, जहां इलेक्ट्रॉन CdS तक सीमित होगा और होल ZnSe में रहेगा। इस प्रकार दूसरी बैंड अंतर सामग्री के साथ पार्श्व आयाम को बदलकर, ऑप्टिकल गुणों को उनकी मोटाई को बदलने के बिना संशोधित किया जा सकता है। अध्याय 7 नैनोमटेरियल्स के कार्यशीलता और गुणों के इंजीनियरिंग के लिए सतह संशोधनों की भूमिका को उजागर करने वाले शोध प्रबंध में प्रस्तुत परिणामों को सारांशित करता है।

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

%	percent
ν	frequency
λ	wavelength
θ	theta
τ	lifetime
Å	angstrom
μL	microlitre
°C	degree centigrade
nm	nanometer
e.g.	for example
g	gram
h	hour
min	minute
Hz	hertz
i.e.	that is
kV	kilovolt
eV	electron volt
E_g	band gap
M	molar
Ar	Argon
mmol	millimole
mL	millilitre
ns	nano seconds
NCs	nanocrystals
TEM	transmission electron microscopy
HR	high resolution
EDX	energy dispersive X-ray analysis
PXRD	powder X-ray diffraction

NPLs	nanoplatelets
CB	conduction band
VB	valence band
EMA	Effective mass approximation
PL	photoluminescence
ODE	1-octadecene
OA	oleic acid