DESIGN AND SYNTHESIS OF SEMICONDUCTOR NANOCRYSTALS TO MODIFY THEIR OPTICAL AND ELECTRONIC PROPERTIES

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by

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to the

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Dedicated to

My Parents

CERTIFICATE

This is to certify that the thesis entitled, “**DESIGN AND SYNTHESIS OF SEMICONDUCTOR NANOCRYSTALS TO MODIFY THEIR OPTICAL AND ELECTRONIC PROPERTIES”** being submitted by me, **Mr. VIKAS ARORA,** 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 me.

Mr. VIKAS ARORA has worked under my guidance and supervision. He has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

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ABSTRACT

Semiconductor nanocrystals have become a significant class of materials with large potential for application varying from medicine to electronic and optoelectronic devices. Quantum dots are a class of semiconductors, which are composed of periodic groups of II-VI, III-V, or IV-VI materials (like CdSe, CdS, CdTe & ZnSe) with size below 10 nm showing size-dependent chemical, optical and electronic properties. Modification of nanocrystal surfaces, doping and deposition of other semiconductor materials alters the optical and structural properties; the key focus of work in the present thesis. The present thesis is primarily focused on the synthesis of new types of semiconductor nanocrystals and controlling their optical and electronic properties by modifying their surfaces. The detail of the research work is as follows:

Chapter I of the thesis is focused on the literature survey of past and present research work on semiconductor nanocrystals. It summarizes in general on the variety of protocols used in the synthesis of nanomaterials, doped nanomaterials and diverse techniques for surface modification of these nanomaterials.

In **Chapter II**, protocols used for the synthesis of nanocrystals and their further modifications are discussed. Brief accounts of the absorption spectroscopy, fluorescence spectroscopy, Time resolved fluorescence spectroscopy, X-ray diffraction and Transmission electron microscopy used to characterize the synthesized nanomaterials are discussed.

In **Chapter III**, the control of optical properties of CdS nanocrystals by altering the capping ligands during their synthesis was studied. It was found that addition of a little amount of

$CdCl_2$:Phosphonic Acid (PA) at the end stages of the synthesis, results in complete elimination of the surface state emission from these nanocrystals and also increases the quantum yield of band edge emission.

In **Chapter IV**, the growth of Cu_2ZnSnS_4 semiconductor nanocrystals via a colloidal route at lower temperatures by the introduction of cationic surfactant cetyltrimethylammonium bromide (CTAB) was monitored. The synthesized nanocrystals were uniform and single crystalline and their size can be tuned by heating them at various temperatures thereby making them suitable candidates in future for application in photovoltaic devices.

Chapter V discusses a new approach by involving the introduction of manganese in (CZTS) semiconductor nanocrystals via a colloidal route and also the synthesis of CMTS nanocrystals. These nanocrystals show optical absorbance in the visible region thereby making them suitable candidates for application in photovoltaic devices. The mechanism of charge transfer in these nanocrystals was further confirmed by dye-degradation studies, showing the possibility of ambient day light photocatalysis.

In **Chapter VI,** the electron-transfer process from CdSe/3ZnS/nCdSe (where n=2, 3, 4, 5) quantum dots to the Au tips as a function of the shell thickness was monitored. Studies show that as the shell thickness increase, the process of charge transfer decreases due to the variation in energy gap between the conduction band of the CdSe shell of dual emitter nanocrystals and gold particles. A combination of steady state and time-resolved photoluminescence studies establish the mechanism of charge transfer in these nanocrystals which can further be used as photocatalysts.

सार

सेमीकंडक्टर नैनोक्रिस्टल सामग्री के एक महत्वपूर्ण वर्ग बन गए हैं जो चिकित्सा से लेकर इलेक्ट्रॉनिक और ऑप्टोइलेक्ट्रोनिक उपकरणों के लिए अलग-अलग आवेदन के लिए बड़ी संभावनाएं हैं। क्वांटम डॉट्स सेमीकंडक्टर्स का एक वर्ग है, जो 2-VI, III-V, या IV-VI सामग्री (जैसे सीडीएसई, सीडीएस, सीडीटीए और जेएनएसई) के आवधिक समूह से बनाये गये हैं, आकार के आधार पर 10 एनएम नीचे आकार के आधार पर, ऑप्टिकल और इलेक्ट्रॉनिक गुण नैनोक्रिस्टल सतहों के संशोधन, अन्य अर्धचालक पदार्थों के डोपिंग और बयान ऑप्टिकल और संरचनात्मक गुणों को बदलते हैं; वर्तमान थीसिस में काम का मुख्य फोकस वर्तमान थीसिस मुख्य रूप से नए प्रकार के अर्धचालक नैनोक्रिस्टल्स के संश्लेषण पर केंद्रित है और उनकी सतहों को संशोधित करके उनके ऑप्टिकल और इलेक्ट्रॉनिक गुणों को नियंत्रित करते हैं। अनुसंधान कार्य का विवरण इस प्रकार है:

थीसिस का अध्याय I अर्धचालक नैनोक्रिस्टल पर अतीत और वर्तमान अनुसंधान कार्य के साहित्य सर्वेक्षण पर केंद्रित है। यह नैनोमिटेरियल्स के संश्लेषण में प्रयुक्त विभिन्न प्रोटोकॉलों पर सामान्य रूप से सारांशित करता है, इन नैनोमेटरीज के सतह संशोधन के लिए ड्रैपड नैनोमिटेरियल्स और विविध तकनीकों का इस्तेमाल किया जाता है।

अध्याय II में, नैनोक्रॉटल के संश्लेषण के लिए प्रयुक्त प्रोटोकॉल और उनके आगे संशोधनों पर चर्चा की जाती है। अवशोषण स्पेक्ट्रोस्कोपी के संक्षिप्त विवरण, प्रतिदीप्ति स्पेक्ट्रोस्कोपी, समय का समाधान प्रतिदीप्ति स्पेक्ट्रोस्कोपी, एक्स-रे विवर्तन और संचरण इलेक्ट्रॉन माइक्रोस्कोपी संश्लेषित nanomaterials को चिह्नित करने के लिए उपयोग किया जाता है चर्चा कर रहे हैं।

अध्याय III में, उनके संश्लेषण के दौरान कैपिंग लिगैंड्स को बदलकर सीडीएस नैनोकस्ट्रीस्ट के ऑप्टिकल गुणों का नियंत्रण अध्ययन किया गया। यह पाया गया कि संश्लेषण के अंत चरण में सीडीसीएल 2: फॉस्फोनिक एसिड (पीए) की थोड़ी मात्रा के अलावा, इन नैनोक्रिस्टल्स से सतह के राज्य के उत्सर्जन का पूरा उन्मूलन और इसके परिणामस्वरूप बैंड के किनारों के उत्सर्जन की मात्रा बढ़ जाती है।

अध्याय IV में, Cu2ZnSnS4 अर्धचालक नैनोक्रॉस्टल का विकास कैथिक सर्फटेक्ट सीटीएलटीमथिलमोनियम ब्रोमाइड (सीटीएबी) की शुरूआत से कम तापमान पर एक कोलाइडयन मार्ग के माध्यम से किया गया था। संश्लेषित नैनोक्रिस्टल एकसमान और एकल क्रिस्टलीय थे और उनके आकार को विभिन्न तापमानों पर उन्हें गर्म करके ट्यून किया जा सकता है जिससे उन्हें फोटोवोल्टिक उपकरणों में आवेदन के लिए भविष्य में उपयुक्त उम्मीदवार बनाते हैं।

अध्याय वी एक कोलाइडयन मार्ग के माध्यम से सेमीकंडक्टर नैनोक्रॉस्टल (सीजीटीएस) में मैंगनीज़ की शुरुआत और सीएमटीएस नैनोक्रिस्टल के संश्लेषण के द्वारा एक नए दृष्टिकोण की चर्चा करता है। ये नैनोकस्ट्रीस्टल दृश्यमान क्षेत्र में ऑप्टिकल शोषक दिखाते

हैं जिससे उन्हें फोटोवोल्टिक उपकरणों में आवेदन के लिए उपयुक्त उम्मीदवार बनाते हैं। इन नैनोक्रॉस्टल्स में चार्ज अंतरण की व्यवस्था को डाई-डिग्रेडेशन अध्ययनों से भी पुष्टि की गई, जो कि परिवेशी दिन के प्रकाश फोटोकैलेटिसिस की संभावना दिखाते हैं। अध्याय छठी में, सीडीएसई / 3ZnS / nCdSe (जहां n = 2, 3, 4, 5) से इलेक्ट्रॉन हस्तांतरण की प्रक्रिया को एयू युक्तियों में खोल मोटाई के एक समारोह के रूप में निगरानी की गई थी। अध्ययनों से पता चलता है कि खोल मोटाई में वृद्धि के रूप में, दोहरी एमिटर नैनोक्रिस्टल्स और सोना कणों के सीडीएसई खोल के प्रवाहकत्त्व बैंड के बीच ऊर्जा अंतर में अंतर के कारण प्रभार हस्तांतरण की प्रक्रिया कम हो जाती है। स्थिर राज्य और समय-समाधान किए गए फोटोल्युमिनेसिस अध्ययनों का एक संयोजन इन नैनोक्रॉस्टल में चार्ज अंतरण के तंत्र की स्थापना करता है, जिसे आगे फोटोकेटिस्टिस्ट के रूप में इस्तेमाल किया जा सकता है।

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

%	percent
ν	frequency
Å	angstrom
Abs	absorption
a.u.	arbitrary unit
μL	microlitre
ca.	calculated
°C	degree centigrade
EDX	energy dispersive X-ray analysis
FWHM	full width at half maximum
g	gram
h	hour
Hz	hertz
i.e.	that is
eV	electron volts
M	molar
mmol	millimole
mol	mole
mL	milliliter
m.p.	melting point
nm	nanometer
SNCs	semiconductor nanocrystals

TEM	transmission electron microscopy
HR	high resolution
PXRD	powder X-ray diffraction