INVESTIGATION OF ENERGY AND CHARGE TRANSFER DYNAMICS IN SEMICONDUCTOR NANOMATERIALS

MONA

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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INVESTIGATION OF ENERGY AND CHARGE TRANSFER DYNAMICS IN SEMICONDUCTOR NANOMATERIALS

by

Mona

Department of Chemistry

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CERTIFICATE

It is to certify that the thesis entitled, "**Investigation of Energy and Charge Transfer Dynamics in Semiconductor Nanomaterials**" being submitted by **Ms. MONA** 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. MONA** 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

Dr. SAMEER SAPRA
ASSOCIATE PROFESSOR
Department of Chemistry
Indian Institute of Technology Delhi
New Delhi- 110016

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ABSTRACT

Semiconductor nanocrystals (NCs), also known as colloidal quantum dots, show size, shape, and composition dependent optoelectronic properties, which make them suitable for various applications such as light emitting diodes, biomedical imaging, solar cells, and photocatalysis. They also offer extensive advantages over organic fluorophores or dyes owing to the quantum confinement, high extinction coefficients, the possibility of hot carrier collection, and multiple charge carrier generation in NCs as well as their broad absorption with narrow emission profiles, and highly resistant nature towards photobleaching. Most of the applications involve either energy or charge transfer between semiconductor NCs and respective molecular species for a particular application. Therefore, the present thesis is focussed on the investigation of the energy and charge transfer dynamics in semiconductor nanomaterials via interaction between semiconductor NCs and molecular species such as dye and proteins, photocatalysis under the visible light irradiation, and Mn^{2+} ions doping in perovskite NCs.

Chapter 1 deals with the extensive literature survey on the semiconductor NCs. **Chapter 2** includes several methods of synthesis and a variety of characterization techniques for synthesis and characterization of NCs, respectively. The safe and effective implementation of NCs in a particular application requires an interaction between NCs and respective molecular species. Hence, next two chapters (**Chapter 3 and 4**) are dedicated towards the interaction of semiconductor NCs with proteins and dye, which can have future applications in *invitro* bioimaging and hybrid sensitized solar cells, respectively. The interaction mechanism has been probed by steady-state and time-resolved photoluminescence spectroscopy. The Poisson binding model has been used to

understand the kinetics of the interaction. In **Chapter 5**, we have studied the effect of shell thickness and shape on charge transfer dynamics at the heterojunction of ZnSe/CdS nanoheterostructures via photocatalysis, such as photocatalytic degradation of dye and hydrogen evolution reaction. Then, we move towards newbie optoelectronic materials, *i.e.*, metal halide perovskites, as the photovoltaic devices based on these materials have attracted tremendous attention due to their power conversion efficiencies around 20 %. In **Chapter 6**, we have carried out the synthesis of perovskite NCs at room temperature using different approaches such as ligand assisted reprecipitation technique and solid state method. The band gap of $MAPbBr_3$ (methylammonium lead bromide) perovskite NCs is tuned by inserting the ethylammonium (EA) cation and varying the ratio of EA and MA cations, resulting in the formation of $(EA)_x(MA)_{1-x}PbBr_3$ NCs (where x varies between 0 and 1). The energy transfer dynamics in these perovskite NCs have been investigated viz. solid state Mn^{2+} ions doping. **Chapter 7** summarizes the results of the present thesis, emphasizing the importance of energy and charge transfer dynamics in semiconductor NCs.

सार

अर्धचालक नैनोक्रिस्टल्स, जिन्हे कोलॉइडल क्वांटम डॉट्स के रूप में भी जाना जाता है, आकार, आकृति और संरचना निर्भर प्रकाश इलेक्ट्रॉनिकी गुण दिखाते हैं, जो उन्हें विभिन्न अनुप्रयोगों जैसे लाइट एमिटिंग डायोड, बायोमेडिकल इमेजिंग, सोलर सेल, और फोटोकैटालिसिस के लिए उपयुक्त बनाती हैं। क्वांटम कॉनफाइनमेन्ट, हाई एक्सटिंक्शन कोएफ़िशिएंट, हॉट कर्रिएर कलेक्शन की संभावना, और नैनोक्रिस्टल्स में कई चार्ज वाहक उत्पादन के साथसाथ संकीर्ण उत्सर्जन प्रोफाइल के साथ उनके व्यापक - अवशोषण और अत्यधिक प्रतिरोधी प्रकृति की वजह से वे आर्गेनिक फ्लोरोफोर्स या डाई पर व्यापक फायदे भी प्रदान करते हैं। अधिकांश अनुप्रयोगों में किसी विशेष उपयोग के लिए अर्धचालक नैनोक्रिस्टल्स और संबंधित आणविक प्रजातियों के बीच ऊर्जा या चार्ज अंतरण शामिल होता है। इसलिए, वर्तमान थीसिस, अर्धचालक नैनोक्रिस्टल्स और आणविक प्रजातियों जैसे डाई और प्रोटीन के बीच इंटरेक्शन के माध्यम से अर्धचालक नैनोमैटेरियल्स में ऊर्जा और चार्ज अंतरण गतिशीलता की जांच, दृश्य प्रकाश विकिरण के तहत फोटोकैटालिसिस, और परोव्सकाइट्स नैनोक्रिस्टल्स में Mn^{2+} आयन डोपिंग पर केंद्रित है।

अध्याय 1अर्धचालक नैनोक्रिस्टल्स पर व्यापक साहित्य सर्वेक्षण दिखाता है। **अध्याय 2** में नैनोक्रिस्टल्स के संश्लेषण और लक्षण वर्णन के लिए संश्लेषण और कई प्रकार की लक्षण वर्णन तकनीक शामिल हैं। किसी विशेष उपयोग में नैनोक्रिस्टल्स के सुरक्षित और प्रभावी कार्यान्वयन के लिए नैनोक्रिस्टल्स और संबंधित आणविक प्रजातियों के बीच इंटरेक्शन की आवश्यकता होती है। इसलिए, अगले दो अध्याय)**अध्याय और 3** प्रोटीन और डाई के साथ सेमीकंडक्टर (**4**नैनोक्रिस्टल्स की इंटरेक्शन के लिए समर्पित हैं, जो कि इन विट्रो बायोइमेजिंग और हाइब्रिड सेंसीटाइज़्ड सोलर सेल में भविष्य में उपयोग कर सकते हैं। स्टेडी स्टेट और टाइम रिसॉल्व्ड फोटोल्युमिनेसिसेंस स्पेक्ट्रोस्कोपी द्वारा इंटरेक्शन की जांच हो रही है। पोइसन बाइंडिंग मॉडल का उपयोग इंटरेक्शन के गतिशीलता को समझने के लिए किया गया है। **अध्याय 5**में, हमने फोटोकटैलिसीस के माध्यम से शैल की मोटाई और आकृति के प्रभाव को ZnSe/CdS नैनोइटरोस्ट्रक्चर्स के उत्परिवर्तन पर चार्ज ट्रांसफर गतिशीलता का अध्ययन किया है, जैसे डाई का फोटोकेटैलिटिक डिग्रेडेशन और हाइड्रोजन विकास प्रतिक्रिया। फिर, हम नवागंतुक ऑप्टोइलेक्ट्रोनिक मैटेरियल्स की ओर बढ़ते हैं, अर्थात्, धातु हलाइड परोव्सकाइट्स, क्योंकि इन मैटेरियल्स पर आधारित फोटोवोल्टिक डिवाइस ने %20के आसपास अपनी पावर कन्वर्शन एफिशिएंसी के कारण बहुत ध्यान आकर्षित किया है। **अध्याय 6** में, हमने

कमरे के तापमान पर परोव्सकाइट्स नैनोक्रिस्टल्स का संश्लेषण किया है, जैसे कि लिगैड़ सहायता प्रदान करने वाली तकनीक और ठोस स्टेट विधि। $MAPbBr_3$) का बैंड अंतर एथिलैमोनियम (मिथाइलअमोनियम लेड ब्रोमाइड)EAधनायन को डालने (औरEA और MA के अनुपात को बदलकर किया गया है जो $(EA)_x(MA)_{1-x}PbBr_3$ नैनोक्रिस्टल्स जहां) x (के बीच होता है 1 और 0 बनाता है। इन परोव्सकाइट्स नैनोक्रिस्टल्स में ऊर्जा हस्तांतरण गतिशीलता की जांच की गई है, अर्थात ठोस स्टेट Mn^{+2}आयन डोपिंग। **अध्याय 7**, अर्धचालक नैनोक्रिस्टल्स में ऊर्जा और चार्ज अंतरण गतिशीलता के महत्व पर जोर देते हुए, वर्तमान थीसिस के परिणामों को सारांशित करता है ।

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

NCs	nanocrystals
MA	methylammonium
EA	ethylammonium
CdTe	cadmium telluride
ZnSe	zinc selenide
CdS	cadmium sulphide
CB	conduction band
VB	valence band
CdSe	cadmium selenide
PL	photoluminescence
SV	Stern-Volmer
FRET	Förster resonance energy transfer
DET	Dexter energy transfer
μL	microlitre
°C	degree centigrade
nm	nanometer
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	nanoseconds
ms	milliseconds
ps	picoseconds
TRPL	time resolved photoluminescence
TA	transient absorption
TEM	transmission electron microscopy
HRTEM	high resolution transmission electron microscopy
EDX	energy dispersive X-ray
PXRD	powder X-ray diffraction
ICP-OES	inductively coupled plasma optical emission spectrometry
EPR	electron paramagnetic resonance
SAED	selected area electron diffraction
STEM	scanning transmission electron microscopy
HAADF	high angle annular dark field