Computational Insights into Surface Engineering of Nanocrystals for Enhanced Optoelectronic Properties

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A Thesis

Submitted to the
Indian Institute of Technology, Delhi, India, for the degree of
Doctor of Philosophy (Ph.D.)
in the Faculty of Materials Science and Engineering

by

Kushal Samanta



Indian Institute of Technology, Delhi, India.
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To my Mother and Father

Declaration

I hereby declare that the matter embodied in the thesis entitled "Computational Insights into Surface Engineering of Nanocrystals for Enhanced Optoelectronic Properties" is the result of investigation carried out by me at the Indian Institute of Technology, Delhi, India, under the supervision of Prof. Dibyajyoti Ghosh and that it has not been submitted elsewhere for the award of any degree or diploma.

In keeping with the general practice in reporting scientific observations, due acknowledgement has been made whenever the work described is based on the findings of other investigators. Any omission that might have occurred by oversight or error of judgment is regretted.

Kushal Samanta

Certificate

This is to certify that the thesis entitled "Computational Insights into Surface Engineering of Nanocrystals for Enhanced Optoelectronic Properties" being submitted by Mr. Kushal Samanta for the award of the degree of Doctor of Philosophy (Ph.D.) is a record of the original, bona fide research work carried out by him under my guidance and supervision. He has fulfilled the requirements for the submission of this thesis. The results presented in this thesis have not been submitted, either in part or in full, to any University or Institution for the award of any degree or diploma.

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सार

सेमीकंडक्टर नैनोक्रिस्टल और क्वांटम डॉट्स आज के ऑप्टोइलेक्ट्रॉनिक्स, डिस्प्ले, लेज़र, फोटोडिटेक्टर, सौर ऊर्जा रूपांतरण और क्वांटम-फोटोनिक्स में प्रमुख सामग्री वर्ग बन चुके हैं। इनके गुणों का मूल आधार क्वांटम कंफाइनमेंट है, जो आकार के साथ बैंडगैप और उत्सर्जन रंग को नियंत्रित करता है। फिर भी, वास्तविक उपकरण-प्रदर्शन अक्सर केवल आकार से तय नहीं होता। नैनोक्रिस्टल में बड़ी संख्या में परमाणु सतह पर होते हैं, इसलिए सतह का फेसट (facet) वितरण, सतही बिंदु-दोष (point defects), और लिगैंड शेल की रसायनिकी तथा गतिशीलता अक्सर निर्णायक भूमिका निभाती है। इस कारण, ट्रैप-स्टेट निर्माण, गैर-विकिरणीय पुनर्संयोजन, स्पेक्ट्रल ब्रॉडनिंग और स्थिरता जैसी समस्याएँ उत्पन्न होती हैं। साथ ही, कैडमियम-आधारित क्वांटम डॉट्स (जैसे CdSe) की विषाक्तता के कारण InP जैसे कैडमियम-मुक्त विकल्पों पर भी व्यापक रुचि है। इसलिए एक ऐसा सामान्य, सटीक और स्केलेबल डिज़ाइन-फ्रेमवर्क आवश्यक है, जो सतह-रसायन और इलेक्ट्रॉनिक-गुणों को परमाणु-स्तर पर जोड़ सके।

इस शोध-प्रबंध का उद्देश्य सेमीकंडक्टर नैनोक्रिस्टल सतह इंजीनियरिंग के लिए एक एकीकृत संगणकीय रणनीति विकसित करना है। इस रणनीति में प्रथम-सिद्धांत (first-principles) इलेक्ट्रॉनिक-स्ट्रक्चर गणनाएँ, सीमित-तापमान परमाणु-गतिकी, उत्तेजित-अवस्था (excited-state) गैर-एडियाबैटिक डायनेमिक्स, और व्याख्यायोग्य मशीन-लर्निंग को एक साथ जोड़ा गया है। यह फ्रेमवर्क दो प्रमुख सामग्री परिवारों पर लागू किया गया है। पहला, II-VI प्रणाली में CdSe नैनोक्रिस्टल और अल्ट्रास्मॉल Cd-rich क्वांटम डॉट्स। दूसरा, लीड-हैलाइड पेरोव्स्काइट में $CsPbCl_3$ नैनोक्रिस्टल, जो नीली रोशनी उत्सर्जन के लिए महत्वपूर्ण है परन्तु क्लोराइड-वैकेंसी-जनित ट्रैप-स्टेट्स से सीमित रहता है।

सबसे पहले, wurtzite CdSe नैनोक्रिस्टल में फेसट-निर्भर संरचना और इलेक्ट्रॉनिक-गुणों का परमाणु-स्तर पर विश्लेषण किया गया। यह पाया गया कि ध्रुवीय (polar) और अध्रुवीय (non-polar) फेसट्स अलग-अलग प्रकार की सतह पुनर्निर्मिति (reconstruction) दिखाते हैं। सतह पर उपस्थित कम-समन्वित (under-coordinated) Se साइट्स वैलेंस-एज के पास लोकलाइज़्ड स्टेट्स उत्पन्न कर सकती हैं। इसके बाद, $CdCl_2$ और $InCl_3$ जैसे अकार्बनिक साल्ट-पासिवेशन के माध्यम से इन ट्रैप-मैनिफोल्ड्स को दबाने की प्रक्रिया को स्पष्ट किया गया। पासिवेशन के बाद बैंड-एज स्टेट्स अधिक डीलोकलाइज़्ड हो जाते हैं और निम्न-ऊर्जा ऑप्टिकल ट्रांजिशन में सुधार दिखता है। यह निष्कर्ष दर्शाता है कि सतह उपचार का प्रभाव समान नहीं होता, बल्कि वह फेसट-पोलैरिटी और स्थानीय समन्वय से नियंत्रित होता है।

इसके बाद, CdSe नैनोक्रिस्टल में सतह बिंदु-दोषों का फेसट-निर्भर प्रभाव व्यवस्थित रूप से स्थापित किया गया। अध्ययन में न्यूट्रल Se-वैकेंसी और Cd-वैकेंसी को अलग-अलग फेसट्स, एज और वर्टेक्स साइट्स पर बनाया गया। मुख्य निष्कर्ष यह है कि किसी दोष का "हानिकारक" होना केवल उसकी रासायनिक पहचान से तय नहीं होता। यह इस बात पर निर्भर करता है कि स्थानीय संरचना कितनी प्रभावी रूप से पुनर्संयोजित होकर डैंगलिंग-बॉन्ड्स को संतृप्त कर पाती है। कुछ स्थानों पर Cd–Cd या Se–Se बंध-निर्माण से दोष-स्थल "सेल्फ-हील" होकर उथले (shallow) स्टेट्स देता है। कुछ ज्यामितीय रूप से बाधित स्थानों पर यह पुनर्संयोजन अधूरा रहता है और गहरे (deep) मिड-गैप ट्रैप-स्टेट्स बनते हैं। ऑप्टिकल अवशोषण में ध्रुवीय फेसट-दोषों से पहली ब्राइट एक्साइटॉन ऊर्जा में परिवर्तन दिखाई देता है, जबकि कई अध्रुवीय फेसट-दोष ऑप्टिकली लगभग निष्क्रिय रहते हैं। इससे फेसट-आधारित दोष-सहनशीलता के स्पष्ट डिज़ाइन नियम प्राप्त होते हैं।

थीसिस का अगला भाग अल्ट्रास्मॉल Cd-rich CdSe क्वांटम डॉट्स में लिगैंड-नियंत्रित उत्तेजित-अवस्था गतिकी पर केंद्रित है। यहाँ विभिन्न X-type लिगैंड्स (कार्बोक्सिलेट, हाइड्रॉक्साइड, क्लोराइड और थायोलेट मॉडल) के साथ सतह पासिवेशन के प्रभावों का अध्ययन किया गया। यह दिखाया गया कि लिगैंड रसायनिकी बैंड-एज लोकलाइजेशन, कंपन-स्ट्रक्चर और इलेक्ट्रॉन-फोनॉन कपलिंग को बदल देती है। परिणामस्वरूप, बैंडगैप फ्लक्चुएशन, नॉन-एडियाबैटिक कपलिंग, और गैर-विकिरणीय रिकॉम्बिनेशन लाइफटाइम में महत्वपूर्ण अंतर आता है। क्लोराइड और थायोलेट पासिवेशन में बैंड-एज अधिक डीलोकलाइज़्ड रहते हैं और नॉन-एडियाबैटिक कपलिंग कम होती है, जिससे कैरियर लाइफटाइम लंबा और लाइनविड्थ संकीर्ण होती है। इसके विपरीत, कुछ ऑक्सीजन-आधारित लिगैंड्स अधिक गतिशील सतह बनाते हैं और ट्रैप-जैसा लोकलाइजेशन बढ़ा देते हैं, जिससे गैर-विकिरणीय नुकसान तेज होता है। इसी अध्ययन में LUMO और LUMO+1 के बीच इंट्राबैंड ऊर्जा अंतर (ΔE_{gap}) पर भी ध्यान दिया गया, जो हॉट-कैरियर रिलैक्सेशन और "फोनॉन-बॉटलनेक" जैसी अवधारणाओं के लिए महत्वपूर्ण है। यह भाग दिखाता है कि लिगैंड चयन न केवल स्थिर पासिवेशन बल्कि हॉट-कैरियर कूलिंग और उत्सर्जन-गुणवत्ता दोनों को नियंत्रित कर सकता है।

परंतु AIMD-DFT जैसे उच्च-सटीक तरीके समय-मान (timescale) के कारण सीमित होते हैं। इसलिए इस शोध-प्रबंध में एक व्याख्यायोग्य ग्राफ-न्यूरल-नेटवर्क फ्रेमवर्क विकसित किया गया, जो परमाणु-ट्राजेक्टरी से समय-निर्भर बैंडगैप और ΔE_gap की भविष्यवाणी कर सके। ALIGNN आधारित मॉडल को विरल-सैंपलिंग और एन्सेम्बल-लर्निंग के साथ प्रशिक्षित किया गया, जिससे कम DFT पॉइंट्स का

उपयोग करके भी उच्च सटीकता प्राप्त हुई। ट्रांसफर-लर्निंग द्वारा मॉडल को आगे के समय-खंडों में विस्तारित किया गया। सबसे महत्वपूर्ण योगदान यह रहा कि फीचर-नलिफिकेशन जैसी विधियों से मॉडल की व्याख्यात्मकता प्राप्त की गई, और यह पहचाना गया कि कौन-से विशिष्ट परमाणु-स्थल और लिगैंड-मोटिफ्स इलेक्ट्रॉनिक "नॉइज़" तथा फ्लक्चुएशन को नियंत्रित करते हैं। इससे ML मॉडल केवल तेज भविष्यवक्ता नहीं रहता, बल्कि एक परमाणु-स्तर का निदान उपकरण बन जाता है।

थीसिस का अंतिम बड़ा भाग $CsPbCl_3$ नैनोक्रिस्टल में नीली रोशनी उत्सर्जन सुधारने के लिए लिगैंड-स्क्रीनिंग पर आधारित है। $CsPbCl_3$ में सतह पर क्लोराइड वैकेंसी (V_Cl) बनने से अंडर-कोऑर्डिनेटेड Pb साइट्स उत्पन्न होते हैं और गहरे ट्रैप-स्टेट्स बनते हैं, जो PLQY और स्थिरता घटाते हैं। इस अध्ययन में विभिन्न रासायनिक वर्गों के लिगैंड्स का DFT-आधारित दो-चरणीय फिल्टरिंग किया गया। पहले चरण में adsorption energy द्वारा थर्मोडायनामिक स्थिरता जाँची गई। दूसरे चरण में इलेक्ट्रॉनिक-स्ट्रक्चर द्वारा ट्रैप-रिमूवल जाँचा गया। यह स्पष्ट हुआ कि केवल मजबूत binding पर्याप्त नहीं है। लिगैंड का बैकबोन, π-कंजुगेशन, और समन्वय ज्यामिति यह तय करती है कि बैंड-एज के पास नए molecular states आएँगे या नहीं। इस प्रकार नीली-एमिशन के लिए उपयुक्त लिगैंड-डिज़ाइन नियम स्थापित हुए, जिनमें मल्टिडेंटेट समन्वय और सही हेड-ग्रुप रसायनिकी का महत्व प्रमुख है।

अंत में, DFT-स्क्रीनिंग की स्केलेबिलिटी सीमा को हटाने के लिए $CsPbCl_3$–लिगैंड इंटरफेस हेतु एक GNN-आधारित ML interatomic potential विकसित किया गया। ट्रांसफर-लर्निंग के साथ प्रशिक्षित इस MLIP ने संरचना-रिलैक्सेशन और adsorption energy की गणना को बहुत तेज बनाया, जिससे बड़े लिगैंड-लाइब्रेरी पर उच्च-थ्रूपुट स्क्रीनिंग संभव हुई। यह भाग एक व्यावहारिक "डिस्कवरी इंजन" प्रस्तुत करता है, जिसमें MLIP-आधारित प्री-स्क्रीनिंग और चयनित DFT-वैलिडेशन की संयुक्त रणनीति अपनाई गई है।

समग्र रूप से, यह शोध-प्रबंध यह स्थापित करता है कि नैनोक्रिस्टल का प्रदर्शन फेसट-दोष-लिगैंड की संयुक्त भूमिका से तय होता है। यह कार्य सतह-ट्रैप्स को नियंत्रित करने, हॉट-कैरियर रिलैक्सेशन को समझने, और लिगैंड-डिज़ाइन को तेज करने के लिए एक सामान्य मंच प्रदान करता है। यह मंच CdSe जैसी पारंपरिक प्रणालियों के साथ-साथ InP जैसे कैडमियम-मुक्त क्वांटम डॉट्स और अन्य उभरते सेमीकंडक्टर नैनोक्रिस्टल्स पर भी लागू किया जा सकता है। इस प्रकार, यह थीसिस सुरक्षित, स्थिर और उच्च-दक्षता वाले अगली-पीढ़ी के एमिटर-मटेरियल्स की दिशा में परमाणु-स्तर पर डिज़ाइन-आधारित मार्ग प्रस्तुत करती है।

List of Publications

(1) **Samanta, K.**; Deswal, P.; Ghosh, D. Atomistic Insights on Facet-Dependent Functional Properties in CdSe Nanocrystals. **Chem. Mater.** 2024, 36 (10), 5120–5132. https://doi.org/10.1021/acs.chemmater.4c00370.

(2) **Samanta, K.**; Deswal, P.; Alam, S.; Bhati, M.; Ivanov, S. A.; Tretiak, S.; Ghosh, D. Ligand Controls Excited Charge Carrier Dynamics in Metal-Rich CdSe Quantum Dots: Computational Insights. **ACS Nano** 2024, 18 (36), 24941–24952. https://doi.org/10.1021/acsnano.4c05638.

(3) **Samanta, K.**; Mannodi-Kanakkithodi, A.; Ghosh, D. Interpretable Graph Neural Network for Predicting Transient Electronic Structures of Semiconductor Quantum Dots. **ACS Mater. Lett.** 2025, 7 (11), 3724 3732. https://doi.org/10.1021/acsmaterialslett.5c01013.

(4) **Samanta, K.**; Bharti, J.; Mannodi-Kanakkithodi, A.; Ghosh, D. Screening Ligands for Passivating Surface Defects in CsPbCl3 Nanocrystals for Enhanced Blue Light Emission: In-Silico Approach. **Chem. Mater.** 2026, 38 (8), 4092–4103. https://doi.org/10.1021/acs.chemmater.5c03376.

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List of Abbreviations

NCs	Nanocrystals
QDs	Quantum Dots
PL	Photoluminescence
PLQY	Photoluminescence Quantum Yield
DFT	Density Functional Theory
TD-DFT	Time Dependent Density Functional Theory
AIMD	*Ab-Initio* Molecular Dynamics
NAMD	Non-Adiabatic Molecular Dynamics
ML	Machine Learning
GNN	Graph Neural Network
AI	Artificial Intelligence
MLIPs	Machine-Learned Interatomic Potentials
CdSe	Cadmium Selenide
InP	Indium Phosphide
$CsPbX_3$	Cesium Lead Halide (X=Cl, Br, I)
LHP NCs	Lead Halide Perovskite Nanocrystals
V_{Cl}	Chloride Vacancy
V_{Se}^{0}	Neutral Selenium Vacancy
V_{Cd}^{0}	Neutral Cadmium Vacancy
VB	Valence Band
CB	Conduction Band
VBM	Valence Band Maximum
CBM	Conduction Band Minimum
LEDs	Light Emitting Diodes

HER	Hydrogen Evolution Reaction
M3GNet	Materials 3-body Graph Network
GaAs	Gallium Arsenide
SRH	Shockley-Read-Hall
CdS	Cadmium Sulfide
QLEDs	Quantum Light Emitting Diodes
QDSCs	Quantum Dot Solar Cells
MEG	Multiple Exciton Generation
QDPs	Quantum Dot Photodetectors
LCD	Liquid Crystal Display
OLED	Organic Light-Emitting Diode
EQE	External Quantum Efficiency
PeLEDs	Perovskite Light Emitting Diodes
ZB	Zinc Blende
WZ	Wurtzite
CN	Coordination Number
QY	Quantum Yield
LO	Longitudinal Optical
CGCNN	Crystal Graph Convolution Neural Network
MEGNet	MatErials Graph Network
ML-NAMD	Machine Learning driven Non-Adiabatic Molecular Dynamics
FWHM	Full-Width Half-Maxima
G-MLIPs	Graph Machine Learned Interatomic Potentials
HOMO	Highest Occupied Molecular Orbitals
LUMO	Lowest Unoccupied Molecular Orbitals

EDLs	Exciton Delocalizing Ligands
NAC	Non-Adiabatic Coupling
XAI	Explainable Artificial Intelligence
PES	Potential Energy Surface
GAP	Gaussian Approximation Potential
MTP	Moment Tensor Potential
TFD	Thomas-Fermi-Dirac
LDA	Local Density Approximation
GGA	Generalized Gradient Approximation
XC	Exchange Correlation
TDKS	Time-Dependent Kohn Sham
LR-TDDFT	Linear-Response Time-Dependent Density Functional Theory
TDA	Tamm-Dancoff approximation
BO	Born-Oppenheimer
SCF	Self-Consistence Field
CPA	Classical Path Approximation
FSSH	Fewest-Switches Surface Hopping
DISH	Decoherence Induced Surface Hopping
ALIGNN	Atomistic Line Graph Neural Network
MSE	Mean Square Error
PDOS	Projected Density of States
GPW	Gaussian and Plane Wave
PAW	Projector Augmented Wave
GTH	Goedecker-Teter-Hutter
PBE	Perdew-Burke-Ernzerhof

DIIS	Direct inversion in iterative subspace
IPR	Inverse Participation Ratio
RMSF	Root Mean Square Fluctuation
vDOS	Vibrational Density of States
ANN	Artificial Neural Network
RFR	Random Forest Regression
ENI	Energy Noise Index
RMSE	Root Mean Square Error
MAE	Mean Absolute Error
FNA	Feature Nullification Analysis
HSAB	Hard-Soft Acid-Base
EDA	Electric Dipole Approximation

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