PHOTOLUMINESCENT NANOSTRUCTURES FROM SELF-ASSEMBLY OF BLOCK COPOLYMER/QUANTUM DOT HYBRIDS

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by

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Dedicated to my family

CERTIFICATE

This is to certify that the thesis titled '***Photoluminescent Nanostructures from Self-Assembly of Block Copolymer/Quantum Dot Hybrids'*** being submitted by **Mr. Sajan Singh** to the Indian Institute of Technology Delhi, for the award of ***Doctor of Philosophy*** degree, is a record of bonafide research work carried out by him. **Mr. Sajan** 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.

Date

(Prof. Bhanu Nandan)
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Sajan Singh

Sajan Singh

ABSTRACT

Polymer-inorganic hybrid materials offer exciting opportunities as they can exhibit promising properties from both the constituents that are desirable for applications such as sensors, composites, catalysis, energy conversion/storage etc. The self-assembly of block copolymer (BCP) has been one of the fascinating approaches to direct the assembly of inorganic nanoparticles (NPs) for the fabrication of such hybrid materials with well-defined morphologies. In the present work, we demonstrate the self-assembly approach to direct the assembly of quantum dots (QDs) into organized structures. It was further demonstrated that self-assembled morphologies of block copolymer could also be used to obtain isolated photoluminescent core-shell hybrid nano-objects *via* selective solvent approach.

The first part of the present study mostly focused on the fundamental study on the self-assembly behavior of BCP/QDs hybrids. This involved the investigation on the localization of QDs within the self-assembled structure of BCPs and the effect of QDs vis-à-vis its size, shape and surface chemistry on the BCP self-assembly. The cylinder-forming PS-*b*-P4VP block copolymer mixed with TOPO capped CdSe quantum dots of diameter ~3.8 nm was investigated. It was found that quantum dots were enthalpically compatible with P4VP chains *via* ligand displacement of TOPO from the QD surface. However, the QDs were found to localize preferentially at the PS/P4VP interphase plausibly to gain translational entropy in order to further lower the energetics of the self-assembled structure. Interestingly, morphological transformation was observed with increasing weight fraction of the QDs, in the BCP/QD composites, which was driven by the migration of the displaced TOPO from QD surface to the PS phase, effectively raising its total volume fraction. Hence, the PS-b-P4VP BCP with PS as the minority block displayed lamellar morphology in its composite with QDs. Most interestingly, it was found that after addition of TOPO capped QDs of diameter ~7.4 nm, the BCP morphology transformed to the perforated lamellar morphology. Moreover, the QDs were exclusively localized within the P4VP perforations. This is one of the first such observation in the bulk BCP/nanoparticle hybrid systems and the formation of perforated layer morphology was attributed to the alleviation of chain packing frustration after localization of the QDs in the P4VP perforations.

Additionally, to incorporate the quantum dots in the PS phase, QDs were stabilized by thiol terminated PS oligomer *via* ligand displacement approach. It was found that PS-stabilized QDs

also localized in the P4VP phase, driven *via* ligand-displacement of the PS-SH from the QD surface as observed with TOPO coated QDs. This was because of the fact that both TOPO and PS-SH ligands form co-ordinate bond with QD surface and, hence, P4VP was effective, as a multidentate ligand, in displacing them from QD surface. This revealed that the thiol chemistry for binding ligands to QDs behave very differently than that in metallic nanoparticles. Apart from this, self-assembly approach was further used to incorporate anisotropic semiconducting nanoparticles such as nanoplatelets and nanorods with the same surface chemistry, as in QDs, within the self-assembled structure of BCP. It was observed that both nanorods and nanoplates macrophase separated, plausibly due to the stronger inter-rod/inter-platelet interactions in comparison to interaction between P4VP block and ligand bound to the particles surface.

In the second part of this research, the approach was extended to fabricate multifunctional nano-objects by adding second targeted functionality i.e. sulforhodamine 101(S101) during the BCP/QD self-assembly. The organization of two different functionalities within the confined space of the self-organized BCP domains enabled them to localize at distances comparable to their Förster radius enabling an efficient fluorescence resonance energy transfer (FRET) between them. There was a reduction in the mean lifetime and PL quenching of CdSe QDs in the presence of S101 dye, which showed effective energy transfer from donor CdSe QDs to acceptor S101 dye molecules. Similarly, another targeted functionality i.e. Au NPs were also used to fabricate multi-functional nano-objects. The confinement imposed by the nanometer-sized cylindrical core resulted in the localization of the CdSe QDs and Au NPs in close proximity. It was found that photoluminescence properties of QDs could be manipulated by changing the concentration of Au NPs while keeping QDs constant within the nano-dimension geometry of the fibers obtained via self-assembly process of PS-b-P4VP BCP. Interestingly, it was observed that PL intensity of CdSe QDs increased at very low weight ratio of Au NPs. On further increasing the amount of Au NPs, the PL intensity decreased and then completely diminished at high ratios.

The present research not only provides fundamental information on the self-assembly behavior of BCP/QD hybrid systems but also has importance for developing nanostructured materials for potential application in sensing, bio-imaging, and functional optoelectronic devices.

सार

बहुलक-अकार्बनिक संकर सामग्री रोमांचक अवसर प्रदान करते हैं क्योंकि वे दोनों घटकों से आशाजनक गुणों का प्रदर्शन कर सकते हैं जो विविध अनुप्रयोगों जैसे कि सेंसर, कंपोजिट, कैटेलिसिस, ऊर्जा रूपांतरण /भंडारण आदि के लिए वांछनीय हैं। ब्लॉक कॉपोलीमर की स्व-असेंबली अच्छी तरह से परिभाषित आकृति विज्ञान के साथ इस तरह के संकर सामग्री के निर्माण के लिए अकार्बनिक नैनोकणों की सभा को निर्देशित करने के लिए आकर्षक दृष्टिकोणों में से एक रही है। वर्तमान कार्य में, हम क्वांटम डॉट्स की सभा को संगठित संरचनाओं में निर्देशित करने के लिए स्व-असेंबली दृष्टिकोण को प्रदर्शित करते हैं। इसके साथ ही ब्लॉक कॉपोलीमर के आत्म-इकट्ठे आकारिकी को अलग-अलग फोटोल्यूमिनेसेंट कोर-शेल हाइब्रिड नैनो-ऑब्जेक्ट्स को चयनात्मक विलायक दृष्टिकोण के माध्यम से प्राप्त करने के लिए भी इस्तेमाल किया जा सकता है।

वर्तमान अध्ययन का पहला भाग ज्यादातर ब्लॉक कॉपोलीमर/क्वांटम डॉट्स संकरों के स्व-असेंबली व्यवहार के मौलिक अध्ययन पर केंद्रित था। इसमे ब्लॉक कोपोलीमर्स के आत्म-इकट्ठे ढाँचो के भीतर क्वांटम डॉट्स का स्थानीयकरण और ब्लॉक कॉपोलीमर स्व-असेंबली पर क्वांटम डॉट्स के माप, आकार और सतह रसायन विज्ञान के प्रभाव पर जांच शामिल थी। बेलनकार ढांचा बनाने वाले PS-b-P4VP ब्लॉक कॉपोलीमर को टोपो कैप्ड CdSe क्वांटम डॉट्स व्यास लगभग 3.8 नैनोमीटर के साथ मिलाया गया था। यह पाया गया कि क्वांटम डॉट्स सतह से टोपो लिगैंड विस्थापन के माध्यम से पी-4-वीपी श्रृंखलाओं के साथ सहज रूप से संगत थे। हालाँकि, क्वांटम डॉट्स को स्थानीय करने के लिए मिला PS/P4VP इंटेरफेज पर अधिमानतः आत्म-इकट्ठे संरचना के ऊर्जावानों को कम करने के लिए, अनुवादकीय एन्ट्रापी हासिल करने के लिए संभव है। दिलचस्प रूप से, ब्लॉक कॉपोलीमर/क्वांटम डॉट्स मिश्रण में क्वांटम डॉट्स के बढ़ते वजन अंश के साथ रूपात्मक परिवर्तन देखा गया था, जो कि क्वांटम डॉट्स सतह से विस्थापित टोपो के पीएस चरण में प्रभावी रूप से प्रवासित था। जिसके कारण पीएस चरण का कुल आयतन बढ़ गया। इसलिए,

PS-b-P4VP ब्लॉक कॉपोलीमर पीएस के साथ अल्पसंख्यक ब्लॉक के रूप में क्वांटम डॉट्स के साथ अपने समग्र रूप में लैमेलर आकृति विज्ञान प्रदर्शित किया। सबसे दिलचस्प बात, यह पाया गया कि व्यास लगभग 7.4 नैनोमीटर के टोपो कैप्ड क्वांटम डॉट्स को शामिल करने के बाद, बीसीपी आकृति विज्ञान छिद्रित लैमेलर आकारिकी में बदल गयी। इसके अलावा, क्वांटम डॉट्स P4VP वेध के भीतर विशेष रूप से स्थानीयकृत थे। यह बल्क ब्लॉक कॉपोलीमर /नैनोकण मिश्रण प्रणालियों में इस तरह के पहले अवलोकन में से एक है और P4VP वेध में क्वांटम डॉट्स के स्थानीयकरण के बाद श्रृंखला पैकिंग कुंठा के उन्मूलन को छिद्रित लैमेलर आकृति विज्ञान के गठन के लिए जिम्मेदार ठहराया गया था।

इसके अतिरिक्त, पीएस चरण में क्वांटम डॉट्स को शामिल करने के लिए, क्वांटम डॉट्स को लिगैंड विस्थापन दृष्टिकोण के माध्यम से थायोल टर्मिनेटेड PS ऑलिगोमेर द्वारा स्थिर किया गया था। यह पाया गया कि PS-स्थिर क्वांटम डॉट्स भी P4VP चरण में स्थानीयकृत हैं, जो क्वांटम डॉट्स सतह से लिगैंड-विस्थापन के माध्यम से संचालित होता है, जैसा कि टोपो लेपित क्वांटम डॉट्स के साथ पाया गया था। यह इस तथ्य के कारण था कि टोपो और थायोल टर्मिनेटेड पीएस दोनों लिगैंड्स क्वांटम डॉट्स सतह के साथ को-ऑर्डिनेट बॉन्ड बनाते हैं और इसलिए, उनको क्वांटम डॉट्स सतह से विस्थापित करने में, P4VP मल्टीगेट लिगैंड के रूप में प्रभावी था। यह पता चला है कि क्वांटम डॉट्स के साथ बंधन बनाने के लिए थायोल रसायन, धातु नैनोकणों में की तुलना में बहुत अलग व्यवहार करते हैं। इसके अलावा, ब्लॉक कॉपोलीमर के आत्म-इकट्ठे ढांचे के भीतर स्व-असेंबली दृष्टिकोण का उपयोग एनिसोट्रॉपीक अर्धचालकता नैनोकणों जैसे नैनोप्लटेलटेस और नैनोरोड्स को समान सतह रसायन, जैसा कि क्वांटम डॉट्स में है, के साथ शामिल करने के लिए आगे किया गया था। यह देखा गया कि दोनों नैनोरोड्स और नैनोप्लटेलटेस मैक्रोफेज अलग हो गए, संभवतः P4VP ब्लॉक और कणों की सतह पर बंधे लिगैंड के बीच बातचीत की तुलना में मजबूत इंटर-रॉड / इंटर-प्लेटलेट इंटरैक्शन के कारण।

इस शोध के दूसरे भाग में, ब्लॉक कॉपोलीमर/क्वांटम डॉट्स के स्व-असेंबली के दौरान दूसरे लक्षित कार्यक्षमता यानि साल्फोरोडामिन101 को जोड़कर मल्टीफंक्शनल नैनोऑब्जेक्ट्स को बनाने के लिए दृष्टिकोण को बढ़ाया गया था। आत्म-इकट्ठे ब्लॉक कॉपोलीमर डोमेन के सीमित स्थान के भीतर दो अलग-अलग कार्यात्मकताओं के संगठन ने उन्हें अपने फॉस्टर रेडियस के बराबर दूरी पर स्थानीयकरण करने में सक्षम किया और उनके बीच एक कुशल प्रतिदीप्ति अनुनाद ऊर्जा हस्तांतरण को सक्षम किया। साल्फोरोडामिन101 डाई की उपस्थिति में CdSe क्वांटम डॉट्स की औसत जीवनकाल और फोटोल्यूमिनेसेंस शमन में कमी थी, जिसने दाता CdSe क्वांटम डॉट्स से स्वीकर्ता साल्फोरोडामिन101 डाई अणुओं में प्रभावी ऊर्जा हस्तांतरण दिखाया। इसी तरह, एक और लक्षित कार्यक्षमता यानी Au नैनोकणों का उपयोग बहु-कार्यात्मक नैनो-ऑब्जेक्ट्स को बनाने के लिए भी किया गया था। नैनोमीटर के आकार के बेलनाकार कोर द्वारा लगाए गए परिरोध का परिणाम CdSe क्वांटम डॉट्स और Au नैनोकणों के स्थानीयकरण से हुआ। यह पाया गया कि PS-b-P4VP ब्लॉक कॉपोलीमर के स्व-असेंबली प्रक्रिया के माध्यम से प्राप्त तंतुओं के नैनो-आयाम ज्यामिति के भीतर क्वांटम डॉट्स को स्थिर रखते हुए क्वांटम डॉट्स की फोटोल्यूमिनेसेंस गुणों को Au नैनोकणों की एकाग्रता में परिवर्तन करके नियंत्रित किया जा सकता है। दिलचस्प बात यह है कि यह देखा गया कि CdSe क्वांटम डॉट्स की फोटोल्यूमिनेसेंस तीव्रता Au नैनोकणों के बहुत कम वजन अनुपात में बढ़ गई। Au नैनोकणों की मात्रा को और बढ़ाने पर, फोटोल्यूमिनेसेंस की तीव्रता कम हो गई और फिर उच्च अनुपात में पूरी तरह से कम हो गई।

वर्तमान शोध न केवल ब्लॉक कॉपोलीमर/क्वांटम डॉट्स मिश्रण प्रणालियों के स्व-असेंबली व्यवहार पर मौलिक जानकारी प्रदान करता है, बल्कि संवेदी, जैव-इमेजिंग, और कार्यात्मक ऑप्टोइलेक्ट्रॉनिक उपकरणों में संभावित अनुप्रयोग के लिए नैनोस्ट्रक्चर सामग्री को विकसित करने के लिए भी महत्वपूर्ण है।

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LIST OF SYMBOLS AND ABBREVIATIONS

BCP	*Block copolymer*
PS-b-P4VP	*polystyrene-block-poly(4-vinylpyridine)*
PS-b-PMMA	*polystyrene-block-poly(methyl methacrylate)*
QDs	*quantum dots*
NPs	*nanoparticles*
N	*degree of polymerization*
X	*Flory-Huggins interaction parameter*
f	*volume fraction*
SCFT	*self-consistent field theory*
PS-b-PI	*polystyrene-block-polyisoprene*
CPB	*Cylindrical polymer brushes*
ATRP	*Atom transfer radiated polymerization*
ROP	*Ring opening polymerization*
NMP	*Nitroxide mediated polymerization*
PBIEM	*poly(2-(2-bromoisobutyryloxy)ethyl methacrylate*
PS	*polystyrene*
PAA	*poly(acrylic acid)*
PtBA	*poly(t-butyric acid)*
PCL	*polycaprolactam*
PEG	*poly(ethylene glycol)*
PDMAEMA	*poly(N, N-dimethylaminoethyl methacrylate)*
PS-b-PCEMA	*polystyrene-block-poly(2-cinnamoyloxyethyl methacrylate)*
PBMA	*poly(butyl methacrylate)*

PS-b-P2VP	*polystyrene-block-poly(2-vinylpyridine)*
PTEPM-b-PS	*poly 3-(triethoxysilyl)propyl methacrylate block-polystyrene*
PtBA-b-PGMA	*poly(tert-butyl acrylate)-block-poly(glycidyl methacrylate)*
EDA	*Ethylenediamine*
PI-b-PEO	*polyisoprene-block-poly(ethylene oxide)*
PDP	*3-n-pentadecylphenol*
POEGMA	*poly(oligo (ethylene glycol) methacrylate)*
PHEMA	*poly(2-hydroxyethyl methacrylate)*
PMAEMA	*poly(2 methylamino)ethylmethacrylate*
SMA	*Supramolecular assembly*
S101	*Sulphorhodamine 101*
CdO	*Cadmium oxide*
TOPO	*Trioctylphosphine oxide*
ODA	*Octadecylamine*
OA	*Oleic acid*
OLA	*Oleylamine*
TOP	*Trioctylphosphine*
HPA	*Hexylphosphonic acid*
TDPA	*Tetradecylphosphonic acid*
SEM	*Scanning electron microscope*
TEM	*Transmission electron microscope*
EFTEM	*Energy filtered Transmission electron microscope*
SAXS	*Small angle x-ray scattering*
AFM	*Atomic force microscopy*
STM	*Scanning tunneling microscope*

PL	*Photoluminescence*
TRPL	*Time-resolved photoluminescence spectroscopy*
TCSPC	*Time-correlated single photon counting*
FRET	*Fluorescence resonance energy transfer*
QE	*Quantum efficiency*
FTIR	*Fourier transformation infrared spectroscopy*
TTIP	*Titanium isopropoxide*
CdSe	*Cadmium selenide*
CdS	*Cadmium sulphide*
ZnSe	*Zinc selenide*
MNP	*Metal Nanoparticles*
FNP	*Fluorescent Nanoparticles*
PS- b -PAMA	*poly(allyl methacrylate)*
PSS	*polystyrene sulfonic acid*
$NaBH_4$	*Sodium borohydride*
Au	*Gold*
Ag	*Silver*
SPR	*Surface plasmon resonance*
hPS	*homopolystyrene*
hP4VP	*homopoly(4-vinylpyridine)*
LSPR	*localized surface plasmons resonance*