SURFACE ENGINEERING OF UPCONVERSION NANOPARTICLES WITH POLYMER CHAINS USING PHOTOINDUCED ELECTRON/ENERGY TRANSFER REVERSIBLE ADDITION-FRAGMENTATION CHAIN TRANSFER POLYMERIZATION

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Surface engineering of upconversion nanoparticles with polymer chains using photoinduced electron/energy transfer reversible addition-fragmentation chain transfer polymerization

by

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Dedicated to my family

CERTIFICATE

This is to certify that the thesis entitled **"Surface engineering of upconversion nanoparticles with polymer chains using photoinduced electron/energy transfer reversible addition-fragmentation chain transfer polymerization"** being submitted by **Ms. Tina Joshi** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. Ms. Tina Joshi has worked under my guidance and supervision and has fulfilled the requirements for the submission of her thesis, which to our knowledge has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or full, to any University or Institute for the award of any degree or diploma.

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ABSTRACT

This thesis includes an extensive assessment of the design and synthesis of core-shell architecture that uses upconversion nanoparticles as the core and their surface modifications as the shell. The optimization of synthetic procedures and functionalization of upconversion nanoparticles with modified silica and polymers has been documented. The literature review on upconversion nanoparticle production, mechanism, and modifications has been comprehensively reviewed. The utilization of various techniques for inorganic UCNP surface modification employing organic functionalities and their intended applications have been thoroughly discussed. Moreover, the effective modification of the surface of UCNPs with silica and polymer grafting via RAFT/PET-RAFT polymerization has been further discussed in depth.

In chapter 2, Optimization for the hydrothermal approach using a Teflon walled autoclave to synthesize $NaYF_4$ based Er^{3+} (0.5% mmol) and Yb^{3+} (20% mmol) doped UCNPs has been discussed. Formation of cubic phase nanocrystals and the presence of small amount of hexagonal phase was confirmed with XRD analysis. Further, surface functionalization of UCNPs was carried out using ZnO and with silica integrated RAFT agent. The synthesis of core@shell framework was optimized first with ZnO. The uniform and homogeneous surface coating with ZnO was optimized using various concentrations and was characterized morphologically by HR-TEM. Moreover, the strategy of incorporating RAFT agent within the network of silica and its homogeneous coating on UCNP core was optimized. The formation of core@shell framework along with their characterizations has been discussed in detail.

In chapter 3, using the stepwise co-condensation approach, mesoporous silica nanoparticles integrated with RAFT agent were synthesized. Mesoporous silica nanoparticles integrated with

RAFT agent (RAFT-MSNs) were used for facile synthesis of an organic-inorganic hybrid system by surface-initiated RAFT polymerizing a variety of monomers, including hydrophobic and hydrophilic monomers. In order to achieve surface-initiated RAFT polymerization, AIBN was used as a thermal initiator for polymerization while Eosin Y served as a photocatalyst for PET-RAFT polymerization that was controlled by visible light. Compared to thermal RAFT polymerization, the light-regulated PET-RAFT polymerization was carried out effortlessly and quickly. Various characterizations such as thermal, morphological, etc. were performed for these systems confirming the effective growth of polymers from the modified surface. The non-porous silica integrated with RAFT agent was used to perform kinetics of polymerization for all the polymers. Successful polymerization was characterized by size exclusion chromatography (SEC) after de-grafting of polymeric chains from silica surface.

In chapter 4, utilising silica combined with a RAFT agent and polymer functionalization, rare earth (Er^{3+}, 0.5% mmol) doped UCNPs were created with their surfaces modified. Eosin Y, which functions as a photocatalyst when exposed to blue light at room temperature, was present during the PET-RAFT polymerization process used for the functionalization of the polymer. The "grafting-from" technique was utilised to functionalize UCNPs using a variety of polymers, including as poly(N-isopropyl acrylamide), poly(acrylic acid), poly(ethylene glycol)methacrylate, and poly(methyl methacrylate). Numerous characterizations were carried out to support the successful PET-RAFT polymerization-based grafting of polymers. An improvement in photoluminescent efficacy towards the red region/window was seen even after the polymer grafting. The emission in the red region as well as results from cytocompatibility studies for as-synthesized core@shell@shell system is marked as suitable for biological applications.

Further in chapter 5, the facile synthesis of multi-shell architecture of rare earth doped upconversion nanoparticles ($NaYF_4$:Er;Yb@ZnO@RAFT) with ZnO and silica integrated with RAFT agent was carried out. The resultant multi-shell assembly has core of upconversion nanoparticles coated primary with semiconductor (ZnO) which also act as photocatalyst and thus, UCNP@ZnO moiety has been further coated with silica integrated with RAFT agent. This UCNP@ZnO@RAFT has been used effectively for successful polymer grafting of various hydrophobic and hydrophilic monomers. Using PET-RAFT polymerization in the presence or absence of an external photocatalyst (Eosin Y), the polymerization has been successfully carried out. A comparative study between the polymerization in the presence of Eosin Y and ZnO has been performed. The synthesis of $NaYF_4$:Er;Yb@ZnO@RAFT@Polymer are characterized with HR-TEM, XRD, EDX, TGA, FTIR and PL using 980 nm laser.

सारांश

इस थीसिस में, कोर-शेल आर्किटेक्चर के डिजाइन और संश्लेषण को कोर के रूप में अपवर्जन नैनोकणों को शामिल करते हुए और शेल के रूप में उनकी सतह के संशोधनों पर व्यापक रूप से चर्चा की गई है। सिंथेटिक प्रक्रियाओं का अनुकूलन और संशोधित सिलिका और पॉलिमर के साथ अपवर्जन नैनोकणों के कार्यात्मककरण को प्रलेखित किया गया है। संश्लेषण, क्रियाविधि, और अपरूपांतरण नैनोकणों के परिवर्तन पर साहित्य समीक्षा पर गहन चर्चा की गई है। कार्बनिक कार्यात्मकताओं और उनके लक्षित अनुप्रयोगों का उपयोग करके अकार्बनिक यूसीएनपी के सतह संशोधन के लिए विभिन्न विधियों के उपयोग पर विस्तार से चर्चा की गई है। इसके अलावा, RAFT/PET-RAFT पोलीमराइज़ेशन के माध्यम से सिलिका और पॉलीमर ग्राफ्टिंग के साथ UCNPs की सतह के प्रभावी संशोधन पर गहराई से चर्चा की गई है।

अध्याय 2 में, NaYF4 आधारित Er3+ (0.5% mmol) और Yb3+ (20% mmol) डोप्ड UCNPs को संश्लेषित करने के लिए टेफ्लॉन दीवार वाले आटोक्लेव का उपयोग करके हाइड्रोथर्मल दृष्टिकोण के लिए अनुकूलन पर चर्चा की गई है। एक्सआरडी विश्लेषण के साथ घन चरण नैनोक्रिस्टल का गठन और हेक्सागोनल चरण की छोटी मात्रा की उपस्थिति की पुष्टि की गई। इसके अलावा, ZnO का उपयोग करके और सिलिका एकीकृत RAFT एजेंट के साथ UCNPs की सतह का कार्यात्मककरण किया गया। Core@shell ढांचे के संश्लेषण को पहले जिंक ऑक्साइड के साथ अनुकूलित किया गया था। जिंक ऑक्साइड के साथ एक समान और सजातीय सतह कोटिंग को विभिन्न सांद्रता का उपयोग करके अनुकूलित किया गया था और एचआर-टीईएम द्वारा रूपात्मक रूप से चित्रित किया गया था। इसके अलावा, सिलिका के नेटवर्क के भीतर आरएएफटी एजेंट को शामिल करने की रणनीति और यूसीएनपी कोर पर इसकी सजातीय कोटिंग को अनुकूलित किया

गया था। कोर@शैल ढांचे के निर्माण के साथ-साथ उनकी विशेषताओं पर विस्तार से चर्चा की गई है।

अध्याय 3 में, चरणवार सह-संक्षेपण दृष्टिकोण का उपयोग करते हुए, आरएएफटी एजेंट के साथ एकीकृत मेसोपोरस सिलिका नैनोकणों को संश्लेषित किया गया था। RAFT एजेंट (RAFT-MSNs) के साथ एकीकृत मेसोपोरस सिलिका नैनोकणों की सतह से हाइड्रोफोबिक और हाइड्रोफिलिक मोनोमर्स सहित विविध मोनोमर्स का सतह-आरंभित RAFT पोलीमराइज़ेशन कार्बनिक-अकार्बनिक संकर प्रणाली के एक सहज संश्लेषण में किया गया था। भूतल-आरंभित RAFT पोलीमराइज़ेशन AIBN को पोलीमराइज़ेशन के लिए एक थर्मल सर्जक के रूप में और इओसिन वाई को दृश्यमान प्रकाश-विनियमित PET-RAFT पोलीमराइज़ेशन के लिए एक फोटोकैटलिस्ट के रूप में नियोजित किया गया था। थर्मल आरएएफटी पोलीमराइजेशन की तुलना में प्रकाश विनियमित पीईटी-आरएएफटी पोलीमराइजेशन न्यूनतम समय में सहजता से किया गया था। संशोधित सतह से पॉलिमर के प्रभावी विकास की पुष्टि करने वाली इन प्रणालियों के लिए थर्मल, रूपात्मक आदि जैसे विभिन्न लक्षण वर्णन किए गए थे। RAFT एजेंट के साथ एकीकृत गैर झरझरा सिलिका का उपयोग सभी पॉलिमर के लिए पोलीमराइज़ेशन के कैनेटीक्स को करने के लिए किया गया था। सफल पोलीमराइजेशन को सिलिका सतह से पॉलीमेरिक चेन के डी-ग्राफ्टिंग के बाद आकार अपवर्जन क्रोमैटोग्राफी (एसईसी) द्वारा चित्रित किया गया था।

अध्याय 4 में, रेयर अर्थ (Er3+, 0.5% mmol) डोप्ड UCNPs के सतह संशोधन के साथ RAFT एजेंट के साथ एकीकृत सिलिका का उपयोग करके पॉलिमर कार्यात्मकता के साथ संश्लेषण किया गया था। ईओसिन वाई (ईवाई) की उपस्थिति में पीईटी-आरएएफटी पोलीमराइजेशन द्वारा बहुलक के साथ क्रियाशीलता का प्रदर्शन किया गया था जो कमरे के तापमान पर नीली रोशनी के संपर्क में आने पर एक फोटोकैटलिस्ट के रूप में कार्य करता है। "ग्राफ्टिंग-फ्रॉम" विधि के माध्यम से,

यूसीएनपी को कार्यात्मक बनाने के लिए पॉली (एन-आइसोप्रोपिल एक्रिलामाइड), पॉली (एक्रिलिक एसिड), पॉली (एथिलीन ग्लाइकॉल) मेथैक्रिलेट और पॉली (मिथाइल मेथैक्रिलेट) सहित विभिन्न पॉलिमर का उपयोग किया गया। पॉलिमर के सफल पीईटी-आरएएफटी पोलीमराइजेशन-आधारित ग्राफ्टिंग का समर्थन करने के लिए कई लक्षण वर्णन किए गए। पॉलीमर ग्राफ्टिंग के बाद भी, लाल क्षेत्र/विंडो की ओर फोटोल्यूमिनेसेंट दक्षता में वृद्धि देखी गई। लाल क्षेत्र में उत्सर्जन के साथ-साथ संश्लेषित कोर @ शेल @ शेल सिस्टम के लिए साइटोकंपैटिबिलिटी अध्ययन के परिणाम जैविक अनुप्रयोगों के लिए उपयुक्त के रूप में चिह्नित हैं।

इसके अलावा अध्याय 5 में, रेयर अर्थ डोप्ड अपकंवर्जन नैनोपार्टिकल्स (NaYF4:Er;Yb@ZnO@RAFT) के मल्टी-शेल आर्किटेक्चर का सरल संश्लेषण ZnO और RAFT एजेंट के साथ एकीकृत सिलिका के साथ किया गया था। परिणामी मल्टी-शेल असेंबली में सेमीकंडक्टर (ZnO) के साथ प्राइमरी कोटेड अपकंवर्जन नैनोपार्टिकल्स का कोर होता है जो फोटोकैटलिस्ट के रूप में भी काम करता है और इस प्रकार, RAFT एजेंट के साथ एकीकृत सिलिका के साथ आगे कोटेड किया गया है। यह विभिन्न हाइड्रोफोबिक और हाइड्रोफिलिक मोनोमर्स के सफल बहुलक ग्राफ्टिंग के लिए प्रभावी ढंग से उपयोग किया गया है। बाहरी फोटोकैटलिस्ट (इओसिन वाई) की उपस्थिति/अनुपस्थिति में किए गए PET-RAFT पोलीमराइज़ेशन का उपयोग करके पोलीमराइज़ेशन कुशलतापूर्वक किया गया था। इओसिन वाई और ZnO की उपस्थिति में पोलीमराइज़ेशन के बीच एक तुलनात्मक अध्ययन किया गया है। NaYF4 का संश्लेषण: एर; Yb@ZnO@RAFT@Polymer को 980 एनएम लेजर का उपयोग करके एचआर-टीईएम, एक्सआरडी, ईडीएक्स, टीजीए, एफटी-आईआर और पीएल की विशेषता है।

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List of Abbreviations and Symbols

AA	Acrylic acid
AIBN	Azobisisobutyronitrile
CIE	Commission Internationale de l'Elcairage
CR	Cross-relaxation
CS_2	Carbon disulfide
CTAB	Cetyltrimethylammonium bromide
Đ	Polydispersity index
DLS	Dynamic light scattering
EDX	Dispersive X-ray spectroscopy
EBT	Energy back transfer
Er^{3+}	Erbium ions
ET	Energy transfer
EY	Eosin Yellow/ Eosin Y
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
HR-TEM	High resolution-transmission electron microscopy

JCPDS	Joint Committee on Powder Diffraction Standards
PAA	Poly(acrylic acid)
MMA	Methyl methacrylate
MSNs	Mesoporous silica nanoparticles
MTT	3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT)
NIR	Near infrared region
PEGMA	Poly(ethylene glycol) methacrylate
PL	Photoluminescence analysis
PNIPAM	Poly (N-isopropylacrylamide)
PMMA	Poly (methyl methacrylate)
PET-RAFT	Photoinduced electron/energy transfer reversible addition-fragmentation chain transfer polymerization
PPh_3	Triphenylphosphine
P-XRD	Powder X-Ray diffraction
MIP	Molecularly imprinted polymers
M_n	Number-average molecular weight
M_w	Weight-average molecular weight
NIPAM	N- Isopropylacrylamide

NMR	Nuclear magnetic resonance
RAFT	Reversible addition-fragmentation chain transfer polymerization
RAFT agent	Reversible addition-fragmentation chain transfer agent
RAFT-Silica	Silica integrated with RAFT agent
RAFT-MSN	Mesoporous silica nanoparticles integrated with RAFT agent
RGR	Red to green ratio
SEC	Size exclusion chromatography
TEOS	Tetraethyl orthosilicate
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
T_{ini}	Onset degradation temperature
T_{fin}	Offset degradation temperature
UC	Upconversion
UCNPs	Upconversion nanoparticles
UCNP@RAFT	Upconversion nanoparticles functionalized with silica integrated with RAFT agent
UCNP@RAFT@Polymer	Upconversion nanoparticles functionalized with silica integrated with RAFT agent and grafted polymer
UCNP@ZnO@RAFT@Polymer	Upconversion nanoparticles functionalized with zinc oxide, silica integrated with RAFT agent and grafted polymer

UCNP@ZnO@RAFT@Polymer-EY	Eosin Y catalysed PET-RAFT polymerization of monomer on surface of functionalized upconversion nanoparticles
U2OS Line	Human Bone Osteosarcoma Epithelial Cells
XRD	X-ray diffraction
XS	Xylene soluble
Yb^{3+}	Ytterbium ions
ZnO	Zinc Oxide
λ	Wavelength (nm)