SYNTHESIS, CHARACTERIZATION AND MODIFICATION OF QUANTUM DOTS FOR ANALYTICAL AND BIOMEDICAL APPLICATIONS

ABSTRACT
of
THESIS

SUBMITTED TO

BABASAHEB BHIMRAO AMBEDKAR UNIVERSITY

(A CENTRAL UNIVERSITY)

LUCKNOW

BABASAHEB
BHIMRAO
AMBEDKAR
UNIVERSITY

LUCKNOW

प्रज्ञा शील करूणा

ESTABLISHED 1996

FOR THE DEGREE OF

Doctor of Philosophy

IN

APPLIED CHEMISTRY

Submitted by

VIVEK PANDEY

ENROLMENT NUMBER 857/12

CO-SUPERVISOR

Dr. MOHANA KRISHNA REDDY MUDIAM

Principal Scientist, Analytical Chemistry Laboratory & Scientist Incharge, Pesticide Toxicology Laboratory Regulatory Toxicology Group CSIR-Indian Institute of Toxicology Research Lucknow- 226001, INDIA.

SUPERVISOR

Dr. GAJANAN PANDEY

Associate Professor & Head, Department of Applied Chemistry School for Physical Sciences Babasaheb Bhimrao Ambedkar University Lucknow, 226025, INDIA.

2015

ABSTRACT

Quantum Dots (QDs) has revolutionized the field of nanotechnology with its leap towards all branches of natural science. Synthesis of the quantum dots for various applications is need of modern day material chemist. Small size of the material which is in the range of 2-10 nm makes it biologically efficient by easy uptaking of the cells and the strong quantum confinement paves the way of tuning size with optical and electronic properties. Photostability of the material and low background noise due to large stokes shift has been explored to use the QDs for bioimaging and sensing applications. The biological applications of the material can only be done if it proves itself non-toxic while the sensing applications of the material depend on sensitivity and selectivity. Quenching of photoluminescence intensity of QDs by interaction of surface of the material with external environment is the best mechanical property to obtain optical signal. These materials hence must be functionalized at surfaces to explore them for tailor made applications Thus prior to obtain the applications of QDs a lot of material pre-treatment at surface is needed which can be possible during synthesis by surface modification of the nanoparticle. These assumptions and hypothesis form the basis of this research work.

Metal chalcogenides are extensively studied and performed in the thesis. Manganese doped Zinc Sulphide crystal lattice is synthesized and modifications of the lattice at surface has been used to investigate optical and biological properties. Green synthetic approach was utilized to synthesize the Mn doped QDs at room temperature. Nucleation controlled synthesis was done at room temperature while Ostwald growth was controlled by suitable capping agent. The capping agents have thiol group (L-cysteine and MPTS) which binds specifically with the zinc metal ion. Imidazole as donor ligand has been developed as novel capping agent in the thesis

which has Nitrogen as binding site with metal ion. Low temperature and water as solvent employed in the synthesis has been a potent green synthetic route of nanoparticle synthesis. The synthesized QD was characterized by SEM for surface morphology, TEM for size determination and the crystal lattice was studied by XRD for composition and size calculations. The Braggs equation and Scherer calculation was derived to obtain the precise size of the synthesized material. The luminescence properties of the QDs were studied by PL spectrophotometer and UV Spectrometer. The band gap and excitation wavelength was calculated from the UV spectra.

The analytical applications of the QDs were done by fabricating the surface through imprinted polymer and surface defects. The optical properties were explored to develop optical sensors. In subsequent chapters, the sensing ability of Mn doped ZnS by surface modifications with molecularly imprinted polymer (MIP) has been explored for target analyte as 3-phenoxy benzoic acid (urinary metabolite for synthetic pyrethroids) and by creation of surface defects for methyl mercury (an organic form of mercury). The QD-MIP for 3-PBA was formed by imprinted polymers with aminopropyl trimethoxysilane (APTES) as monomer on Mn doped ZnS QDs. The methyl mercury based sensor was developed by creating defects on the QD surface through enriched sulphur. The defect decreases on binding the analyte to the synthesized Mn doped ZnS crystal lattice, as a result of this increase in intensity occurs with increase in concentration of the methyl mercury. The studies shown that, the surface modification not only improves optical sensitivity but also enhances the selectivity towards a desired analyte.

In subsequent later chapters biomedical applications of QDs were performed. The orange emission of the manganese doped zinc sulphide QDs has potential of non-invasive imaging applications. As part of biomedical applications imaging of the cells

by QD have been studied. The biological applications of nanoparticle are dependent on the toxicological tests. Here in various toxicity assessments have been done to evaluate and find the suitability of the material in biological environment of the cells. L-Cysteine and imidazole as capping agents lowers the toxicity of the QDs upto many fold. The toxicity evaluation of the as synthesized manganese doped zinc sulphide QDs is performed by *in-vitro* method.

Neuronal cell lines and human lung cell lines are used for uptaking the nanoparticles. The in-vitro toxicity assessment was performed by checking cell viability through MTT and NRU assays. The other parameters like oxidative degradation of lipids (LPO), reactive oxygen species, Lactate dehydrogenase activity, Glutathione, Oxidative stress and catalase assay was performed to determine oxidative stress in the cells by the entrance of QD in the cell. Genetic toxicology was performed by analysis of chromosomal aberration and micronucleus test. Through these analysis we can predict the biocompatibity of the as synthesized quantum dots and the usage of these materials in biomedical applications. The L-Cysteine and imidazole as capping has been used to synthesize small sized quantum dots and also to reduce toxicity. Both of the capping agents were tested with QD for its bio-applicability. The L-cysteine capped QD has shown toxicity above 1500 ppm and the as synthesized QD capped with L-Cysteine was also used as imaging probe. The red luminescence and its bright field contrast image confirm that QD has been uptake by cells without rupturing the cell membrane. The antioxidant property of L-cysteine was the key for its reduction in toxicity up to higher concentration. L-cysteine being a biomolecule which can be further functionalized for targeted applications as well. Imidazole capped Mn doped ZnS QDs were also prepared and passed through cytotoxic assessment. The toxicity at cellular, molecular and genetic level was done for

imidazole capped QDs. It was found that the synthesized Imidazole capped QD was non toxic upto 1000 ppm. Hence water soluble non-toxic Mn doped QDs was synthesized by various capping agents has shown that the synthesized QDs are biocompatible and can be used in biomedical sciences. Thus biomedical applications of the QDs were studied by toxicity assessment and imaging methods.