SYNTHESIS AND CHARACTERIZATION OF CORE-SHELL NANOSTRUCTURES

by

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CERTIFICATE

This is to certify that the thesis entitled, **"Synthesis and characterization of core-shell nanostructures"**, being submitted by **Ms Sonalika Vaidya**, 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 Sonalika Vaidya has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or full, to any other university or institute for award of any degree or diploma.

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To

My Loving Parents

and

Sister

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ABSTRACT

Core shell nanostructures are materials that have an inner core surrounded by a shell. These materials exhibit interesting properties. These exhibit improved physical and chemical properties over their single counterparts. The shell alters the reactivity of the surface and imparts stability and dispersibility to the colloidal core. With these improvements in the properties these materials find a wide range of application in medicines, pharmaceuticals, protection of light and moisture sensitive materials etc. In this thesis, an attempt has been made to synthesize core-shell nanostructures.

Chapter 1 gives a brief overview of the state of knowledge existing in the area of core-shell nanostructures. Synthetic methodologies and a brief description of various characterization techniques that have been employed to synthesize and characterize core-shell nanostructures have been discussed. Apart from this, the chapter discusses the motivation for carrying out the research work.

Chapter 2 discusses the synthesis of nanostructures of $NiO@SiO_2$, $Co_3O_4@SiO_2$ and $Mn_2O_3@SiO_2$. It was observed that the shell thickness for $NiO@SiO_2$ core-shell nanostructures could be varied in the range of 5- 25 nm with appropriate loading of tetraethylorthosilicate (TEOS). Highly uniform silica shell was grown on Co_3O_4 and Mn_2O_3 nanoparticles using the colloidal solutions of Tergitol and cyclohexane. Addition of 1-octanol and varying the amount of water was effective in increasing the shell thickness on Co_3O_4 nanoparticles from 5 nm to 20 nm. The quantity of water (required for hydrolysis) was found to be the key factor for controlling the shell thickness. The formation of the shell was confirmed by transmission electron microscopy and energy dispersive x-ray analysis. Zeta potential studies of these core-shell nanostructures show a

negative value compared to the bare nanoparticles. Electron paramagnetic resonance studies indicate the presence of free radicals on the surface of the SiO_2 shell. The magnetic susceptibility increased with shell thickness possibly due to the free radicals associated with the silica shell.

In **Chapter 3,** core-shell nanostructures of Mn_2O_3@amino-functionalized silica, Mn_2O_3@vinyl-functionalized silica and Mn_2O_3@allyl-functionalized silica were synthesized using the hydrolysis of the respective organosilane precursor. The synthetic methodology does not make use of the commonly used post-grafting or co-condensation method. These core-shell nanostructures were characterized using TEM, IR and zeta potential studies. TEM shows the formation of core-shell with a core diameter of 25-30 nm and a shell thickness of 5-15 nm. We observed that the zeta potential value increased (towards positive) compared to the bare Mn_2O_3 and silica coated Mn_2O_3 core-shell nanostructures which also confirm the presence of functional groups over the surface of the core-shell. The amino-functionalized core-shell nanostructures were used for the immobilization of glucose and L-methionine.

Apart from these, the chapter also discusses the synthesis of hollow shells of silica which were obtained by the dissolution of the oxide core of Co_3O_4@SiO_2 core-shell nanostructures. We have shown that these hollow shells have the potential to entrap hydrophilic moieties present in trace amount in the aqueous environment. From the spectrophotometric studies it was observed that up to 18% of methyl orange could be entrapped using these hollow shells.

Chapter 4 discusses the synthesis of Ag@TiO_2 core-shell structures using reverse micellar route. Two different shell-forming reagents viz. titanium isopropoxide and titanium hydroxyacylate were used to obtain core-shell nanostructures of Ag@TiO_2. It was observed that nanocomposites were formed when the shell forming agent, titanium isopropoxide, was added before breaking the micelles whereas uniform core-shell structures of Ag@TiO_2 (core diameter ranging from 10-40 nm and a shell thickness of 10-50 nm) were formed when titanium hydroxyacylate (first time) was employed as a shell forming agent. The most uniform shell formation was realized using titanium hydroxyacylate as the shell forming agent with an optimum ratio of Ag : Ti :: 1:0.67. Formation of a uniform shell structure was disrupted when 2-mercaptoethanol was used as a capping agent to synthesize Ag@TiO_2 core-shell nanostructures. HRTEM, IR and XPS studies of Ag@TiO_2 synthesized using capping agent show the formation of Ag_2S coated with an amorphous layer of TiO_2. Surface plasmon band of silver was red shifted by 25 nm and 10 nm for Ag@TiO_2 core-shell structures (compared with that of silver nanoparticles) synthesized using titanium hydroxyacylate and titanium isopropoxide respectively. The surface plasmon peak was masked by the presence of capping agent (2-mercaptoethanol) by demetallizing the silver particles through Ag-S bond formation. An increase in the emission intensity, for the core-shell structures when compared to that of TiO_2 nanoparticles, was observed which was attributed to SERS effect. The PL intensity of TiO_2 also decreases in the core-shell nanostructures in presence of 2-mercaptoethanol due to the formation of Ag_2S as an intervening shell.

In **Chapter 5** reverse micellar route was employed to synthesize core-shell nanocomposites of CdS@TiO_2 and ZnS@TiO_2 using titanium hydroxyacylate as the shell-forming agent. HRTEM studies show the size of 3-5 nm for sulphide nanoparticles forming the core. The size of CdS particles (observed from HRTEM studies and calculated from absorption studies) in the composite decreased as compared to bare CdS particles which suggest the restriction in the growth of particles by the titania shell. A strong quantum confinement of these nanocomposites was observed for bare nanoparticles and core-shell nanocomposites from the optical studies. The size of CdS and ZnS, calculated from absorption studies, corroborated with that observed from HRTEM studies. The size of CdS core in these nanostructures was found to be smaller in presence of 2-mercaptoethanol when compared to that of bare CdS and core-shell nanostructures synthesized in absence of 2-mercaptoethanol No quenching in the emission band of CdS was observed for the core-shell nanostructures which indicated quantum confinement in the TiO_2 shell. No change in the optical properties was observed for ZnS@TiO_2 core-shell nanostructures when compared to bare ZnS nanoparticles.

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