Chapter 1

Introduction

1.1 Objective of the Thesis: The Scope of Studies with Copper and Copper oxide nanoparticles:

Nanomaterials are materials in which at least one dimension is in the nanometer size regime. They have unique physical and chemical properties. Nanomaterials have thus found wide application in optics, electronics, catalysis, chemical sensing, biomedicine etc. Among nanomaterials, metal nanomaterials especially those of gold, silver and copper have been widely studied in the past. This is mainly due to the fact that nanoparticles of these noble metals show absorption in the visible region of the spectrum due to surface plasmon resonance. All the interesting behavior exhibited by the metal nanoparticles depend on their size and shape. Thus synthesis of these nanoparticles is designed with a strong focus on controlling their size and tailoring their shape. Among the noble metal nanoparticles, copper is the most abundantly used in electronics applications and catalysis due to its high conductivity and low cost.

This thesis is a detailed account of the synthesis of copper-based nanomaterials in different organized assemblies. The organized assemblies employed are all based on surfactants. Detailed characterization and some applications of the synthesized nanomaterials are also included.

1.2 Summary of the Work Done:

1.2.1 Shape control of Copper Nanostructures in a Cationic Surfactant:

Special-shaped metal nanoparticles are an interesting topic of research due to their superior performance over their spherical counterparts. Composite nanomaterials of special shapes are important for manufacture of catalysts with high selectivity. Thus establishment of suitable synthetic procedures for such nanomaterials is important. Among all procedures, the soft chemical approach involving the chemical reduction of metal precursor solutions in presence of structure directing agents like surfactants is popular. This work was designed with an aim to synthesize special shaped copper nanomaterials by simply varying the surfactant concentration.

Using the cationic surfactant cetyltrimethylammonium bromide, it was found that the microstructure of surfactant assemblies dictate the size and particularly the shape of the nanomaterials. It has been found that unlike polymers, the surfactant micelles do not act as templates for copper nanorod formation but are actively involved in controlling the nanorod structure. The shape variations of the copper nanomaterials are determined by a delicate balance of the [surfactant]: [copper ion] ratio and the alignments of the initially formed particles.
1.2.2 Synthesis of Copper Nanoparticles using AOT surfactant – “Micelles versus conventional Reverse Micelles”:

One of the more popular methods of synthesis of copper nanoparticles (CuNPs) has been the use of functionalized Aerosol OT (AOT) reverse micelles. The microenvironment of the water pools in w/o microemulsions formed by AOT is significantly different from bulk water. Thus both the oxidation and aggregation of the CuNPs can be prevented by modulating the \([\text{H}_2\text{O}] : [\text{AOT}]\) mole ratio i.e. \(w_0\).

In this work, AOT micelles and reverse micelles were explored as prospective media for preparing CuNPs. Here for the first time AOT micelles were used for nanoparticle synthesis. Metallic CuNPs were found to form above the critical micellar concentration (CMC) of AOT while aggregates of copper oxide nanoparticles were formed below CMC. It was also shown that AOT micelles are better templates for NP synthesis compared to reverse micelles composed of Na-AOT.

1.2.3 Synthesis of Copper Nanoparticles in non-ionic Polysorbate micelles-Dye catalysis and Fluorescence studies:

Polysorbates or Tweens are nontoxic non-ionic surfactants that have been widely approved as pharmaceutical excipients for use in medicinal formulations. A homologous Polysorbate surfactant series was used to prepare stable copper nanoparticles. It was found that the Polysorbates function as efficient stabilizers for the synthesis of stable CuNPs. The size, shape and crystallinity of the nanoparticles are modulated by the Hydrophile: Lipophile Balance (HLB) values of the surfactants and also the surfactant concentration. Among the three Polysorbates used, Polysorbate 20 and 40 lead to the formation of metallic CuNPs while in Polysorbate 60 copper oxide NPs are formed. The low HLB value of Polysorbate 60 leads to solvent exposure of the initially formed seed CuNPs which subsequently get coated by a surface layer of copper oxide. The high HLB value of Polysorbate 20 helps in the formation of stable spherical metallic CuNPs. The metallic CuNPs and copper oxide NPs can catalyse dye reduction, the former being more efficient as catalysts.

1.2.4 Synthesis of Copper Nanoparticles in Niosomal Vesicles and their Catalytic Activity:

The synthesis of CuNPs was carried out in the confined volume of a membrane-mimicking liposome-type vesicle for the first time in literature. Vesicles are highly ordered, curved bilayers existing in aqueous media. Niosomes or vesicles formed by non-ionic surfactants were first introduced by Handjani-Vila et al. Niosomes are of higher chemical stability than phospholipid vesicles or liposomes. The niosomal bilayers are stabilized by the addition of cholesterol. This work showed that the niosomal cavity provides good control over the size, shape and polydispersity of the nanoparticles. The quality of the CuNPs produced is guided largely by the specific effects exerted by the niosomes. The HLB values
of the span surfactants used, their transition temperature ($T_c$), entrapment ability and “leakiness” of the niosomes are important factors affecting the CuNP characteristics. It is found that the “less leaky” niosomes formed by the surfactant Span 40 result in spherical, monodisperse and highly crystalline CuNPs. These CuNPs of diameter 11-15 nm produced in Span 40 based niosomes function as efficient catalysts for dye reduction.

1.3 Plan of the thesis:

Chapter 1: This chapter gives a summary of the work done.

Chapter 2: This chapter includes a review on nanoparticles- their synthesis in organized surfactant assemblies, their characterization and their catalytic activity in solution.

Chapter 3: This chapter includes all the experimental details of the work and description of equipment used and/or techniques employed.

Chapter 4: This chapter is an outline of how a cationic surfactant can be used to control the shape of CuNPs.

Chapter 5: This chapter is an account of the use of micelles and reverse micelles of the anionic surfactant Aerosol OT (AOT) for synthesis of CuNPs.

Chapter 6: This chapter outlines how a homologous series of non-ionic surfactants has been used to prepare copper nanoparticles. It also includes a description of the catalytic and fluorescence applications of the nanomaterials.

Chapter 7: This chapter describes the synthesis of copper nanomaterials in niosomal vesicles and their catalytic activity.
References:


