Name of Scholar : Aparna Ganguly

Name of Supervisor : Dr Tokeer Ahmed , JMI, New Delhi

Name of Co-Supervisor : Prof A.K.Ganguli, IIT – Delhi

Department of Chemistry

Title of thesis : Precursor mediated synthesis to nanooxides : synthesis, characterization and properties.

Abstract

Design of nanostructures with controlled size and shape using low temperature solution based routes has been a major area of research in the field of nanoscience and nanotechnology. This interdisciplinary area has contributed to several important applications in industries with wide ranging products like pharmaceuticals, semiconductors and abrasives. Among all, the oxide nanoparticles form the major category of material being used commercially. One of the important methodologies used to synthesize nanosized particles is by using microemulsion where emulsifying agents or surfactants are used as aggregates to control the size and shape of tiny aqueous droplets. These droplets can be effectively used to synthesize inorganic materials having nanodimensions. The size and shape of the product nanoparticles may be controlled through a proper choice of parameters which are involved in the formation of surfactant aggregates.

Chapter 2 discusses the microemulsion method for the synthesis of anisotropic nanostructures of alkaline - earth metal oxalates with the aid of a cationic surfactant, CTAB. We discuss the synthesis of magnesium oxalate dihydrate, calcium oxalate dihydrate and the mixed metal oxalate of the two. These oxalate precursors were decomposed under aerial conditions to obtain the corresponding oxides. The surface area of magnesium oxide nanoparticles was measured to be 108 m^2/g. Nanoparticles of magnesium oxide were used as a catalyst for Claisen Schmidt condensation. Chalcone formation was found to increase with time as observed using gas chromatography-mass spectrometry (GC-MS). The reusability of the catalyst was checked by using the same catalyst twice which showed a reduced percentage (50% compared to first cycle) conversion. Nanoparticles of alkaline earth metal have also been studied for its removal capacity for toxic ions. High adsorption capacity has been observed for cadmium and lead ions by calcium oxide and magnesium oxide respectively.

In chapter 3, the role of the dicarboxylate ligand in controlling the aspect ratio of these anisotropic mesostructures and the oxidation state of the transition metal ion in the formation of anisotropic structures has been investigated. We have studied the conditions required for the self assembly of the nanoparticles to form ordered nanostructures and control the anisotropy. We observe the formation of rod – like structures of copper succinate that are formed by an ordered assembly of spherical particles of size ~ 4-5 nm which is facilitated by water molecules and is

driven by the permanent dipole moment of the succinate ion that leads to the oriented attachment of the nanoparticles in the presence of the surfactant. The requirement of + 2 oxidation state of the metal ion for the formation of anisotropic structures has also been discussed. We observe formation of spherical particles for the + 3 oxidation state of metal ion. The succinate precursors have been decomposed to obtain metal and metal oxide nanoparticles. Both the precursor and the oxide nanoparticles have been characterized and studied for their magnetic properties.

In chapter 4 we discuss the synthesis of mesoporous silica using surfactant assemblies. A simple route has been developed for the fabrication of mesoporous particles by manipulating the cooperative assembly of the surfactant and silicate species using the hydrothermal method. A control over the pore size, particle morphology and surface area has been achieved using both microemulsion and hydrothermal method. We have systematically studied the effect of different types of stabilizers like PEG and surfactants of different types like the cationic, cetyl trimethyl ammonium bromide (CTAB) to anionic sodium lauryl sulfate (SLS) on the porosity of the mesoporous silica samples. We observe that the pore size can be controlled in a wide size distribution (3.4 to 22 nm) by the systematic variation of the surfactant i.e. from non-ionic to cationic surfactants. With the combined effect of the hydrothermal conditions on the CTAB templated synthesis, uniform spherical particles with pores as large as 22 nm and surface area of ~ 1100 m^2/g have been obtained.

Mesoporous silica nanoparticles (MSN) are of immense importance owing to their high surface area, large pore size, uniform particle size and chemical inertness. In chapter 5 we discuss some of the applications associated with the mesoporous silica particles whose synthesis is discussed in the previous chapter. We have used the anisotropic silica nanostructures for DNA encapsulation studies and observed a loading capacity of ~ 8 $\mu g\ mg^{-1}$ of the sample. We have also used MSNs' as nanocontainer for the removal of aromatic dyes and have also been used for the controlled release of any molecule. We chose pyrene as our model molecule to study the release profile of the dye from the core of the silica mesostructures.

We have also looked into the possibilities of using the pores of the silica particles as the template for the synthesis of nanomaterials with the specific size and shape offered by the pore. Large surface area MSNs have been synthesized using the basic amino acid, arginine, acting both as the template and the hydrolyzing agent.

In chapter VI, nanoparticles of perovskite based manganese oxides have been synthesized using microemulsion method. The $RE^{3+}{}_{(1-x)}A^{2+}{}_{x}$ MnO_3-type manganites where R.E. = Pr, Nd and A= Sr have been synthesized, characterized and studied for its magnetic properties. The half doped manganites are important compositions owing to their charge ordering ~ (CO) effect, i.e. a regular arrangement of the Mn (III) and Mn (IV) species that are in equal amounts, below a certain temperature T_{CO} which coincides with T_N. A comparison to the properties exhibited by the bulk material, shows that the FMM transition gets pushed down to 265 K and the anti-ferromagnetic (AFM) transition at T_N = 150K disappears in the nanoparticles .