Abstract

In view of intrinsic fundamental interest and manifold technological applications we have undertaken a study on the synthesis, characterization and some important properties of a few selected first row transition metal oxide nanomaterials. Simple strategies under mild reaction condition afforded nanomaterials of various sizes and shapes. The content of entire thesis is distributed over six chapters.

Chapter-1 of the thesis presents a general introduction to the field of nanoscience and nanotechnology. How the properties of materials differ according to their size and in which respect a nanoparticle is more important than bulk material are discussed. Syntheses of transition metal oxide nanomaterials by various strategies are reviewed. A few specific applications of the nanostructured transition metal oxides are also mentioned in this chapter.

Chapter-2 of the thesis describes experimental methods, chemicals and materials, and details of the equipment used for physical measurements.

Chapter-3 of the thesis describes a low-temperature surfactant-assisted thermal decomposition strategy for the synthesis of some selected first row transition metal oxide nanomaterials. Various transition metal precursors like metal dicarboxylates, metal(II, III) acetylacetonates, metal(II) salicylates were thermally decomposed in the presence of surfactant stabilizers oleylamine, octadecylamine, and triphenylphosphine (TPP) under appropriate reaction conditions. Thermal decomposition of cobalt malonate in the presence of surfactants oleylamine and TPP resulted in monodispersed phase pure cubic Co$_3$O$_4$ nanoparticles. However, thermal decomposition of copper malonate gives rise to multiply twinned copper nanoparticles. The surfactant oleylamine, plays a two-
fold role - as reaction medium and stabilizer, which prevents oxidation of copper nanoparticles. Thermal decomposition of zinc malonate under identical reaction condition afforded photoluminescent zinc oxide (ZnO) nanoflowers. The band gap luminescence was observed at 354 nm (~3.50 eV) along with defect related blue emission at 450 nm (~2.75 eV). As the surface of the ZnO nanocrystals were capped with oleylamine a possible hole trapping effect of amine group is attributed for the blue emission. Thermal decomposition of cobalt and copper succinate resulted in cobalt oxide (mixture of CoO and Co₃O₄) and copper nanoparticles of various sizes and shapes. Thermal decomposition of zinc succinate however is incomplete at the experimental temperature. Thermal decomposition of cobalt(II) acetylacetonate in the presence of surfactant octadecylamine resulted in monodispersed phase pure cubic CoO solid nanoparallelepipeds of size 10-20 nm. Thermal decomposition of nickel(II) and copper(II) acetylacetonates resulted in nearly spherical Ni/NiO and Cu/Cu₂O nanoparticles. Thermal decomposition of zinc(II) acetylacetonate afforded ZnO nanorods of diameter 30 nm and length 200 nm. The obtained ZnO nanorods possess good optical and structural quality. Thermal decomposition of manganese(III), iron(III), and cobalt(III) acetylacetonates in the presence of surfactant octadecylamine successfully produced monodispersed phase pure Mn₃O₄, Fe₃O₄, and CoO nanoparticles of various shapes. Superparamagnetic NiO nanoparticles of sizes 5-15 nm were accessed via thermal decomposition of nickel(II) salicylate. Photoluminescent ZnO nanoparticles of sizes 5-10 nm were also accessed via thermal decomposition of zinc(II) salicylate. The surfactant stabilizers oleylamine and TPP plays a decisive role in controlling the growth of the particles and lowering the calcination temperature.
Chapter-4 of the thesis describes a modified sol-gel route for obtaining Co₃O₄ nanoparticles. The average crystallite sizes of Co₃O₄ were found to increase with the rise in calcination temperature. The as-synthesized Co₃O₄ nanoparticles exhibited a faceted morphology. This chapter also describes a low-temperature solid state thermal decomposition of bis(dimethylglyoximato)copper(II) complex as an access to cupric oxide (CuO) nanoparticles. The obtained CuO nanoparticles have been demonstrated to be a potent antioxidant.

Chapter-5 of the thesis describes synthesis of NiO and ZnO nanoparticles by a homogeneous chemical precipitation route in the presence of urea as precipitating agent. The obtained NiO and ZnO nanoparticles were found to be photoluminescent. Room temperature photoluminescence (PL) spectrum of NiO nanoparticles showed UV-emission band at 337 nm which is attributed to recombination of electrons in conduction band and holes in the valence band. The spectrum also showed a visible emission at 423 nm due to defects-related to deep level emission such as oxygen vacancies and Ni-interstitials. PL spectrum of ZnO nanoparticles showed a strong band at 384 nm arising from recombination of free excitons indicating the synthesized particles to be perfectly crystalline having low density of deep-level defects.

Chapter-6 includes a brief summary of the thesis.

At the end all References are collected in order of their appearance in the text. Finally a list of research publications emanating from the research are appended at the end alongwith the copies of published/accepted papers.