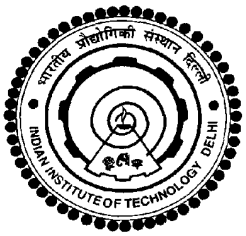
MICROEMULSION BASED SYNTHESIS OF BIMETALLIC ALLOY NANOPARTICLES: MAGNETIC AND ELECTRO-CATALYTIC PROPERTIES

JAHANGEER AHMED



DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
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by

JAHANGEER AHMED

Department of Chemistry

Submitted in accordance with the requirement for the Degree of Doctor of Philosophy

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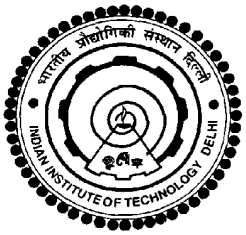

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

INDIA

DECEMBER, 2010

Dedicated
To
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CERTIFICATE

This is to certify that the thesis entitled, "**MICROEMULSION BASED SYNTHESIS OF BIMETALLIC ALLOY NANOPARTICLES: MAGNETIC AND ELECTRO-CATALYTIC PROPERTIES**", being submitted by Mr. Jahangeer Ahmed, 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 him. Mr. Jahangeer Ahmed 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.

Date :

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ABSTRACT

Nanomaterials are among the most challenging areas of current scientific and technological research because of interesting changes in their optical, magnetic, electrical and catalytic properties accompanied with improved physical properties like mechanical hardness, thermal stability or chemical passivity. Many physical properties of nanoparticles often differ drastically from those of bulk materials with the same chemical composition. At nanometer size, crystallites are influenced by the presence of significant number of surface atoms and by the quantum confinement effect of the electronic states and this influences the property of nanomaterials as compared to their bulk phases. Nanomaterials include metals, semiconductors, core-shell, alloy nanostructures and organic polymeric materials.

In chapter 1, a detailed survey of the background literature has been carried out for the state of knowledge existing in the area of alloy nanoparticles with interesting magnetic and electrochemical properties. We also discuss the synthesis of binary alloy nanoparticles using the microemulsion method and characterization techniques.

In chapter 2, we discuss the synthesis of cobalt (hcp and fcc) and cobalt-nickel (1:1) alloy nanoparticles by choosing appropriate microemulsion systems. Initially at room temperature the precursor was amorphous (observed from PXRD), this precursor when annealed in hydrogen atmosphere at 500°C for 5 hrs led to the formation of monophasic Co and Co-Ni (1:1) alloy nanoparticles. The PXRD pattern of Co – Ni alloy nanoparticles could be indexed on the basis of a face centered cubic unit cell. Microscopy studies show the formation of spherical nanoparticles of Co (hcp and fcc) and Co – Ni (1:1) alloy nanoparticles with the average size of 4, 8 and 20 nm respectively. The microemulsion

method thus stabilizes the hcp cobalt structures even at sizes (< 10 nm) at which normally fcc cobalt is predicted to be stable. On annealing the hcp cobalt nanoparticles in H_2 at 700°C we could transform them to fcc cobalt nanoparticles. Cobalt (hcp and fcc) and alloy (Co-Ni) nanoparticles show ferromagnetism at 4K. The saturation magnetization of Co-Ni nanoparticles is reduced compared to the bulk possibly due to surface oxidation. Electrochemical studies show that the catalytic property towards oxygen evolution is dependent on the applied voltage. At low voltage (less than 0.65 V) the Co (hexagonal) nanoparticles are superior to the alloy (Co-Ni) nanoparticles while above this voltage the alloy nanoparticles are more efficient catalysts.

In chapter 3, we discuss the microemulsion based synthesis, characterization, magnetic and electrocatalytic properties of binary Fe – Co alloy nanoparticles of varying stoichiometry. Initially the as-synthesized products (precursor for Fe – Co nanoparticles) were amorphous at room temperature. These precursors were annealed in hydrogen at 700°C for which led to the formation of pure crystalline nanoparticles of Fe – Co alloy and x-ray could be indexed on the basis of a body-centered cubic (bcc) unit cell. Microscopic studies show the formation of spherical, uniform and highly monodisperse nanoparticles of $Fe_{75}Co_{25}$, $Fe_{67}Co_{33}$, $Fe_{50}Co_{50}$ and $Fe_{33}Co_{67}$ with an average size of 20, 25, 10 and 40 nm respectively. These nanoparticles crystallize in body centered cubic cell. Higher cobalt content (x > 70 %) in the binary system of $Fe_{100-x} – Co_x$ led to formation of biphasic mixtures of hcp cobalt and bcc iron – cobalt alloy. Energy dispersive x-ray spectroscopy (EDS) studies confirmed the Fe/Co ratios. Nanoparticles of $Fe_{33}Co_{67}$ alloy show higher hydrogen and oxygen evolution efficiencies (over 100 times)

compared to other Fe-Co alloys of nanocrystalline or bulk form. The Fe-Co alloy nanoparticles also show ferromagnetism.

Chapter 4 deals with the characterization and properties (magnetic and electro-catalytic) of Cu-Ni (1:3, 1:1, 3:1) alloy nanoparticles synthesized using the microemulsion method followed by reduction in hydrogen atmosphere at 500°C. Powder x-ray diffraction patterns of Cu – Ni alloy nanoparticles could be indexed on the basis of a face centered cubic unit cell. Microscopic studies show nearly uniform, monodisperse and spherical nanoparticles with the size from 7 to 30 nm. XPS studies confirm the expected Cu/Ni ratios in these alloys. These bimetallic nanoparticles show ferromagnetic behavior and the magnetization decreases with increase in concentration of copper. Cu – Ni (1:1) alloy nanoparticles show better electro-catalytic efficiencies for hydrogen generation compared to the other nanocrystalline Co-Ni and Fe-Co compositions.

Chapter 5 describes the characterization and properties (magnetic and electro-catalytic) of fcc and bcc Fe – Ni alloy nanoparticles of varying stoichiometry synthesized by the microemulsion method using Triton X-100 and hydrazine and then further reduction in H_2 atmosphere at 500°C. The microemulsion method has been used by us for the first time for the synthesis of both fcc and bcc Fe – Ni alloy nanoparticles. Fe – Ni alloy nanoparticles ($Fe_{38}Ni_{62}$ and $Fe_{50}Ni_{50}$) crystallizes in the fcc structure while for higher Fe - content ($Fe_{64}Ni_{36}$ and $Fe_{75}Ni_{25}$) the bcc structure is stabilized. The average size of these nanoparticles lies from 18 to 50 nm. The formation of fcc and bcc structures Fe-Ni alloy nanoparticles have been confirmed from EDAX, electron diffraction (ED) and HRTEM studies. Iron rich nanoparticles of Fe-Ni alloy show higher hydrogen and oxygen

evolution efficiencies. The field dependent magnetization of these nanoparticles show ferromagnetism at 5K.

In chapter 6, we discuss the microemulsion based synthesis of an unusual core - shell (Cu-Co composite@Cu-Co alloy) nanostructures at 700°C in H_2. The core (dia ~100 nm) consists of Cu-Co composite particles while the shell (thickness ~20 nm) is composed of Cu-Co alloy particles. It is to be noted that in bulk Cu-Co binary system there is practically no miscibility. Microscopic studies show formation of uniform, monodisperse and spherical nanoparticles of core-shell structures. XPS studies have been used to confirm the composition of the core (Cu-Co composite) and shell (Cu-Co alloy). The formation of the Cu-Co alloy as the shell is mainly driven by surface energy considerations. We have also obtained Cu-Co nanocomposites (by controlling the concentration of reducing agent) with an average particle size of ~ 10 nm. These Cu-Co nanostructures show ferromagnetic behavior at 4K. The saturation magnetization of the core – shell (Cu-Co composite@Cu-Co alloy) nanostructure (125 emu/g) is found to be higher than that of pure Cu-Co nanocomposite or alloy, which may be useful for applications as soft magnet. Detailed electrochemical measurements have been carried out to establish the efficiency of this material as a catalyst for hydrogen evolution (greater than five times than any previous report using the same binary system).

Chapter 7 describes the microemulsion based synthesis and electrochemical studies of nanocrystalline copper nanoparticles with varying morphology, nanocubes (~ 50 nm), nanorods (diameter of ~ 3 nm and length of ~50 nm) and nanospheres (5 nm). Powder x-ray diffraction patterns of the above nanostructures could be indexed on the basis of face centered cubic unit cell. We have used the characterization techniques like powder X-ray

diffraction, high resolution transmission electron microscopy (HRTEM), and X-ray photoelectron spectroscopy (XPS) to characterize the copper nanostructures. The role of concentration in the self-assembly of nanoparticles in varying dimensionality has been brought out in this study. Copper nanoparticles are known to be efficient electro-catalysts for a variety of reactions. In addition, the ability of copper catalyst to generate hydrogen and oxygen in electrochemical reactions provided the impetus to understand size and shape dependence of such electro-catalytic reactions of copper in nanocrystalline form. Cube - shaped Cu nanoparticles show significantly high hydrogen and oxygen evolution efficiencies compared to the nanorods and spherical nanoparticles. The nanospheres show higher hydrogen and oxygen evolution efficiencies than the nanorods.

In annexure, we discuss investigations on the controlling the shape, size and crystal structures of calcium carbonate by optimizing the concentration, temperature and aging of the reaction in microemulsions. The process resulted in uniform micron-sized hexagonal plates (~1μm) of vaterite where 9.375 μmol of Ca^{2+} and CO_3^{2-} ions was used while at lower ionic concentration (0.625 μmol) cubes of calcite phase were obtained at 20°C. High magnification TEM images of the hexagonal plates show an assembly of spherical nanoparticles (~50 nm). The rod-shaped vaterite particles were obtained at 40°C at an optimal concentration. The length and diameter of the rods have been found to be ~250 nm and ~30 nm respectively using high resolution transmission electron microscope. The high pressure orthorhombic phase of calcium carbonate (aragonite) has been obtained at 40°C using 0.375 μmoles of Ca^{2+} and CO_3^{2-} ions, which normally crystallizes in the sea as abalone shells and as natural pearls. The aragonite phase undergoes morphological changes under higher temperatures with long Y-junctions (at

40°C) to shorter rod-like structures (at 85°C). Pure calcite is also obtained at higher reaction temperature (105°C) using the ionic concentration of 0.375 μmoles.

In chapter 8, we record our conclusions from this body of work and discuss the scope for further research in alloy nanostructures.

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