INVESTIGATION OF NANOSTRUCTURED METAL COBALTITES AND MANGANITES FOR ELECTROCATALYTIC AND MAGNETIC PROPERTIES

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by

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Submitted in fulfillment of the requirements of the Degree of

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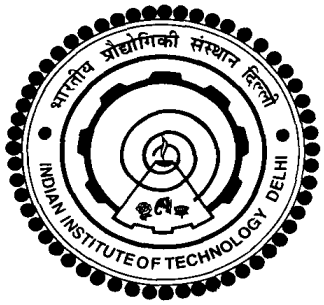

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INDIA

January 2016

Dedicated to

My Parents and My Husband

CERTIFICATE

This is to certify that the thesis entitled, **"Investigation of nanostructured metal cobaltites and manganites for electrocatalytic and magnetic properties"**, being submitted by **Mrs. Neha Garg**, 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. Mrs. Neha Garg 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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ABSTRACT

Growing environmental pollution and depleting energy resources are major issues in the present scenario. One of the prime reasons behind the arising environmental pollution is combustion of fossil fuels and their depletion. Therefore, the need of the hour has generated an extensive interest in researchers to develop technologies that provide clean, sustainable, cheap, renewable energy which are also environmentally benign. Electrochemical storage and conversion devices have attracted a great interest to solve these issues. Electrochemical water splitting reaction provides one of the efficient sources of renewable energy (Hydrogen evolution and oxygen evolution). Spinel based mixed transition metal oxides (MTMOs) is important for future energy requirements due to their low cost, high abundance and environmental friendly behavior. Electrocatalytic properties of the functional materials depend on the composition, structure, crystalline phase, and morphology (size and shape). Due to the presence of various cations with more than one oxidation state and unpaired electrons, cobaltite and manganite spinel nanostructures show interesting and highly tunable electrocatalytic properties. Although, various physical and chemical methodologies are known for synthesis of MTMOs, rational design of the efficient electrode material for effective electrochemical technologies is still a challenge.

Motivation of the present thesis is to develop alternate approaches for the synthesis of nanostructured spinel cobaltites and manganites with various morphologies. We focus on the development of an efficient electrocatalyst with controlled size, morphology, composition and structure. Nanostructured electrodes (with high surface/volume ratio, efficient electrochemical activities and cycling performance) have been synthesized using

hydrothermal, microemulsion and coprecipitation methods under ambient conditions. We have investigated various parameters that cooperatively enhance the electrocatalytic efficiency of the material. This thesis deals with the synthesis, characterization and properties of various shapes and size of cobaltites and manganites nanostructures and their properties suitable for electrochemical storage/conversion devices.

In chapter 1, a detailed review of the background literature has been carried out to know the existing research and the major challenges in the area of the available energy source and the materials especially manganites and cobaltites, which are useful for the electrochemical devices. We have also discussed the importance of the nanostructured cobaltites and manganites as efficient electrocatalyst. Although, various high temperature routes, physical and chemical methods known, rational design of the efficient electrode material is still a challenge. So, in this chapter we have discussed the methodologies used for obtaining cobaltites and manganites of controlled size and morphology for efficient electrocatalytic applications.

The controlled synthesis procedure for obtaining $NiCo_2O_4$ nanorods (assembled from small nanoparticles) with different aspect ratio has been discussed in **chapter 2**. To control the anisotropy of the $NiCo_2O_4$ nanorods, a surfactant mediated reverse micellar route was used. The effect of surfactants and non-polar phases was studied by varying the chain length of the co-surfactants. Cationic surfactant (CTAB) prefers the alignment of $NiCo_2O_4$ nanorods with high aspect ratio (~12) while non-ionic surfactant (Tergitol) led to the formation of much lower aspect ratio (~5) nanorods. We also investigated the electrocatalytic activity of the $NiCo_2O_4$ nanostructures towards oxygen evolution

reaction. The current work focuses to understand the effect of size of nanostructured electrode towards the electrochemical applications.

In **chapter 3**, we have discussed a template free hydrothermal route for the synthesis of $NiCo_2O_4$ nanostructures. Different morphologies of $NiCo_2O_4$, like square sheets, hexagonal sheets and spheres were synthesized by fine tuning the reaction conditions as well as the selection of the hydrolyzing agents. These synthetic parameters were studied in detail. Shape dependent electrocatalytic study showed significant electrochemical behavior with improved supercapacitance as well as good electrocatalytic properties towards oxygen evolution reaction. Studies showed the enhanced efficiency of $NiCo_2O_4$ square sheets with enhanced stability.

In **chapter 4**, the role of the surfactant, co-surfactant and non-polar phase during the synthesis of $NiMn_2O_4$ nanospheres and hexagonal particles using the reverse micellar route are discussed. Slow decomposition of the oxalate precursor (aspect ratio > 3) is the key to maintain the anisotropic morphology of the oxide $NiMn_2O_4$ nanorods (assembled with smaller nanoparticles). Cationic surfactants lead to anisotropic growth while non-ionic surfactant preferred isotropic growth of nanostructures. The detailed magnetic properties of the above have been studied.

Chapter 5 highlights, the methodology used for the synthesis of novel Mg and Cd based manganites (Mg_2MnO_4 and $CdMn_2O_4$) under ambient conditions. Mg_2MnO_4 nanorods (assembled from small nanoparticles) have been synthesized using reverse micellar route while $CdMn_2O_4$ nanocubes have been obtained via a facile co-precipitation route at room temperature. Electrochemical studies showed that Mg_2MnO_4 nanorods act as efficient

electrode towards oxygen evolution reaction and $CdMn_2O_4$ nanocubes show good anodic behavior towards Li-ion battery applications.

In **chapter 6**, we have discussed composition and phase dependent electrochemical behavior of cobalt manganite nanostructures. The chapter focuses on synthesis of two distinct phases, cubic Co_2MnO_4 and tetragonal $CoMn_2O_4$ using a simple hydrothermal method without any further annealing. Cubic Co_2MnO_4 nanocubes show efficient electrochemical behavior towards oxygen reduction reaction while tetragonal $CoMn_2O_4$ nanocubes show better performance towards oxygen evolution reaction (OER) than Co_2MnO_4.

Conclusions and future prospects of the work carried out are described in **chapter 7**. The thesis has led to the development of low temperature methodologies using co-precipitation, microemulsion route and hydrothermal mediated precursors to obtain various morphologies of nanostructured cobaltites and manganites. Various factors that affect the electrochemical performance have been studied in this thesis and the above study can be extended to a detailed study of the growth controlling parameters for various morphologies of spinel cobaltites and manganites.

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Abbreviations and Symbols

Å	Angstroms
^{o}C	Centigrade
μm	Micrometer
nm	Nanometer
T	Temperature
T_N	Neel Temperature
Tc	Curie Temperature
τ_N	Néel Relaxation Time
T_B	Blocking Temperature
K	Kelvin
°	Degree
Hz	Hertz
2θ	Two Theta
λ	Wavelength
cP	Centipoise
eV	Electron volt
ECs	Electrochemical Capacitors
LIBs	Lithium-ion Batteries
MOBs	Metal Oxide Batteries
FCs	Fuel Cells
RM	Reverse Micelle

MTMOs Mixed Transition Metal Oxides

CTAB Cetyltrimethylammonium bromide

XRD X-ray Diffraction

PXRD Powder X-ray Diffraction

TGA Thermogravimetric Analysis

DTA Differential Thermal Analysis

FT IR Fourier Transform Infrared Spectroscopy

FESEM Field Emission Scanning Electron Microscopy

TEM Transmission Electron Microscopy

HRTEM High Resolution Transmission Electron Microscopy

ED Electron diffraction

EDAX Energy Dispersive X-ray Analysis

BET Brunauer-Emmett-Teller

XPS X-ray Photoelectron Spectroscopy

CV Cyclic Voltammetry

LSV Linear Sweep Voltammetry

μ Magnetic Moment

H Magnetic Field

μ_B Bohr-Magneton

M Magnetization

χ_m Molar Magnetic Susceptibility

χ_m^{-1} Inverse Molar Magnetic Susceptibility

Ms Saturation Magnetization

Mr	Remnant Magnetization
Oe	Oersted
emu	Electromagnetic Unit
vs.	Versus
J	Current Density
H	Applied Field
eq.	Equation
°C	Centigrade
μm	Micrometer
nm	Nanometer
mm	Millimetres
min	Minutes
h	Hours
s	Seconds
NHE	Normal Hydrogen Electrode
HER	Hydrogen Evolution Reaction
OER	Oxygen Evolution Reaction