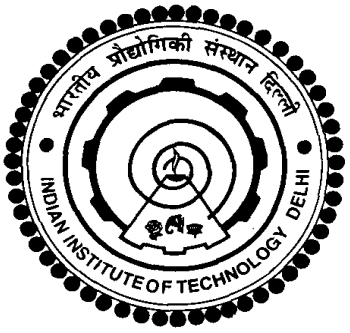
METAL AND METAL OXIDE NANOCOMPOSITES FOR EFFICIENT ELECTROCATALYTIC AND MAGNETIC PROPERTIES

BHARAT KUMAR



DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

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MAY, 2015

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By

BHARAT KUMAR

Department of Chemistry

Submitted in fulfillment of the requirements for the Degree of Doctor of Philosophy

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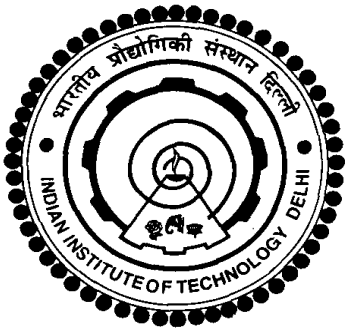

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MAY, 2015

Dedicated to my

Parents and

Supervisor

CERTIFICATE

This is to certify that the thesis entitled, **"Metal and metal oxide nanocomposites for efficient electrocatalytic and magnetic properties"** being submitted by **Mr. Bharat Kumar** 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. Bharat Kumar 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:

Professor A. K. Ganguli

Department of Chemistry

Indian Institute of Technology, Delhi

New Delhi – 110016, INDIA

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ABSTRACT

Energy resources and environmental issues are the two important topics of concern at present global level scenario. To effectively address these issues, there has been extensive research for technologies that provide energy and help in environmental remediation that is a renewable, safe, clean, cheap and viable alternative to fossil fuels. To meet the energy demand, materials are designed to capture solar energy and new renewable energy. It is universally accepted that hydrogen is one of the best energy source because it can be used as clean fuel (by product is H_2O) in a variety of energy sectors including the conversion to electricity without CO_2 emission, producing CH_4 by absorbing CO_2 from the environment. One of the potential ways to combat these present energy and environmental crises will be electrocatalysis and photocatalysis. Water splitting reaction, hydrogen evolution reaction (HER) and oxygen evolution reaction has been a growing interest in search of materials with electrocatalytic and photocatalytic properties. Metal and metal oxides based electrocatalyst & photocatalysts have been proven to be potentially advantageous for splitting of water to supply clean and recyclable hydrogen energy as well as environmental pollutant remediation for complete decomposition of organic compounds into H_2O and CO_2 at ambient conditions. Also, the magnetic nanostructured materials are of intense interest due to their potential use in magnetic resonance imaging, biomedicine, data storage and environmental remediation. The new materials are being explored and examined in order to meet all these requirements for electrocatalytic and magnetic applications.

The design of nanostructured metal and metal oxide based materials has become one of the most challenging fields of nanoscience and technology due to its unique properties and important applications in catalysis, electronics and photonic devices. Due to the small sizes

and large surface area, of nanosized materials are known to have unique features in high reactivity and enhanced catalytic activity.

So, the motivation of the present thesis is to develop alternate approaches for the synthesis of nanostructured metal, metal oxide and their nanocomposites to investigate their electrocatalytic properties and to establish factors influencing the efficiency of catalysis. The magnetic properties of materials have importance in magnetic resonance imaging, biomedicine, data storage and environmental remediation.

In the present investigation, we focus our study on the enhancement of the efficiency of electrocatalysts and magnetic materials (metal, metal oxide and composites) with the control of size, morphological features, and surface area by increasing the surface/volume ratio. These nanomaterials were synthesized by coprecipitation, hydrothermal and microemulsion methods under varying reaction conditions. Such size and shape tunable materials have the potential to enhance the production of hydrogen and oxygen as well as magnetic properties. This thesis deals with the synthesis, characterization, electrocatalytic (HER & OER) and magnetic properties of various metal, metal oxide nanostructures and composites.

Chapter 1 deals with the detailed survey of the literature background of metal and metal oxide in the area relevant interesting electrocatalytic and magnetic properties. We also discuss various possibilities of synthetic process for obtaining metal, metal oxide in bulk as well as nano regime. The details of characterization techniques, basics of electrocatalytic (HER & OER), magnetic and photocatalytic properties have been discussed.

In chapter 2, copper oxalate nanorods were synthesized by modified microemulsion method. Using copper oxalate and CuO, we have synthesized Cu, Cu_2O nanoparticles and Cu/Cu_2O nanocomposites at 350 °C. These materials were characterized with various

characterization techniques such as FESEM, TEM and XPS. The hydrogen and oxygen evolution reaction have been carried out using these electrocatalysts in which Cu/Cu_2O nanocomposites are more efficient than Cu & Cu_2O for HER as well as OER. These electrocatalyst are very stable over 50 cycles of electrocatalysis. Photocatalytic degradation of Methylene blue is also carried out by using Cu_2O which show 98 % degradation of Methylene blue dye in visible light.

Chapter 3 deals with the morphology based synthesis of Cu/Cu_2O nanocomposites by one step hydrothermal method at different reaction times (24, 72, 120 h). The study of role of reaction time is to see the effect on growth of particles inside the hydrothermal reaction as well as on the reduction of Cu^{2+} to Cu^{+} & Cu^{0}. The TEM studies show the morphology varying from nanorods at higher reaction time to agglomerated nanoparticles at lower reaction time. The nanorods shape Cu/Cu_2O nanocomposites produce higher current in hydrogen & oxygen evolution reaction (amount of H_2 and O_2) as compared to assemble nanoparticles (72 h) and agglomerated (24 h) nanoparticles. Sonogashira cross couple product was also higher in case of rod shaped morphology.

In chapter 4, the synthesis nano-micron (n-μ) composites of CuO by mixing of the micron sized CuO and copper oxalate at 350 °C and their characterization by powder X-ray diffraction, diffuse reflectance spectroscopy, transmission electron microscopy and surface area measurements along with hydrogen evolution reaction and magnetic properties have been discussed. It was observed that pure nano sized particles produce more current density as compared to pure micron sized particles and nano-micron composites due to more surface area and alignment of the nanoparticles. The highest and lowest magnetizations were found for pure nano and micron sized CuO respectively.

In chapter 5, the synthesis of Co nanoparticles (from cobalt oxalate obtained by reverse micellar method) with varying size and their electrocatalytic & magnetic properties is discussed. It is observed that as the heating rate was slower, the size of nanoparticles was smaller which produce more H_2 and O_2 due to higher surface area (more active site) as compared to higher heating rate synthesis methodology. The magnetization value was the opposite. The smaller size of nanoparticles has lower saturation magnetization value.

In chapter 6, we discuss about the synthesis of $BaTiO_3$ obtained by hydrothermal route and $CoFe_2O_4$ by coprecipitation as well as by hydrothermal route. The heterostructures of $BaTiO_3$@$CoFe_2O_4$ were synthesized by four different reaction protocols and it named as CS1, CS2, CS3 and CS4. The TEM study shows the variation of morphology as well as particles size of the above synthesized materials. The magnetic study of these $CoFe_2O_4$ nanoparticles and heterostructures of $BaTiO_3$@$CoFe_2O_4$ was carried out which show the ferromagnetic behavior at 100 as well 300 K. The coercivity, saturation magnetization and remnant magnetization of these materials were calculated and compared with each other. CS4 have lowest coercive field value at 100 and 300 K whereas the CS3 has the highest magnetization value.

Chapter 7 discusses the synthesis of nano-micron (n-μ) composites of $La_{0.82}Sr_{0.18}MnO_3$ by mixing the micron sized $La_{0.82}Sr_{0.18}MnO_3$ and nano sized $La_{0.82}Sr_{0.18}MnO_3$ at 1200 °C in air. The density of these nano-micron composites was found to be 95 to 99 % of the theoretical density. The entire series of the $La_{0.82}Sr_{0.18}MnO_3$ shows ferromagnetic behavior. The enhancement in the saturation magnetization (30%) is observed on addition of~ 1.0 weight percent of nanoparticles of $La_{0.82}Sr_{0.18}MnO_3$ to micron-size $La_{0.82}Sr_{0.18}MnO_3$.

In Chapter 8, conclusions and future prospects of the work described in the thesis have been discussed. The low temperature methodologies have been developed using microemulsion and hydrothermal mediated precursors to obtain various morphologies of nanostructured metal and metal oxide based materials. The synthesis temperature was lowered by 200ºC to 400ºC in metal and metal oxides by the above reaction protocol.

We suggest metal and metal oxide system which may be pursued for both basic scientific interest and attractive applications in near future. These nanomaterials have sufficient research interest to a variety of researchers working on fuel cells, batteries, nanocapacitors, memory devices etc.

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Abbreviations and Symbols

Å	Angstroms
°C	Centigrade
μm	Micrometer
nm	Nanometer
min	Minutes
h	Hours
s	Seconds
μE	Microemulsion
PXRD	Powder X-ray diffraction
TEM	Transmission Electron Microscopy
HRTEM	High Resolution Transmission Electron Microscopy
FESEM	Field Emission Scanning Electron Microscopy
EDAX	Energy Dispersive X-ray Analysis
DRS	Diffuse reflectance spectroscopy
BET	Brunauer – Emmett – Teller
VB	Valence band
CB	Conduction band
NHE	Normal hydrogen electrode
CTAB	Cetyl trimethylammonium bromide
UV-vis	Ultraviolet -visible
MB	Methylene blue
Ms	Saturation Magnetization
Mr	Remnant Magnetization

Oe	Oersted
HER	Hydrogen evolution reaction
OER	Oxygen evolution reaction
ESA	Electroactive surface area
emu	Electro magnetic unit