Metal Organic Materials Derived Nanostructures for Energy Conversion and Storage Applications

A Thesis

submitted by

Bandhana Devi

(D15035)

for the award of the degree of

Doctor of Philosophy

SCHOOL OF BASIC SCIENCES
INDIAN INSTITUTE OF TECHNOLOGY, MANDI
Mandi, Himachal Pradesh, 175005.

Dedicated to

Maa Sukrala Devi Ji

And My Husband

INDIAN INSTITUTE OF TECHNOLOGY MANDI
MANDI-175005 (H.P.), INDIA
www.iitmandi.ac.in

Declaration by the Research Scholar

I hereby declare that the entire work personified in this thesis entitled**, "Metal Organic Materials Derived Nanostructures for Energy Conversion and Storage Applications"** is the result of investigations carried out by me in the School of Basic Sciences, Indian Institute of Technology Mandi, under the supervision of **Dr. Aditi Halder (Guide) and Dr. Rik Rani Koner (Co-Guide**) for the award of the degree of **Doctor of Philosophy** and that it has not been submitted elsewhere for any degree or diploma. In keeping with the general practice, due acknowledgements have been made wherever the work described is based on findings of other investigators.

Place: Mandi

Signature:

Date:

Name: **Bandhana Devi**

INDIAN INSTITUTE OF TECHNOLOGY MANDI
MANDI-175005 (H.P.), INDIA
www.iitmandi.ac.in

Declaration by the Research Advisor

I hereby certify that the entire work in this thesis titled, **"Metal Organic Materials Derived Nanostructures for Energy Conversion and Storage Applications"** has been carried out by **Bandhana Devi** under our supervision in the **School of Basic Sciences**, Indian Institute of Technology Mandi for the award of the degree of **Doctor of Philosophy** and that no part of it has been submitted elsewhere for any degree or diploma.

Signature:

Name of the Guide: **Dr. Aditi Halder**
Associate Professor
School of Basic Sciences
Indian Institute of Technology, Mandi
Mandi (H.P.), 175005

Date:

Signature:

Name of the Co-Guide: **Dr. Rik Rani koner**
Associate Professor
School of Engineering
Indian Institute of Technology, Mandi
Mandi (H.P.), 175005

Date:

Acknowledgements

Writing this thesis entitled "***Metal Organic Materials Derived Nanostructures for Energy Conversion and Storage Applications***" marks the successful culmination of a long campaign characterized as scholarly work that was started in July 2015 and has finally been accomplished, not all by my endeavours. There were many seen and unseen hands who pushed me forward, put me on the right path and enlightened me with their knowledge and experience. This page is a heartfelt acknowledgement to those people who helped me in one or other way in this entire journey of Ph.D.

At the very outset, I would like to thank Almighty from the core of my heart for bestowing endless blessings upon me to carry out my research work successfully as no work is accomplished without His grace and guidance.

I express my deep gratitude to my supervisors Dr. Aditi Halder and Dr. Rik Rani Koner for their supervision and guidance. Their continuous support, immense knowledge, tireless efforts and constant motivation helped me to complete my Ph.D. research work within stipulated time. I am fortunate enough to have their teaching about how to cultivate scientific thoughts.

I am grateful to Director, IIT Mandi for his support and encouragement to all research scholars. I also wish to acknowledge the members of my doctoral committee, Dr. Venkata Krishnan, Dr. Subrata Ghosh, Dr. Pradeep Parmeswaran, and Dr. Viswanath Balakrishnan for their critical appraise of my research work, invaluable comments and insights which made a deep impact on my research.

The research facility at Advanced Materials Research Centre (AMRC) is gratefully acknowledged. My wholehearted thanks to all members of AMRC staff for their assistance in lab work. I am also thankful to the library staff for the help, whenever it was needed.

I wish to acknowledge my seniors at IIT Mandi, Mangili Venkataswarulu, Himmat Singh Kushwaha, Pawan Kumar and Davender Kumar who helped me in my research work during its initial phase. I would like to acknowledge my labmates and friends, Mohammad Saquib, Ankita Mathur, Lalita Sharma, Ravinder Kaushik, Chetna Madan, Harpreet Kaur, Trivender Kumar, Biswajit Roy, Piyush Avasthi, Divya Verma, Deepa Thakur, Nitika Arya, Diksha Gambhir, Naggaraju Nakka, Moolchand Sharma, Ashish Bhatia and Ajay Thakur. I learnt from you all, both professionally and personally.

I wish to acknowledge Dr. Sumit Sinha Ray, Dr. Narsa Reddy Tummuru, Ashish Kakoria and Bhaskara Rao for collaboration. I also acknowledge Dr. Ankush Bag for helping us in our experimental work.

I like to acknowledge Puneet Sood for his help during solving of crystal structures of our compounds. I also acknowledge the staff members, Arjun, Satuti, Anoop Kumar, Pratik Pathania, Sushma, Rakhi Verma, Soniya Gupta and Alka Thakur for their helpful and supporting attitude.

I would like to express my wholehearted gratitude to Ministry of Human Resource Department (MHRD), India for the fellowship during my journey of Ph.D.

I would like to thank my friends, Sumiti Sharma and Priyanka Khandelwal for their selfless support as true friends. Thankyou Sumiti for always helping me in my difficult times.

Last but not least, I would like to share my deep eternal gratitude to my parents and in-laws family. I manifest special thanks to my mother who holds a very high place in my life for teaching me deep morality, discipline, respect to hard work and willingness to make efforts without which I would not have found myself in the current place. I also thank my maternal grandmother who is the most influencing person in my life. Thank you for your unconditional love, wisdom, deep patience, endless blessings and unwavering faith in me. I would like to

mention my mother-in-law, Shanti Devi Ji who is in Heavenly world and always shower her blessings upon us. A special mention goes to my sister-in-law's, Veena Devi and Pooja Devi who are like my own sisters. Thank you, Veena dee for spending tough days with me in IIT campus during my thesis writing.

I would like to express my warm words of gratitude to my husband, Kulbir Singh who motivated me to start and then supported me throughout this journey, taught me to be a strong person, helped me to balance my academic and personal life. Thank you for being so selfless, wise and strong to bear all the responsibilities, which I would like to share with you in future. A special thanks goes to my son, Dhiren Singh. Your twinkling eyes, eternal smile and innocence make me forget all my tiredness and worries. You have made me stronger and more responsible than I was before.

Bandhana Devi

Preamble

The increasing population of the world and decreasing fossil fuel reserves have put a lot of focus on renewable energy sources. Energy conversion systems like fuel cell and energy storage system like supercapacitors have carved an important niche in energy field with a lot of scope for improvement. The development of nanomaterials with dual application for energy conversion as well as energy storage will decrease the energy loss and increase the overall energy efficiency. Metal organic materials (MOMs) which include metal organic frameworks, metal organic gels and coordination polymers are very important class of hybrid materials having potential of energy conversion and energy storage application. These hybrid materials can act as a template for generating various kinds of heterostructures like metal/carbon, metal oxide/carbon, metal/metal oxide/carbon with favourable heteroatom doping of N, O, P etc. In addition, these developed heterostructures do not require external conductive substrate like Vulcan carbon because of in-situ graphitization which adds to their long-term stability and durability for concerned energy processes. In this direction, we synthesized some new MOMs derived nanostructures and explored their application for energy conversion (electrocatalysis) and energy storage (supercapacitors). The complete chapter wise thesis overview has been given below:

Chapter 1 describes the general overview of energy conversion and energy storage devices and their importance in daily life. The energy conversion system includes the detailed explanation about fuel cell and electrolyzer, their importance, advantages, drawbacks and various parameters required for their improvement in practical applications. Energy storage devices like supercapacitors, their types, advantages and current requirements for improvement have also been explained. Then synthesis techniques for MOMs, importance of pyrolysis and application of MOM derived nanomaterials for energy conversion as well as energy storage

have been explained. The need for dual application in energy conversion as well as energy storage has been highlighted.

Chapter 2 begins with the synthesis of a new iron containing metal organic gel, its conversion into xerogel which acts as a precursor for synthesis of a bifunctional nanocomposite (Fe_3O_4/Fe/C). The synthesized nanocomposite was found to have dual application for electrocatalysis (ORR) and energy storage (supercapacitor).

Chapter 3 shows the synthesis of a new Ni based dimeric complex and generation of a trifunctional electrocatalyst from this dimeric complex by optimizing the annealing/pyrolysis conditions. The synthesized electrocatalyst Ni-NC700 showed highly efficient electrocatalytic activity for oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). The excellent durability and stability of Ni-NC700 catalyst has been explained and also compared with the state-of-the-art catalyst i.e. Pt/C for ORR and HER and RuO_2 for OER.

Chapter 4 continues with the synthesis of a new Co based MOF containing 1,3, 5-trimesic acid and 1,10-phenanthroline. This MOF was used as a precursor for synthesis of Co-NC3 nanostructure by optimizing the pyrolysis conditions. Co-MOF was pyrolyzed at 700 °C for duration of 1 h, 3 h and 5 h. The obtained Co-NC3 (annealing at 700 °C for 3 h) showed highly efficient ORR activity comparable to commercial 20 wt.% Pt/C. The same was also explored for supercapacitor application. As a proof of concept, solid state supercapacitor device was assembled showing application in glowing of light emitting diode (LED). The device was also used for wireless sensor node application.

Chapter 5 describes the synthesis of a new lanthanide (Dy) based coordination polymer and its application for oxygen reduction reaction has been explored. Optimized pyrolysis process (800 °C, Ar, 1 h) was used for formation of a porous nanostructure (Dy_2O_3/C) which was

represented as Dy-800. Role of graphitization in enhancement of ORR activity has been studied. The ORR activity of self-supported annealed sample has been compared with the parent coordination polymer using Vulcan carbon as a support, in order to justify the role of annealing for enhancing the durability of the catalyst.

Chapter 6 This is the last chapter which includes the overall summary and conclusion of the research work explained above with focus on its importance and applicability in day to day life. This research work is expected to be useful in the field of energy conversion and energy storage especially in the development of devices involving multifunctional application. The following publications are related to the research work shown in this thesis:

Publications:

1. **B. Devi**, R. R. Koner and A. Halder "A dysprosium based new coordination polymer and its application towards the oxygen reduction reaction" ***New Journal of Chemistry,*** 2017, 41(16), 7972-7979.
2. **B. Devi**, M. Venkateswarulu, H. S. Kushwaha, A. Halder and R. R. Koner "A PolyCarboxyl Decorated Fe^{III} -Based Xerogel -Derived Multifunctional Composite (Fe_3O_4/Fe/C) as an Efficient Electrode Material towards Oxygen Reduction Reaction and Supercapacitor Application" ***Chemistry A European Journal,*** 2018, 24(25), 6586-6594.
3. **B. Devi**, R. R. Koner and A. Halder "Ni (II) -Dimeric Complex -Derived Nitrogen -Doped Graphitized Carbon -Encapsulated Nickel Nanoparticles: Efficient Trifunctional Catalyst for Oxygen Reduction Reaction, Oxygen Evolution Reaction and Hydrogen Evolution Reaction" ***ACS sustainable chemistry and Engineering,*** 2019, 7(2), 2187-2199.

4. **B. Devi**, A. Jain, B. Roy, B. Rao, N. R. Tummuru, A. Halder and R. R. Koner "Cobalt -Embedded N-Doped Carbon Nanostructures for Oxygen Reduction and Supercapacitor Applications" ***ACS Applied Nanomaterials***, 2020, DOI: 10.1021/acsanm.0c00732.

Other Publications:

1. A. Kakoria, **B. Devi**, A. Anand, A. Halder, R. R. Koner and S. S. Ray "Gallium Oxide Nanofibers for Hydrogen Evolution and Oxygen Reduction***" ACS Applied Nanomaterials,*** 2019, 2, 64-74.
2. S. Singh, S. Moun, **B. Devi**, R. R. Koner, A. Halder and C. S. Yadav "Field induced single molecule magnet behavior in Dy-based coordination polymer" ***Europhysics Letters***, 2020, 130, 47002.
3. M. R. Mulay, **B. Devi**, A. Mathur and A. Halder "Flax Meal Assisted Controlled Green Synthesis of Nanostructured Nickel Ferrite as Durable Bi-functional Oxygen Electrocatalyst" **(Under preparation)**.
4. **B. Devi**, P. K. Samal, V. Thakur and A. Halder "Walnut shell derived Activated Carbon- Polyaniline Porous Nanocomposite for Supercapacitors" **(Under Preparation)**.

Table of Contents