

# **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**



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*Dedicated to*  
*Maa Sukrala Devi Ji*  
*And My Husband*





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**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.

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**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.

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## *Preamble*

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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 ( $\text{Fe}_3\text{O}_4/\text{Fe}/\text{C}$ ). 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  $\text{RuO}_2$  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 ( $\text{Dy}_2\text{O}_3/\text{C}$ ) 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<sup>III</sup> -Based Xerogel -Derived Multifunctional Composite (Fe<sub>3</sub>O<sub>4</sub>/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**).

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