# Photocatalytic and Electrocatalytic Investigations on Perovskite-based Catalysts for Energy and Environmental Applications

*A Thesis*

Submitted

by

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**(D12081)**

For the award of the degree of

**Doctor of Philosophy**


**SCHOOL OF ENGINEERING**

**INDIAN INSTITUTE OF TECHNOLOGY MANDI**

**Mandi, Himachal Pradesh -175005**

**June, 2017**

Dedicated to

My Parents

## Declaration by the Research Scholar

I hereby declare that the entire work embodied in this thesis entitled "**Photocatalytic and Electrocatalytic Investigations on Perovskite-based Catalysts for Energy and Environmental Applications**" is the result of investigations carried out by me in the **School of Engineering**, Indian Institute of Technology Mandi, under the supervision of **Dr. Rahul Vaish** for the award of the degree of **Doctor of Philosophy** is a bona fide record of the research work carried out by me 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 finding of other investigators.

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## Thesis Certificate

I hereby certify that the entire work in this thesis titled "**Photocatalytic and Electrocatalytic Investigations on Perovskite-based Catalysts for Energy and Environmental Applications**" has been carried out by **Himmat Singh Kushwaha**, under my supervision in the **School of Engineering,** Indian Institute of Technology Mandi for the award of the degree **Doctor of Philosophy**. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

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# *Preamble*

A sustainable energy supply and environmental protection are two of the most important issues in the development of our future world. Photocatalysis and electrocatalysis are two of the most important routes for the green energy production and degradation of organic waste in water into harmless substances. Perovskite are the second most important class of electronic materials after semiconductors and are slowly gaining momentum in various novel applications. This has allowed them to break free of the traditional applications of actuators and sensors to novel technologies like solar energy harvesting, wastewater treatment and fuel cell catalysts. The perovskites materials can be an efficient catalyst for wastewater treatment and energy generation using fuel cells. These kind of materials have unique tunable properties like wide absorption spectra, low band gap and oxygen deficiency which support in efficient photocatalysis and electrocatalysis process. Another successfully approach to improve the stability of catalysts can be perovskite derived polymer and glass composites. In this regards, this study attempts to shed light on the photocatalytic and electrocatalytic investigation of $CaCu_3Ti_4O_{12}$ (CCTO) perovskites for pharmaceutical wastewater treatment and alkaline fuel cells.

**Chapter 2** begins with detailed explanation of fabrication techniques for CCTO perovskite catalysts and their characterization. The photocatalytic, electrocatalytic and photoelectrocatalytic properties have been investigated for different kind of pharmceutical wastewater pollutants.

**Chapter 3** is followed by synthesis and characterization of polyaniline-CCTO composites. The photocatalytic efficiency of synthesized polymer composites has

been investigated for methyl orange and Congo red degradation. The stability and reusability of the catalysts has been studied for the similar system.

**Chapter 4** continues with fabrication of xCCTO- (1-x) $TeO_2$ glass ceramic plates. The photocatalytic activity of fabricated glass plates has been investigated for estrogenic pollutants removal and hydrogen production under visible light irradiation. The self cleaning ability of CCTO-$TeO_2$ glass ceramic has also been analyzed.

**Chapter 5 demonstrates** the bifunctional electrocatalytic behavior of CCTO perovskite in alkaline fuel cell. We have investigated the potential of CCTO electrocatalyst for oxygen reduction and evolution reaction in alkaline fuel cell. Hydrodynamic studies have been performed to study the oxygen reduction reaction mechanism and quantification of generated radicals.

**Chapter 6** describes the role of the ferroelectric polarization to improve the electrocatalytic performance of ferroelectric perovskite. $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) was selected to investigate the effect of ferroelectric polling on oxygen evolution reaction (OER) involve in alkaline fuel cells. This chapter demonstrates that the ferroelectric polarization can be a constructive approach to improve the performance of electrocatalysts in a fuel cell, solar cells and energy storage beyond the limitation of chemistry and structure optimization.

The thesis concludes by summarizing the key findings of the investigation and highlighting the best results obtained during individual studies. This research is expected to greatly benefit the field of photocatalysis and electrocatalysis and to expedite the development of cost effective systems for wastewater treatment and energy generation. The following publications are largely based on the studies conducted as a part of the research work reported over here.

1. H. S. Kushwaha, N. A Madhar, B. Ilahi, P. Thomas, Aditi Halder, **Rahul Vaish**, "Efficient solar energy conversion using $CaCu_3Ti_4O_{12}$ photoanode for photocatalysis and photoelectrocatalysis" ***Nature Scientific Reports*** **6**, 18557 (2016).
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**Other publications include:**

1. Monisha Rastogi, A.Chauhan, H.S.Kushwaha, RV Kumar and Rahul Vaish "Reaping the benefits of ferroelectricity in selectively precipitated lithium niobate microcrystals in silica matrix for photocatalysis" ***Applied Physics Letters*** **109 (22), (2016)**

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