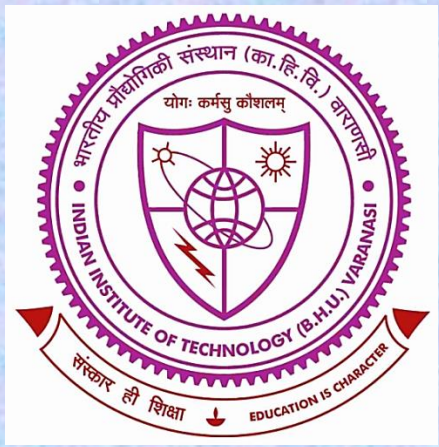
Synthesis of Co-Pd-Si nanocomposite and its Application in Oxygen Evolution Reaction



Thesis submitted in partial fulfillment for the Award of Degree

DOCTOR OF PHILOSOPHY

By

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It is certified that the work contained in the thesis titled **"Synthesis of Co-Pd-Si nanocomposite and its Application in Oxygen Evolution Reaction"** by **Chitra Singh** has been carried out under my supervision and this work has not been submitted elsewhere for a degree.

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DECLARATION BY THE CANDIDATE

I, **"Chitra Singh"**, certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of **"Prof. P. C. Pandey"** from **"July-2019"** to **"June-2024,"** at the **Department of Chemistry, Indian Institute of Technology, (BHU), Varanasi**. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not wilfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, theses, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

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ACKNOWLEDGEMENTS

*I take this opportunity to express my deep sense of gratitude to my supervisor "**Prof. P. C. Pandey**", for his scrupulous guidance and whole-hearted cooperation in carrying out this work. His meticulous and valuable review and constructive criticism of the manuscript have greatly improved the quality of work. Sir, for your faith in me and the desire to live up to your expectations, has constantly pushed me to work harder.*

*My grateful appreciation also goes to "**Prof. Y. C. Sharma**", Department of Chemistry, IIT (BHU), Varanasi, "**Prof. Sushant Kumar Shrivastava**" , Pharmaceutical Medicinal and Computational chemistry, IIT (BHU), for serving on my research progress evaluation committee (RPEC). Thank you all for sparing your valuable time and assisting me throughout my research and completion of this thesis.*

*I wish to extend my sincere thanks to "**Prof. Sundaram Singh**" (Head) and "**Prof. Y.C. Sharma**" (former Head) of Department of Chemistry, IIT (BHU), Varanasi for providing me the necessary resources to enable me to complete this research work. I am also thankful to my thesis coordinator **Dr. Prabhat Tripathi** and all the teaching and non-teaching staffs of Department of Chemistry IIT (BHU) for their kind support and for extending all required facilities to carry out my research work smoothly.*

*I am thankful and indebted to **UGC-JRF** for providing me financial support during my research work. I gratefully acknowledge the facilities provided by **CIFC, IIT (BHU)**, Varanasi for doing various characterizations of samples.*

I want to thank my colleagues at IIT (BHU) Varanasi, especially Mrs Maneesha Pandey, Mr. Kulveer, Mr. Kuldeep, Ms Khushboo Rajput, Mrs Neha Kamal, Ms Vartika Verma , Ms Sunita , Ankita Sharma for encouraging me to finish this work.

I would like to express my deepest affection to my Brothers, ***" Herjindra Singh, Balvindra Singh,*** *and* ***Parvendra singh" ,*** *Sister in laws* ***Mrs Neetu Singh*** *and* ***Reeta Singh*** *and Nephew* ***Devraj Singh*** *and* ***Dhanraj Singh*** *for their love, concern, continuous moral support and encouragement which enabled me to perform my liabilities without any reservations.*

I would like to acknowledge ***MY PARENTS, "Smt. Prakasho Devi"*** *and* ***"Mr. Chhatrapal Singh,"*** *for not engaging me in any other affairs during my research duration and handling all the matters by themselves. I thank my father for assisting me financially whenever needed and motivating me for my work.*

I would also like to thank ***GOD*** *the Almighty for giving me the strength to remain on the path to success.*

Date:

Place: **(Chitra Singh)**

List of Figures

CC	: Carbon Cloth
K_2PdCl_4	: Potassium tetrachloropalladate (II)
PdNPs	: Palladium nanoparticles
NPs	: Nanoparticles
NC	: N doped carbon
3-APTMS	:3-Aminopropyltrimethoxysilane
EETMS	: 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane
PVP	: Polyvinylpyrrolidone
GPTMS	:3 Glycidoxypropyltrimethoxysilane
HRTEM	: High Resolution Transmission electron microscopy
HRSEM	: High Resolution Scanning Electron Microscope
XRD	:X-ray Diffraction
NTA	: Nitrilotriacetic Acid
EDX	: Energy dispersive xray-spectroscopy
SAED	: Selected area electron diffraction
XPS	: X-ray photoelectron spectroscopy
CV	: Cyclic Voltammetry
LSV	: Linear sweep voltammetry
EIS	: Electrochemical impedance spectroscopy
R_{ct}	: Charge transfer resistance
θ	: Angle (degree)
µ	: micro
µl	: micro liter
µm	: micro meter
µM	: micromolar

mM	: millimolar
Nm	: nanometer
µA	: microampere
S	: Time (second)
N	: Scan rate
E	: Potential
V	: Volt
mV	: millivolt
eV	: electron Volt
I	: current
I_p	: peak current
E_{pa}	: anodic peak potential
E_{pc}	: cathodic peak potential
kΩ	: kiloohm
°C	: degree Celsius

Preface

The quest for sustainable and renewable energy solutions has become a pivotal focus in modern scientific research. Among the various strategies explored, the oxygen evolution reaction (OER) stands out as a critical process in technologies such as water splitting for hydrogen production, metal-air batteries, and regenerative fuel cells. The efficiency of these technologies' hinges significantly on the development of effective and durable catalysts that can facilitate the OER with minimal energy input. Although noble metal nanocatalysts are widely used in heterogeneous catalysis, they have not yet reached the target catalytic efficiency per noble metal atom. This shortfall underscores the need for innovative approaches in catalyst design and synthesis. The present work, embodied in this Ph.D. thesis, delves into the realm of functional nanomaterial-based composites and their remarkable applications in the field of oxygen evolution reaction, with a specific focus on the integration of heterogenous catalysis. This thesis explores the synthesis and application of cobalt-palladium nanocatalysts (Co@Pdnps) mediated by organotrialkoxysilane within an N-doped carbon matrix. The primary objective is to enhance the catalytic performance and durability of these nano catalysts for the OER by leveraging the structural and compositional advantages imparted by nanostructured silica. This doctoral thesis delves into the intricate world of functional nanoparticles and their multifaceted applications in the realm of oxygen evolution reaction. The outcomes of this research provide valuable insights into the design of advanced nano catalysts for OER, with potential implications for the broader field of renewable energy technologies. This work not only advances our understanding of catalyst behaviour at the nanoscale but also

opens new avenues for the development of more efficient, cost-effective, and durable catalysts for sustainable energy applications.

The remarkable properties of nanoparticles, including their tuneable size, shape, and surface chemistry, have opened up unprecedented avenues for their utilization in a diverse array of oxygen evolution reaction applications. This thesis embarks on a comprehensive journey through the realms of oxygen evolution reaction role in the burgeoning field of Hydrogen evolution reaction. The interdisciplinary nature of this research underscores the critical importance of bridging the gap between materials science, biology, and medicine, as we seek to harness the full potential of these nanomaterials.

The thesis is structured into 5 distinct chapters; each contributing to a comprehensive understanding of the research.

Chapter 1 Introduction and overview of an efficient, environmentally friendly, and inexpensive technique of producing a significant amount of H_2 gas is electrochemical water splitting, which uses the cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction (OER). The mechanism of the reaction and the optimum catalyst in terms of activity and stability have not yet been identified. The OER is therefore surrounded by many unanswered questions and formidable obstacles. The creation of a highly active, reliable, and affordable electrocatalyst is urgently needed in order to hasten the market penetration of water electrolyzers. The OER mechanism on metal oxides has traditionally been drawn from that on metal catalysts, where overpotential is the primary factor controlling the reaction. according to the Sabatier principle, the oxygen's ability to attach to the catalyst surface. In the hydrothermal approach, the current work belongs to a simple Co-based coordination polymerization with nitrilotriacetic acid (NTA) as the chelating ligand. The Co-NTA nanowires were

employed as precursors for the Co@NC catalyst, which may be used to alter the catalytic activity of as-made Co-NTA for efficient OER by doping noble metal catalysts like palladium at a much lower ratio.

Chapter 2 Describe a comprehensive overview of the materials and experimental methodologies used to synthesize a range of materials, including Co-NTA, PdNPs, Co@NC, Co@PdNPs1, Co@PdNPs2, Co@PdNPs3, PdNPs1, and PdNPs2. Nanomaterials and nanocomposites are thoroughly characterized using X-ray Diffractometer (XRD), Scanning Electron Microscope (SEM), Transmission Electron Microscopy (TEM), Energy Dispersive Spectroscopy (EDX), BET, and X-ray Photoelectron Spectroscopy (XPS). These techniques provide detailed insights into the structural, morphological, compositional, and surface properties of the materials. Cyclic voltammetry (CV) is employed for electrochemical characterization, while Linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS) are used for electrochemical application. Each technique is briefly discussed to provide essential background information.

Chapter 3 Describe the seed-mediated growth event, Pd-doped bimetallic nanoparticles, known as Co@Pdnps, created using a chemical reduction method. The synthesized material was analysed by XRD, TEM, SEM, XPS, and EDX. Three systems of bimetallic nano catalysts of composition after calcination: (i) Co@Pdnps1: Si=4.54%; Pd=4.36% and Co=91.10%; (ii) Co@Pdnps2: Si=2.81%; Pd=5.83% and Co=91.36% and (iii) Co@Pdnps3: Si=0.00, Pd=9.48, Co=90.52 are made justifying the impact of nanostructured silica and palladium nano geometry on OER. The presence of nanostructured silica facilitates (a) re-cyclability of nano catalyst, (ii) significantly improves the palladium nano geometry, (iii) Effective interaction of Cobalt and palladium components during OER. A nanostructured silica-derived thin film composed

of Co@Pdnps produced a very high current density at a low overpotential with a minor Tafel slope of 39 mV dec^{-1} and a catalyst loading of 3.5 mg cm^{-2} on the carbon cloth. In the absence of silica, the nano catalysts are relatively larger with comparatively less current density (19 $mAcm^{-2}$) as compared to (20.5 $mAcm^{-2}$) recorded with high silica content. As the amount of silica increases, the Pd nanoparticle's shape changes from hexagonal to round, and its polycrystallinity decreases in size, boosting its rate of oxygen evolution reaction.

Chapter 4 This chapter sheds light on the integration of Co-NTA nanowires were utilized as precursors in the synthesis of Co@NC, CoPd@NC-1, and CoPd@NC-2, facilitated by the active participation of 3-aminopropyltrimethoxysilane (3-APTMS). To regulate the presence of nanostructured silica after calcination at 700°C, which is beneficial for the oxygen evolution reaction (OER), porous CoPd@NC was created with varying amounts of nanostructured silica in an N-doped carbon matrix. CoPd@NC-1, with a high silica content, and CoPd@NC-2, with relatively less silica content, were analyzed using XRD, TEM, SEM, and EDX. The presence of nanostructured silica enabled the formation of stabilized bimetallic nanogeometry of cobalt and palladium, leading to improved OER performance compared to catalysts without nanostructured silica. CoPd@NC-1, with a small Tafel slope of 28 mV/dec, and CoPd@NC-2, with a Tafel slope of 44 mV/dec, both at a catalyst loading of 3.5 mg/cm^2 on carbon cloth, generated very high current densities at low overpotentials, with CoPd@NC-1 achieving 0.79 V vs RHE at 10 mA/cm^2. In the absence of silica, the nano catalysts were larger and exhibited lower current densities than those with higher silica content. The regulation of Pd nanoparticle nucleation on cobalt surfaces and the promotion of improved nano shape during pyrolysis by the sol-gel approach resulted in a several-fold increase in the catalytic activity of the heterogeneous catalyst in OER.

Chapter 5 The outcomes of this research provide valuable insights into the design of advanced nanocatalysts for OER, with potential implications for the broader field of renewable energy technologies. This work not only advances our understanding of catalyst behavior at the nanoscale but also opens new avenues for the development of more efficient, cost-effective, and durable catalysts for sustainable energy applications. I extend my deepest gratitude to my advisors, colleagues, and family for their unwavering support and encouragement throughout this journey. This thesis is a culmination of their invaluable guidance and the collaborative spirit that has driven this research forward. As we navigate the intricate pathways of these applications, we hope to inspire further research, collaboration, and innovation in the relentless pursuit of improving human health and well-being.