

Preface

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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 heterogeneous catalysis. This thesis explores the synthesis and application of cobalt-palladium nanocatalysts (Co@Pd_nps) 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 H₂ 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@Pdnp, 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@Pdnp1: Si=4.54%; Pd=4.36% and Co=91.10%; (ii) Co@Pdnp2: Si=2.81%; Pd=5.83% and Co=91.36% and (iii) Co@Pdnp3: 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@Pdncs 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.