

COBALT METAL/METAL OXIDE-BASED NANOMATERIALS
SUPPORTED ON CARBON NANOSTRUCTURES FOR HIGH-
PERFORMANCE ELECTRO-CATALYSIS

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Cobalt Metal/Metal Oxide-based Nanomaterials Supported on Carbon Nanostructures for High- Performance Electro-catalysis

by

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Dedicated to my Parents and Teachers

CERTIFICATE

This is to certify that the thesis entitled, '**Cobalt Metal/Metal Oxide-based Nano-materials Supported on Carbon Nanostructures for High-performance Electro-catalysis**' being submitted by Shwetambara Jha to the Indian Institute of Technology Delhi for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by her. Shwetambara Jha has worked under guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or full, to any other university or institute for award of any degree or diploma.

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ABSTRACT

Due to ever increasing demand of energy and due to the environmental pollution caused by energy system based on fossil fuel, the scientific community has been driven to develop adequate clean energy generating and storage technologies. Energy sources such as fuel cells, supercapacitors, metal-air batteries, and lithium-ion batteries are non-polluting alternatives as compared to sources of energy that are non-renewal such as fossil fuel. These clean energy source has arisen opportunities for the researchers and scientific community to make them mainstream and more affordable for the end consumers. Furthermore, it is desirable that these devices be efficient and cost-effective in order to assure their penetrability in the energy market. The oxygen reduction reaction (ORR) is the rate-determining step in metal-air batteries and fuel cells, for example, and the ideal catalyst is one that helps with the reaction at low overpotential. However, in the special case of rechargeable metal air battery, since ORR as well as OER are equally important and therefore catalyst's multiple roles become even more important. The energy efficiency of such electrochemical systems are greatly impacted by the the electrode processes of ORR and OER and therefore it is very important to find the right catalysts which are both energy efficient as well as cost effective. The electrocatalysts that has been proven as most energy efficient in the ORR and OER reactions are the noble metals such as platinum, iridium, palladium, and their alloys, however, as we know these noble metals are extremely costly, rare and do not last long in adverse conditions. Because of their tunable properties and ease of usage, first-row transition metals are widely investigated as feasible and cost-effective alternatives to Pt for ORR. Some of the catalysts that are known to show very good energy efficiency in ORR and OER are oxides of transition metals, oxynitrides, chalcogenides and their complexes. There has been attempts to build hybrid catalysts, such as heteroatom doped carbon framework, metal alloys and metal oxide composites, and it has helped to improve the performance significantly. It is important to note that when N-doped graphene or N-doped carbon nanotubes were used as supports for nanoparticles of the oxides of early transition metal like CoO, Co₃O₄, MnCo₂O₄, ZnFe₂O₄, CuCo₂O₄, NiFe hydroxides which has its size in nanometers, NiCo₂O₄, ZnCo₂O₄, and CoO, the ORR and OER activity was exceptional. Other parameters such as shape and size of particles, and also the dispersion of catalyst on a conducting substrate, as well as the involvement of

surface intermediates in the reaction process, are found to have a significant impact on the intrinsic activities of these systems. For cobalt based nano alloys and spinel bi-metal oxide atoms, we investigated the synergism effect between nanoparticles and conducting carbon support and also spinel bi- metal oxides which are decorated over carbon support, are helpful in the facilitation of reactions like ORR and OER. The results of the several chapters are summarized here: Chapter 2 is brief highlights of Material and their characterization techniques, In the chapter 3, we report a simplistic and facile approach for the fabrication of highly efficient oxygen reduction reaction (ORR) electro-catalyst based on PtCo alloy nanoparticles supported on carbon fiber paper (PtCo@CFP) via potentiostat electro-deposition method. Besides being rapid and facile, this method is highly effective and allows easy control over the kinetics of nucleation and growth process as a function of electro-deposition parameters varied by changing electrodeposition time. We have optimized the electro-deposition time to obtain the PtCo@CFP electro-catalyst that show enhanced electro-catalytic activity for ORR. The results demonstrate that the PtCo@CFP electro-catalyst obtained at electro-deposition time of 600 seconds exhibited the best ORR activity among others, following four electron transfer pathways with minute peroxide formation. We report the multifunctional electrocatalysis activity by platinum-cobalt nanoalloy in chapter 4 with different molar ratios decorated over graphene oxide (PtCo/GO) nanosheet based electrocatalysts synthesized via hydrothermal treatment. All catalysts were thoroughly characterized by XRD, FESEM, XPS, and Raman spectroscopy. The catalyst with 1:1 molar ratio PtCo catalyst anchored on GO shows the excellent multifunctional electro catalytic activity towards ORR, Methanol oxidation reaction (MOR), Hydrogen evolution reaction (HER). The combination of Pt and Co lowers the cost of catalyst by alloying and also its comparable activity with 20% wt. Pt/C is attractive catalyst of choice for fuel cells. Among the possible alternative metals to Pt for better ORR activity, a first-row transition metal Cobalt, Nickel and Iron and its bimetallic composite are regarded as most promising material due to its low cost, abundance, and moderate binder capacity of O₂ molecules towards oxygen electrocatalyst. In chapter 5, development of non-precious platinum free, cost-effective and efficient bi-functional oxygen electro-catalyst is critical for energy conversion devices. Inverse spinel CoFe₂O₄ nano-cubes supported on nitrogen doped graphene oxide (NGO) sheets prepared by simple hydrothermal process. NGO is used as supporting material which increases the conductivity and provides surface area of the CoFe₂O₄. The crystal structure and composition have been investigated by X-ray diffraction, Raman Spectroscopy as well as X-ray photoelectron spectroscopy

indicating the formation of inverse spinel CoFe_2O_4 and its composite with NGO. In chapter 6, we have synthesized mix Cobalt iron sulfide supported on nitrogen/sulfur doped graphene oxide sheets which is prepared by simple reflux method followed by annealing process namely, CoFe-S/NGO. The crystal structure and their composition were investigated by PXRD, FTIR, Raman spectroscopy as well as X-ray photoelectron spectroscopy indicating the formation of composite CoFe-S/NGO. We have investigated the ORR and OER activity and discussed the variation of annealing temperature. CoFe-S/NGO annealed at 250°C shows enhanced ORR and OER activity. In chapter 7 the spinel $\text{NiCo}_2\text{O}_4/\text{rGO}$ nanocomposite can be considered as a promising precious metal-free electrocatalyst owing to its high surface area and abundant catalytic active sites. In this study $\text{NiCo}_2\text{O}_4/\text{rGO}$ nanoplates were synthesized using a simple refluxing technique, followed by annealing in inert atmosphere. The as synthesized materials were characterized using Scanning electron microscopy, X-ray diffraction, Transmission electron microscopy. The $\text{NiCo}_2\text{O}_4/\text{rGO}$ showed enhanced electrocatalytic activities and high stability towards ORR, and OER. This outstanding electrochemical performance could be attributed to the remarkable structural characteristic of the electrocatalyst with a morphology of small nanoparticle assembled nanoplate. These exceptional electrochemical performances could be ascribed to the remarkable structural feature of the electrocatalyst with a nanoplate morphology exhibiting high surface area and void spaces within the surface of nanoplates, which provide large contact areas between electrolyte and active materials for electrolyte diffusion. The as prepared catalyst showed high electrocatalytic activity owing to its synergism between graphene oxide and abundant active sites. The chapter 8 presents an overview of the of the chapters. In the search of new and hybrid materials as an electrocatalyst alternative replacement to precious metal (Pt and Ir), we have investigated lowering the cost of catalyst from precious to non-precious metal-based compounds and their composite for efficient multifunctional catalyst. Several modification and hybridization have been carried out with Co- based compounds e.g., PtCo, Pt_3Co , CoFe_2O_4 , CoFe-S and $\text{NiCo}_2\text{O}_4/\text{rGO}$. The composites were investigated in detail for electrochemical study, using linear sweep voltammetry, cyclic voltammetry, chronopotentiometry. However, much work is needed to be done on it. New materials exhibiting promising applications are always attractive to the researchers. However, finding of promising materials alternative to Pt for electrocatalysis is still an open challenge to the scientific community.

सार

पारंपरिक जीवाश्म ईंधन आधारित ऊर्जा प्रणालियों के बढ़ते प्रतिकूल प्रभावों और ऊर्जा की मांग में निरंतर वृद्धि के कारण वैज्ञानिक समुदाय को पर्याप्त स्वच्छ ऊर्जा उत्पादन और भंडारण प्रौद्योगिकियों को विकसित करने के लिए प्रेरित किया गया है। लिथियम-आयन बैटरी, सुपरकैपेसिटर, ईंधन सेल, और मेटल-एयर बैटरी सभी पारंपरिक गैर-नवीकरणीय ऊर्जा स्रोतों के स्वच्छ विकल्प के रूप में उभरे हैं, जिससे इस प्रक्रिया में बहुत अधिक वैज्ञानिक और तकनीकी रुचि पैदा हुई है। इसके अलावा, यह वांछनीय है कि ये उपकरण ऊर्जा बाजार में अपनी पैठ सुनिश्चित करने के लिए कुशल और लागत प्रभावी हों। इलेक्ट्रोड सामग्री, सामान्य रूप से, इन उपकरणों का सबसे महंगा घटक है। किसी पदार्थ की इलेक्ट्रोड सामग्री के रूप में कार्य करने की क्षमता इस बात से निर्धारित होती है कि यह विभिन्न इलेक्ट्रोड प्रक्रियाओं को सुविधाजनक बनाने में कितनी अच्छी तरह सहायता कर सकता है। हालांकि, एक रिचार्जबल मेटल-एयर बैटरी के मामले में, उत्प्रेरक की बहुक्रियाशीलता पर बल देते हुए, ओआरआर और ऑक्सीजन विकास प्रतिक्रिया (ओईआर) दोनों ही महत्वपूर्ण हो जाते हैं। क्योंकि ओआरआर और ओईआर दो प्रमुख इलेक्ट्रोड प्रक्रियाएं हैं जिनका ऊपर उल्लिखित कुछ विद्युत रासायनिक प्रणालियों की ऊर्जा दक्षता पर सीधा प्रभाव पड़ता है, इन प्रतिक्रियाओं की सहायता के लिए लागत प्रभावी और ऊर्जा-कुशल उत्प्रेरक खोजना महत्वपूर्ण है। इन कारकों के आलोक में नोबल-मेटल कंपोजिट के निषेधात्मक कारकों को कम करने के उद्देश्य से कई अध्ययन किए जा रहे हैं। उनके ट्यून करने योग्य गुणों और उपयोग में आसानी के कारण, पहली पंक्ति संक्रमण धातुओं की व्यापक रूप से जांच की जाती है क्योंकि ओआरआर के लिए पीटी के लिए व्यवहार्य और लागत प्रभावी विकल्प हैं। इन महत्वपूर्ण प्रक्रियाओं में संक्रमण धातु ऑक्साइड, चाकोजेनाइड्स, ऑक्सीनिट्राइड्स और उनके परिसरों ने उत्कृष्ट उत्प्रेरक प्रदर्शन का प्रदर्शन किया है। ग्रेफाइटिक कार्बन फ्रेमवर्क और मेटल ऑक्साइड कंपोजिट जैसे हाइब्रिड उत्प्रेरक बनाने के प्रयासों ने भी प्रदर्शन में काफी सुधार किया है। अधिक दिलचस्प बात यह है कि जब एन-डॉप्ड ग्रेफीन या एन-डॉप्ड कार्बन नैनोट्यूब का उपयोग प्रारंभिक संक्रमण धातु ऑक्साइड जैसे CoO , Co_3O_4 , MnCo_2O_4 , ZnFe_2O_4 , और CuCo_2O_4 , के नैनोकणों के लिए समर्थन के रूप में किया गया था, तो हेटेरोएटम-डॉप्ड कंडक्टिंग कार्बन का संभावित सहक्रियात्मक प्रभाव। नैनोकणों के परिणामस्वरूप उत्कृष्ट ओआरआर गतिविधि हुई। इसी तरह, नैनोमीटर आकार के NiFe हाइड्रॉक्साइड्स, NiCo_2O_4 , ZnCo_2O_4 , और CoO में OER के लिए उच्च गतिविधि और स्थायित्व है। हालांकि ये ऑक्साइड दिलचस्प उत्प्रेरक गतिविधि विशेषताओं को प्रदर्शित करने में सक्षम हैं, अन्य पैरामीटर जैसे कण आकार, आकारिकी, और उत्प्रेरक कणों को एक संवाहक सबस्ट्रेट पर कितनी अच्छी तरह फैलाया जाता है, साथ ही साथ प्रक्रिया में शामिल सतह मध्यवर्ती भी पाए जाते हैं। इन प्रणालियों की आंतरिक गतिविधियों पर महत्वपूर्ण प्रभाव। इस प्रकार, हमने एक संवाहक कार्बन पर सक्रिय कणों के फैलाव विशेषताओं के घनिष्ठ संबंध, अन्य धातुओं के प्रतिस्थापन प्रभाव और कोबाल्ट आधारित नैनो मिश्र धातुओं और द्वि-धातु ऑक्साइड स्पिनल परमाणुओं के लिए सतह मध्यवर्ती के नियंत्रित परस्पर क्रिया का पता लगाया है ओआरआर और ओईआर। अध्याय 3 में, हम पोर्टेंशिएशन इलेक्ट्रो-डिपोजिशन विधि के माध्यम से कार्बन फाइबर पेपर (PtCo@CFP) पर समर्थित PtCo मिश्र धातु नैनोकणों पर आधारित अत्यधिक कुशल ऑक्सीजन कमी प्रतिक्रिया (ORR) इलेक्ट्रो-उत्प्रेरक के निर्माण के लिए एक सरल और आसान दृष्टिकोण की रिपोर्ट करते हैं। तेज और सुगम होने के अलावा, यह विधि अत्यधिक प्रभावी है और इलेक्ट्रो-डिपोजिशन मापदंडों के एक कार्य के रूप में न्यूक्लियेशन और विकास प्रक्रिया के कैनेटीक्स पर आसान नियंत्रण की अनुमति देती है। हमने PtCo@CFP इलेक्ट्रो-उत्प्रेरक प्राप्त करने के लिए इलेक्ट्रो-डिपोजिशन समय को अनुकूलित किया है जो अलग-अलग समय अंतरालों के लिए CFP पर PtCo के इलेक्ट्रो-डिपोजिशन के माध्यम से PtCo@CFP इलेक्ट्रोड का निर्माण करके ORR के लिए बढ़ी हुई इलेक्ट्रो-कैटलिटिक गतिविधि दिखाते हैं। 300, 600, 900 और 1200 सेकंड। परिणाम प्रदर्शित करते हैं कि सीएफपी में जमा पीटीसीओ मिश्र धातु ऑक्सीजन की कमी प्रतिक्रिया की दिशा में उत्कृष्ट विद्युत रासायनिक गतिविधि प्रदर्शित करता है। पीटीसीओ@सीएफपी इलेक्ट्रो-उत्प्रेरक 600 सेकंड के इलेक्ट्रो-डिपोजिशन समय पर प्राप्त होता है/ हम अध्याय 4 में प्लैटिनम-कोबाल्ट नैनोएलॉय द्वारा

बहुक्रियाशील इलेक्ट्रोकेटलिसिस गतिविधि की रिपोर्ट करते हैं, जिसमें हाइड्रोथर्मल उपचार के माध्यम से संश्लेषित विभिन्न दाढ़ अनुपातों से सजाए गए ग्राफीन ऑक्साइड (PtCo / GO) नैनोशीट आधारित इलेक्ट्रोकेटलिस्ट हैं। सभी उत्प्रेरकों को एक्सआरडी, एफईएसईएम, एक्सपीएस और रमन स्पेक्ट्रोस्कोपी द्वारा पूरी तरह से चित्रित किया गया था। हाल की रिपोर्टों ने प्रदर्शित किया है कि बड़े सैद्धांतिक सतह क्षेत्र (ca. 2600 m²/g), अल्ट्राहाई विद्युत चालकता और कार्बोनिल, एपॉक्साइड और हाइड्रॉक्सिल की उपस्थिति। लक्षण वर्णन इस बात की पुष्टि करता है कि ये PtCo नैनो मिश्र धातु और ग्रेफीन ऑक्साइड उत्प्रेरक के साथ उनके सम्मिश्रण को पूरी तरह से ग्राफीन ऑक्साइड शीट में वितरित किया जाता है। GO पर लगे 1:1 मोलर अनुपात PtCo उत्प्रेरक के साथ उत्प्रेरक ऑक्सीजन रिडक्शन रिएक्शन (ORR), मेथनॉल ऑक्सीडेशन रिएक्शन (MOR), हाइड्रोजन इवोल्यूशन रिएक्शन (HER) के लिए उत्कृष्ट बहुक्रियाशील इलेक्ट्रो उत्प्रेरक को दर्शाता है। तैयार उत्प्रेरक के रूप में इलेक्ट्रो-कैटलिटिक गतिविधि का अध्ययन साइक्लिकवोल्टमेट्री (सीवी), लीनियर स्वीपवोल्टमेट्री द्वारा किया जाता है। अध्याय 5 में, गैर-कीमती प्लेटिनम मुक्त, लागत प्रभावी और कुशल द्वि-कार्यात्मक ऑक्सीजन इलेक्ट्रो-उत्प्रेरक का विकास ऊर्जा रूपांतरण उपकरणों के लिए महत्वपूर्ण है जो उलटा स्पिनल CoFe₂O₄ नैनो-क्यूब्स पर आधारित नाइट्रोजन डोप्ड ग्रेफीन ऑक्साइड (एनजीओ) शीट पर आधारित है। एक कुशल द्वि-कार्यात्मक ऑक्सीजन इलेक्ट्रोकेटलिस्ट के रूप में सरल हाइड्रोथर्मल प्रक्रिया। एनजीओ का उपयोग सहायक सामग्री के रूप में किया जाता है जो चालकता को बढ़ाता है और CoFe₂O₄ का सतह क्षेत्र प्रदान करता है। क्रिस्टल संरचना और संरचना की जांच एक्स-रे विवर्तन, रमन स्पेक्ट्रोस्कोपी के साथ-साथ एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी द्वारा की गई है जो स्पिनल CoFe₂O₄ और इसके समग्र एनजीओ के गठन का संकेत देती है। बेहतर ओआरआर और ओईआर गतिविधि के लिए पीटी के लिए संभावित वैकल्पिक धातुओं में, पहली पंक्ति संक्रमण धातु कोबाल्ट और आयरन और इसके द्विधात्विक मिश्रित को इसकी कम लागत, बहुतायत और O⁻² अणुओं की मध्यम बाइंडर क्षमता के कारण सबसे आशाजनक सामग्री माना जाता है। अध्याय 6 में गैर-कीमती कुशल द्वि-कार्यात्मक इलेक्ट्रो-उत्प्रेरक को ऑक्सीजन इलेक्ट्रोकेटलिस्ट में कीमती धातु (Pt और Ir) के विकल्प के रूप में खोजा जा रहा है। इस रिपोर्ट में, हमने नाइट्रोजन फंक्शनलाइज ग्राफीन ऑक्साइड शीट्स पर समर्थित मिक्स कोबाल्ट आयरन सल्फाइड को संश्लेषित किया है, जिसे सरल रिफ्लक्स विधि द्वारा तैयार किया जाता है, जिसके बाद एनीलिंग प्रक्रिया अर्थात् CoFe-S/NGO होता है। क्रिस्टल संरचना और उनकी संरचना की जांच एक्स-रे विवर्तन के साथ-साथ एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी द्वारा की गई थी। अध्याय 7 में स्पिनल NiCo₂O₄ / rGO नैनोकम्पोजिट को इसकी उच्च सतह क्षेत्र और प्रचुर मात्रा में उत्प्रेरक सक्रिय साइटों के कारण एक आशाजनक कीमती धातु-मुक्त इलेक्ट्रोकेटलिस्ट माना जा सकता है। इस अध्ययन में NiCo₂O₄/rGO नैनोप्लेट्स को एक साधारण रिफ्लक्सिंग तकनीक का उपयोग करके संश्लेषित किया गया, इसके बाद निष्क्रिय वातावरण में एनीलिंग की गई। संश्लेषित सामग्री के रूप में स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी, एक्स-रे विवर्तन, ट्रांसमिशन इलेक्ट्रॉन माइक्रोस्कोपी का उपयोग करके विशेषता थी। NiCo₂O₄/rGO ने बड़ी हुई इलेक्ट्रोकेटलिटिक गतिविधियों और ओआरआर, और ओईआर के प्रति उच्च स्थिरता दिखाई। इन असाधारण विद्युत रासायनिक प्रदर्शनों को इलेक्ट्रोकेटलिस्ट की उल्लेखनीय संरचनात्मक विशेषता के लिए एक नैनोप्लेट आकारिकी के साथ उच्च सतह क्षेत्र और नैनोबेल्ड की सतह के भीतर शून्य रिक्त स्थान प्रदर्शित किया जा सकता है, जो इलेक्ट्रोलाइट प्रसार के लिए इलेक्ट्रोलाइट और सक्रिय सामग्री के बीच बड़े संपर्क क्षेत्र प्रदान करते हैं। इस काम में, ग्रेफीन ऑक्साइड शीट नैनोकणों पर समर्थित नैनो प्लेट निकल-कोबाल्ट ऑक्साइड को रिफ्लक्स-आधारित संश्लेषण विधि का उपयोग करके तैयार किया गया था, जिसके बाद एनीलिंग तकनीक का उपयोग किया गया था और फिर क्षारीय परिस्थितियों में ओआरआर और ओईआर के लिए एक इलेक्ट्रोकेटलिस्ट के रूप में विशेषता थी। तैयार उत्प्रेरक ने ग्राफीन ऑक्साइड और प्रचुर मात्रा में सक्रिय साइटों के बीच तालमेल के कारण उच्च इलेक्ट्रोकेटलिटिक गतिविधि दिखाई। अध्याय 8 अध्यायों का एक सिंहावलोकन प्रस्तुत करता है। उच्च ऊर्जा घनत्व वाले ऊर्जा भंडारण और रूपांतरण उपकरण महंगे और सड़ने योग्य इलेक्ट्रोड सामग्री की भागीदारी से ग्रस्त हैं, जो उनकी व्यावसायिक व्यवहार्यता को प्रतिबंधित करते हैं।

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ABBREVIATIONS

CV-	Cyclic Voltammetry
LSV-	Linear Sweep Voltammetry
GCE-	Glassy Carbon Electrode
CE-	Counter Electrode
RE-	Reference Electrode
WE-	Working Electrode
EIS-	Electro Chemical Impedance Spectroscopy
PXRD-	Powder X-ray Diffraction
SEM-	Scanning Electron Microscopy
FTIR-	Fourier Transformed Infra-Red Spectroscopy
TGA-	Thermogravimetric Analysis
XPS-	Xray-Photoelectron Spectroscopy
ORR-	Oxygen Reduction Reaction
MOR-	Methanol Oxidation Reaction
HER-	Hydrogen Evolution Reaction
OER-	Oxygen Evolution Reaction
ECSA-	Electrochemical Active Surface Area
RHE-	Reversible Hydrogen Electrode
J° -	Exchange Current Density
K° -	Kinetic Rate Constant
eV-	Electron Volt
TSC-	tri-Sodium Citrate
CFP-	Carbon Fiber Paper
GO-	Graphene Oxide
rGO-	Reduced Graphene Oxide