

Article

Exploring Enhanced Oxygen Reduction Reactions: A Study on Nanocellulose, Dopamine, and Cobalt Complex-Derived Non-Precious Electrocatalyst

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Abstract: Cobalt-based catalysts are recognized as promising electrocatalysts for oxygen reduction reactions (ORRs) in fuel cells that operate within acidic electrolytes. A synthesis process involving a cobalt complex, nanocellulose, and dopamine, followed by pyrolysis at 500 °C under a nitrogen atmosphere, was used to create a cobalt and nitrogen-doped carbonaceous material. Additionally, urea was incorporated to enhance nitrogen doping in the carbonaceous material. The morphology and structure of the material were examined using Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD), where SEM unveiled dispersed metal oxides within the carbonaceous framework. Energy Dispersive X-ray Spectroscopy (EDS) analysis showed an even distribution of elements across the cobalt-doped carbonaceous material. X-ray Photoelectron Spectroscopy (XPS) analysis further highlighted significant alterations in the elemental composition due to pyrolysis. The electrochemical behavior of the cobalt-doped carbonaceous material, with respect to the oxygen reduction reaction (ORR) in an acidic medium, was investigated via cyclic voltammetry (CV), revealing an ORR peak at 0.30 V against a reversible hydrogen reference electrode, accompanied by a notably high current density. The catalyst's performance was evaluated across different pH levels and with various layers deposited, showing enhanced effectiveness in acidic conditions and a more pronounced reduction peak with uniformly applied electrode layers. Rotating disk electrode (RDE) studies corroborated the mechanism of a four-electron reduction of oxygen to water, emphasizing the catalyst's efficiency.

Keywords: cobalt catalyst; nanocellulose; polydopamine; electrochemistry; oxygen reduction reaction; clean energy; fuel cell



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1. Introduction

Fuel cells offer a viable alternative to the non-renewable energy sectors, such as petroleum and natural gas, by harnessing catalysts to accelerate the oxygen reduction reaction (ORR) crucial for their operation. Platinum (Pt) catalysts are favored for their high ORR efficiency and minimal overpotential [1]. Nevertheless, Pt's high cost poses significant economic challenges for widespread commercial adoption [2]. The escalating global demand for energy, driven by a growing population, higher living standards, and the ubiquity of portable devices, has led to an increased reliance on fossil fuels, which account for more than 85% of the energy used worldwide for stationary and automotive purposes [3]. This reliance on fossil fuels, which are depleting while also damaging the environment

through contributions to global warming [4], highlights the urgent need for a shift toward alternative and renewable energy sources [5]. Efforts to utilize geothermal, hydro, wind, and solar power for energy production are underway, paralleled by research into batteries, fuel cells, and electrochemical supercapacitors for efficient energy storage [6–8]. Fuel cells stand out among alternative energy storage technologies, offering higher energy density compared to both flow batteries and lithium-ion batteries [9]. Although lithium-ion batteries boast portability, they are hindered by short lifespans, environmental pollution, and reduced effectiveness in extreme temperatures [10].

The interest in alternative energy systems is on the rise, with Proton Exchange Membrane Fuel Cells (PEMFCs) emerging as the leading technology in the field. PEMFCs are distinguished among fuel cell technologies for their superior energy conversion efficiency and power density, which ranges between 40% and 65% [11]. These fuel cells are also valued for their rapid startup and warmup times, ability to operate at relatively low temperatures (60 to 80 °C) [12], and their lightweight, compact design [13]. In PEMFCs, electricity is generated through an electrochemical reaction as protons move from the anode to the cathode. This setup includes a bipolar plate (flow field plate), a gas diffusion layer (GDL), and a catalyst layer (CL) at both the anode and cathode sides. At the anode, the hydrogen oxidation reaction (HOR) occurs, where hydrogen molecules are absorbed onto the catalyst layer, resulting in the detachment of electrons and the release of protons (H^+). These electrons then make their way to the cathode via an external circuit, whereas the protons move through the membrane to reach the cathode. At this point, the oxygen reduction reaction (ORR) occurs, facilitating the production of electricity. The reactions within PEMFCs can be summarized as follows:

Anode (HOR):	$2H_2 \rightarrow 2H^+ + 4e^-$	$E^\circ = 0.00 \text{ V vs. SHE}$
Cathode (ORR):	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$E^\circ = 1.23 \text{ V vs. SHE}$
Overall reaction:	$2H_2 + O_2 \rightarrow 2H_2O$	SHE = Standard Hydrogen Electrode

The primary challenge faced by Proton Exchange Membrane Fuel Cells (PEMFCs) is the need for high loadings of noble metal catalysts, such as platinum (Pt) and its alloys, at the cathode to accelerate the inherently slow ORR. These catalysts are essential for both the hydrogen oxidation reaction (HOR) and the ORR, with Pt and its alloys currently recognized as the most effective electrocatalysts due to their high catalytic activity, electronic conductivity, low overpotential, and outstanding stability [14–16]. However, the high cost of Pt significantly hinders the mass commercialization of PEMFCs [17,18]. This has led to efforts to develop non-precious metal catalysts (NPMCs) aimed at replacing Pt-based catalysts for the ORR, with recent research making considerable progress in improving the ORR performance of NPMCs, particularly those based on iron and cobalt [19]. A carbon-based bifunctional electrocatalyst offers a more efficient approach to constructing superior electrocatalysts. This is likely achieved by combining specific heteroatom doping and engineered carbon defects, which simultaneously have positive effects. To create porous B and N co-doped nanocarbon (also known as B, N-carbon) materials that are composed of interconnected cuboidal hollow nanocages with fine graphitization and ample carbon defects, a convenient strategy for facile construction has been developed. The resultant nanocarbon material, which combines carbon defects and B and N co-dopants, is an extremely reactive and long-lasting electrocatalyst for the ORR and the oxygen evolution reaction (OER) [20]. These advances have positioned NPMCs as viable alternatives to Pt and its alloys.

Polydopamine (PDA) has emerged as a novel, bio-inspired material attracting significant attention for its unique properties and applications in energy, the environment, and catalysis [21]. PDA, a synthetic polymer, demonstrates a strong affinity for solid substrates through chemical bonds and physical interactions, courtesy of its functional groups like amines, imines, and catechol [22,23]. Its excellent biocompatibility and surprising prop-

erties in terms of optics, electricity, and magnetism [21], along with similarities to mussel proteins, have spurred interest in its application across various domains, including coatings, environmental and catalytic applications, and energy storage and conversion [24–26]. The synthesis of N-doped carbon materials typically involves direct reactions with nitrogen precursors or the carbonization of nitrogen-containing polymers, with PDA polymerization offering a straightforward method for creating carbonaceous nanostructures [27–29].

Cellulose, the most abundant natural polymer, presents an opportunity for the synthesis of N-doped carbonaceous materials, including those containing metals [30]. Nanocellulose (NC), derived from cellulose, is noted for its environmental friendliness and excellent mechanical properties attributed to its nano-scale structure. This has led to its widespread application in engineering and functional materials [31]. NC, with dimensions in the nanometer range, is obtained from a variety of sources including plants, algae, and bacteria, and is characterized by its high surface area, mechanical strength, and biodegradability, making it suitable for high-performance energy devices [32]. The increasing demand for renewable energy solutions has catalyzed research into NC-based conductive materials. Despite the advancements, the stability of NPMCs remains a challenge, preventing them from being considered direct replacements for Pt/C catalysts in PEMFCs [19].

In this manuscript, we discuss the synthesis and application of a cobalt and nitrogen-doped carbonaceous catalyst. The catalyst is synthesized by pyrolyzing a mixture of cobalt complex, NC, PDA, and urea at 500 °C under a nitrogen atmosphere, aiming to enhance the oxygen reduction reaction (ORR) efficiency in acidic fuel cells. We hypothesize that incorporating cobalt and nitrogen into the carbonaceous material matrix significantly boosts the electrocatalytic activity for the ORR in acidic environments, a critical aspect for fuel cell technology. The innovative aspect of our work lies in the synthesis strategy, which involves a unique blend of a well-dispersed cobalt complex, nanocellulose, and polydopamine, followed by pyrolysis with urea under an inert atmosphere. Characterization techniques such as SEM, XRD, and EDS have confirmed the presence of uniformly dispersed metal nanoparticles and an even elemental distribution. CV assessments demonstrated robust ORR activity, evidenced by a significant peak at 0.30 V against a reversible hydrogen electrode (RHE), particularly under acidic conditions and with uniformly layered electrodes. RDE experiments have further validated the four-electron reduction pathway of oxygen to water, highlighting the catalyst's potential in improving fuel cell performance.

2. Results and Discussions

2.1. Synthesis

The PPh_4^+ salt of the cobalt complex and nanocellulose were mixed together in the presence of dopamine (hydrochloride salt), which was allowed to polymerize under an oxidative environment at a slightly elevated pH. The reaction mixture turned black, and a composite material precipitated, which is supposed to contain the cobalt complex along with nanocellulose coated with polydopamine. PDA plays a dual role: it is involved in the synthesis of the nanocellulose and cobalt complex nanocomposite, and it contains nitrogen atoms. Upon pyrolysis, these nitrogen atoms can dope the carbonaceous material, altering its structure and properties. After collecting the nanocomposite material post-polydopamine reaction, we added urea so that during pyrolysis, the carbonaceous material could be further doped with nitrogen atoms, which in turn can synergistically enhance ORR (oxygen reduction reaction) activities. NC contains several hydroxyl groups ($-\text{OH}$), which allow well dispersion and possible binding of the cobalt complex on its surface to enable uniform distribution of the catalytic site. NC also acts as a source of carbon when the catalyst is synthesized under pyrolysis. This unique synthesis route aims to achieve a homogeneous distribution of cobalt nanoparticles and nitrogen doping within the carbonaceous material matrix, hypothesized to synergistically improve the ORR performance by facilitating a more efficient four-electron reduction pathway of oxygen to water.

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2.2. Characterizations

2.2.1. SEM and EDS

SEM characterization was conducted to assess the morphology of the carbonaceous material. The SEM images, presented in Figure 1a,b, depict the formation of the cobalt-doped material, characterized by aggregates of various shapes [33]. The SEM analysis also reveals that the carbon produced through pyrolysis exhibits flake-like structures with some porosity [34]. The surface features distinct white and gray areas, clearly distinguishable from each other. To verify the composition of the cobalt-doped carbonaceous material, EDS analysis was performed. Figure 1c displays the EDS results and the associated spectrum for the selected area, indicating the atomic percentages of elements. The EDS spectrum shows peaks for C, Co, and O, suggesting the formation of metal oxides. The higher atomic percentage of carbon (C) can be attributed to the use of carbon tape during the EDS analysis, where the powder sample was affixed to the sample holder with carbon tape. Furthermore, the presence of nitrogen in the sample is highly likely. It is assumed that the peak nearest to C corresponds to nitrogen.

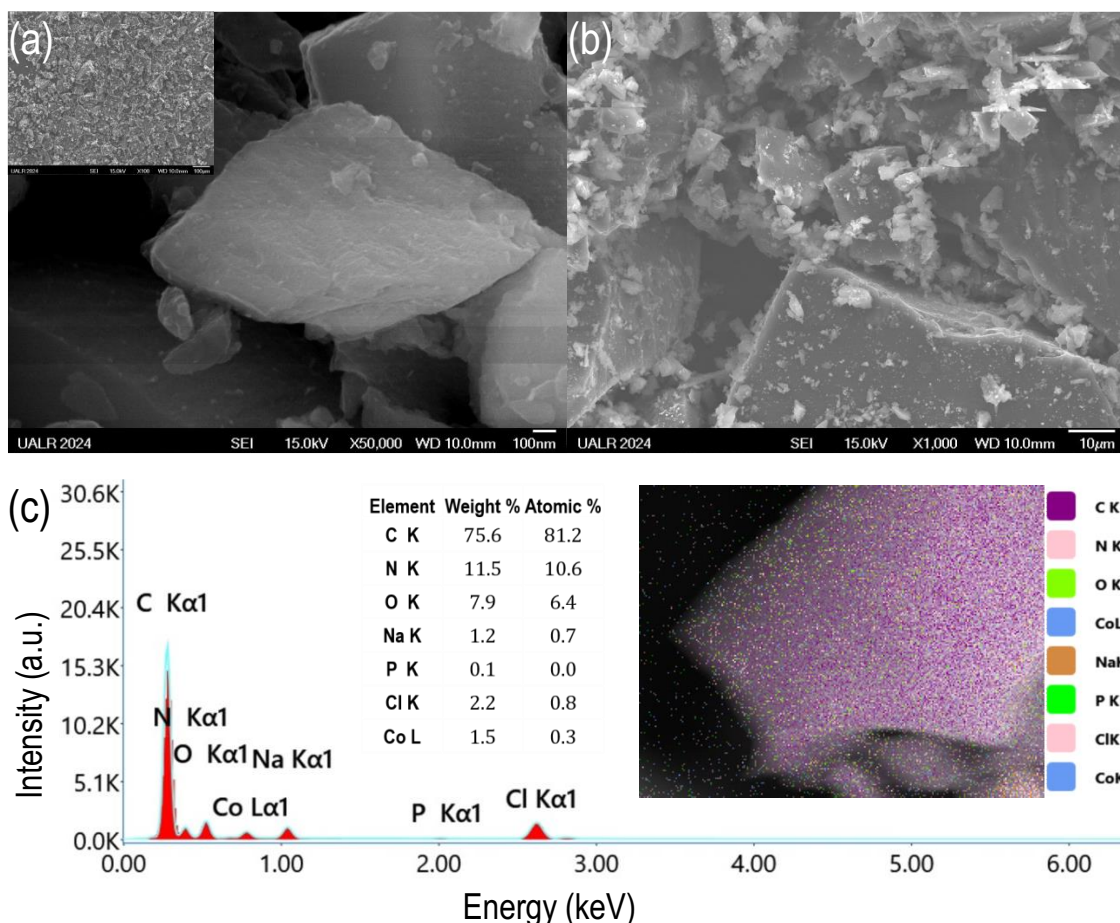


Figure 1. SEM images of cobalt-doped carbonaceous ORR catalytic material at (a) 50k magnification and (b) 1k magnification. (c) EDS spectra showing element mapping image of elements of carbonaceous material.

2.2.2. XRD

X-ray Diffraction (XRD) characterization was conducted to investigate the phase, structure, and crystallinity of the pyrolyzed material. The XRD patterns reveal the presence of cobalt oxides. The XRD pattern, depicted in Figure 2, confirms the crystalline nature of the sample. The diffraction peaks corresponding to Co_3O_4 were observed at 2θ values of 27.33° , 31.66° , 45.43° , 56.45° , 66.23° , and 75.32° , which correspond to the (111), (220),

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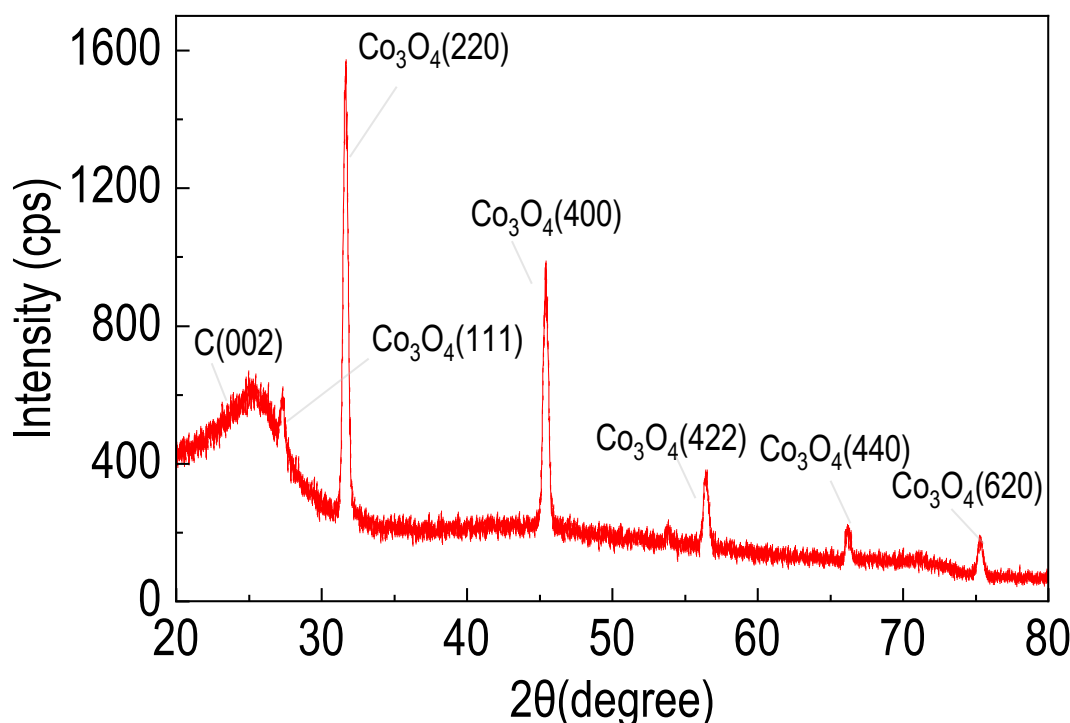


Figure 2. XRD pattern of pyrolyzed cobalt-doped carbonaceous ORR catalytic material.

2.2.3. XPS Study

X-ray Photoelectron Spectroscopy (XPS) analysis was performed on the pyrolyzed carbonaceous material to determine its surface elemental composition and the chemical states of carbon and cobalt (Co), which are crucial for its electrocatalytic activity. Initially, a survey scan of the material revealed the presence of major elements including C, N, O, and Co. During this survey, peaks were observed for both nitrogen and oxygen atoms. An oxygen peak was noted at approximately 532.6 eV, suggesting the presence of carbonyl oxygen in the sample [38]. A nitrogen peak was detected at 400.3 eV, indicating nitrogen doping in the carbonaceous material [39]. Nitrogen doping can enhance the material's properties, potentially altering its electronic structure, improving conductivity, or enhancing its catalytic properties. These modifications can be tailored for specific applications, such as energy storage devices, catalysis, sensors, and electronic devices. The C1s XPS peaks shown in Figure 3b reveal the chemical composition and bonding present in the carbonaceous material. The C1s spectrum exhibits distinct peaks at binding energies of

284.8 eV, 286.0 eV, and 288.5 eV, corresponding to various carbon functional groups in the material [40]. The primary peak at 284.8 eV represents carbon atoms in sp^3 -hybridized structures prevalent in the sample. The peak at 286.0 eV is attributed to carbon atoms involved in C-O (carbon-oxygen) bonds, indicating the presence of oxygen-containing functional groups. Furthermore, the peak at 288.5 eV suggests the presence of carbon atoms in carbonyl (C=O) functionalities [41]. The relative intensities and positions of these C1s peaks offer insights into the surface chemistry, molecular structure, and composition of the carbonaceous material.

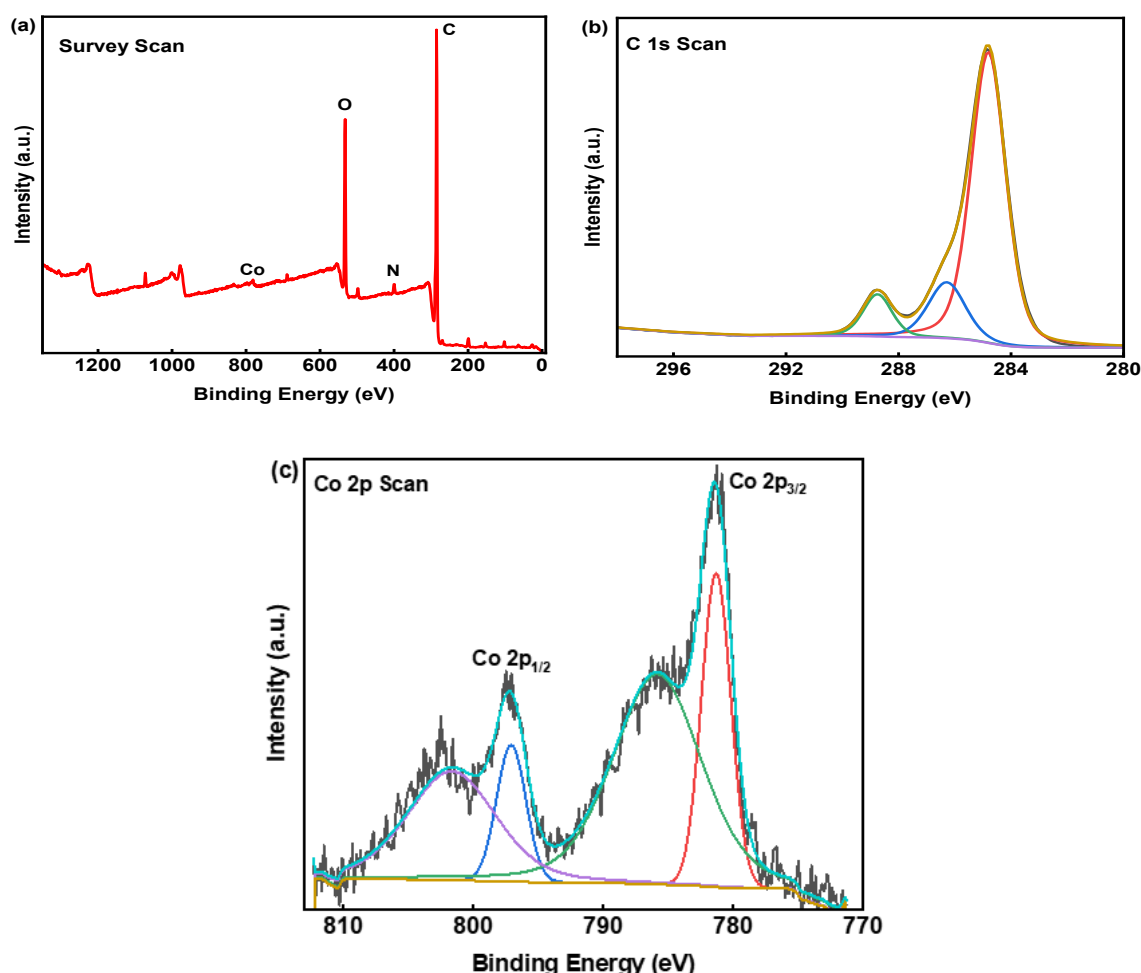


Figure 3. XPS results of cobalt-doped carbonaceous material: (a) survey scan, (b) C1s narrow scan, and (c) Co 2p narrow scan. [The red line means sum of peaks, the green line means background line and other color line represents peak fitting curve].

2.3. Cyclic Voltammetry (CV)

A comprehensive analysis of the cobalt complex through Co 2p XPS scans unveiled two distinct peaks depicted in Figure 3c. The first peak, observed at 781.8 eV, is attributed to the Co 2p_{1/2} orbital, and the second peak, located at 796.9 eV, is associated with the Co 2p_{3/2} orbital. The 15.1 eV difference between the Co 2p_{1/2} and Co 2p_{3/2} levels signifies the presence of Co(II) in the sample, as indicated by references [42–44]. Additionally, satellite peaks at binding energies of 802.6 eV and 786.8 eV, with a 15.8 eV separation between the Co 2p_{1/2} and Co 2p_{3/2} levels, further corroborate the existence of Co(II), supported by references [45–49]. Given the XRD and Raman (Figure S6) results indicating both CoO and Co₃O₄, it is plausible that our sample contains both Co(I) and Co(III) states and CoO itself comprises both.

Distinguishing between Co(III) and Co(II) in XPS analysis is challenging due to their similar peak positions, leaving room for both possibilities. Prior XPS data for similar, the assessment of other ORR catalysts in both acidic and alkaline electrolytes [51]. The electrocatalytic activity of the cobalt-doped carbonaceous material toward the ORR was initially examined using cyclic voltammetry (CV). CV measurements were taken at various scan rates (100 mV/s, 50 mV/s, 25 mV/s, and 10 mV/s) across different pH levels (1, 3, 5, and 7) of a 0.1 M H₂SO₄ electrolyte solution, within a potential range of 0.0 V to 1.1 V (vs. RHE), under both O₂- and Argon (Ar)-saturated conditions, as illustrated in Figure 4a,b. The results from the pH studies indicated that the catalyst displayed a sharper reduction peak in the electrolyte with a pH of 3 (Figure 4a), noting a significant reduction in the current at 0.30 V (vs. RHE) and 0.35 V (vs. RHE) at scan rates of 100 mV/s and 10

non-pyrolyzed complexes showed peak positions akin to those reported here [50], albeit identified in the Co(III) oxidation state. The presence of deprotonated amide peaks complicates the assignment further, as deprotonated amides significantly donate electrons to the metal. Despite the sample being subjected to a pyrolysis temperature of 500 °C, which typically leads to the decomposition of such complexes into metal oxides, it is conceivable that some original complex structures were retained, especially when polydopamine was involved. Pyrolysis is expected to break down the complex, as indicated by previous XRD and Raman analyses, potentially reducing Co(III) to Co(II) through the production of reducing gases during the process. The pyrolysis of our sample, enriched with nitrogen doping from dopamine, the amidomacrocyclic ligand, and urea, fundamentally altered the original complex structure. This transformation decomposed the metal complex and integrated metal and nitrogen into the matrix, potentially enhancing the material's oxygen reduction reaction (ORR) activities. This enhancement could be attributed to a synergistic interaction, with the metal or the nitrogen dopants serving as active sites for the ORR, illustrating the intricate relationship between material composition and electrocatalytic performance.

2.3. Cyclic Voltammetry (CV)

Electrochemical tests were conducted to evaluate the carbonaceous material's capability to electrochemically reduce oxygen in the oxygen reduction reaction (ORR). The most common method for efficiently evaluating the performance of a catalyst is to measure its half-wave potential ($E_{1/2}$). Assessing the ORR performance of a catalyst entails benchmarking against the ORR performance of a cutting-edge commercial Pt/C catalyst, typically featuring 20% Pt loading. The established average $E_{1/2}$ value of 0.84 ± 0.03 V (vs. RHE) serves as the "Golden reference" for commercial Pt/C (with Pt 20 wt%), facilitating the assessment of other ORR catalysts in both acidic and alkaline electrolytes [51]. The electrocatalytic activity of the cobalt-doped carbonaceous material toward the ORR was initially examined using cyclic voltammetry (CV). CV measurements were taken at various scan rates (100 mV/s, 50 mV/s, 25 mV/s, and 10 mV/s) across different pH levels (1, 3, 5, and 7) of a 0.1 M H_2SO_4 electrolyte solution, within a potential range of 0.0 V to 1.1 V (vs. RHE), under both O_2 - and Argon (Ar)-saturated conditions, as illustrated in Figure 4a,b. The results from the pH studies indicated that the catalyst displayed a sharper reduction peak in the electrolyte with a pH of 3 (Figure 4a), noting a significant reduction in the current at 0.30 V (vs. RHE) and 0.35 V (vs. RHE) at scan rates of 100 mV/s and 10 mV/s, respectively, in the O_2 -saturated environment. Additionally, a CV test was performed under the same conditions but in an Ar-saturated environment to determine if the catalyst could reduce oxygen in its absence, where no peak was observed (Figure 4b).

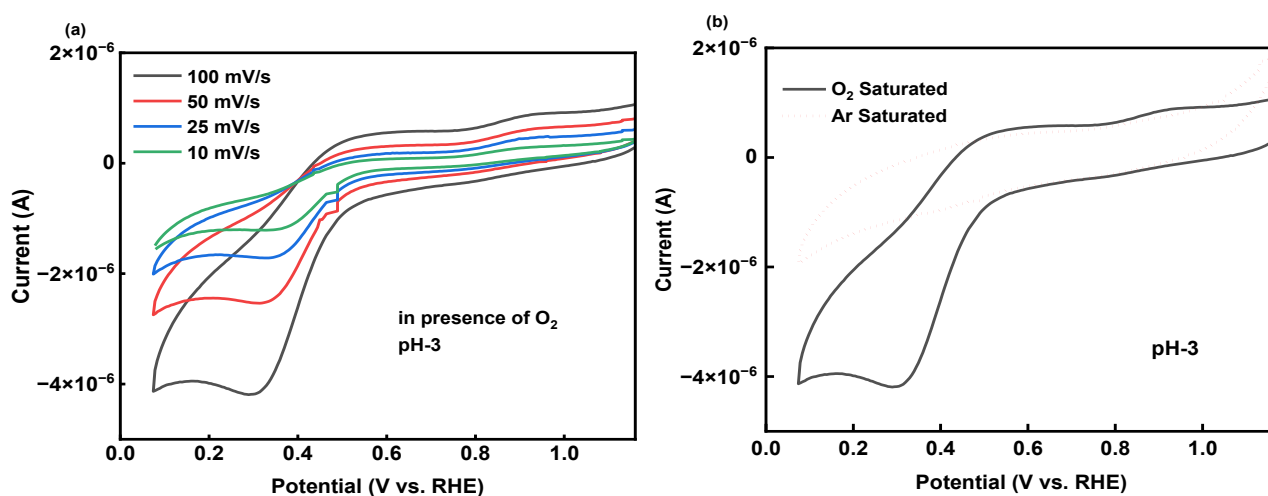


Figure 4. Cyclic voltammograms of pyrolyzed cobalt-doped carbonaceous material at pH 3 in (a) O_2 -saturated 0.1 M H_2SO_4 and (b) Ar-saturated 0.1 M H_2SO_4 , with $v = 100$ mV/s.

2.3.1. Electrocatalyst Layer Studies

The oxygen reduction reaction (ORR) studies utilized different numbers of deposited layers (1, 3, 5, 7) on glassy carbon electrodes to investigate variations in the peak potential position and/or current density. Cyclic voltammetry tests were extended to seven layers,

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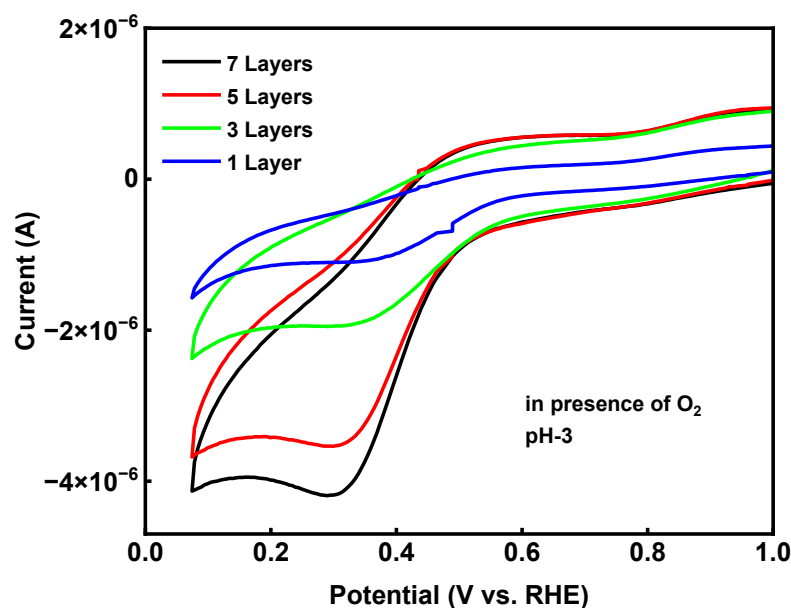


Figure 5. Cyclic voltammogram comparison for different layers in 0.1 M H_2SO_4 electrolyte solution, with $v = 100$ mV/s.

2.3.2. Electrocatalyst pH and Stability Studies

The performance of the catalyst was evaluated using cyclic voltammetry (CV) tests under various pH conditions (1, 3, 5, 7) in both O_2 -saturated and Ar-saturated environments. In Figure 6a, the cobalt-doped carbonaceous catalyst exhibited a pronounced reduction peak at pH 3 in an oxygen (O_2)-saturated environment at a scan rate of 100 mV/s, indicating its optimal performance in acidic conditions. At pH 1 and 5 in an O_2 -saturated environment, only modest reduction peaks were detected, suggesting a decrease in catalytic activity compared to pH 3. Remarkably, at pH 7, the catalyst showed no reduction peak, indicating a significant drop in activity in less acidic environments. This trend confirms that the catalyst's efficiency is maximized in more acidic conditions. In contrast, the CV tests conducted in an Ar-saturated environment revealed no significant reduction peaks for any pH level, with only a very slight peak observable for pH 1, 3, and 5 (Figure 6b), and again, no peak was detected from pH 7 upwards. The absence of significant activity in the Ar-saturated tests across all pH levels emphasizes the catalyst's specificity for the oxygen reduction reaction in acidic media, highlighting its potential application in environments where efficient ORR activity is critical. The electrochemical stability study

again, no peak was detected from pH 7 upwards. The absence of significant activity in the Ar-saturated tests across all pH levels emphasizes the catalyst's specificity for the oxygen reduction reaction in acidic media, highlighting its potential application in environments where efficient ORR activity is critical. The electrochemical stability study aims to examine the stability of the carbonaceous material through cyclic voltammetry (CV) measurements. The stability of the catalyst is an important requirement for its operation. It has been recently discovered that ensuring the long-term stability of the Membrane/Electrode Assembly (MEA) is crucial for commercializing fuel cells. An investigation through XPS data has revealed that the amount of fluorine atoms in the fuel cell gradually decreases over time due to the degradation of Nafion [52]. In this study, we investigated the chemical stability of our material up to 500 cycles at pH 3 under an oxygen (O₂)-saturated environment at a scan rate of 100 mV/s with a voltage window from 0.0 V to 1.1 V (vs. RHE). During the 500 cycles, drop-cast working electrode materials experienced a significant loss during the experiment, and it resulted in a consequential decrease in the reduction peak (Figure 6c). This degradation of active materials on the electrode surface may have resulted from irreversible reactions in the electrolyte. The effect of binders can be another factor for this kind of decrease in reduction peak. We used Nafion as a binder due to its high ionic conductivity and chemical stability. However, Nafion tends to swell in certain electrolytes or solvent environments, which can compromise the stability and electrocatalytic performance of the material over time. Although Nafion is chemically stable, its hydrophobic nature may impede the wetting of electrode surfaces, affecting electrochemical reactions and leading to reduced performance, particularly in aqueous environments. We have planned to experiment with different electrolytes and binders to improve the stability of the pyrolyzed cobalt-doped carbonaceous material.

2.3.3. Rotating Disk Electrode (RDE)

RDE studies were conducted on the carbonaceous material to determine the number of electrons involved in the ORR. In acidic conditions, oxygen can be reduced to water in a four-electron process. However, sometimes, oxygen can be reduced to hydrogen peroxide through a two-electron exchange process. Even though the reduction of oxygen to hydrogen peroxide is also an ORR process, generating peroxide is undesirable since it has an oxidative character that degrades the catalyst, which decreases its ORR activity. RDE tests were performed by rotating a drop-cast glassy carbon electrode at different rotation speeds ($\omega = 400$ to 2500 rpm) with a 10 mV/s scan rate in O₂-saturated 0.1 M H₂SO₄ (Figure 7a).

To calculate the number of electrons involved in an electrochemical process, the convective movement between the analyte solution and the electrode surface is related using the Koutecky–Levich equation. The Levich current (J_{lev}) is calculated using the equation $J_{lev} = 0.620nFCD^{2/3}\omega^{1/2}\nu^{-1/6}$, where n is the number of electrons transferred, F is the Faraday constant, C is the molar concentration of the analyte, D is the diffusion coefficient of O₂, ω is the angular rotation rate of the electrode, and ν is the kinematic viscosity of the solution. The kinetic current (J_k) and the observed limiting current (J_{lim}) from the experimental RDE data are used to construct the Koutecky–Levich equation. The slope of J_{lev} is obtained by plotting the graph between J_{lim}^{-1} and $\omega^{-1/2}$.

$$1/J_{lim} = 1/J_{lev} + 1/J_k$$

where J_{lim} is the limiting current density, J_{lev} is the Levich current, and J_k is the kinetic current.

From the slope of the K-L plot, the number of electrons involved in the oxygen reduction mechanism is determined using the equations mentioned above. According to the calculated results, the catalyst performs the ORR through a 3.58 electron process at pH 3, which matches the theoretical $n = 4$ value (Figure 7b).

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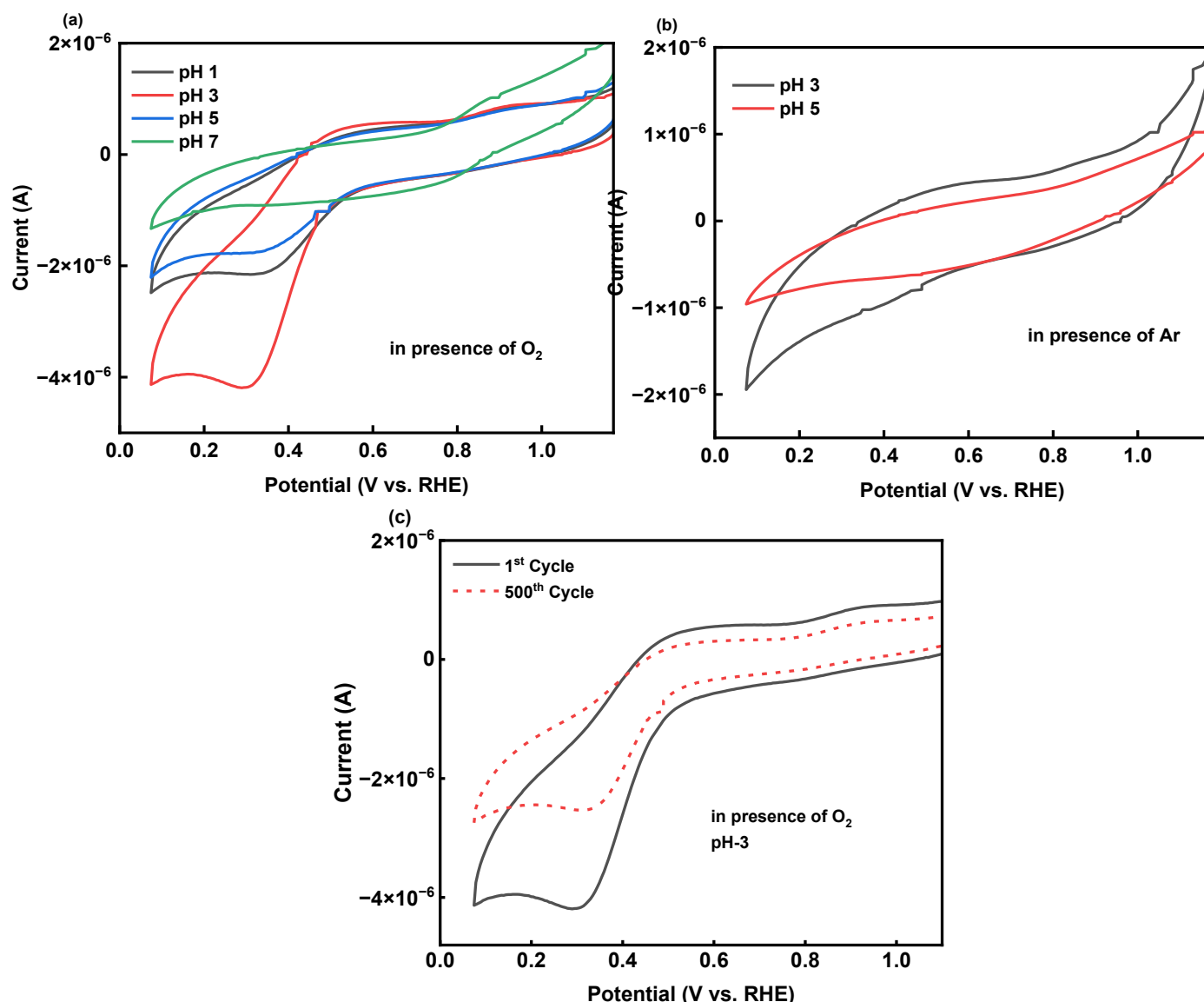


Figure 6. Cyclic voltammograms of cobalt-doped carbonaceous catalyst with different pH values in (a) O₂-saturated 0.1 M H₂SO₄ and (b) Ar-saturated 0.1 M H₂SO₄. (c) Electrochemical stability at pH 3 in 0.1 M H₂SO₄ with $v = 100$ mV/s.

2.3.3. Rotating Disk Electrode (RDE)

2.4. Proposed Mechanism

RDE studies were conducted on the carbonaceous material to determine the number of electrons involved in the ORR. The RDE studies provide clear evidence that the material catalyzes the oxygen reduction reaction (ORR) through a four-electron mechanism in acidic environments, a conclusion supported by electrochemical analyses at pH 3. This efficient four-electron pathway is shown in Figure 8. XPS analysis has confirmed the presence of both Co(II) and Co(III) species within the catalytic material, indicating that these Co centers could serve as the critical active sites for the ORR, with molecular O₂ initially binding to them. Although tests were performed by rotating a drop-cast glassy carbon electrode at different rotation speeds ($\omega = 400$ to 2500 rpm) with a 10 mV/s scan rate in O₂-saturated 0.1 M H₂SO₄ (Figure 7a), adding nitrogen to the material is expected to greatly improve the reactivity and effectiveness of these active sites for the ORR process. Interestingly, during the ORR, the Co center temporarily reaches a higher oxidation state when it first binds with an O₂ molecule. The reaction ends with the reduction of O₂ to water, which interestingly brings the Co center back to its original oxidation state, either II or III, thus completing the catalytic cycle in the challenging environment of acidic conditions. This reversible oxidation–reduction

cycle highlights the durability and effectiveness of the catalytic process, pointing out the catalyst's potential as an excellent catalyst for ORRs [53,54].

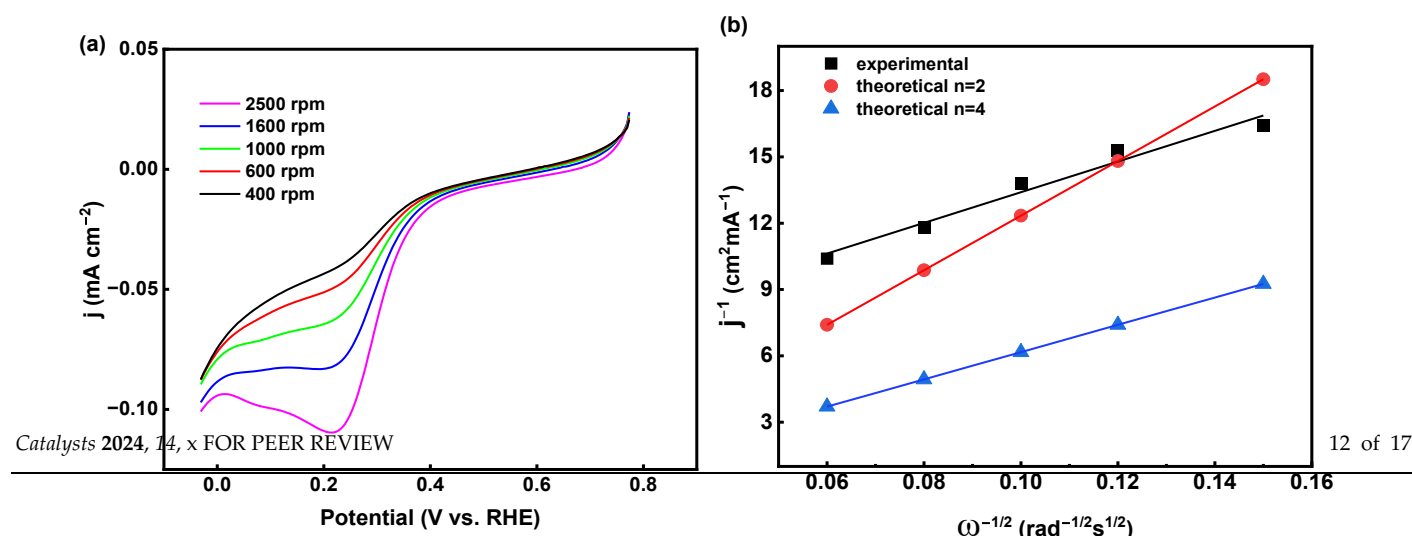
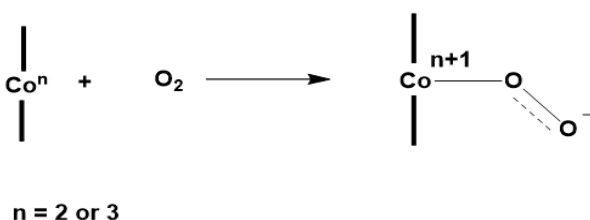


Figure 7. (a) RDE voltammograms of the catalytic process at different rotation speeds (400 to 2500 rpm) with cobalt-doped carbonaceous material in 0.1 M H₂SO₄ at different rotation speeds (400 to 2500 rpm), with $v = 10$ mV/s; (b) Koutecky–Levich plot (j^{-1} vs. $\omega^{-1/2}$).

Acidic to neutral medium

(a) Addition of Oxygen



(b) Reduction of Oxygen

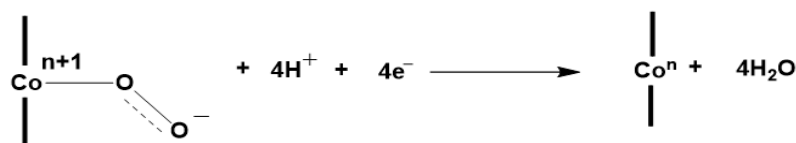


Figure 8. Proposed mechanism for ORR using cobalt-doped carbonaceous material.

3. Materials and Methods

3.1. Materials

The chemicals used in this study were sourced from Aldrich Chemical Co., St. Louis, MO, USA, and Fisher Scientific Company, San Jose, CA, USA and were utilized as received unless specified otherwise. Nanocellulose was sourced from Blue Goose Bio refining (91 Sparks Road, 26066 Canada). Scanning Electron Microscopy (SEM) analysis was performed using a JEOL SEM-1000 (JEOL, Tokyo, Japan) with a 10 kV accelerating voltage. Energy Dispersive X-ray Spectroscopy (EDS) analysis was performed with a JEOL JED-2300 (JEOL, Tokyo, Japan). The electrochemical measurements were carried out using a Pine Instruments Co. potentiostat (Echem Analyst 1.10) in a 0.1 M H₂SO₄ solution. The Co center temporarily reaches a higher oxidation state when it first binds with an O₂ molecule, using a Rinko-Miniplex instrument (Tokyo, Japan). The values of elements in the carbonaceous material was determined using X-ray Photoelectron Spectroscopy (XPS) on a Thermo Scientific (Waltham, MA, USA) K-Alpha instrument with Al K α radiation. Cyclic voltammetry (CV) experiments to assess electrocatalytic activity were conducted with a Pine Instruments potentiostat (Raleigh, NC, USA) in a 0.1 M H₂SO₄ solution. Pyrolysis was performed in an MTI Corporation (GSL-1100X, Richmond, CA, USA)

(Waltham, MA, USA) K-Alpha instrument with Al K α radiation. Cyclic voltammetry (CV) experiments to assess electrocatalytic activity were conducted with a Pine Instruments potentiostat (Raleigh, NC, USA) in a 0.1 M H₂SO₄ solution. pH and layer deposition studies also utilized the Pine Instruments potentiostat in a 0.1 M H₂SO₄ solution. Pyrolysis was performed in an MTI Corporation (GSL-1100X, Richmond, CA, USA) high-temperature furnace. Oxygen and argon gases for the research were supplied by Airgas, and deionized water was used for all washing procedures.

3.2. Synthesis of Cobalt-Doped Carbonaceous Material

The cobalt complex of the amidomacrocyclic ligand was synthesized using a previously published synthetic method with slight modifications [55]. Initially, the lithium salt of the cobalt complex was synthesized. Tetraphenylphosphonium (PPh₄⁺) salts of inorganic or metalloorganic anions are commonly utilized due to their ease of crystallization. Consequently, the counteranion was switched from lithium (Li⁺) to tetraphenylphosphonium (PPh₄⁺) by dissolving 300.0 mg of the initial cobalt complex in deionized water and incrementally adding a 3.0 M solution of tetraphenylphosphonium chloride (PPh₄Cl). The resulting precipitate was collected through filtration, and the product was subsequently dried under vacuum for 5–6 h.

Next, 120.0 mg of nanocellulose was combined with the newly synthesized cobalt complex in deionized water, and the pH of the solution was adjusted to 8. To facilitate binding, 338.0 mg of dopamine hydrochloride (DA HCl) was introduced to the mixture. This mixture was then placed on a hotplate and stirred gently for 12 h in an open allow for polydopamine formation via an oxidative polymerization process. Afterward, the contents were collected and dried under vacuum. Finally, 220.0 mg of (Co(CO)₄N₂)₆ was finely ground and added to the dried sample. The prepared mixture (refer to Figure 9) underwent pyrolysis at 500 °C in a nitrogen atmosphere.

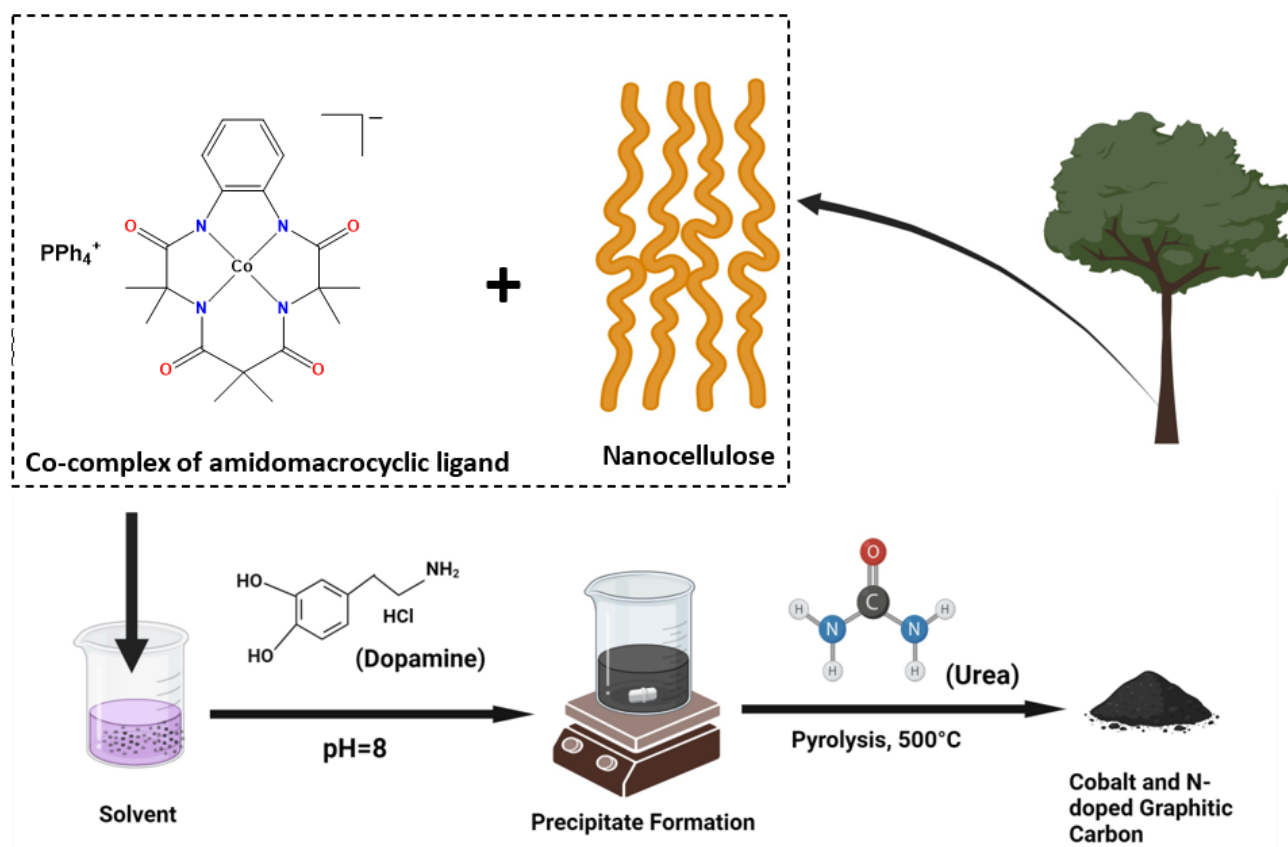


Figure 9. Schematic illustration of the synthesis of the cobalt-doped carbonaceous material catalyst for enhanced ORR activity.

3.3. Electrochemical Studies

A potentiostat facilitated the cyclic voltammetry (CV) experiments. For these tests, a glassy carbon electrode from BASi Research Product (Lafayette, IN, USA) served as the working electrode. The reference electrode, Ag/AgCl, and the counter electrode, a plati-

3.3. Electrochemical Studies

A potentiostat facilitated the cyclic voltammetry (CV) experiments. For these tests, a glassy carbon electrode from BASi Research Product (Lafayette, IN, USA) served as the working electrode. The reference electrode, Ag/AgCl, and the counter electrode, a platinum wire, were sourced from Pine Instruments and BASi Research Product, respectively. The setup included a 100 mL glass vial as the electrochemical cell, sealed with a three-holed stopper. Concentrated sulfuric acid was diluted to a 0.1 M H₂SO₄ solution, yielding a predicted pH of 1.0. CV measurements spanned potential ranges from 0.0 V to 1.1 V (vs. RHE) at various scan rates. These electrochemical studies were conducted at an ambient temperature (25 °C) using a freshly prepared 0.1 M H₂SO₄ electrolyte solution. An O₂-saturated environment was established for the experiments by bubbling oxygen gas through the electrolyte solution for at least one hour prior to testing, a condition that was maintained during the experiments. To evaluate the activity of the synthesized carbonaceous material, the electrolyte solution was deoxygenated with argon (Ar) gas. Throughout this study, all potential values are reported relative to the reversible hydrogen electrode (RHE), as per the specified expression.

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E^{\circ}_{\text{Ag/AgCl}} + 0.059\text{pH}$$

E_{RHE} is the potential versus RHE in this equation. The potential measured against the Ag/AgCl reference electrode is denoted by $E_{\text{Ag/AgCl}}$. The standard electrode potential of the Ag/AgCl reference electrode in 0.1 M H₂SO₄ is $E^{\circ}_{\text{Ag/AgCl}}$.

Layer and pH studies were carried out by performing CV tests at different scan rates ranging from 0.0 V to 1.1 V (vs. RHE) in both O₂- and Ar-saturated 0.1 M H₂SO₄ or buffered electrolytes.

3.4. Electrode Preparation

A homogeneous catalyst suspension was prepared by dissolving 5 mg of the catalyst in 5 mL of methanol, achieving a 1:1 weight/volume (w/v) ratio. To ensure uniformity, the mixture was sonicated for 10 min. Subsequently, after sonication, 40 µL of Nafion solution (5 wt.%) was added to the homogeneous suspension. The surface of the glassy carbon electrode was initially polished with a 0.05 µm alumina slurry and then thoroughly rinsed with deionized water. Following this, 20 µL of the catalyst suspension was drop-cast onto the polished glassy carbon electrode surface and allowed to dry under vacuum. For the electrocatalyst layer studies, the procedure was similar to that used for cyclic voltammetry (CV) testing; however, 10 µL of the catalyst suspension was drop-cast onto the glassy carbon surface for each layer, with each application followed by drying under vacuum.

4. Conclusions

A cobalt complex along with nanocellulose, polydopamine, and urea composite material was synthesized for use as a cathode catalyst in fuel cell applications. Characterizations of the metal-doped carbonaceous material were conducted using SEM, EDS, XRD, and XPS. SEM analysis revealed the morphology and nanostructure of the material, with some agglomeration observed. EDS confirmed the uniform distribution of elements within the carbonaceous material, while XRD identified the crystalline structures of Co₃O₄ and CoO. The electrocatalytic behavior of the cobalt-doped carbonaceous material toward the oxygen reduction reaction (ORR) in acidic media was investigated through cyclic voltammetry (CV) and rotating disk electrode (RDE) techniques. CV analysis demonstrated the ORR activity of the Co-doped carbonaceous material across different pH levels, with a pronounced peak at pH 3, showing a peak potential of 0.30 V (vs. RHE) in an oxygen-saturated 0.1 M H₂SO₄ electrolyte solution at a scan rate of 100 mV/s. This indicates the material's capability for ORRs. Further pH and layering studies were conducted using the CV system. RDE measurements determined that the cobalt complex catalyzes the ORR via a four-electron pathway. These findings offer new insights that could be beneficial for various applica-

tions, including acidic fuel cells, electrocatalytic reduction processes, batteries, biosensors, and supercapacitors.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal14090613/s1>, Figure S1: Raman spectrum of pyrolyzed cobalt-doped carbonaceous ORR catalytic material. References [56–58] are cited in the Supplementary Materials.

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