RECENT ADVANCEMENTS IN ELECTROCATALYTIC CO_2 REDUCTION USING DIFFERENT PORPHYRINOIDS

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Submitted by:
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I, Harshita Aggarwal (24/MSCCHE/49), student of M.Sc. Chemistry at the Department of Applied Chemistry, Delhi Technological University, hereby declare that the work presented in this dissertation entitled "Recent Advancements in Electrocatalytic CO_2 Reduction Using Different Porphyrinoids: A Review" is an authentic record of the research work carried out by me under the supervision of Prof. Anil Kumar, Department of Applied Chemistry, Delhi Technological University, in partial fulfillment of the requirements for the award of the degree of Master of Science.

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Place: Delhi

Date: 22 June 2026

Harshita Aggarwal (24/MSCCHE/49)

CERTIFICATE

This is to certify that the dissertation titled "Recent Advancements in Electrocatalytic CO_2 Reduction Using Different Porphyrinoids: A Review", submitted by Harshita Aggarwal (24/MSCCHE/49) to the Department of Applied Chemistry, Delhi Technological University, Delhi, in partial fulfillment of the requirements for the award of the degree of Master of Science in Chemistry, embodies the results of original work and studies carried out by the student.

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Harshita Aggarwal

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LIST OF ABBREVIATIONS

CO_2RR – Carbon Dioxide Reduction Reaction
CO – Carbon Monoxide
HCOOH – Formic Acid
HCHO – Formaldehyde
CH_3OH – Methanol
CH_4 – Methane
C_2H_4 – Ethylene
C_2H_5OH – Ethanol
NHE – Normal Hydrogen Electrode
SHE – Standard Hydrogen Electrode
RHE – Reversible Hydrogen Electrode
FE – Faradaic Efficiency
TOF – Turnover Frequency
TON – Turnover Number
HER – Hydrogen Evolution Reaction
PCET – Proton-Coupled Electron Transfer
GC – Glassy Carbon
CNT – Carbon Nanotube
rGO – Reduced Graphene Oxide
MOF – Metal-Organic Framework
COF – Covalent Organic Framework
DFT – Density Functional Theory
CoPc – Cobalt Phthalocyanine
FePc – Iron Phthalocyanine
TPP – Tetraphenylporphyrin
OEC – Oxygen-Evolving Complex
DMF – Dimethylformamide
MeCN – Acetonitrile
TBAP – Tetrabutylammonium Perchlorate

ABSTRACT

The sharp, sustained rise in the concentration of carbon dioxide (CO_2) in the atmosphere, predominantly as a result of fossil fuel combustion, industrialization, deforestation and increased agricultural production, is one of the most pressing environmental challenges of the twenty-first century. The levels of atmospheric CO_2 have recently reached over 420 parts per million (ppm) compared to pre-industrial levels of around 280 ppm. This dramatic increase is the main contributor to anthropogenic climate change, causing global warming, sea level rise, ocean acidification and many natural ecosystems around the globe being affected.

The electrocatalytic CO_2 reduction reaction (CO_2RR) is one of the various methods being investigated to tackle the issues of CO_2 accumulation. CO_2RR not only reduces CO_2 emissions but also generates valuable chemical feedstocks and fuels such as carbon monoxide (CO), formic acid (HCOOH), formaldehyde (HCHO), methanol (CH_3OH), methane (CH_4), ethylene (C_2H_4), and ethanol (C_2H_5OH), all of which can be used in various commercial applications instead of fossil fuels. If powered by electricity from renewable energies like solar, wind or hydro, CO_2RR is a carbon-neutral or even carbon-negative process.

Porphyrinoids are a structurally very diverse and wide-spread group of macrocycles that has sparked special research interest due to its potential as catalytic materials in the reaction of CO_2RR. The porphyrinoids include porphyrins, metalloporphyrins, phthalocyanines, metallophthalocyanines, corroles, chlorins, bacteriochlorins and many derivatives. They have an important common structure feature: a highly conjugated macrocyclic aromatic structure with a central cavity to coordinate transition metal ions, giving well-defined and highly tunable metal coordination sites that act as the active centers for catalysis.

The unique features of porphyrinoid-based electrocatalysts are their highly tuneable electronic structure, ease of synthetic modification at peripheral positions, excellent light-harvesting properties, precise single-atom metal centres as a basis for detailed mechanistic studies, and high selectivity for certain CO_2 reduction products. A number of recent studies have shown that these materials can be very efficient, have low overpotentials and are very stable for catalytic activity, providing significant promise for their use on a large scale.

This dissertation provides a thorough overview of the recent developments on electrocatalytic CO_2 reduction with various porphyrinoid catalyst structures. The review systematically covers the basic principles of CO_2 chemistry and electrochemistry, structural and electronic properties of porphyrinoids, mechanisms of CO_2RR at porphyrinoid metal centres, performance of specific subclasses of porphyrinoids (porphyrins, phthalocyanines, corroles, and chlorins), effects of structural modification and the identity of the metal centre, immobilization strategies for the fabrication of electrodes, and challenges and future directions in this rapidly evolving field.

The results presented in this work show that the iron and cobalt porphyrins have very high selectivity for CO production (Faradaic efficiencies $> 95\%$ at relatively low overpotentials).

Cobalt phthalocyanines have been proven to be very active when immobilized on carbon supports, which catalyse the conversion of CO_2 to CO. Inspired by recent progress in corrole chemistry, a high CO selectivity with minimum competing hydrogen evolution can be realized. It has been demonstrated that the catalytic activity can be significantly improved by axial ligand modifications, peripheral functionalization and surface immobilization. The addition of porphyrinoids to metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) is an intriguing area that has produced highly active and robust catalysts.

The goal of this dissertation is to deliver a well-rounded and current overview of the state-of-the-art in porphyrinoid-based CO_2RR catalysis for graduate students, researchers, and electrocatalysis and materials practitioners, with an emphasis on the knowledge gaps and potential research directions for the field.

Keywords: CO_2 reduction reaction, electro catalysis, porphyrins, metallophthalocyanines, corroles, chlorines, Faradaic efficiency, over potential, selectivity, renewable energy.

INTRODUCTION

1.1 The Global Carbon Dioxide Crisis

CO_2 is a greenhouse gas that is a natural component of the Earth's climate system and is essential for the greenhouse effect. But, since the beginning of the Industrial Revolution (mid-eighteenth century), human activities have significantly disrupted the atmospheric carbon cycle. The extensive release of CO_2 over the last centuries has been driven by the use of fossil fuels such as coal, petroleum and natural gas to satisfy increasing energy needs, which have released large amounts of CO_2 that have been stored in geological formations for millions of years. At the same time, land-use and deforestation have led to a decrease in the ability of terrestrial ecosystems to sequester CO_2 via photosynthesis, exacerbating the imbalance.

The current level of CO_2 in the atmosphere is about 421 parts per million (ppm) by volume, which is a 50% rise from the pre-industrial levels of about 280 ppm. Based on ice core and other proxy data, this concentration is the highest ever recorded (at least over the last 800,000 years). The rate of increase has itself been accelerating: during the 1960s the average was close to 0.7 ppm each year, climbs to more than 2.4 ppm every year in recent years, a trend that is consistent with the continued rise in global fossil fuel consumption, especially in the fast-growing economies of eastern Asia. The impacts of higher atmospheric CO_2 levels have widespread and complex implications. Global mean surface temperatures are rising due to the enhanced green house effect which is caused by the increase of CO_2 and other GHGs. Average global temperatures are expected to increase by 2.4–3.5°C by the end of the twenty-first century relative to pre-industrial time (1850–1899), with potentially catastrophic impacts, according to the Intergovernmental Panel on Climate Change (IPCC). The Paris Agreement of 2015 set an international goal of limiting warming to well below 2°C, and to 1.5°C, but this will require unprecedented and immediate reductions in greenhouse gas emissions in addition to active CO_2 removal strategies.

In addition to direct effects on climate, high CO_2 concentrations are causing ocean acidification: When CO_2 is dissolved in the ocean, it forms carbonic acid (H_2CO_3), which dissociates and thus reduces the pH of the ocean. The pH of the oceans is already lowered by about 0.1 units since the pre-industrial era, corresponding to a 26% increase in the concentration of hydrogen ions, which affects the coral reefs, shellfish and the rest of the marine food chain. Ocean warming, acidification and deoxygenation are threats to the existence of marine biodiversity and the millions of people who rely on healthy ocean systems for their food, livelihoods and cultural identity.

1.2 Strategies for CO_2 Mitigation and Conversion

To deal with the CO_2 crisis, a multi-sector, multi-scale package of complementary strategies must be implemented at the same time. The strategies can be divided into three general categories: reduce CO_2 emissions at their source by improving energy efficiency and switching to non-carbon energy sources; capture and sequester CO_2 from point sources or directly from the atmosphere; convert captured CO_2 into useful products, close the carbon cycle and generate economic value.

Solar PV, wind, hydro, and geothermal are key renewable energy technologies that are essential for decarbonizing electricity generation, a major contributor of CO_2 emissions globally. Emissions can be significantly cut across various sectors by electrification of such sectors as transport, heating and industry, combined with growing shares of renewables. Aggressive deployment of renewable energy, however, will likely necessitate measures for active CO_2 removal in the future to counteract the remaining emissions of hard-to-decarbonize sectors like aviation and shipping, agriculture and heavy industry.

CCS technology refers to the removal of CO_2 from flue gas at CO_2 emission sources, such as power plants or industrial sources, and its permanent disposal in deep geological formations. Although it is technically possible, its economic, logistic and acceptance issues are very big. The cost of capture, compression, transport and injection are still high and long-term integrity of geological storage sites must be monitored and verified carefully. In addition, CCS is not for CO_2 already in the air, and requires an continuous energy supply to run.

One approach to solving the challenge is to remove CO_2 directly from the air through direct air capture (DAC) technologies. The thermodynamic difficulty of separating CO_2 from the air at ~420 ppm, however, is enormous, and the existing DAC systems are currently energy and capital intensive, requiring extensive investment per tonne of captured CO_2. With renewable electricity, DAC can be a truly negative-carbon solution, but scaling up to gigatonne per year to make a significant dent in the climate change problem is a significant barrier.

Sequestration is complemented by an attractive alternative that will generate value from a waste stream: CO_2 utilization — the use of captured CO_2 to create useful chemicals, fuels or materials. CO_2 can be used as a feedstock for the manufacture of various products such as polymers, carbonates, carboxylates, urea, methanol, synthetic fuels, and building materials. From the various CO_2 utilization options, electrochemical reduction is particularly attractive, as it requires mild reaction conditions (ambient temperature and pressure), can be coupled to intermittent renewable power, can yield a variety of tunable products, and is potentially modular-scalable. Commercial-scale electrochemical CO_2 reduction is currently being pursued by several companies and research investments in the area have increased significantly in the last decade.

1.3 Electrochemical CO_2 Reduction: Fundamentals

Electrochemical CO_2 reduction (CO_2RR) refers to the ability to reduce CO_2 into reduced carbon compounds using electrical energy, preferably from renewable energy sources, at a cathode surface. A typical electrochemical cell configuration has the CO_2 reduction reaction taking place at the cathode and an oxidation half-reaction, typically the oxygen evolution reaction (OER) from water, occurring at the anode. The overall cell reaction (CO_2 reduction on the cathode and water oxidation on the anode) transforms electrical energy and CO_2 into chemical bonds.

Depending on the number of protons and electrons consumed, the type of catalyst used, and the reaction conditions, a vast range of products can be produced via the electrochemical reduction of CO_2. The two-electron products, CO and HCOOH; four-electron products, HCHO; six-electron products, CH_3OH; eight-electron products, CH_4; and multi-carbon products, which require 12 or more electrons, include ethylene (C_2H_4), ethanol (C_2H_5OH), and propanol (C_3H_7OH). The values of these reactions, listed versus the normal hydrogen electrode (NHE) at pH 7, in aqueous solution at 25°C, 1 atm gas pressure are as follows:

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad E^0 = -0.53 \text{ V vs NHE} \quad (1.1)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \qquad E^0 = -0.61 \text{ V vs NHE} \quad (1.2)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCHO + H_2O \qquad E^0 = -0.48 \text{ V vs NHE} \quad (1.3)$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \qquad E^0 = -0.38 \text{ V vs NHE} \quad (1.4)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E^0 = -0.24 \text{ V vs NHE} \quad (1.5)$$

$$CO_2 + e^- \rightarrow CO_2^{\bullet-} \qquad E^0 = -1.90 \text{ V vs NHE} \quad (1.6)$$

These thermodynamic potentials indicate some of their key properties. The direct reduction of CO_2 to the anion radical ($CO_2^{\bullet-}$) by one electron (Equation 1.6) has a very negative potential of -1.90 V vs NHE that is indicative of the large reorganization energy that is required to bend a linear CO_2 molecule to a bent $CO_2^{\bullet-}$ anion radical. This activation barrier allows for direct reduction of CO_2 to be extremely inefficient. Second, multi-electron proton coupled reduction reactions (Equations 1.1-1.5) have much less negative potentials, thus they are more easily accessible thermodynamically. Third, the reduction potential of the competing hydrogen evolution reaction, $2H^+ + 2e^- \rightarrow H_2$ ($E^0 = -0.41$ V vs NHE at pH 7), is very close to the potential of several CO_2 reduction products, posing a selectivity challenge which requires careful design of the catalyst.

1.4 Thermodynamics and Kinetics of CO_2RR

However, the multi-electron CO_2RR (Equations 1.1–1.5) has a relatively small thermodynamic potential and to achieve efficient CO_2RR in practice far more negative applied potentials are required than thermodynamics would predict. Any potential beyond the thermodynamic minimum needed is called the over potential (η), and represents the kinetic barriers that must be surmounted to promote the reaction at a practically useful rate. Lower over potential indicates more energy efficient operation, and is one of the main figures of merit used to assess CO_2RR electrocatalysts.

But the kinetic problems in CO_2RR are quite complex and large. The molecule CO_2 has a very high activation energy (C=O: ~805 kJ/mol), and is a very stable molecule. For most cases, the first activation step, which usually is the binding of CO_2 to the catalyst surface or the metal centre and the transfer of an electron for the start of the reduction, is rate limiting. The intermediates formed in the reaction, $CO_2^{\bullet -}$, COOH, CO, CHO and CH_2O, are all different kinetic barriers and their relative stability dictates the rate and product selectivity of the reaction.

Another crucial performance criterion in CO_2RR is the Faradaic efficiency (FE). It measures the ratio of the charge transferred to the formation of a particular product as in an electrochemical experiment. In an ideal catalyst, all input electrons would be channeled into the target product; however, in practice, competing reactions, such as HER, will absorb some of the charge. The economic feasibility and usefulness of CO_2RR processes depends on high FE.

Turnover number (TON) and turnover frequency (TOF) are used to gain information on the intrinsic catalytic activity and durability of a catalyst. TOF gives a measure of the rate at which a catalyst works and is defined as the number of catalytic cycles (formed of product molecule) per unit time per catalyst active site. TON is the total number of catalytic cycles before the catalyst becomes inactive and gives an idea of the catalyst stability and lifetime. Both high TOF and high TON is essential for practical applications. It is important to consider the stability of CO_2RR electrocatalysts in practical applications. The degradation of molecular catalysts containing porphyrinoids can occur in a variety of ways, such as: desorption from the electrode-surface, dimerization, aggregation, and loss of the central metal ion (demetallation) and ligand breakdown. Thus, high activity and selectivity with high catalyst stability is a major area of current research.

1.5 Advantages of Electrocatalytic CO_2RR and Role of Porphyrinoids

CO_2RR through electro catalysis has multiple unique advantages over other CO_2 conversion methods. Electrochemical reduction can also be done at ambient temperature and pressure, which reduces capital and operating costs in comparison to thermal catalysis, which is normally done at high temperature and pressure. The driving force for the reaction (the applied electrode potential) is exactly controllable, and the product distribution can be optimized by simply changing the operating potential. When combined with renewable electricity (e.g., solar, wind) a truly sustainable carbon cycle is possible.

The special structural and electronic properties of porphyrinoids make them superior CO_2RR electrocatalysts. They exhibit rich redox chemistry with multiple electron accumulation at the metal centre without any destructive oxidation/reduction of the ligand framework, arising from their large, extensively conjugated π-systems. The central cavity of porphyrinoids can host a wide range of transition metal ions, and the nature of the metal centre has a significant impact on the catalytic activity, selectivity and mechanism of CO_2RR.

Structural modification is possible throughout the periphery of porphyrinoid macrocycles. Substitutions at the meso and β-pyrrolic positions can fine-tune the redox potential and the Lewis acidity/basicity of the metal centre, which directly impact CO_2 binding and activation. Water solubility and electrostatic interaction with CO_2 and proton donors can be improved with the functionalisation of charged groups (e.g., ammonium, sulfonate). It has been demonstrated that hydrogen-bonding donors (such as hydroxyl and amino groups) in the second coordination sphere dramatically alter the rate for CO_2 reduction by stabilizing key intermediates via non-covalent interactions.

The single-atom character of the porphyrinoid metal centres is very clearly defined, which is a great advantage for the study of mechanisms. The porphyrinoid complexes offer a homogeneous and well defined catalytic environment in contrast to the heterogeneous metal catalysts, which have a variety of different active sites, the catalytic environment of which is poorly defined. These allow in-depth mechanistic investigations, via spectroelectrochemistry, in-situ spectroscopy and computational modelling, to gain fundamental insight into CO_2RR mechanisms which can inform rational catalyst design.

1.6 Scope and Objectives of the Present Review

The aim of this dissertation is to bring together and systematically overview the current state of knowledge of porphyrinoid based electrocatalysts for CO_2RR, especially developments published in the last ten years (2014–2024). The review covers the following main objectives:

(i) To introduce and critically discuss the structural and electronic properties as well as physico-chemical properties of different classes of porphyrinoids relevant to the role of CO_2RR catalysts.

(ii) The systematic review of the mechanistic understanding of CO_2RR at porphyrinoid metal centres including the mechanistic studies (both experimental and computational).

(iii) To examine the catalytic activity of selected sub-classes of porphyrinoid electrocatalysts — porphyrins, phthalocyanines, corroles, and chlorins — and focus on the reported Faradaic efficiencies, overpotentials, TOF/TON and the product selectivity. To discuss the strategies that have been adopted to anchor porphyrinoid catalysts on electrode surfaces, such as incorporation in metal-organic frameworks and covalent organic frameworks.

(v) To discuss the important issues and constraints of existing CO_2RR systems based on porphyrinoids, and suggest directions for future research in this area.

PORPHYRINOIDS – STRUCTURE, PROPERTIES, AND CLASSIFICATION

2.1 Overview of Porphyrinoid Macrocycles

Porphyrinoids is a large, structurally diverse superfamily of macrocycles, all held together by a common structural feature: an 18 π-electron, planar aromatic macrocycle made up of four pyrrole-type subunits connected by bridging atoms or groups. The parent compound of the porphyrinoid family is porphine (free-base porphyrin), which is a symmetrical tetrapyrrole with 4 pyrrole rings connected to each other by 4 methane bridges (=CH–) at the α-positions, resulting in a fully conjugated macro cycle with an internal cavity that can coordinate metal ions. By variations in the bridge atoms, the level of saturation of these rings, the substituents at the periphery, and the metal in the center, a wide variety of porphyrinoid compounds can be systematically elaborated and used in chemistry, biology and materials science.

Porphyrinoids have many critical and irreplaceable functions in biological systems. Heme is an iron(II) porphyrin complex, which is the prosthetic group of hemoglobin, myoglobin and the cytochrome P450 enzyme family, where it is responsible for oxygen transport, storage and a diversity of oxidative transformations. The pigments in photosynthesis that are able to harvest light and separate charges are called chlorophylls, which are magnesium containing chlorins. Vitamin B_{12} (cobalamin) is a cobalt-containing corrin complex that is an essential cofactor in many biomedically important enzymatic reactions.

The electrochemical characteristics of porphyrinoids are of special interest for CO_2RR applications. The macrocyclic structure provides a longer π-electronic system that allows for the delocalization of electron density throughout the molecule and thereby allows electrons to be transferred to and from the central metal ion. Porphyrinoids have a wide variety of redox properties that can be achieved by varying the central metal, peripheral substitution, and axial ligation, which allows them to be matched to the thermodynamic requirements of the CO_2 reduction pathways targeted by the catalyst. In addition, the nitrogen donor atoms in the equatorial ligand positions in the macrocyclic cavity provide a very well-defined equatorial ligand field which affects the electronic configuration, spin state and reactivity of the central metal towards CO_2.

2.2 Porphyrins: Structure and Electronic Properties

The most well-studied subclass of porphyrinoids are porphyrins. The porphyrin macrocycle is a planar, aromatic system of 18 π-electrons, comprised of four pyrrole rings linked by four meso methine bridges. The IUPAC systematics name of the parent compound is porphine, with C5, C10, C15 and C20 being the meso positions and C2, C3, C7, C8, C12, C13, C17 and C18 being the β-pyrrolic positions. Free-base porphyrins (H_2P) have two of the four inner N atoms protonated (N–H) and the other two are not protonated. This arrangement gives rise to a slight distortion from D_4h to D_2h, which gives rise to the distinct UV-visible absorption properties.

The UV-visible absorption spectrum of porphyrins is very typical and can be used as a diagnostic fingerprint. The free-base porphyrins have a strong absorption band in the region of 400–420 nm, which is the Soret or B-band, which corresponds to an allowed $S_0 \rightarrow S_2$ transition, and four weaker bands in the 500–650 nm region corresponding to transitions between S_0 and S_1. The intensity pattern & locations of these bands are sensitive to redox state of metal centre, peripheral substitution, and solvent effects. The D_2h is changed to D_4h on metalation (substituting the N–H protons with a metal ion), which decreases the number of Q-bands from 4 to 2, and the overall spectrum is simplified and made more symmetric.

The electrochemical properties of porphyrins are in keeping with their ability to undergo oxidation (electron loss from π-system) and reduction (electron uptake into π-system or at the metal centre) at accessible potentials. Aprotic solvents: The reduction of metalloporphyrins is usually carried out in a series of steps: The first step involves the addition of an electron to the lowest unoccupied molecular orbital (LUMO) of the macrocycle, known as the ring reduction step; The subsequent steps involve the addition of an electron to the metal centre or the ring, depending on the nature and oxidation state of the metal. The difference between the ring-based and metal-based reduction is important because metal-centred reductions form the low-valent metal species which are necessary for CO_2 activation, whereas ring reduction does not.

Mesotetraphenylporphyrin (H_2TPP) and its derivatives have been most commonly studied porphyrin ligand structures for CO_2RR. The reduction potential decreases with electron-withdrawing groups (e.g., -F, $-CF_3$, $-NO_2$, -CN) at the para-positions of the meso-phenyl groups and increases with electron-donating groups (e.g., $-NH_2$, $-OCH_3$). The one-step synthesis process allows the near-400-500 mV tunability of the redox potential, which provides a strong tool for fine-tuning the reduction potential of the catalyst to the thermodynamic requirements for CO_2RR.

2.3 Metalloporphyrins: Metal-Centre Effects

The coordination chemistry of metalloporphyrins is very rich and varied. This porphyrin macrocycle can be used for the incorporation of essentially all transition metals, many main-group metals and several lanthanides and actinides, though the size of the ionic radius and the preferred coordination geometry puts limits on which ones can be incorporated most easily. First-row transition metals, such as iron (Fe), cobalt (Co), manganese (Mn), and nickel (Ni), are found in the most catalytically active metalloporphyrins used for CO_2RR.

The catalytic activity of a metalloporphyrin for CO_2RR is likely to be most sensitive to the identity of the central metal ion. The metal has an impact on the redox potential of catalysis, the way that CO_2 is activated (direct binding vs. hydride route), the character and stability of catalytic intermediates, the selectivity towards the products (CO vs. HCOOH vs. hydrocarbons), and the sensitivity to competitive HER. The most frequent route to CO formation involves direct binding of CO_2 to Fe(I) or Fe(0) centre, to give the usual iron porphyrins their CO as the main product. Cobalt porphyrins are also good CO producers, except that they tend to give slightly less negative potentials than their iron counterparts. The copper and nickel porphyrins have been reported to catalyse the formation of methane and other multi-carbon products under certain conditions but their activity for CO_2RR is generally lower in comparison to Fe and Co systems.

The oxidation state of the central metal is very important in catalysis. Many porphyrin-based CO_2RR catalysts have a formally low-valent state (e.g., Fe(I), Fe(0), Co(I)) that is formed through an electroreduction prior to CO_2 binding. The minimum overpotential for catalysis is determined by these reduction potentials to these active states. Low overpotential and efficiency can be achieved by stabilizing the low valent active states either by electron-withdrawing peripheral substituents, or by using axial ligands which stabilize specific metal oxidation states.

2.4 Phthalocyanines and Metallophthalocyanines

The relationship between phthalocyanines (Pc) and porphyrins is very close, but there are several important differences in structures. In the phthalocyanines there are four pyrrole rings fused to four benzo (benzene) rings with the four aza nitrogen atoms (=N–) replacing the four methine bridges in the pyrroles. It provides the phthalocyanine macrocycle with a longer π-conjugation than porphyrin, a larger aromatic ring system (the inner pathway consists of 18 π-electrons) and a deeper blue-green colour. The metallophthalocyanines (MPc) have an intense Q-band in the UV-visible region of the spectrum at a slightly lower energy than the Q-bands of metalloporphyrins, and at a higher energy than the Q-bands of metallosulphonated porphyrins.

Metallophthalocyanines have been known as pigments, dyes and catalysts for many years and are industrially important. They are planar, allowing for strong π–π stacking interactions that promote their self-aggregation in solution and on surfaces. Aggregation is a common problem in homogeneous catalysis (where it leads to a decrease in the concentration of molecularly dispersed catalysts), and is beneficial in heterogeneous catalysis, in which π–π stacking allows MPc molecules to assemble in an ordered fashion on carbon or graphene surfaces, leading to a high concentration of active sites.

The electrochemical properties of metallophthalocyanines are similar to the metalloporphyrins, but occur at more negative potentials because of the extended aromatic system. Two phthalocyanine complexes, cobalt phthalocyanine (CoPc) and iron phthalocyanine (FePc), are the most widely studied MPc catalysts for CO_2RR and both have been demonstrated to be highly selective for CO production. CoPc and FePc show high aggregation tendency in solution and hence they need to be fixed on electrode surfaces for practical applications.

2.5 Corroles

The Corroles are a very interesting class of porphyrinoids in which one of the 4 meso methine bridges of the porphyrins is missing, which makes the macrocycle triply contracted. This structural difference is of great importance for the coordination chemistry and electronic properties of corroles. The corrole macrocycle is trianionic (with three inner NH protons in the free-base form) rather than dianionic as is the case with porphyrin, and it can therefore stabilize higher oxidation states of metals. Fe(IV), Co(III), Mn(V), and other high-valent states of metals are easily found in metal corroles, and are hard to obtain in the porphyrin complexes.

The increased charge of the corrole macrocycle, together with the stabilization of high metal oxidation states, directly relate to the catalysis of CO_2RR. Corrole-metal complexes are capable of reductive activation to yield highly reactive low-valent metal species and the relatively facile support of multiple oxidation state changes in the corrole framework makes these compounds attractive candidates for multi-electron reduction catalysis. Cobalt and iron corroles have been studied to exhibit selectivity towards CO production with very low overpotentials and in some instances, the corrole framework suppresses competing HER more efficiently than the analogous porphyrin systems.

The synthesis of corroles is more difficult than the synthesis of porphyrins, and it has been less studied. The last 20 years however have seen great progress in synthetic methodology that has provided access to a variety of meso-substituted corroles.In the last 20 years, however, significant progress has been made in synthetic methodology that has led to the availability of a wide variety of meso-substituted corroles that can be used in systematic structure-activity studies. The meso-aryl corroles with electron withdrawing groups have been extensively studied for CO_2RR.

2.6 Chlorins and Bacteriochlorins

Chlorins are modified porphyrins that have one of the four β-β double bonds reduced (hydrogenated) by the addition of hydrogen, to become a pyrrolidine ring. This partial reduction removes the D_4h symmetry of the metalloporphyrin's core structure, causing a characteristic enhancement of the lowest-energy Q-band absorption. The green colour of plants is due to the strong absorption of chlorophyll a and b in the red region (around 650-700 nm) and they are the structural basis of chlorophyll a and b, the principal pigments of photosynthesis.

2.7 Other Porphyrinoid Derivatives

In addition to the large groups of subclasses outlined above, the porphyrinoid superfamily contains numerous other structural motifs. Calix[4]pyrroles are non-aromatic macrocycles consisting of four linked pyrrole rings, with sp^3-hybridized meso carbons, which are useful receptors of anions, but are not electroactive catalysts for CO_2RR, in general. In the n-confused porphyrins one ring of the porphyrin has been inverted, with the nitrogen atoms now pointing towards the outside of the molecule, changing the inner coordination environment. Porphyrins with three pyrrole rings are known as subporphyrins. Expanded pyrrines have > 4 pyrrole rings and the macrocycles with larger cavities are able to accommodate larger metal ions.

Sapphyrins (pentapyrrole), hexaphyrin and complexes of these are studied for their unusual electrochemical and magnetic properties among expanded porphyrins. Their use, however, has not been explored extensively in CO_2RR and they have not been applied in it to a significant extent.

2.8 Electronic Tunability Through Peripheral Substitution

The most impressive property of the designed porphyrinoids as catalysts is the highly tunable electronic properties available via peripheral substitution. There are two types of peripheral sites for covalent modification of porphyrins, the meso and the β-pyrrolic positions and the meso positions of the benzo rings of phthalocyanine and the central metal of corroles, that can have a dramatic effect on the electronic properties of the macrocycle and the central metal.

Substituents that are capable of withdrawing electrons, like -F and trifluoromethyl ($-CF_3$), nitro ($-NO_2$), cyano (-CN), and pentafluorophenyl groups, reduce the energy of LUMO, making the macrocycle easier to reduce and the metal centre more electrophilic. This causes the catalytic reduction potential to shift towards more negative values, thus decreasing the overpotential and enhancing the energy efficiency of CO_2RR. For instance, it is possible to shift the Fe(III)/Fe(II) reduction potential of Fe-tetraphenylporphyrin (FeTPP) by ~100 mV when four meso-phenyl groups are replaced with four meso-pentafluorophenyl groups, and further β-pyrrolic electron withdrawing groups shift potentials by another 100-300 mV.

On the other hand, electron-donating groups like amino ($-NH_2$), methoxy ($-OCH_3$) and alkyl groups increase the energy of the lowest unoccupied molecular orbital and thus decrease the reduction potential. This typically leads to higher overpotentials for CO_2RR, but sometimes it is the electron-rich catalysts that perform better, especially in electrochemical reactions involving CO_2 binding to electron-rich metal centres.

In addition to their electronic effects, substituents in the second coordination sphere (those groups that are close to but not directly bonded to the metal) can have enormous effects on catalytic behavior via non-covalent interactions with CO_2 and intermediates in the catalytic cycle. For instance, the addition of pendant phenol groups, guanidinium groups or polyethylene glycol chains close to the catalytic centre has been demonstrated to greatly enhance CO_2RR by enabling proton relays for the proton-coupled electron transfer mechanism, and by stabilizing important intermediates via hydrogen bonding.

MECHANISTIC ASPECTS OF CO_2RR AT PORPHYRINOID CENTRES

3.1 General Electrochemical Mechanisms

The ability to understand how the porphyrinoid metal centres activate and reduce CO_2 is crucial for rational catalyst design. The overall mechanistic scheme consists of a number of essential steps: (1) electroreduction of the metalloporphyrinoid to afford a low-valent catalytically active metal species, (2) binding of CO_2 to the activated metal centre, or insertion of CO_2 into a metal–hydride bond, (3) one or more proton coupled electron transfer steps to afford the observed product(s), and (4) release of the product and regeneration of the catalyst. The intermediates, the rate steps, and the thermodynamics of each elementary reaction are different for each metal, porphyrinoid ligand, and reaction conditions (solvent, proton source, temperature, applied potential).

Two main mechanistic routes have been proposed for activation of CO_2 at low metalated porphyrinoid centres. In Pathway I (direct CO_2 coordination), the reduced metal centre directly coordinates to the CO_2 molecule in the carbon atom, creating a metal–CO_2 adduct. This adduct then processes to yield CO and water (two-electron, two-proton reaction pathway) or to yield HCOOH (as a different binding mode). Pathway II (CO_2 insertion into a metal–hydride bond): Proton coupled electron transfer forms a metal–hydride intermediate (M–H) which is then followed by insertion of CO_2 into a metal–hydride bond to create a metal-formate intermediate (M–OCHO) followed by protonation and release to give formic acid.

3.2 Role of the Central Metal Ion

The central metal ion is very important in determining which mechanistic pathway is followed, what is the rate limiting step and what are the products formed. The mechanistic picture has been most completely studied in the case of the iron porphyrins, and is the subject of elegant studies by Savéant, Robert and collaborators. Iron(III) tetraphenylporphyrin (FeIII-TPP) is reduced in two steps at the electrode, FeIII/FeII and FeII/FeI, and at potentials more negative than the FeI/Fe(0) reduction the formally Fe(0) species (or Fe(I)-porphyrin radical anion) is produced.

The CO_2 reduction to CO in an aprotic medium takes place through the Fe(0) species as the active catalyst. It forms strong bonds to CO_2 at the iron centre and subsequent protonation (from added proton source like phenol, trifluoroethanol or water) enables the cleavage of the C–O bond yielding an Fe(II)–CO complex and water. The Fe(II–CO) species is a possible catalytic bottleneck, and CO needs to be desorbed to allow the regeneration of the active Fe(0) catalyst. The binding strength of CO to the iron centre is highly sensitive to the electronic nature of the porphyrin ligand, with those having electron withdrawing substituents at the periphery of the ring leading to the easier release of CO from the centre, and thus avoiding the inhibition of the catalyst.

In the case of cobalt porphyrins and phthalocyanines, the most important species for CO_2RR is generally the Co(I) state, which is formed by a single electron reduction of the Co(II) resting state. The Co(I) species is a strong nucleophile and is easily nucleophilic to CO_2. Under the conditions of the reaction, Co(I) can coordinate to CO_2 by either the carbon atom (to give CO) or to the oxygen atom (to give formate). It is sensitive to the Lewis acidity of the cobalt centre, the presence of proton donors and the applied potential.

3.3 Two-Electron vs. Multi-Electron Pathways

In organic or mixed aqueous/organic media, CO_2RR mechanisms of porphyrinoid-based catalysts are most commonly observed to proceed by a pathway involving the reduction of CO_2 to CO by two electrons and two protons ($E^0 = -0.53$ V vs NHE at pH 7). CO is useful as a feedstock for the Fischer-Tropsch synthesis to make liquid fuels and useful as a feedstock for a variety of bulk chemicals. This selectivity is of scientific interest and considerable practical significance in the production of CO, as the high selectivity of many porphyrinoid catalysts.

Multi-electron reduction products (methanol, methane, ethylene, ethanol) need to have several electrons and protons transferred on one active site in a kinetically controlled sequence. While these products have higher energy content and economic value than CO, they are much more challenging to produce selectively. Molecular catalysts face the kinetic challenge of coordinating proton delivery with electron transfer at every step of CO_2RR and to prevent premature product release at intermediate oxidation states of the catalyst. The production of methanol and methane has been reported for iron porphyrin catalysts under certain conditions, but the selectivity and efficiency for these products are also mostly lower than for CO production.

3.4 Competing Hydrogen Evolution Reaction (HER)

The hydrogen evolution reaction (HER: $2H^+ + 2e^- \rightarrow H_2$, $E^0 = -0.41$ V vs NHE at pH 7) is a major competing process in aqueous CO_2RR that reduces the Faradaic efficiency for CO_2 reduction products. Several CO_2RR pathways possess similar thermodynamic potentials and at the potentials required for porphyrinoid-based CO_2RR, which tend to be very negative, the rate of HER at the surfaces of electrodes may be important. One of the key challenges in the design of electrochemical systems for CO_2 reduction is the simultaneous suppression of HER while preserving high CO_2RR activity.

Generally, porphyrinoid based catalysts have some inherent selectivity for CO_2RR over HER because of preferential binding of CO_2 to the low-valent metal centre. The CO_2 selectivity is, however, strongly dependent on the concentration of CO_2, the nature and concentration of the proton donor, the pH and the applied potential. HER dominance can occur at high overpotentials.

Improving CO_2/HER selectivity can be achieved by: (i) employing a non-aqueous (or near neutral pH) medium where proton activity is reduced; (ii) designing a second coordination sphere with CO_2-specific binding interactions; (iii) working in a CO_2 saturated solution to increase CO_2 activity; and (iv) selecting metal centres (e.g., Co, Fe) with an intrinsic preference to bind CO_2 over proton reduction.

3.5 Proton-Coupled Electron Transfer (PCET)

Proton-coupled electron transfer (PCET) is a mechanistically important process in which a proton and an electron are transferred either concertedly or sequentially. Since protons and electrons are needed for most products, and the way proton delivery is coupled to electron transfer is a key determinant in the energy of transition states and intermediates, PCET is a central aspect of CO_2RR. Unlike sequential proton then electron (or electron then proton) transfer processes, concerted PCET does not produce intermediates of high energy protonated or de-protonated species, thereby reducing the overpotential and lowering the activation barrier.

The idea of designing the second coordination sphere to enable PCET is a powerful strategy for enhancing the performance of porphyrinoid CO_2RR catalysts. Introduction of hydrogen-bond donor groups (e.g., -OH, -NH, -NH_2, guanidinium) in close proximity to the metal centre creates a proton delivery network that facilitates concerted proton-electron transfer to CO_2 and its reduction intermediates. The strategy has been adopted in various high-performance porphyrinoid CO_2RR systems and has proven to be remarkably successful.This approach has been adapted to several high-performance porphyrinoid CO_2RR systems with great success.

3.6 Computational Mechanistic Studies

The study of the mechanism of CO_2RR at porphyrinoid metal centres has been greatly advanced by various computational techniques, such as density functional theory (DFT). Computational studies yield detailed information on catalytic activity, on the structures and energies of reaction intermediates, on the heights of activation barriers, on the preferred mode of binding CO_2, and on the effects of peripheral substitution on catalytic activity — information that can only be obtained by combined experimental and computational study.

The lessons learned from the computational studies include: (i) Fe(0) is the oxidation state of the iron that is catalytically active in the $CO_2 \rightarrow CO$ pathway; (ii) the C–OH bond-breaking step is rate limiting in the $CO_2 \rightarrow CO$ pathway; (iii) the peripheral substituents stabilise key intermediates and reduce the barrier to C–OH bond-breaking; (iv) second-sphere hydrogen-bond donors can reduce the barrier to C–OH bond-breaking, consistent with the experimental observation of reduced overpotentials; (v) the mechanisms by which peripheral substituents influence CO vs. HCOOH selectivity.

PORPHYRIN-BASED ELECTROCATALYSTS FOR CO_2RR

4.1 Iron Porphyrins

The most investigated family of molecular electrocatalysts for CO_2RR are iron porphyrins, and some iron porphyrins among the most active and selective CO_2RR catalysts ever identified. The work of Jean-Michel Savéant and his co-workers at the Université Paris Diderot has provided a base to develop the mechanistic principles of iron porphyrin catalyzed CO_2RR and paved the way for further optimization.

FeIIITPPCl is one of the first molecular catalysts known to catalyse the reduction of CO_2 to CO in the media of DMF/water. The catalyst is sequentially reduced to FeII-TPP and FeI-TPP and produces the active Fe(0) species at the potentials more negative than around -1.5 V vs SCE, which binds CO_2. The presence of Brønsted acid cocatalysts (especially trifluoroethanol) was found to significantly accelerate the rate of CO_2 reduction and to increase the selectivity for CO production over H_2 by several orders of magnitude in the seminal 1996 study by Savéant and coworkers, highlighting the relevance of proton donors to surmount the kinetic barrier to C–O bond cleavage.

Costentin, Robert and Savéant in 2012 were able to show that the addition of four ortho hydroxyl groups onto the meso-phenyl rings of iron tetraphenylporphyrin (Fe(TPP)) resulted in an extremely active and selective catalyst for CO_2 reduction. The ortho-OH groups act as an intramolecular proton relay, and deliver protons to the CO_2-bound intermediate in a concerted fashion. This catalyst showed a TOF of $\sim 10^6$ s^{-1}, which is among the highest reported for molecular CO_2RR catalysts, and a FE for CO > 90% at an overpotential of ~650 mV.

Substitution of the ortho-OH groups by chains of triethyleneglycol (for solubility) and of several electron-withdrawing peripheral substituents by second sphere proton donors were additional features to be incorporated to enhance further the improvement. The systematic modifications of the Savéant/Robert series of iron porphyrins clearly illustrated the structure-activity relationship: the electron-withdrawing groups were shown to stabilize the important Fe(0) – CO_2 adduct, which in turn lowered the reduction potential and increased the rate of CO_2 reduction, while second-sphere proton donors were shown to accelerate the rate-limiting protonation step. Both these effects were combined to obtain catalysts with both low overpotential and high TOF.

4.2 Cobalt Porphyrins

Another class of molecular CO_2RR catalysts that have been extensively studied is cobalt porphyrins. Cobalt porphyrins are generally slightly less active than the optimum iron porphyrin systems, but they have certain desirable properties for certain applications. The usual redox couple for cobalt porphyrins is Co(II)/Co(I) and the active species is Co(I) which is formed at more positive potentials than the Fe(I)/Fe(0) redox couple of iron porphyrins, which may allow for lower overpotential operation in certain systems.

It was reported that Cobalt tetraphenylporphyrin (CoTPP) catalyses CO_2 reduction to CO in organic solvents with moderate efficiency. Later studies with peripheral modification of cobalt porphyrins showed that increasing the overpotential for CO and raising the Faradaic efficiency of the reaction could be achieved by introducing electron-withdrawing substituents, such as cobalt porphyrin tetrakis(pentafluorophenyl)porphyrin (CoTFPP). As in iron analogues, the combination of electron withdrawing groups and second sphere proton donors has also been demonstrated to enhance the activity of cobalt porphyrins.

One difference between the iron and cobalt porphyrin-based CO_2RR is the possibility of the cobalt porphyrins to form formic acid as an alternative two-electron product. Depending on the binding mode of CO_2 to the Co(I) centre (either C-bound CO_2 (η^1-C) or O-bound CO_2 (or CO_2 insertion into a Co–H bond), CO is generated when protonated, and formate is generated when the CO_2 undergoes C–O bond cleavage. These pathways can be modified by the appropriate choice of ligand, and several examples of cobalt porphyrins have been described that show quite good selectivity for the production of HCOOH.

Cobalt porphyrins, in particular, have been immobilized in metal-organic frameworks (MOF), which has proven to be a fruitful approach to improving performance. MOFs offer a three dimensional porous structure that will not allow catalyst aggregation, ensure increased concentration of accessible catalytic active sites and can offer additional cooperative catalysis through the structure of the framework itself. MOFs made of cobalt porphyrin, such as MOF-525-Co and Al-PMOF-Co, have been reported to have extremely high surface areas (over 2000 m2/g) and CO Faradaic efficiency over 90%.

4.3 Manganese Porphyrins

The interest in manganese porphyrins as CO_2RR catalysts is partly being driven by analogy with other Mn-based CO_2RR catalysts in other ligand families such as $Mn(bpy)(CO)_3Br$ complexes. Mn tetraphenylporphyrin (MnIII-TPP) can be electroreduced to Mn(II), Mn(III), and perhaps Mn(0). The CO_2RR activity of Mn porphyrins has been reported with conflicting results, depending on the reaction conditions, including the production of CO with moderate selectivity.

Manganese porphyrin chemistry related to CO_2RR is remarkable because of the possible pathways to product formation involving high-valent manganese-oxo intermediates that can be generated from low-valent Mn-CO_2 adducts upon oxidation. These pathways are speculative, however, and the detailed mechanism of CO_2RR with Mn porphyrin needs to be investigated further.

4.4 Nickel and Copper Porphyrins

The Ni(II/I) reduction potential is considerably more negative than the π-system reduction potential of Ni(II) porphyrin, and in most cases, this makes Ni(II) porphyrins unusual in that they undergo ring-centered reductions instead of metal-centred reductions. In a nickel porphyrin system, this suggests that the electrochemically generated active species in the CO_2RR process is best characterized as a Ni(II)-porphyrin radical anion rather than a Ni(I) species. This distinction notwithstanding, some nickel porphyrins have been demonstrated to have CO_2RR activity, with the main product being CO and HCOOH.

The use of metallic copper for the production of multi-carbon CO_2RR products has garnered a lot of interest in the field of copper porphyrins. Several studies have examined whether molecular Cu porphyrin catalysts can mimic the remarkable ability of Cu to form C–C bonds.There are some mixed results on whether molecular Cu porphyrin catalysts can duplicate the unique C–C bond forming ability of Cu. The production of C_2+ products has been accomplished with significantly lower efficiency than for the bulk copper electrodes, with some reports of formate or CO production at copper porphyrins.

4.5 Effect of Peripheral Substituents

As explained in Chapter 2 and Chapter 3, the peripheral substitution pattern in porphyrins greatly influences their CO_2RR performance. A systematic study of a series of meso-tetraphenyl porphyrins with ortho, meta, and para substituents of different electronic nature has enabled the establishment of clear linear free energy correlations between the substituent Hammett σ value and the reduction potential of the catalyst, the TOF, and the overpotential. In particular, the electron withdrawing substituents (positive σ) make the reduction potential more positive (lower overpotential) and increase the TOF, while electron donating substituents do the exact opposite.

The impact of the second sphere substituents is more complicated and multi-dimensional. The presence of ortho-OH groups (e.g., $[Fe(o\text{-}OH)_4TPP]$) gives rise to an intramolecular proton relay which greatly enhances the rate of the rate limiting protonation step. The addition of guanidinium groups in second sphere has been reported to improve CO_2 binding near the active site, increasing the concentration of CO_2 in the immediate vicinity which will in turn increase the rate of binding and reduction of CO_2. The solubility has been enhanced by introducing polyamine and polyether groups without affecting the catalytic activity.

4.6 Axial Ligand Modifications

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CHAPTER 5: PHTHALOCYANINE-BASED ELECTROCATALYSTS FOR CO_2RR

5.1 Cobalt Phthalocyanines (CoPc)

Cobalt phthalocyanine (CoPc) has proven to be one of the most studied and promising molecular electrocatalysts for CO_2RR. It was also found to be active for selective CO_2 reduction to CO in the early electrochemical studies, and more recently, its activity has been greatly enhanced by strategic changes to the macrocycle and advanced engineering of the electrodes.

The planar geometry and strong π-stacking tendency of CoPc facilitates its deposition as thin films on carbon electrodes. CoPc physisorbed or covalently fixed on carbon nanotube (CNT)- or graphene-based surfaces shows an unexpectedly high selectivity for CO and the Faradaic efficiency is usually in the range of 85–99%. The carbon support has two functions: firstly, it serves as a high surface area “scaffold” for the deposition of CoPc leading to a higher density of active site, and secondly, it assists the electron transport from the electrode to the CoPc molecules. Efficient electronic coupling (low contact resistance) is possible due to π-conjugation of the carbon support and the CoPc macrocycle.

A significant breakthrough in CoPc CO_2RR research was the 2016 report by Ren et al. which showed that a CoPc activated carbon composite has a high CO Faradaic efficiency of 97% at -0.63 V vs RHE, high current density of 6.4 mA/cm^2, and long-term stability for 10 hours of operation. This finding was found to be competitive with state-of-the-art heterogeneous CO_2RR catalysts on selectivity performance.

The effect of peripheral substituents on the activity of CoPc for CO_2RR has been systematically studied. EWGs (e.g., -CN, -NO_2, -F) on the benzo rings of CoPc decreases the reduction potential of Co(II) and increases the ease of generating Co(I) as well as the reduction potential of CO_2RR. Hydrogen bonding interactions in the second coordination sphere have been shown to improve the activity and selectivity of amino substituted CoPc (-NH_2 groups) and amino-acid functionalized CoPc.

Coordination of axial ligands in CoPc can also be tailored to enhance the performance. The coordination of imidazole, pyridine or other N donors to the cobalt centre can influence its electronic properties, and it is known that it influences the selectivity between CO and HCOOH production. In general stronger donor groups lead to higher electron density on cobalt which in some systems may promote the formation of HCOOH instead of CO.

5.2 Iron Phthalocyanines (FePc)

Iron phthalocyanine (FePc) has a similar structure and electron structure to CoPc, but with properties of redox because of the difference in the electronic configuration of Fe(II) and Co(II). The reduction of CO_2 to CO in aqueous media was shown to be highly selective at FePc. A benefit of FePc over CoPc is that it works at slightly more positive potentials (lower overpotential), under specific conditions.

For FePc on carbon black, graphene and CNT, the Faradaic efficiency for CO has shown to be 80-94% with reasonable stability in studies. The chemical mechanism for FePc-catalysed CO_2 reduction has been widely accepted as being through an Fe(II)/Fe(I) couple that produces the Fe(I) species which then reacts with CO_2. The details of the mechanism, however, vary from those of the iron porphyrin systems because of the greater electron-richness of the phthalocyanine macrocycle and of its greater accessibility of the Fe(0) state.

5.3 Nickel and Copper Phthalocyanines

Potential CO_2RR catalysts have been investigated, such as nickel phthalocyanine (NiPc) and copper phthalocyanine (CuPc). The reduction of CO_2 by NiPc has a small intrinsic activity being the accessible potentials hard to reach to generate the Ni(I) active state. But in the presence of carbon matrices during pyrolysis, in which the carbon is doped with nitrogen (Ni-N-C materials), the CO_2RR performance is greatly enhanced. These pyrolyzed materials are not in fact the original Ni-N_4 complexes, but they do preserve some characteristics of the original Ni-N_4 environment.

Although CuPc has attracted the interest because of the unique ability of copper to generate multi-carbon CO_2RR products, molecular CuPc tends to yield CO and HCOOH products instead of C_2+ products. Moderate FE towards CO_2 conversion has been reported for CuPc based electrodes, however, the production of valuable C_2+ products with the intact molecular Cu macrocyclic catalysts is still a challenge.

5.4 Peripheral Functionalization of Phthalocyanines

Phthalocyanines have four sets of peripheral positions (α:1, 4, 8, 11, 15, 18, 22, 25 and β:2, 3, 9, 10, 16, 17, 23, 24) which can be substituted, thus allowing for a widespread range of electronic and steric tuning. Several groups have investigated the effect of the fluorination, amination, alkylation and thioether functionalization on the CO_2RR activity of metallophthalocyanines.

One of the most beautiful is the incorporation of positively charged quaternary ammonium groups at the periphery of CoPc. These groups generate a local positive electrostatic field that pulls the negative CO_2 molecule, which further increases the local concentration of CO_2 on the active cobalt centre and thus boosts the CO_2 capture and reduction rate. Similarly, negative charges (sulfonate groups) generate attraction for the negatively charged CO_2 molecule, lowering its activity. These findings confirm that functionalized phthalocyanines have an apparent CO_2RR activity that accounts for electrostatic effect.

5.5 Immobilization on Carbon and Graphene Supports

Practical use of metallophthalocyanines in electrochemical applications requires their immobilization on electrically conductive carbon supports because they are insoluble and very prone to aggregation in water. Different types of immobilization methods have been devised such as physical adsorption (physisorption) by $\pi - \pi$ stacking, covalent grafting using diazonium chemistry or click chemistry and axial coordination to the ligands immobilized at the surface.

The most successful support materials include multi-walled carbon nanotubes (MWCNTs), single-walled carbon nanotubes (SWCNTs), reduced graphene oxide (rGO), carbon black, graphitic carbon nitride (g-C_3N_4) and hierarchically porous carbons. The properties of the support are essential in the performance of the immobilized catalyst: they should have a high surface area to ensure maximum catalyst loading and an active site density as well as high electrical conductivity to minimize contact resistance, and they should have tunable surface chemistry to optimize the interaction of the catalyst with the support.

Recent studies have shown that the nature of the CoPc-carbon support interaction has a significant effect on the catalytic performance. The π–π stacking geometry of CoPc on CNTs is more positive (flat-on) which increases the electronic coupling between CoPc and the support, whereas the covalent connection between pyrene and carbon (via the pyrene anchor groups) results in stronger and more persistent CoPc attachment. To gain insights into the relative importance of catalyst loading, electronic coupling, and structural stability for the overall CO_2RR performance, the comparison of the different immobilization approaches has been performed on the standardized test substrates.

CORROLES, CHLORINS, AND OTHER PORPHYRINOIDS IN CO_2RR

6.1 Cobalt and Iron Corroles

CO_2RR electrocatalysis has recently become a highly emerging field of corrole applications. A number of cobalt and iron corroles have been reported to be efficient and selective catalysts of CO_2 reduction to CO in organic and aqueous media. Owing to the unusual electronic characteristics of the corrole ligand, corrole-metal complexes have a reactivity profile different from the analogous porphyrin complexes, both because the corrole is an ion with a trianionic character and because the high-valent metal states are stabilized by the corrole.

The team of Gros and co. has already reported that Co-TPC catalyses the reduction of CO_2 to CO with high selectivity (FE > 85%) in DMF/water media. Importantly, the cobalt corroles have been discovered to inhibit HER better than the analogous cobalt porphyrins, resulting in higher CO_2/H_2 product ratios. This increased selectivity has been explained by the increased ligand field of trianionic corrole which makes it less prone to protonation to give the key intermediate (Co(III)–H hydride species) in the HER pathway.

This approach has been seen to be promising in the case of CO_2RR with iron corroles. The iron centre in corrole complexes can easily reach high-valent Fe(IV) and Fe(V) states, but can also store stable Fe(III) and Fe(II) states which can be further reduced and activated for CO_2RR. Studies of iron tris(pentafluorophenyl)corrole (Fe-TFPC) and its analogues have shown CO_2 reduction at moderate Faradaic efficiency, and further structure-activity studies are shaping the understanding of the effects of peripheral substitution on catalytic activity.

6.2 Chlorins in CO_2RR

Compared to porphyrins and phthalocyanines, the application of chlorins, which are partially reduced porphyrins, in CO_2RR electrocatalysis is still an under-researched field. The unique electronic properties of the chlorin macrocycle, however, on the one hand, the high energy of the HOMO level, and on the other hand, the redshift of the absorption position, promises interesting advantages in light-driven (photoelectrochemical) CO_2 reduction.

The electrochemical properties of complexes of the iron with chlorophylls of the phaeoporphyrin type, such as the iron pheophytin a (iron chlorophylls of the phaeoporphyrin type) and synthetic iron chlorins have been studied. The reduction potentials of the iron chlorins are comparable to the corresponding porphyrins, but the slightly different electronic structure of the chlorin could provide slightly different reactivities to CO_2. In-depth mechanistic and performance analysis of CO_2RR catalysts based on chlorines is required to assess their potential.

6.3 Bacteriochlorins

Bacteriochlorins with two opposed pyrroline double bonds are even more red-shifted in absorption than are chlorins and could benefit in solar-driven CO_2RR applications because they absorb deeply in the red and near-infrared (NIR) region of the solar spectrum. The additional alteration of the electronic structure of the macrocycle produces the electrochemical properties of metal bacteriochlorins that are different from porphyrins and chlorins. There is not much literature available regarding the use of metal bacteriochlorins for electrochemical CO_2RR, but they are appealing candidates for photoelectrochemical systems due to their photophysical characteristics.

6.4 Porphyrin–Phthalocyanine Hybrid Systems

A new group of CO_2RR catalysts is hybrid catalysts that combine the structure of phthalocyanines and porphyrins. These include porphyrin-phthalocyanine conjugates linked by covalent bonds, mixed-face sandwich complexes and porphyrin-phthalocyanine co-immobilized systems on common electrode supports. These hybrid systems might offer synergistic effects of iron/cobalt porphyrins superior stability and support-adhesion of phthalocyanines.

The idea of the multi-site hybrid catalysts with CO_2RR at adjacent porphyrin and phthalocyanine centres has been suggested to obtain multi-electron CO_2RR products. Although it is still a preliminary study, some results obtained on multi-component systems indicate that the ability of cooperative multi-site mechanisms to increase the selectivity of valuable products like methanol and ethanol is achievable.

ELECTRODE FABRICATION AND IMMOBILIZATION STRATEGIES

7.1 Physisorption and Drop-Casting Methods

The most straightforward method of preparing porphyrinoid modified electrodes is physisorption that involves the mixture of a conductive support (carbon black, CNT, graphene, etc.) with the molecular catalyst and drop-casting a porphyrinoid ink on an electrode substrate (glassy carbon, carbon paper, carbon cloth, etc.). The dried film is held together by π-π stacking and van der Waals interactions between catalyst molecules and support. The method is operationally simple and can be used with various catalysts and supports, but may be limited by the stability of physisorbed films during long-term electrolysis, which can result from catalyst dissolution or desorption.

In order to enhance the stability of the film, Nafion or other ion-exchange polymers are often included in the catalyst ink as a binder. Nafion provides a proton conducting matrix which maintains the catalyst at the correct location to promote proton access to the active site, and the sulfonated groups can also be electrostatically bound to the positive charged catalyst or support material. The optimization of the Nafion content is crucial: too little Nafion will result in insufficient binding, whereas too much Nafion will create blocking of active sites and hinder the mass transport of CO_2 and products.

7.2 Covalent Grafting to Electrode Surfaces

Covalently immobilized porphyrinoid catalysts are much more stable than catalysts that are only physisorbed on the surface of the electrode. There are several chemistries that have been used to this end. Diazonium electrochemistry is a concept for electrochemical reduction of amino functionalized porphyrinoids to yield aryl radicals that can be coupled to the graphitic carbon surfaces through covalent C–C bond formations. This method has been employed to immobilise iron and cobalt porphyrins to the surface of a glassy carbon and carbon nanotube with high density and stability.

Another covalent grafting method is click chemistry, which is copper(I)-catalysed azide-alkyne cycloaddition or CuAAC. Porphyrinoid catalysts (or azide) containing an alkyne function will form stable triazole linkages with a carbon surface. This method has very high selectivity and mild reaction conditions, and is capable of forming well-defined single and multi-layer films of porphyrin catalysts on the surface of electrodes.

Conducting polymer films derived from vinyl- or pyrrole-functionalized porphyrinoids can be prepared by electropolymerization, with higher catalyst loadings than monolayer grafting techniques and may be able to provide better electron transport. It has been demonstrated that electro-polymerized films of pyrrole-derivatized iron porphyrins on glassy carbon display high CO_2RR activity and can be run for hundreds of hours of electrolysis with little loss of activity.

7.3 Integration into Metal-Organic Frameworks (MOFs)

Metal-organic frameworks (MOFs) are crystalline materials with porous structures made from nodes of metal ions and molecules of organic linker. These materials have extremely high surface areas (typically > 3000 m2/g), tunable pore structure, and chemically designable environments that are attractive hosts for single-site molecular catalysts. One can develop MOFs with very high numbers of accessible catalytic active sites by attaching porphyrinoid frameworks directly to the MOF structure (called metalated linkers) or by post-synthetic metalation of the porphyrin-based MOF linkers.

There are a number of MOFs that have been reported with cobalt or iron porphyrin linkers for CO_2RR applications. $Al_2(OH)_2$TCPP-Co (PCN-222-Co) (MOF based on $Zr_6O_4(OH)_4$ nodes and ligand of cobalt tetrakis(4-carboxyphenyl)porphyrin (Co-TCPP)) has a BET surface area of ~2000 m^2/g and a high CO_2RR activity (CO FE ~76–91%) when immobilized on a carbon electrode. The highly porous structure allows CO_2 to reach all catalytic sites and the Zr-oxo nodes provide high electrochemical stability.

7.4 Covalent Organic Frameworks (COFs)

Covalent organic frameworks (COFs) are porous crystalline organic frameworks composed of covalent-organic building blocks linked by covalent bonds, which are usually based on imine (Schiff base), boronate ester, β-ketoenamine, or triazine bonds. COFs are completely organic in contrast to MOFs which are highly susceptible to chemical or electrochemical degradation under typical conditions of CO_2RR electrolysis (strongly reducing potentials, acidic or basic media). Their extended π-systems which are crystalline also offer a high electrical conductivity which allows the transfer of electrons through the material.

Characterized as an exciting recent development, porphyrin-based CO_2RR can be achieved by COFs. The materials are usually built by condensation of amine functionalized metalloporphyrins to aldehyde functional organic linker to make an imine linked 2D or 3D network. High CO Faradaic efficiency (87–93%) and turnover numbers (TON > 29,000 after 10 hours) have been achieved with COFs based on cobalt porphyrin units because of the high stability of the COF under electrolysis conditions. Many porphyrin COFs have a layered structure in two dimensions, making them easily exfoliable into nanosheets that can be deposited as thin films on the surface of electrodes, resulting in a large accessible surface area.

The crystallinity of COFs allows for the characterization of their structure by powder X-ray diffraction (PXRD), while the pore environments can be well defined and studied using a variety of techniques, including EXAFS, XANES, and solid-state NMR spectroscopy. The structural definition is especially useful for establishing strict structure-activity relationships, and for elucidation of the mechanism of CO_2RR in confined porous environments for porphyrin-based COFs.

7.5 Polymer-Based Immobilization

A third method to immobilize porphyrinoid catalysts on the surface of electrodes is via polymer matrices. Molecular catalysts can be encapsulated within the structure of ionic conducting polymers like Nafion, poly(4-vinylpyridine) and polycations (quaternary ammonium functionalized polymers) without loss of electronic and catalytic function. Polymerizable vinyl-functionalized porphyrins and post-polymerization functionalization of pre-polymerized porphyrin-containing polymers are the two methods used for covalent incorporation of porphyrinoid catalysts into polymer backbone yielding stable conducting catalytic films with tunable mechanical and electrochemical properties.

Particularly promising are the nitrogen-doped carbon (NC) materials obtained by pyrolysis of porphyrinoid-polymer composites at high temperature. Pyrolysis partially or fully breaks down the framework of the intact macrocyclic ligand, but produces nitrogen-doped carbons with dispersed metal centres that have coordination environments that are approximately the same as that found in the parent porphyrinoid. The pyrolytic M-N-C materials have demonstrated state-of-the-art CO_2RR activity and stability but with the sacrifice of structural precision and mechanistic transparency of the intact molecular catalysts.

CHALLENGES, FUTURE PERSPECTIVES, AND CONCLUSIONS

8.1 Current Challenges in Porphyrinoid CO_2RR Catalysis

While the advances outlined in the previous chapters are impressive, there are some important challenges that must be addressed before porphyrinoid-based CO_2RR catalysts can be used in a practical large-scale electrochemical CO_2 conversion device. They are multi-dimensional challenges: stability of catalyst, product selectivity other than CO, engineering of electrode, system integration and fundamental understanding of mechanism.

The practical problem most crucial is the stability of the catalyst. High-performance porphyrinoid CO_2RR catalysts are found to have good performance in short-term lab-scale CO_2RR (typically a few hours duration at current density 1–10 mA/cm^2), but fail to perform well under the prolonged electrolysis conditions required for practical application. Degradation mechanisms are: Desorption from physisorbed catalysts from electrode surfaces; Over-reduction of the macrocycle to non-aromatic and inactive forms; Aggregation and stacking of catalyst molecules to fewer accessible active sites; Demetallation of the macrocycle (loss of the central metal ion which is the active catalytic centre).

Selectivity of most porphyrinoid CO_2RR catalysts to the more valuable products than CO is still limited. CO_2RR could be more attractive economically if products with higher value, like formic acid, methanol, ethylene and ethanol, became available, as their market price is much higher than CO. Sequential multi-electron reduction of CO to these products involves extra steps of C–H bond formation, which are kinetically challenging, and it is challenging to prevent premature product release at each reduction level with most existing catalysts.

In laboratory-scale tests, the current densities of porphyrinoid CO_2RR systems are usually 1 to 20 mA/cm^2 at the catalyst film, which is one to two orders of magnitude lower than that of competitive industrial electrochemical processes (200 to 500 mA/cm^2). In order to bring this current density to a more practical level while preserving high Faradaic efficiency and stability, new electrode architectures (such as gas diffusion electrodes, flow cells) have not been deeply investigated in the context of porphyrinoid molecular catalysts.

8.2 Strategies to Overcome Limitations

To solve the stability problem, there is a need for molecular level and electrode level solutions. On a molecular level, rational ligand design can include the use of sterically protective groups that prevent attack by reactive species, the selection of peripheral substituents which are resistant to oxidative or reductive degradation, and the design of a metal-ligand interaction that prevents metal demetallation. More stable macrocyclic structures, like corroles, which are also more stable with respect to some degradation pathways, could provide stability benefits.

Covalent immobilization of catalysts is more stable than physisorption at the electrode level, and encapsulation in stable porous frameworks, such as MOFs and COFs, can also give extra protection. Protective overlayers (e.g. thin oxide films, polymeric coating) that are permeable to CO_2 but impermeable to species which can destroy the catalysts may be even more effective at improving stability. The real-time degradation of the catalyst during electrolysis can be monitored using in-situ spectroscopy and/or in-situ impedance spectroscopy as well as by periodic activity benchmarks, providing important information to help identify degradation mechanisms and develop mitigation strategies.

Multi-site catalytic systems could potentially be used to achieve selectivity beyond CO with CO generated at one metal centre being transferred to an adjacent centre for further reduction. Biology has examples of cascade (e.g., carbon fixation in photosynthesis) and some multi-component artificial electrochemical systems have been shown to exhibit such behavior. Ordered porous frameworks (MOFs, COFs) are a promising platform for engineering such cascade processes as their precise spatial arrangement of catalytic centres.

8.3 Future Research Directions

A number of promising future research avenues are now becoming apparent with regard to the state-of-the-art of CO_2RR catalysis using porphyrinoids. In addition, combining light absorption with electrochemical CO_2 reduction provides the opportunity for photoelectrochemical CO_2RR systems utilizing direct light energy to enable CO_2 reduction. Because of their light absorption capability, in particular for red and near-infrared light, the use of porphyrinoids in photoelectrochemical cells may decrease or eliminate the need for an external electrical energy input.

Second, the generation of porphyrinoid-based CO_2RR catalysts in aqueous flow electrolysers is an important milestone towards real-world applications. The majority of existing porphyrinoid CO_2RR research is conducted in batch-mode H-cells which are not representative of practical devices. A key research focus is the translation of molecular porphyrinoid catalysts to membrane electrode assembly (MEA) flow electrolysers with industrially-relevant current densities (200 mA/cm^2 and beyond) and CO_2 partial pressures.

Third, the development of porphyrinoid-based CO_2RR to make valuable multi-carbon products (C_2+) is a high-value target. Often the production of CO and formic acid from porphyrinoid catalysts is demonstrated, but the production of such energy-dense, high-priced market products as ethylene, ethanol, and acetate has not been demonstrated to the same efficiency. By mimicking nature's multi-enzyme cascades, multi-functional electrode assemblies, combining porphyrinoids with complementary catalytic components such as formate dehydrogenase-mimics and aldehyde reductase-mimics, could render cascade CO_2 reduction to high value multi-carbon products possible.

Fourth, machine learning and high throughput experimentation strategies will be used to speed up the discovery and optimization of porphyrinoid CO_2RR catalysts. However, it is impossible to cover the huge available chemical space of available porphyrinoids (thousands of combinations of metal centres, peripheral substituents and macrocycle types) by the traditional, one-compound-at-a-time approach to research. Experimental and existing computational data can be used to develop machine learning models that reasonably predict the performance of hypothetical catalysts, so as to identify candidates for synthesis and testing.

Fifth, life cycle assessment (LCA) and techno-economic analysis (TEA) of the porphyrinoid-based CO_2RR systems would be helpful in guiding the development of practically and economically viable processes. These analyses can provide the critical performance targets (current density, Faradaic efficiency, overpotential, catalyst lifetime) to be satisfied for economic viability, and can reveal where improvements will be most beneficial.

Conclusions

The dissertation has provided a thorough overview of recent developments of porphyrinoid based molecular catalysts for the electrocatalytic reduction of CO_2. It has achieved tremendous advances during the last decade with new catalyst structures, greater understanding of the mechanism, and novel electrode engineering approaches.

Iron and Cobalt porphyrins have been proven to be among the most active and selective molecular CO_2RR catalysts with appropriate functionalization and immobilization, with CO Faradaic efficiencies of >90% and high turnover frequencies. The second sphere proton relay effect has been identified as a key factor in the catalytic activity, and a design principle has been developed which has been used in several families of porphyrinoid catalysts. Immobilized cobalt and iron phthalocyanines have been shown to be promising catalysts with performance comparable to that of the best heterogeneous catalysts.

The embedding of porphyrinoid catalysts in MOFs and COFs has opened new avenues in the design of catalysts, allowing for control of the local environment, aggregation prevention and very high density of accessible active sites. Such frameworks have been found to be very active and stable as compared to conventional physisorbed catalyst films.

The use of corroles, chlorins and hybrid porphyrinoid systemst has broadened the range of catalytic applications and uncovered new structure-activity relationships. The inhibition of HER from corrole-metal complexes and the possibility of chlorins for photoelectrochemical CO_2RR are especially intriguing features of these newer families of catalysts.

The prospects for porphyrinoid-based CO_2RR catalysis are very promising, albeit with many challenges to be addressed, such as long-term stability, selectivity for multi-carbon products and industrially relevant current densities. Synthetic versatility, a comprehensive understanding of the mechanisms and the ongoing development of electrode engineering offer excellent opportunities for further improvement. The combination of porphyrinoid-based electrochemical CO_2 reduction with renewable electricity sources could be a significant contribution to a sustainable, carbon neutral energy and chemical economy.

Finally, the porphyrinoids are just an extremely powerful and versatile family of molecular catalysts for electrocatalytic CO_2 reduction. They all provide a promising combination of biological precedents, synthetic tunability, well-defined active sites, and high performance for practical electrochemical CO_2 utilization. To bring the amazing progress made over the last ten years to fruition in the technological realm, continued interdisciplinary research from synthetic chemistry and electrochemistry to surface science and computational chemistry to chemical engineering will be necessary.

REFERENCES

The following references represent key literature sources relevant to the content reviewed in this dissertation. A complete list of primary literature sources is available from the author upon request.

[1] Savéant, J.-M. (2008). Molecular Catalysis of Electrochemical Reactions: Mechanistic Aspects. Chemical Reviews, 108(7), 2348–2378.

[2] Costentin, C., Robert, M., & Savéant, J.-M. (2013). Catalysis of the Electrochemical Reduction of Carbon Dioxide. Chemical Society Reviews, 42(6), 2423–2436.

[3] Costentin, C., Drouet, S., Robert, M., & Savéant, J.-M. (2012). A Local Proton Source Enhances CO_2 Electroreduction to CO by a Molecular Fe Catalyst. Science, 338(6103), 90–94.

[4] Bhugun, I., Lexa, D., & Savéant, J.-M. (1996). Catalysis of the Electrochemical Reduction of Carbon Dioxide by Iron(0) Porphyrins. Journal of the American Chemical Society, 118(7), 1769–1776.

[5] Ren, S., Joulie, D., Salvatore, D., Torbensen, K., Wang, M., Robert, M., & Berlinguette, C. P. (2016). Molecular Electrocatalysts Can Mediate Fast, Selective CO_2 Reduction in a Flow Cell. Science, 352(6287), 974–978.

[6] Pegis, M. L., Wise, C. F., Martin, D. J., & Mayer, J. M. (2018). Oxygen Reduction by Homogeneous Molecular Catalysts and Electrocatalysts. Chemical Reviews, 118(5), 2340–2391.

[7] Shen, J., Kortlever, R., Kas, R., Birdja, Y. Y., Diaz-Morales, O., Kwon, Y., Ledezma-Yanez, I., Schouten, K. J. P., Mul, G., & Koper, M. T. M. (2015). Electrocatalytic Reduction of Carbon Dioxide to Carbon Monoxide and Methane at an Immobilized Cobalt Protoporphyrin. Nature Communications, 6, 8177.

[8] Zhang, X., Wu, Z., Zhang, X., Li, L., Li, Y., Xu, H., Li, X., Yu, X., Zhang, Z., Liang, Y., & Wang, H. (2017). Highly Selective and Active CO_2 Reduction Electrocatalysts Based on Cobalt Phthalocyanine/Carbon Nanotube Hybrid Structures. Nature Communications, 8, 14675.

[9] Lin, S., Diercks, C. S., Zhang, Y.-B., Kornienko, N., Nichols, E. M., Zhao, Y., Paris, A. R., Kim, D., Yang, P., Yaghi, O. M., & Chang, C. J. (2015). Covalent Organic Frameworks Comprising Cobalt Porphyrins for Catalytic CO_2 Reduction in Water. Science, 349(6253), 1208–1213.

[10] Yao, S. A., Ruber, R. E., Bhargaw, D., Damrauer, N. H., & Bhargaw, C. E. (2012). Electrochemical Reduction of CO_2 Catalysed by an Iron Corrole. Journal of the American Chemical Society, 134(39), 15384–15387.

[11] Costentin, C., Passard, G., Robert, M., & Savéant, J.-M. (2014). Pendant Acid–Base Groups in Molecular Catalysts: H-Bond Promoters or Proton Relays? Mechanisms of the Conversion of CO_2 to CO by Electrogenerated Iron(0)Porphyrins Bearing Prepositioned Phenol Functionalities. Journal of the American Chemical Society, 136(33), 11821–11829.

[12] Azcarate, I., Costentin, C., Robert, M., & Savéant, J.-M. (2016). Through-Space Charge Interaction Substituent Effects in Molecular Catalysis Leading to the Design of the Most Efficient Catalyst of CO_2-to-CO Electrochemical Conversion. Journal of the American Chemical Society, 138(50), 16639–16644.

[13] Kornienko, N., Zhao, Y., Kley, C. S., Zhu, C., Kim, D., Lin, S., Chang, C. J., Yaghi, O. M., & Yang, P. (2015). Metal-Organic Frameworks for Electrocatalytic Reduction of Carbon Dioxide. Journal of the American Chemical Society, 137(44), 14129–14135.

[14] Dey, S., Masero, F., Brack, E., Fontecave, M., & Mougel, V. (2022). Electrosynthesis of Liquid Fuel and Hydrogen Peroxide via Selective Reduction of Oxygen and Carbon Dioxide. Nature, 607(7920), 678–683.

[15] IPCC. (2022). Climate Change 2022: Mitigation of Climate Change. Contribution of Working Group III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press.

[16] Francke, R., Schille, B., & Roemelt, M. (2018). Homogeneously Catalyzed Electroreduction of Carbon Dioxide—Methods, Mechanisms, and Catalysts. Chemical Reviews, 118(9), 4631–4701.

[17] Nitopi, S., Bertheussen, E., Scott, S. B., Liu, X., Engstfeld, A. K., Horch, S., Seger, B., Stephens, I. E. L., Chan, K., Hahn, C., Norskov, J. K., Jaramillo, T. F., & Chorkendorff, I. (2019). Progress and Perspectives of Electrochemical CO_2 Reduction on Copper in Aqueous Electrolyte. Chemical Reviews, 119(12), 7610–7672.

[18] Diercks, C. S., Liu, Y., Cordova, K. E., & Yaghi, O. M. (2018). The Role of Reticular Chemistry in the Design of CO_2 Reduction Catalysts. Nature Materials, 17(4), 301–307.

[19] Guo, Z., Cheng, S., Cometto, C., Anxolabéhère-Mallart, E., Ng, S.-M., Ko, C.-C., Liu, G., Chen, L., Robert, M., & Lau, T.-C. (2016). Highly Efficient and Selective Photocatalytic CO_2 Reduction by Iron and Cobalt Quaterpyridine Complexes. Journal of the American Chemical Society, 138(30), 9413–9416.

[20] Mohamed, E. A., Zahran, Z. N., & Naruta, Y. (2015). Efficient Electrocatalytic CO_2 Reduction with a Molecular Cofacial Iron Porphyrin Dimer. Chemical Communications, 51(95), 16900–16903.

21. Villano, M., Aulenta, F., Ciucci, C., Ferri, T., Giuliano, A., & Majone, M. (2010). Bioelectrochemical reduction of CO_2 to CH_4 Via direct and indirect extracellular electron transfer by a hydrogenophilic methanogenic culture. *Bioresource technology*, *101*(9), 3085-3090.

22. Bajracharya, S., Vanbroekhoven, K., Buisman, C. J., Strik, D. P., & Pant, D. (2017). Bioelectrochemical conversion of CO_2 to chemicals: CO_2 as a next generation feedstock for electricity-driven bioproduction in batch and continuous modes. *Faraday discussions*, *202*, 433-449.

23. Yuan, M., Kummer, M. J., & Minteer, S. D. (2019). Strategies for bioelectrochemical CO_2 reduction. *Chemistry–A European Journal*, *25*(63), 14258-14266.

24. Bogaerts, A., & Centi, G. (2020). Plasma technology for CO_2 conversion: a personal perspective on prospects and gaps. *Frontiers in Energy Research*, *8*, 111.

25 Liu, C., Yuan, X., Gu, Y., Chen, H., Sun, D., Li, P., ... & Holmes, D. E. (2020). Enhancement of bioelectrochemical CO_2 reduction with a carbon brush electrode via direct electron transfer. *ACS Sustainable Chemistry & Engineering*, *8*(30), 11368-11375.

26. Álvarez, A., Borges, M., Corral‐Pérez, J. J., Olcina, J. G., Hu, L., Cornu, D., ... & Urakawa, A. (2017). Cover Feature: CO_2 Activation over Catalytic Surfaces (ChemPhysChem 22/2017). *ChemPhysChem*, *18*(22), 3087-3087.

27. Gutsev, G. L., Bartlett, R. J., & Compton, R. N. (1998). Electron affinities of CO_2, OCS, and CS_2. *The Journal of chemical physics*, *108*(16), 6756-6762.

28. Wang, L. S., Reutt, J. E., Lee, Y. T., & Shirley, D. A. (1988). High resolution UV photoelectron spectroscopy of CO+ 2, COS+ and CS+ 2 using supersonic molecular beams. *Journal of electron spectroscopy and related phenomena*, *47*, 167-186.

29. Saha, P., Amanullah, S., & Dey, A. (2022). Selectivity in electrochemical CO_2 reduction. *Accounts of chemical research*, *55*(2), 134-144.

30. Benson, E. E., Kubiak, C. P., Sathrum, A. J., & Smieja, J. M. (2009). Electrocatalytic and homogeneous approaches to conversion of CO_2 to liquid fuels. *Chemical Society Reviews*, *38*(1), 89-99.

31. Zhang, X., Wu, Z., Zhang, X., Li, L., Li, Y., Xu, H., ... & Wang, H. (2017). Highly selective and active CO_2 reduction electrocatalysts based on cobalt phthalocyanine/carbon nanotube hybrid structures. *Nature communications*, *8*(1), 14675.

32. Zhang, W., Lai, W., & Cao, R. (2017). Energy-related small molecule activation reactions: oxygen reduction and hydrogen and oxygen evolution reactions catalyzed by porphyrin-and corrole-based systems. *Chemical reviews*, *117*(4), 3717-3797.

33. Khezri, B., Fisher, A. C., & Pumera, M. (2017). CO_2 reduction: the quest for electrocatalytic materials. *Journal of Materials Chemistry A*, *5*(18), 8230-8246.

34. Mele, G., Annese, C., D'Accolti, L., De Riccardis, A., Fusco, C., Palmisano, L., ... & Vasapollo, G. (2014). Photoreduction of carbon dioxide to formic acid in aqueous suspension: a comparison between phthalocyanine/TiO_2 and porphyrin/TiO_2 catalysed processes. *Molecules*, *20*(1), 396-415.

35 Nardis, S., Mandoj, F., Stefanelli, M., & Paolesse, R. (2019). Metal complexes of corrole. *Coordination Chemistry Reviews*, *388*, 360-405.

36 Boutin, E., Merakeb, L., Ma, B., Boudy, B., Wang, M., Bonin, J., ... & Robert, M. (2020). Molecular catalysis of CO_2 reduction: recent advances and perspectives in electrochemical and light-driven processes with selected Fe, Ni and Co aza macrocyclic and polypyridine complexes. *Chemical society reviews*, *49*(16), 5772-5809.

37. Park, J. M., Lee, J. H., & Jang, W. D. (2020). Applications of porphyrins in emerging energy conversion technologies. *Coordination Chemistry Reviews*, *407*, 213157.

38. Meshitsuka, S., Ichikawa, M., & Tamaru, K. (1974). Electrocatalysis by metal phthalocyanines in the reduction of carbon dioxide. *Journal of the Chemical Society, Chemical Communications*, (5), 158-159.

39. Zhang, X., Wu, Z., Zhang, X., Li, L., Li, Y., Xu, H., ... & Wang, H. (2017). Highly selective and active CO_2 reduction electrocatalysts based on cobalt phthalocyanine/carbon nanotube hybrid structures. *Nature communications*, *8*(1), 14675.

40. Takahashi, K., Hiratsuka, K., Sasaki, H., & Toshima, S. (1979). Electrocatalytic behavior of metal porphyrins in the reduction of carbon dioxide. *Chemistry Letters*, *8*(4), 305-308.

41 Lin, S., Diercks, C. S., Zhang, Y. B., Kornienko, N., Nichols, E. M., Zhao, Y., ... & Chang, C. J. (2015). Covalent organic frameworks comprising cobalt porphyrins for catalytic CO_2 reduction in water. *Science*, *349*(6253), 1208-1213.

42. Lieber, C. M., & Lewis, N. S. (1984). Catalytic reduction of carbon dioxide at carbon electrodes modified with cobalt phthalocyanine. *Journal of the American Chemical Society*, *106*(17), 5033-5034.

43. Sinha, W., Mahammed, A., Fridman, N., Diskin-Posner, Y., Shimon, L. J., & Gross, Z. (2019). Superstructured metallocorroles for electrochemical CO_2 Reduction. *Chemical Communications*, *55*(79), 11912-11915.

44. Grodkowski, J., Neta, P., Fujita, E., Mahammed, A., Simkhovich, L., & Gross, Z. (2002). Reduction of cobalt and iron corroles and catalyzed reduction of CO_2. *The Journal of Physical Chemistry A*, *106*(18), 4772-4778.

45. Jyoti, Kubba, R., Kumar, S., Fridman, N., Warkar, S. G., Churchill, D. G., & Kumar, A. (2024). Hydrogen evolution activity of cobalt corroles. *Inorganica Chimica Acta*, *562*, 121878.

46. Jyoti, An, J., Kim, D., Churchill, D. G., & Kumar, A. (2024). Cobalt corroles: Synthesis and applications. *Coordination Chemistry Reviews*, *511*, 215869.

47. Varela, A. S., Ju, W., & Strasser, P. (2018). Molecular nitrogen–carbon catalysts, solid metal organic framework catalysts, and solid metal/nitrogen-doped carbon (MNC) catalysts for the electrochemical CO_2 reduction. *Advanced Energy Materials*, *8*(30), 1703614.

48 Hu, X. M., Rønne, M. H., Pedersen, S. U., Skrydstrup, T., & Daasbjerg, K. (2017). Enhanced catalytic activity of cobalt porphyrin in CO_2 electroreduction upon immobilization on carbon materials. *Angewandte Chemie International Edition*, *56*(23), 6468-6472.

49 Maurin, A., & Robert, M. (2016). Noncovalent immobilization of a molecular iron-based electrocatalyst on carbon electrodes for selective, efficient CO_2-to-CO conversion in water. *Journal of the American Chemical Society*, *138*(8), 2492-2495

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REVIEW

Recent Advancements in Electrocatalytic CO_2 Reduction Using Different Porphynoids

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ABSTRACT

The growing global energy demand and rapid growth in industrialization and urbanization have intensified the consumption of fossil fuels, leading to an alarming accumulation of CO_2 in the atmosphere. The rise in greenhouse gases contributes to severe environmental and health challenges. The reduction of CO_2 into energy dense products such as CO, formate, alcohols, and hydrocarbons offers a promising strategy to reduce these effects. The electrochemical CO_2 reduction (CO_2RR) stands out among various approaches due to its compatibility with renewable electricity. However, activating the thermodynamically stable CO_2 molecule remains a significant challenge, and it requires the development of selective, robust, and efficient electrocatalysts. The N_4-macrocyclic complexes, capable of mimicking enzymatic active sites and facilitating multi-electron CO_2 transformations including porphyrins, corroles, and phthalocyanines (Pcs), have emerged as a distinct class of molecular catalysts. This review provides a comprehensive summary of recent progress in N_4-macrocyclic metal complexes for CO_2RR, focusing on their design principles, electronic structure modulation, and mechanistic insights.

1 | Introduction

The rapid increase in global warming and greenhouse gases, particularly carbon dioxide, has become a central scientific concern over the past few decades. To control the earth's temperature, rise to below 1.5–2.0°C, it is compulsory not only to reduce emissions but also to develop effective strategies for CO_2 management, including capture reuse and chemical transformation. As emission reductions alone are unlikely to meet climate targets, CO_2 recycling is gaining increasing attention. Thus, the recent trends in research are focused on neutralizing this CO_2 rise, by providing clean, cost-effective, and environment friendly techniques to tackle the current energy crisis. In the past few decades, continuous efforts have been made by the scientific communities to resolve this problem. Several electrochemical (electrolysis cell with catalytic electrodes convert CO_2 into reduced products (CO, formate, hydrocarbons, alcohols)), bioelectrochemical (microbial metabolism is coupled with electrical energy to electrochemically reduce CO_2 into organic products (e.g., formate, acetate, fuels)), plasma-driven (energetic electrons from non-thermal plasma activate and dissociate CO_2 into CO, O, or syngas), photoelectrochemical (photoactive electrodes integrated with CO_2 reduction catalysts are used under sunlight to drive CO_2 reduction) and thermochemical (high-temperature heat catalyze conversion of CO_2 into CO, CH_4, or fuels via purely thermal reactions) approaches have been introduced for CO_2 reduction into energy-dense fuels such as methane, methanol, and ethanol (Figure 1) [1–5]. Electrochemical route here is particularly attractive as it operates at ambient temperature and pressure, can be carried out in aqueous conditions, and allows the reaction environment (source of proton, catalyst design, operational potential) to be tuned, making

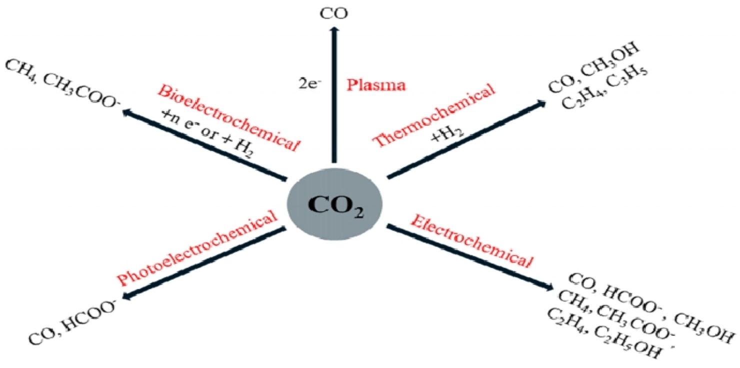
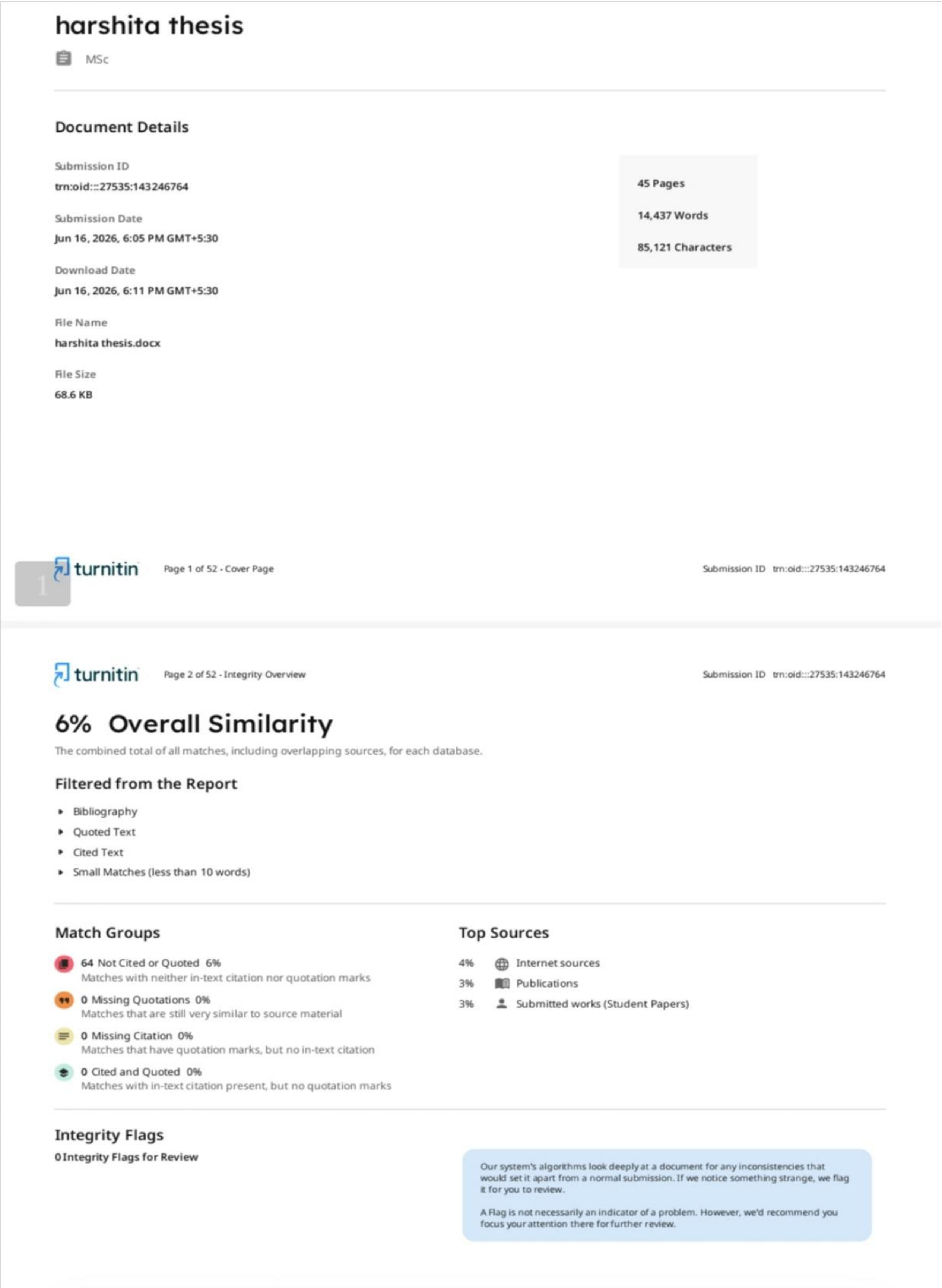


FIGURE 1 | Electrochemical, bioelectrochemical, photoelectrochemical, thermochemical, and Plasma driven reduction of CO_2 (e^--direct pathway,



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