

Electrocatalytic Reduction of Nitrate Pollution and Electrocatalytic Oxygen Evolution Reaction from Water Resources

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Amid the pursuit of modernization, the urbanization process continues to advance, accompanied by rapid industrial and economic growth, the frequent occurrence of water resource abuse, pollution, and wastage. Water resource recycling stands as a crucial approach to addressing the water crisis, while the treatment of water pollution and the regeneration of water resources are of paramount importance. Groundwater, a vital freshwater resource, finds widespread application across nations worldwide. However, over the past few decades, contamination of groundwater by nitrate due to factors such as agricultural nitrogen fertilizer use, livestock industry growth, sewage irrigation, and domestic wastewater discharge, has emerged as a severe environmental concern. Furthermore, the oxygen evolution reaction (OER) at the anode during water electrolysis is relatively complex, requiring a significant overpotential. The development of high-performance OER catalysts to reduce the overpotential of OER and enhance energy conversion efficiency is crucial, especially in promoting the widespread adoption of water electrolysis technology within renewable energy systems. Hence, this thesis focuses on the treatment and conversion of nitrate pollution in water, as well as the reuse of transformed products, and investigates the oxygen evolution reaction (OER) at the anode during water electrolysis. The main contents are summarized as follows:

(1) Electrocatalytic nitrate reduction reaction (NO_3^- RR) technology provides a promising solution to recover the nitrate nutrition from wastewater through catalyzing nitrate reduction into value-added NH_3 . However, the selectivity and efficiency of electrocatalysts are frustrated due to the imbalance of $^*\text{H}$ adsorption (for NO_3^- hydrogenation) and unavoidable adjacent $^*\text{H}$ self-coupling on active sites, resulting in competitive hydrogen evolution reaction (HER). This research reports a PdCu single-atom alloy (SAA) catalyst, that allows isolated Pd sites to produce $^*\text{H}$ for the hydrogenation process of $^*\text{NO}_3^-$ on neighboring Cu sites, which can restrain the $^*\text{H}$ self-coupling through extending the distance between two $^*\text{H}$ and thus effectively suppress competitive HER. Consequently, the PdCu SAA catalyst exhibits ultrahigh NH_3 Faraday efficiency (FE) of 97.1% with a yield of $15.4 \text{ mol cm}^{-2} \text{ h}^{-1}$ from the electrocatalytic NO_3^- RR in the neutral electrolyte, outperforming most of the reported catalysts.

(2) To date, electrocatalytic CO_2 reduction in KHCO_3 electrolyte is the closest technology to industrialization, but its long-term stability under industrial current density ($>200 \text{ mA cm}^{-2}$) are severely limited by the counter reaction, oxygen evolution reaction (OER). This research focuses on Ru doped IrOx catalyst (IrOx/Ru) for OER in KHCO_3 electrolyte under large industrial current density. The catalyst as anode electrocatalyst delivers a cell voltage of 3.9 V at 200 mA cm^{-2} for 500 hours exhibits boosted activity and ultrahigh stability. It can guide the design of future OER catalysts with high stability under large industrial current density in KHCO_3 electrolyte, which is of great meaning for accelerating industrialization process of electrocatalytic CO_2 reduction technology.

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Chapter 1 Introduction

1.1. Research background and overview

Water resources are intertwined with all life on Earth, exerting the potential to both propel and hinder societal development, to bestow fulfillment or inflict suffering upon individuals, and to engender both cooperation and conflict. Water stands as an indispensable and finite resource, fundamental to life, ecosystems, agricultural systems, and industrial processes. Nonetheless, the world confronts significant challenges encompassing water scarcity, pollution, and inefficient utilization.^[1] Approximately 80% of the global populace grapples with elevated vulnerabilities concerning water security^[1], as the amplification of planetary water scarcity ensues from the interplay of climate impetus, population escalation, and economic progress.^[2,3] Escalating climatic extremities, marked by both droughts and inundations, give rise to intensifying disjunctions in time and space between water provision and requisites, thereby heightening the complexities of safeguarding consistent provisions of sustenance and water resources globally.^[4] Such mounting challenges impede the assurance of dependable provisions of sustenance and water on a worldwide scale. The ramifications of prolonged droughts combined with near-exclusive dependence on surface water sources have precipitated scenarios where prominent urban centers teeter on the verge of water depletion. Illustratively, São Paulo confronted such a predicament in 2015, while Cape Town experienced a similar crisis in 2018.^[5-7] Water plays a pivotal role in responding to the challenges posed by climate shifts and socioeconomic advancement, particularly in its recognition as a pivotal nexus within the climate framework, the global economic landscape, and the vital life support systems.^[8] This acknowledgment has engendered a fresh impetus in the global discourse concerning water security. Initiatives aimed at fortifying water security have manifested at the highest echelons of government, commerce, and civil society. Notably, from 2012 to 2020, the World Economic Forum's rankings of high-impact risks featured water crises on eight occasions, prominently highlighting its significance. Further underlining the urgency, the 77th UN General Assembly in 2022 sounded a red alert regarding the confluence of climate change and water supply.^[9-14] While it is widely acknowledged that water is "vital to all life," including humanity, water is often taken for granted, at least by those who have easy access to safe and abundant water supplies. Consequently, phenomena of water mismanagement, contamination, or squandering are frequently encountered. To address this challenge, water recycling is considered a pivotal approach in tackling the water resource crisis. Water recycling involves the collection, treatment, and reuse of both wastewater and rainwater. Through wastewater treatment, valuable water resources within wastewater can be reclaimed, transforming it into reusable water resources. This method serves to augment the supply of available water resources, alleviating pressure on groundwater and surface water resources.^[15] Water recycling contributes to the reduction of pollution and overexploitation of natural

water bodies, thus safeguarding the ecological environment. Through wastewater treatment, pollutants and nutrients can be removed from the wastewater, diminishing contamination of natural water bodies and conserving the habitats of aquatic organisms. Furthermore, water recycling aids in decreasing the development of natural wetlands and rivers, thereby preserving the integrity of aquatic ecosystems^[16,17] In addition, Water pollution is a severe threat to global water resources and ecosystems. Various human activities, including industrial discharges, agricultural runoff, and improper waste disposal, release pollutants into water bodies. These pollutants encompass a wide range of substances, such as heavy metals, organic compounds, nutrients (e.g., nitrogen and phosphorus), and microplastics. The consequences of water pollution are far-reaching, affecting aquatic life, human health, and the environment. It leads to the degradation of water quality, eutrophication of lakes and rivers, and loss of biodiversity^[18,19]. Efficient water pollution treatment is crucial to safeguard water quality and protect human health and ecosystems. Wastewater treatment plants play a vital role in removing contaminants from domestic and industrial wastewater before it is discharged into water bodies. Advanced treatment technologies, such as biological treatment, chemical oxidation, and membrane filtration, can effectively remove various pollutants from wastewater. Proper wastewater treatment prevents the discharge of harmful substances into natural water bodies, mitigating the negative impacts of water pollution on aquatic life and human populations^[20,21]. Therefore, the treatment of water pollution and the recycling of water resources are very important.

Meanwhile, clean energy is one of the key factors in achieving sustainable development and combating climate change. Among all kinds of renewable energy, water as a clean energy plays an important role in the global energy supply. Nobel Laureate Richard E. Smalley proposes that energy, water and the environment are 3 of the ten challenges facing humanity now and in the decades to come^[22]. According to the data of the International Energy Agency, about 70% of the world's energy consumption in 2018 came from fossil fuels, which caused serious environmental pollution and climate warming, and it is urgent to solve the problem of environment and climate change, which also promotes mankind to find a new generation of renewable clean energy^[23-25]. The excessive consumption of fossil fuels has led to increasingly pressing energy crises, global warming, environmental pollution, and other issues, posing significant challenges to the sustainable development of human society.^[26-29] Therefore, establishing and developing green and renewable new energy systems has become an urgent task. Electrocatalytic energy conversion and storage technologies, represented by hydrogen production via water electrolysis and fuel synthesis through electrochemical CO₂ reduction, have garnered widespread attention due to their simplicity, environmental friendliness, and high conversion efficiency.^[30] The anodic oxygen evolution reaction, also known as the anodic water oxidation reaction, serves as the anodic half-reaction of hydrogen production via water electrolysis and is also involved in the electrocatalytic CO₂ reduction

process. The overall electrocatalytic CO₂ reduction reaction consists of two half-reactions: the anodic oxygen evolution reaction and the cathodic CO₂ reduction reaction. The anodic oxygen evolution reaction involves multiple electron transfer steps, leading to a relatively high overpotential and substantial energy losses.^[31,32] On the other hand, the cathodic CO₂ reduction reaction yields complex and poorly selective products, which in turn increases the subsequent separation and purification costs, making practical production challenging. Obtaining suitable and efficient catalysts is at the heart of addressing these challenges, and a deeper understanding of the reaction principles and processes can guide catalyst research and preparation.

1.2. Objectives and Scopes of the research project

Building upon the preceding discussion, this thesis first studies the treatment and transformation of nitrate pollution in water, and generates high value-added NH₃ by electrocatalytic nitrate reduction, which provides a promising solution for recovering nitrate nutrition in wastewater. Subsequently, this paper focuses on the anodic oxygen evolution reaction (OER) in electrolytic water, and studies an efficient OER electrocatalyst, which can run stably for a long time under high current density, and provides a promising solution for promoting the development of industrial hydroelectrolysis and electrocatalytic reduction of CO₂.

1.3. Outline of the thesis

The thesis is divided in three main chapters. The Chapter 2 covers brief review about the related work Ammonia Synthesis from Nitrate Ions in Aqueous Solution via Electrocatalytic Reduction at normal temperature and pressure and Neutral electrolytic oxygen evolution reaction catalyst at high current density. In Chapter 3, Selectively reducing nitrate into NH₃ in neutral media by PdCu single-atom alloy electrocatalysis will be discussed. In Chapter 4, Ultra-stable Ru doped IrO_x catalyst for oxygen evolution reaction paired with CO₂ reduction under large industrial current density will be presented. In Chapter 5, summarizes the research work and proposes the future work.

Chapter 2. Literature Review

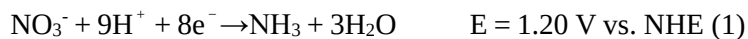
2.1. Ammonia Synthesis from Nitrate Ions in Aqueous Solution via Electrocatalytic Reduction at normal temperature and pressure

Nitrate ion (NO_3^-) represents the most stable nitrogen-containing compound in aerobic environments [33]. The escalating living standards and swift progress of contemporary industry and agriculture have led to a gradual surpassing of the natural environment's capacity to purify NO_3^- . The World Health Organization specifies a maximum nitrate nitrogen content of 10mg/L in drinking water [34], yet a grave situation concerning NO_3^- in drinking water sources is prevalent worldwide [35]. NO_3^- pollution stems from a diverse array of sources, primarily rooted in the extensive application of nitrogen fertilizers, leaching and percolation of solid waste, as well as the release and seepage of domestic sewage and nitrogen-laden industrial effluents [35]. When NO_3^- concentration surpasses a certain threshold, it poses a severe threat to human health. Initially, NO_3^- can be converted to NO_2^- within the human body, binding with hemoglobin and impeding its oxygen-carrying capacity, thereby inducing asphyxia. Concurrently, NO_2^- reacts with ammonia nitrogen in the stomach, generating carcinogenic nitrosamines and their derivatives [35], resulting in a spectrum of ailments impacting the brain, nervous system, bones, intestines, skin, thyroid, and other physiological systems [36]. Consequently, the imperative to mitigate and rectify NO_3^- pollution in water bodies is evident. Standard techniques for addressing NO_3^- include reverse osmosis [37], ion exchange [38], electrodialysis [39], biological denitrification [40], and chemical reduction [41]. Among these, the electrocatalytic reduction method is gaining prominence due to its merits of safety, operational ease, mild reaction conditions, elevated removal efficiency, robust selectivity, and absence of secondary pollution [42].

Synthetic ammonia carries profound significance for the progression of human society [43]. Beyond its role as a pivotal fertilizer and chemical precursor, ammonia emerges as a crucial conduit for clean energy, notably hydrogen. Demonstrating its prowess, ammonia presents itself as an optimal hydrogen storage medium, boasting a hydrogen storage capacity of 17.6% (mass fraction) and an energy density reaching 3000 Wh/kg [44]. Moreover, NH_3 touts a range of virtues as an energy carrier: (1) High Energy Density: Ammonia has a high volumetric energy density, making it an efficient energy carrier for long-term storage and transportation. (2) Hydrogen Carrier: Ammonia contains approximately 17.65% hydrogen by weight, making it a dense source of hydrogen for various applications. (3) Existing Infrastructure: The ammonia industry has a well-established infrastructure for production, storage, and distribution, which can be repurposed for energy applications. (4) Global Availability: Ammonia is produced and traded globally, ensuring reliable access and distribution as an energy carrier. (5) Carbon-Free Production: Ammonia can be produced using green hydrogen, generated from renewable energy

sources, making it a carbon-free energy carrier. (6) Versatility: NH_3 can be utilized as a direct fuel in various combustion engines, gas turbines, and fuel cells, as well as a feedstock for hydrogen production. (7) Long-Term Storage: Ammonia can be stored for extended periods without significant energy losses or degradation, providing stability to energy systems.^[45] Currently, the global annual production of synthetic ammonia nearly reaches 200 million tons, and in light of the growing concern for environmental and energy matters, the call for ammonia is anticipated to steadily increase. The primary approach to engineered ammonia synthesis rests on the Haber-Bosch method^[46], whereby N_2 and H_2 are transformed into NH_3 on catalyst surfaces under elevated temperatures (650 ~ 750 K) and high pressures (10 MPa). However, this process incurs substantial energy consumption due to its rigorous reaction conditions and yields a mere conversion rate of around 15%^[46]. According to statistics, the world consumes 2% of energy every year for industrial ammonia synthesis, which produces about 400 million tons of CO_2 ^[47]. Amidst the escalating concerns over energy and environmental challenges, the trajectory of synthetic ammonia research is veering towards the exploration of novel technologies that can mitigate reaction conditions and energy demands. This directional shift holds significant implications for the sustainable advancement of human society.

To minimize the energy outlay in synthetic ammonia production, extensive investigations have focused on the N_2 reduction reaction (NRR). The utilization of water as a hydrogen source for ammonia synthesis through electrocatalysis and photocatalytic nitrogen reduction has gained escalating interest^[48-53]. Nevertheless, the cleavage of the robust $\text{N}\equiv\text{N}$ triple bond (with an energy of 941 kJ mol^{-1}) in nitrogen presents a formidable challenge, compounded by the impedance posed by concurrent hydrogen evolution reactions, which impede Faraday efficiency.^[54-56] Therefore, the prospect of converting waterborne nitrate contamination into a reusable ammonia solution is indeed appealing. Furthermore, this innovation can seamlessly integrate into prevailing procedures, generating value-added ammonium/ammonia compounds and pristine water^[51]. The reduction of NO_3^- to NH_3 involves $8e^-$ transfer in thermodynamics, and the catalyst is more inclined to reduce NO_3^- to N_2 through $5e^-$. In addition, like N_2 reduction, NO_3^- reduction also faces competition from HER. Equation (1) shows the reduction of NO_3^- to NH_3 :



In fact, the process of NO_3^- reduction is very complicated, and the valence state of N changes from +5 to -3. In the reduction process, NO_3^- is first reduced to NO_2^- and then to NO , and NO is further hydrogenated to generate HNO , H_2NO , and finally NH_3 ^[57-60]. The key to NO_3^- reduction is that the highest occupied d orbital of the metal in the catalyst matches the LUMO level of NO_3^- to promote the transfer of e^- of the metal d orbital to the LUMO level of NO_3^- . Current research shows that Cu and Ru-based catalysts have higher selectivity for NO_3^- reduction to NH_3 , while Fe, Ni, Co and other metals are more inclined to

reduce NO_3^- to N_2 [61]. Wang *et al.* [62] used anodic oxidation to grow $\text{Cu}(\text{OH})_2$ nanoarrays on the Cu substrate, and then $\text{Cu}(\text{OH})_2$ was heat treated in O_2 atmosphere to obtain CuO nanoarrays. In the electrochemical test, CuO is finally converted to Cu/Cu₂O, and the comparison experiment proves that Cu/Cu₂O is the effective component of NO_3^- reduction. In 0.5 mol/L Na_2SO_4 electrolyte with a concentration of 200 mg/L NO_3^- , the Cu/Cu₂O catalyst reduced NO_3^- to produce NH_3 with a yield of 0.24 mmol•h⁻¹•cm⁻¹, a conversion rate of 81.2% and a Faraday efficiency of 95.8%. [62] Isotope experiments with $\text{Na}^{15}\text{NO}_3$ confirmed that the formation of NH_3 came from NO_3^- reduction. DFT calculations showed that Cu/Cu₂O could reduce the formation barrier of HNO and effectively inhibit HER competition [62]. Li *et al.* [63] designed Ru/RuO₂ nanoclusters with core-shell structure, the average size of Ru particles was 2 nm, the ammonia conversion rate was close to 100%, and the yield was 5.56 mol•gcat⁻¹•h⁻¹. The development of efficient NO_3^- reduction catalyst to NH_3 is of great significance for ammonia synthesis at normal temperature and pressure. The aforementioned experimental findings demonstrate the feasibility of attaining ammonia synthesis with enhanced efficiency and selectivity within a high-concentration NO_3^- environment. However, it is crucial to acknowledge that the actual NO_3^- concentration in water is significantly lower than the experimental conditions, resulting in a substantial occupation of the NO_3^- -reduction active sites by a large quantity of H^+ . Furthermore, electrocatalytic NO_3^- reduction encounters formidable competition from the hydrogen evolution reaction (HER). Therefore, it becomes imperative to address the challenge posed by HER competition during catalyst design.

2.2. Neutral electrolytic oxygen evolution reaction catalyst at high current density

Electrolytic water oxygen evolution reaction (OER) is a process in which oxygen in water is oxidized to oxygen by electric energy under the action of catalyst. It is not only an important half reaction in the process of electrolysis of water, but also plays an important role in many energy conversion and storage technologies, such as CO_2 electrocatalytic reduction, metal air batteries, fuel cells, and so on. The total electrocatalytic CO_2 reduction reaction can be divided into two half reactions, which are anodic oxygen evolution reaction and cathodic CO_2 reduction reaction. Because of the multiple electron transfer steps involved in the anodic oxygen evolution process, it has a high overpotential and is one of the main sources of excessive total reaction energy consumption. Therefore, efficient OER catalysts are a prerequisite for driving the technology towards eventual industrialization. [64-66] In the past few decades, substantial progress has been made in the development of catalysts for water electrolysis, especially in the exploration of active sites and the development of new catalysts [67-70]. However, these catalysts are usually studied under laboratory conditions, focusing on basic catalyst kinetics [71]. Among them, the OER reaction process needs to transfer 4 electrons, which is the speed control step of electrolytic water reaction

and the main bottleneck of electrolytic water. Therefore, the development of highly efficient OER electrocatalysts with low overpotential, especially at high current density, will undoubtedly promote the development of industrial hydropower electrolysis and electrocatalytic CO₂ reduction ^[72]. In recent years, although the research on high performance water electrolysis and electrocatalytic CO₂ reduction catalysts has been greatly developed, there is still a long way to go before large-scale industrialization. At present, most of the catalysts for water electrolysis have excellent performance at low current density. The current densities commonly used in industrial electrolytic cells are 200, 500 and 1000 mA·cm⁻², and the catalyst needs to work stably under the high current densities greater than 200 mA·cm⁻² or even up to 1000 mA·cm⁻². In order to be suitable for industrial applications, OER catalysts need to meet more stringent standards ^[73], and their performance at high current densities is crucial to move electrocatalysts from the academic stage to industrial use. Through the study of OER mechanism, it is found that OER reaction has a faster reaction rate under high current density, and a large number of O₂ bubbles tend to form on the electrode ^[74]. In this case, the accumulation of bubbles at the interface between the electrocatalyst and the electrolyte will seriously hinder the mass transfer of the liquid, slow down the electron transfer, reduce the exposure of the active site, and lead to poor electrocatalytic activity and durability. Therefore, higher basic requirements should be put forward for the development of catalysts: (1) At high current density, especially in the strong oxidation process, the catalyst should have stable long-term durability and corrosion resistance; (2) The catalyst should have structural and chemical stability to prevent the shedding and deactivation of the catalyst at high current density; (3) The faster reaction rate requires the catalyst to have high activity and the electrode to have good electron transfer performance; (4) The electrode should have a large electrochemical active surface area (ECSA) to ensure abundant active sites; (5) The catalyst should have rapid reaction kinetics. When the current density is very high, the electron and mass transfer process at the reaction interface is the key step ^[75].

Oxygen evolution reaction (OER) is the most energy-intensive step in the electrochemical water decomposition reaction, which involves the transfer of four protons and four electrons, O–H bond fracture and O–O bond formation, etc. Its mechanism and pathway are far more complex than hydrogen evolution reaction. Therefore, OER is a thermodynamically unfavorable process that requires a high potential to overcome the energy barrier. So far, OER is still the bottleneck of water decomposition. The reaction mechanism of OER can be changed according to the pH value of the electrolyte, and its reaction process is different in acidic environment and alkaline environment. At present, the widely accepted oxygen evolution reaction mechanism is as follows ^[76] :

In alkaline media: (1) $* + OH^- \rightarrow *OH + e^-$; (2) $*OH + OH^- \rightarrow *O + H_2O + e^-$; (3) $*O + OH^- \rightarrow *OOH + e^-$; (4) $*OOH + OH^- \rightarrow * + O_2 + H_2O + e^-$

In acidic media: (1) $\text{H}_2\text{O} + * \rightarrow *\text{OH} + \text{H}^+ + \text{e}^-$; (2) $*\text{OH} \rightarrow *\text{O} + \text{H}^+ + \text{e}^-$; (3) $\text{H}_2\text{O} + *\text{O} \rightarrow *\text{OOH} + \text{H}^+ + \text{e}^-$; (4) $*\text{OOH} \rightarrow * + \text{O}_2 + \text{H}^+ + \text{e}^-$

Among them: * indicates the site of reaction on the surface of the catalytic agent; *OH, *OOH, and *O represent the intermediate body in the reaction. Whether in acidic or alkaline media, OER involves four REDOX reactions in which electrons and protons are transferred at each step. In acidic media, the first step of OER is the dissociation of water molecules, which will cause great obstacles to the process of OER, and many catalysts show poor durability in acidic environment. In alkaline media, the presence of OH^- ions, which can be utilized directly and do not involve the dissociation of water molecules, contributes to the OER reaction.

The OER process requires the transfer of 4 electrons in multiple steps, each step only involves the transfer of a single electron, and the accumulation of energy in each step makes OER blocked in kinetics, so that it has slow kinetics. The development of effective and stable OER electrocatalyst, reducing the energy barrier of reaction, is helpful to improve the efficiency of electrocatalytic water splitting reaction. At present, OER catalysts are mainly divided into two categories: noble metal oxygen evolution catalysts and transition metal catalysts. Noble metal based oxygen evolution catalyst is the most active commercial catalyst for water electrolysis, among which RuO_2 and IrO_2 have excellent corrosion resistance in a wide pH range, and are suitable for OER reaction in acidic, alkaline and other environments^[77]. However, its high cost and scarcity hinder the large-scale application of hydrogen production by electrolysis of water^[78]. Transition metal-based catalysts (Co, Ni, Fe) also have good catalytic activity after a series of modifications, and are more attractive than precious metal catalysts due to their wide source and low price^[79]. However, these catalysts are tested in a small range and rarely work for hundreds of hours continuously, far from meeting the actual application needs. Therefore, it is of great research value to improve the stability and activity of transition metal-based electrocatalysts under high current density.

Although water electrolysis and electrocatalytic CO_2 reduction technologies have achieved some results, they still face severe challenges in further industrial applications. Due to the corrosive nature of acidic or alkaline electrolytes common in water electrolysis and electrocatalytic CO_2 reduction technology, long-term operation will corrode industrial equipment, which further hinders the industrial application of electrolytic water. In particular, a recent popular development in the electrocatalysis community has been the adoption of highly basic (for example, 1 M KOH or higher) electrolytes to enhance catalytic activity in gas diffusion electrode (GDE) environments^[80]. Although the strongly alkaline environment has many advantages, however, the significant drawback of employing a high alkaline electrolyte in practical operating conditions cannot be overlooked. The inevitable reaction between OH^- and CO_2 leads to the creation of carbonate/bicarbonate and irreversibly acidifies the electrolyte. The consequent formation of

carbonates hinders overall cell performance, obstructs gas diffusion pathways, and promotes electrolyte flooding, ultimately leading to cell shutdown. In contrast, while locally generated OH^- at the cathode in a neutral electrolyte may also interact with CO_2 , the resulting carbonate/bicarbonate is, on the whole, balanced with the anodic half-reaction, where carbonate/bicarbonate can react with generated protons and release CO_2 back into the gas phase. Although this results in a net transfer of CO_2 from the cathode to the anode, it presents a more manageable issue compared to the irreversible acidification caused by using KOH. Furthermore, the economic costs are elevated by the consumption of the feeding gas and alkaline electrolyte, which also exerts a considerable inhibitory effect on the CO_2 concentration in the vicinity of the catalyst surface. Therefore, investigating high-performance electrocatalysts in neutral electrolytes will be a direction for future development.

Chapter 3 Selectively reducing nitrate into NH_3 in neutral media by PdCu single-atom alloy electrocatalysis

A larger portion of this chapter has been submitted to the ACS Catalysis and published as: Cheng Du and Siyan Lu *et al.*, “Selectively reducing nitrate into NH_3 in neutral media by PdCu single-atom alloy electrocatalysis^{[81]”}.

3.1. Introduction

With the rapid development of modern industry and agriculture, nitrate waste from industrial sewage and overfertilization has caused serious pollution in the biosphere and water bodies, which is threatening human health and ecological safety.^[82,83] Currently, the removal of nitrate waste in wastewater mainly relies on biological, physical, and chemical treatments, such as bacterial denitrification, ion exchange, and reverse osmosis.^[83] Nevertheless, those traditional methods are severely limited by rigorous operation conditions, high cost of posttreatment, and tedious procedures.^[83] To circumvent these problems, newly developed electrocatalytic nitrate reduction reaction (NO_3^- RR) technology driven by green electric energy has been developed to recover nutrition flexibly and effectively from nitrate in wastewater, by catalyzing aqueous nitrate reduction into N_2 (main product) and NH_3 (by-product) under ambient temperature and pressure.^[84-86] Although promising, the accessibility of such electrocatalytic technology in the industrial treatment of nitrate waste still suffers from an intractable limitation, specifically that the main product N_2 possesses very limited economic value and is difficult to be reused.^[87-89] Moreover, the competitive hydrogen evolution reaction (HER) over the electrocatalyst draws electrons from the nitrate reduction processes, resulting in a low Faraday efficiency (FE) of electrocatalytic NO_3^- RR.^[82,90] Although alkaline electrolytes can suppress HER for selective NO_3^- RR, the strong corrosivity to reactors would severely increase the economic cost of large-scale industrial applications.^[91-93] Therefore, an emerging electrocatalyst is urgently needed to catalyze nitrate reduction selectively and effectively into value-added NH_3 under mild neutral media to increase the economic value of this process, since NH_3 is an important precursor to produce fertilizer and urea for agriculture.

To generate NH_3 from NO_3^- RR, the NO_3^- is typically adsorbed on the surface of the electrocatalyst and then goes through a series of hydrogenation steps.^[94,95] Recently, Cu has been found to have promising nitrate reduction performance due to its excellent $^*\text{NO}_3$ adsorption ability.^[96-98] However, too weak $^*\text{H}$ adsorption on Cu limits the following hydrogenation steps, resulting in low catalytic performance. To meet this challenge, enormous effort has been devoted to introducing an additional $^*\text{H}$ adsorption site in the Cu-based catalyst. For instance, CuNi and CuPd catalysts have been developed for

promoting nitrate reduction, due to the outstanding $^*H$ generation ability of those second elements.^[99-102] However, the $^*H$ produced on those introduced $^*H$ adsorption sites may cross-couple and desorb through the Tafel step, which can not well suppress HER and promote NO_3^- RR.^[103]

To avoid the possibility of HER from the $^*H$ intercoupling, in this work, we design a PdCu single-atom alloy (SAA) with atomic Pd atoms on the surface of Cu nanoparticles. Due to the isolated position of Pd atoms, the produced $^*H$ on Pd sites are separated and hard to intercouple, thus limiting the HER. As a result, the PdCu SAA exhibit ultrahigh selectivity with Faraday efficiency (FE) of 97.1%, accompanied by an NH_3 generation rate of $15.4 \text{ mol cm}^{-2} \text{ h}^{-1}$. To further investigate the catalytic active sites and reaction mechanism, model PdCu SAA was experimentally prepared using the Cu single-crystal with different crystal faces and tested for NO_3^- RR. Combined with density functional theory (DFT) calculations, we conclude that atomically dispersed Pd atoms on Cu (100) are the most active catalytic sites, which can decrease the energy barrier of the rate-determining step (RDS) and promotes NO_3^- RR.

3.2. Method

3.2.1 Chemicals: Toray carbon paper (CP) HCP-060 was purchased from Fuel cell store. D_2O , $^{15}NH_4Cl$, $Na^{15}NO_3$, NH_4Cl , $NaNO_3$, $NaOH$, Na_2PdCl_4 , $Cu(NO_3)_2 \cdot 3H_2O$, sodium citrate dehydrates, salicylic acid, acetone, ethanol, Ethylene glycol, isopropanol, $NaClO$ aqueous solution, sodium nitroprusside ($C_5FeN_6Na_2O$) and p-Dimethylaminobenzaldehyde were purchased from Sigma. Cu single-crystals with different crystal facets were purchased from MTI company. Deionized water was used in the experiments. All reagents were used without further purification.

3.2.2 Electrodeposition of Cu: Before the electrodeposition process, carbon paper (CP) was firstly cut into $1 \text{ cm} \times 2 \text{ cm}$ size and then fully washed with acetone, dilute HCl solution, and water, respectively. The electrodeposition was conducted using a three-electrode system, in which the CP served as the working electrode with a $1 \times 1 \text{ cm}^2$ working area. The reference electrode and counter electrodes were an Ag/AgCl electrode and a graphite rod, respectively. The electrochemical technique used for electrodeposition was the potentiostat method. The potentiostat electrodeposition was conducted in 50 mL 6.5 mM $Cu(NO_3)_2$ aqueous solution with the CP as substrate under the potential of -0.3V (vs. Ag/AgCl) for 30 min.^[104] Under the application of the electric field, the Cu^{2+} was reduced into Cu nanoparticles on the CP. Meanwhile, the H_2O was oxidized into O_2 at the graphite rod. After the electrodeposition, the CP with Cu nanoparticles was washed with isopropanol and water, respectively. After being dried by N_2 flow, the Cu sample was stored in a vacuum or inert gas environment.

3.2.3 Synthesis of PdCu SAA: PdCu SAA was synthesized by the galvanic replacement reaction. The galvanic replacement reaction was spontaneously driven by their reduction potential difference. Typically, 2 mL 0.1 mg mL⁻¹ Na₂PdCl₄ solution was first prepared using ethylene glycol as solvent. Then CP with Cu nanoparticles was immersed into the solution under 80°C for 15min. After washing with isopropanol and water, the CP with PdCu SAA was dried by N₂ flow and was stored in a vacuum or inert gas environment for further experiments. For the synthesis of PdCu alloy NP and Pd NP on Cu, the concentration of Na₂PdCl₄ solution was increased to 5 mg mL⁻¹ and 100 mg mL⁻¹, respectively. The other procedures were the same as that for PdCu SAA on CP. Single-crystal PdCu SAA was synthesized according to a similar procedure, which put single-crystal Cu into a dilute Na₂PdCl₄ solution (0.001mg mL⁻¹) for 15 min under room temperature. The other procedures were the same as that for PdCu SAA on CP. The carbon paper is to enhance the conductivity of the electrode during the electrocatalytic reaction.

3.2.4 Material characterization: Scanning electron microscopy (SEM) images were captured on a Hitachi S4800 with a working accelerating voltage of 10 kV. Glancing-incidence X-ray diffraction (GIXRD) was measured on a PANalytical X'Pert Pro MRD diffractometer with Cu K α radiation (1.54 Å) at an incidence angle of 0.3°. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo-VG Scientific ESCALab 250 microprobe with a monochromatic Al K α X-ray source (1486.6 eV). The obtained spectra were calibrated using the C 1s line. The catalyst was sonicated from the carbon paper in IPA solution. Then the solvent was dropped casting onto ultrathin lacey carbon TEM grids for imaging. Some residue carbon paper is hard to separate from the samples. Aberration-corrected high-angle annular dark field scanning transmission electron microscope (AC-HAADF-STEM) tests were carried out on an FEI Titan 80-300 HB TEM equipped with energy-dispersive X-ray spectroscopy (EDX) at 300 kV. The HAADF-STEM images were recorded by FEI Titan 80-300 HB TEM/STEM with double aberration correctors operating at 300 kV at the Canadian Center for Electron Microscopy (CCEM). Inductively coupled plasma mass spectrometry (ICP-MS) analyses were carried out on an Agilent 8800 triple quadrupole instrument, using He as a collision cell gas, Ge and In as internal standards to correct for instrument drift, and ICP element standards (secondary standards from Delta Scientific Inorganic Ventures; primary calibration standards from Alfa Aesar and Aristar VWR Chemicals BDH) to confirm instrument accuracy (within 5%; relative standard deviation for individual sample analyses was $\leq 11\%$). UV-Vis absorption spectroscopy was tested on a Shimadzu UV-2600i spectrophotometer. Proton nuclear magnetic resonance (¹H-NMR) was measured on Bruker Avance III 300 MHz. XAS measurements were carried out at the 20-BM and 20-ID-C beamline of Advanced Photon Source (APS), Argonne National Laboratory. The measurements at the Pd K-edge were performed in fluorescence mode using a Lytle detector. The Pd K-edge XANES and EXAFS data were analyzed and treated using the software package Athena. The EXAFS data is fitted using the software package Artemis. Pd foil is applied for reference and

calibration samples. In this fitting data, CN represents the coordination numbers of identical atoms; R is assigned as the interatomic distance; δ^2 is considered as Debye-Waller factors. The fitting parameters strictly comply with all experimental requirements.

3.2.5 Electrochemical NO_3^- RR measurements: All electrochemical tests were measured on Autolab PGSTAT 204 electrochemical workstations at room temperature with IR corrected. A three-electrode system was fabricated with the prepared PdCu-based materials, platinum wire, and saturated calomel electrode (SCE) serving as the working electrode, the counter electrode, and the reference electrode, respectively. A gas-tight H-type electrochemical cell equipped with a piece of 211 Nafion membrane was employed to conduct the electrochemical reaction. A platinum wire was in the anode compartment alone to avoid the electrochemical oxidation of produced NH_3 . Before NO_3^- RR tests, the 211 Nafion membrane was firstly activated in 5% H_2O_2 , H_2O , 0.5 M H_2SO_4 , and H_2O for 20min, respectively, and then soaked in water at 80 °C for 12h.^[105] The synthesized CP with PdCu SAA catalyst directly served as the working electrode with an electrode holder. The NO_3^- RR catalytic activities were evaluated using the potentiostatic technique under selective potential for one hour in 0.5M Na_2SO_4 with 600 ppm NaNO_3 solution under an Ar gas environment. All the potential values are presented in RHE unless otherwise stated. For the electrochemical test of single-crystal PdCu SAA samples, the bulk single-crystal PdCu SAA was connected to the electrode holder through Cu foil. To avoid the interference of Cu foil on the electrochemical signal, an inert Kapton tap was used to totally cover the Cu foil.

3.2.6 Determination of ammonia using UV-Vis method: The UV-Vis method for NH_3 concentration determination was modified from the indophenol blue method.^[106] In detail, 2 mL of the electrolyte was taken out after the electrocatalytic reaction and was diluted 5 times. Then, 2mL of the diluted solution was added to 2 mL of a 1 M NaOH solution containing salicylic acid and sodium citrate. Then, 1 mL of 0.05 M NaClO and 0.2 mL of 1 % $\text{C}_5\text{FeN}_6\text{Na}_2\text{O}$ were also added to the above-mixed solution. The UV-Vis absorption spectrum was measured after 2 hours. The concentration of indophenol blue was determined using the absorbance at the wavelength of 655 nm. The concentration-absorbance curves were calibrated using a standard ammonia nitrate solution with a series of concentrations in 0.5 M Na_2SO_4 . The fitting curve ($y = 0.160x + 0.040$, $R^2=0.999$) shows a good linear relationship between the absorbance values and NH_3 concentrations (**Figure 3.1A-B**).

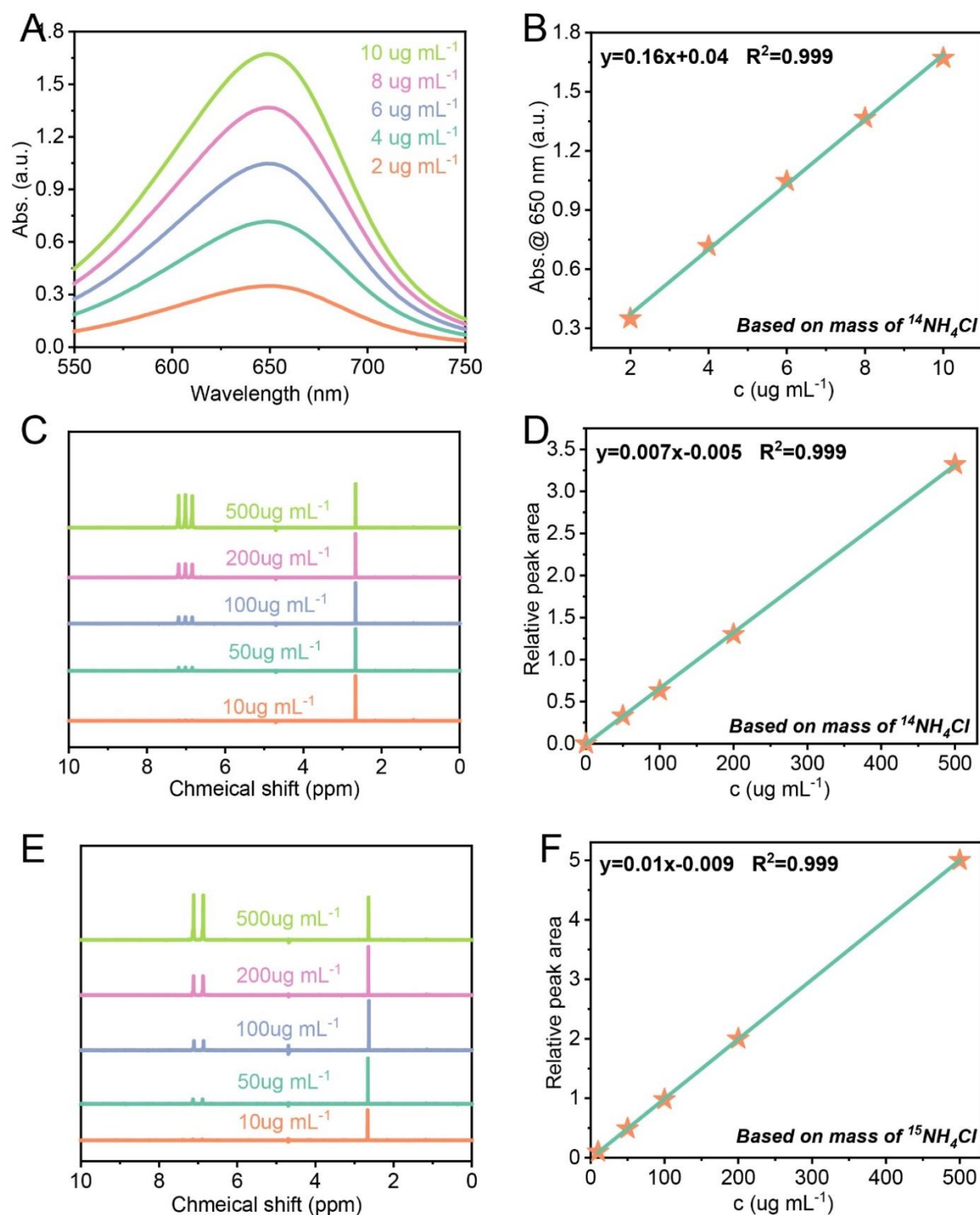


Figure 3.1. Standard curves of NH_3 from different detection methods. (A-B) UV with $^{14}\text{NH}_4^+$, (C-D) ^1H NMR with $^{14}\text{NH}_4^+$, and (E-F) ^1H NMR with $^{15}\text{NH}_4^+$. DMSO shows a peak at 2.6 ppm and serves as the internal standard. The ^1H NMR spectra of $^{15}\text{NH}_4^+$ showed double peaks, while $^{14}\text{NH}_4^+$ showed triple peaks in the range of 7.2 ppm to 6.8 ppm. The calibration curves all show good linearity.

3.2.7 Determination of ammonia using NMR method: The NMR method is based on ¹H-NMR. To better detect the NH₄⁺ using NMR, the solution needs to be acidized to pH~3. Typically, 630 μL electrolyte was taken out after the electrocatalytic reaction and then acidized by adding 5 μL concentrated hydrochloric acid. After that, 100 μL D₂O with certain DMSO was added to the mixed solution and then transferred into an NMR tube for the test. All NMR spectra were obtained by 128 scans. DMSO shows a peak at 2.6 ppm and serves as the internal standard. The concentration of NH₄⁺ was determined by the peak (triplet) area ratio between NH₄⁺ and DMSO. The concentration-NMR peak area ratio curves were calibrated using a standard NH₄Cl solution with a series of concentrations in 0.5 M Na₂SO₄. The fitting curve ($y = 0.007x - 0.005$, $R^2=0.999$) shows a good linear relationship between the absorbance values and NH₃ concentrations (**Figure 3.1C-D**).

3.2.8 Isotope labeling experiments: The isotopic labeling experiments were conducted using ¹⁵NaNO₃ as the feeding in 0.5 M Na₂SO₄. All other experimental operations are the same as that using NaNO₃. Especially, the ¹⁵NH₄⁺ standard curve was built using ¹⁵NH₄Cl with a series of concentrations in 0.5 M Na₂SO₄. The fitting curve ($y = 0.010x - 0.009$, $R^2=0.999$) shows a good linear relationship between the absorbance values and NH₃ concentrations (**Figure 3.1E-F**).

3.2.9 Calculations of the NH₃ formation rate and Faradaic efficiency (FE):

The Faradaic efficiency (FE) and Yield for NH₃ are calculated as follows:

$$Yield = \frac{c_{NH_3} \times V \times M_{NH_3}}{A \times t}$$

$$FE = \frac{c_{NH_3} \times V \times 8 \times F}{\int_0^t idt}$$

Where c_{NH_3} is the determined NH₃ concentration; V is the volume of electrolyte in the cathode compartment, typically 25 mL; M_{NH_3} is the molecular weight of ammonia, 17 g mol⁻¹ for ¹⁴NH₃ and 18 g mol⁻¹ for ¹⁵NH₃; A is the geometric surface area of the electrode, 1 cm²; t is the time of electrolysis, 3600 s; F is the Faraday constant, i.e., 96485 C mol⁻¹. The reported values of *Yield* and FE were calculated based on three separate measurements under the same conditions.

3.2.10 Operando Raman Spectroscopy

The *operando* Raman spectroscopy measurements were performed using a Renishaw inVia Reflex system and Autolab PGSTAT 204 electrochemical workstation. The electrochemical cell was homemade by Teflon with a quartz window between the sample and objective. The working electrode was immersed into the electrolyte through the wall of the cell and kept the electrode plane perpendicular to the laser. A

platinum wire and Ag/AgCl electrode were served as the counter and reference electrode, respectively. IT curves were conducted at 0V, -1,1V, -1,2V, -1,3V VS Ag/AgCl.

3.2.11 Electrochemical surface area (ECSA) measurement

Cyclic voltammetry (CV) curves in electrochemical double-layer capacitance (C_{dl}) determination were measured in a potential window nearly without the Faradaic process at different scan rates of 20, 40, 60, 80, and 100 mV s^{-1} . The plot of current density at set potential against scan rate has a linear relationship and its slope is the C_{dl} . What should be noted that the double-layer capacitance for ideal smooth oxide surface is assumed to be $60 \mu\text{F}\cdot\text{cm}^{-2}$ based on previous reports,^[107-109] which means the ECSAs values can only be used for reference and related comparison.

3.2.12 Determination of NO_2^- using UV-vis-absorption method

The method of NO_2^- using the UV-vis-absorption method is similar from previous report.^[110] A mixture of p-aminobenzenesulfonamide (4 g), N-(1-Naphthyl) ethylenediamine dihydrochloride (0.2 g), ultrapure water (50 mL) and phosphoric acid (10 mL, $\rho=1.70 \text{ g/mL}$) was used as a color reagent. A certain amount of electrolyte was taken out from the electrolytic cell and diluted to 5 mL to detection range. Next, 0.1 mL color reagent was added into the aforementioned 5 mL solution and mixed uniformly, and the absorption intensity at a wavelength of 540 nm was recorded after sitting for 20 min. The concentration-absorbance curves were calibrated using a standard ammonia nitrate solution with a series of concentrations in 0.5 M Na_2SO_4 . The fitting curve ($y = 0.6193x + 0.0022$, $R^2=0.9999$) shows a good linear relationship between the absorbance values and NO_2^- concentrations (**Figure 3.2A-B**). The Faradic Efficiency of NO_2^- was then calculated.

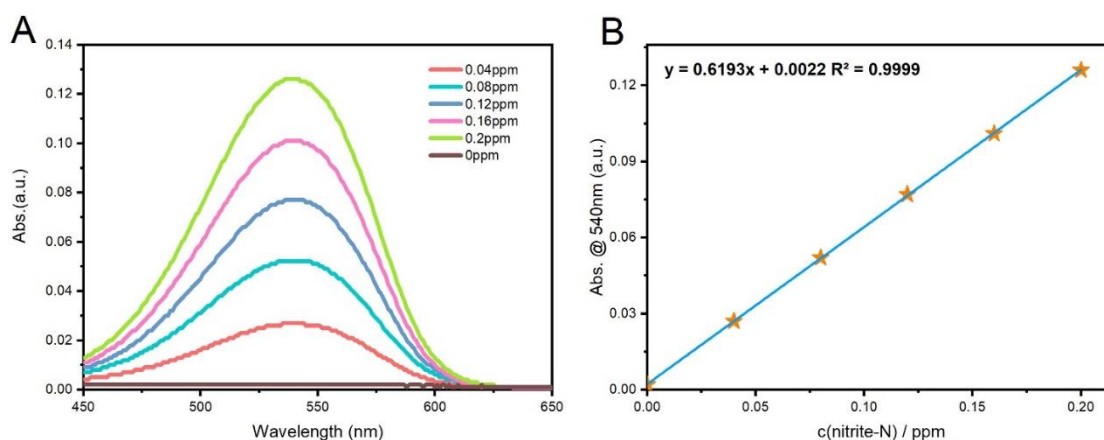


Figure 3.2. The measurement of NO_2^- products. (A-B) The concentration-absorbance calibration curves of NO_2^-

3.2.13 DFT calculations:

Density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP) with projector-augmented wave pseudopotentials.^[111-113] The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional within the generalized gradient approximation (GGA) was chosen in consideration of a balance between accuracy and computational cost.^[114] Van der Waals interactions were considered using DFT-D3 with the Becke-Jonson damping method. The plane wave energy cutoff was 400 eV for each of the slabs. These periodic slabs are separated by 20 Å vacuum space along the z direction to isolate interactions between replicas. The Brillouin zone was sampled on a $3 \times 2 \times 1$ Monkhorst-Pack k-point grid.^[115] For each slab, the top two layers of the slabs and adsorbates were fully relaxed until the maximum forces converged to 0.05 eV/Å. Free energy for the three catalysts was obtained following the same method as the literature.^[116] The free energy correction was implemented for each species by conducting an additional frequency calculation with the same function. To avoid abnormal entropy contribution, frequencies less than 50 cm⁻¹ are set to 50 cm⁻¹.

3.3. Result and Discussions

3.3.1 Synthesis and STEM characterizations

PdCu SAA was prepared through the spontaneous galvanic replacement reaction, which was driven by the reduction potential difference between Na₂PdCl₄ and Cu.^[117,118] As schematically shown in **Figure 3.3**, Cu nanoparticles were firstly electrodeposited on the carbon paper (CP) substrate, and then immersed into extremely dilute 0.1 mg mL⁻¹ Na₂PdCl₄ ethylene glycol solution for 15min under 80°C (for experimental details please see the Supplementary Information). Here, ethylene glycol serves as solvent for the reaction, due to its mild reduction ability to prevent the possible oxidation of Cu.

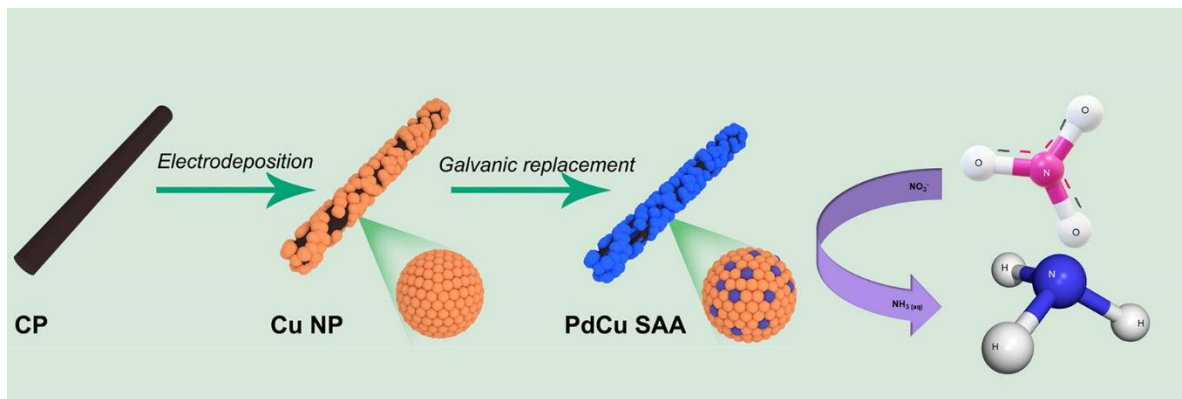


Figure 3.3. Schematic illustration of the synthesis of PdCu SAA

As seen from the scanning electron microscope (SEM) images (**Figure 3.4**), no obvious change was observed in the morphology of Cu after its galvanic replacement reaction with Na_2PdCl_4 . However, compared to the pure Cu sample, many bright atoms can be found from the PdCu SAA in the darker lattice from the aberration-corrected high-angle annular dark-field scanning transmission electron microscope (AC-HAADF-STEM) images (**Figure 3.5A-C** and **Figure 3.7**). Based on the Z-contrast difference between Cu and Pd atoms, the darker contrast belongs to the Cu lattice while the brighter contrast is the Pd atoms, as marked by the arrows (**Figure 3.5B and C**). Those AC-HAADF-STEM images directly demonstrate the atomic dispersion of Pd atoms in PdCu SAA. The scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDX) mapping further prove the co-existence of Pd and Cu elements in the PdCu SAA (**Figure 3.5E-G**). The STEM-EDX mapping image of the Pd signal looks relatively weak, due to its extremely low content of 0.1wt%, as determined by the inductively coupled plasma mass spectrometry (ICP-MS) analysis. EDX cannot be used to quantify the amount of single atoms (**Figure 3.7**).

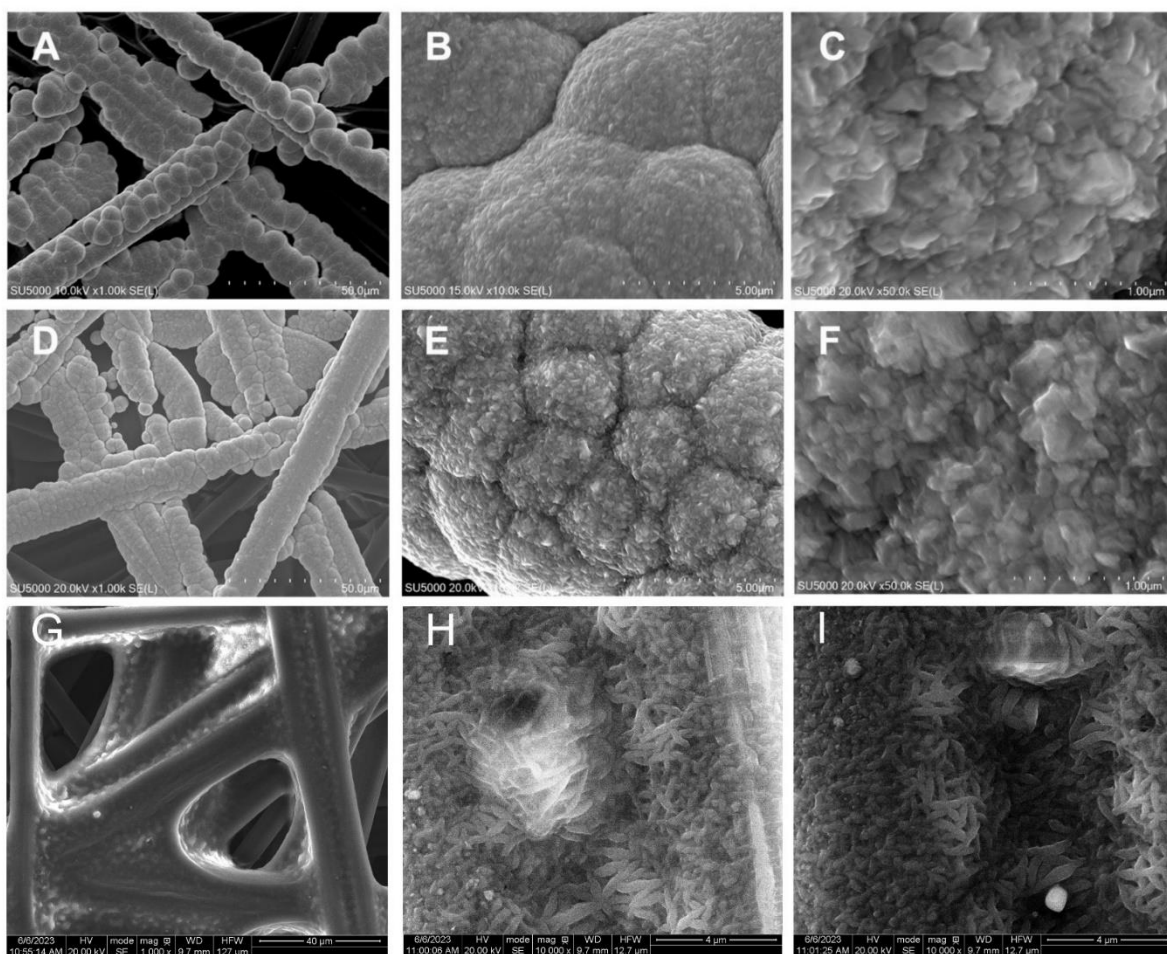


Figure 3.4. SEM images for blank carbon paper and all catalysts samples. (A-C) SEM image of Cu on carbon paper. (D-F) PdCu SAA on carbon paper. (G-I) Blank carbon paper.

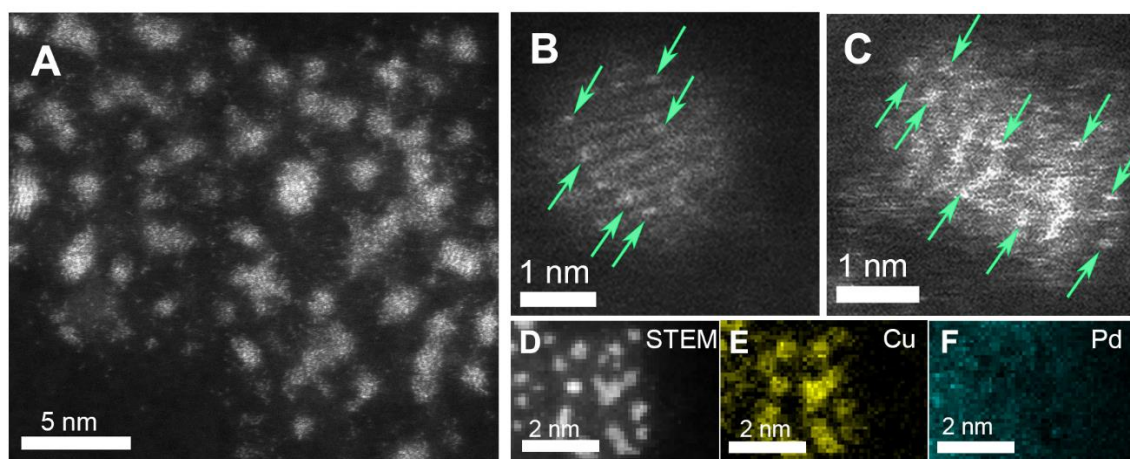


Figure 3.5. STEM characterization. (A) AC-HAADF-STEM image of PdCu SAA; (B-C) enlarged AC-HAADF-STEM images of PdCu SAA; (D) STEM image of PdCu SAA; (E-F) STEM-EDS mapping of Cu and Pd elements in PdCu SAA.

EDX STEM can analyse the homogeneity of chemical composition of materials at low magnification. However, at the atomic scale, the complex electron scattering between the number of X rays detected and number of atoms the probe interacts with, making it impossible to directly relate x ray counts to the number or density of atoms.^[119,120]

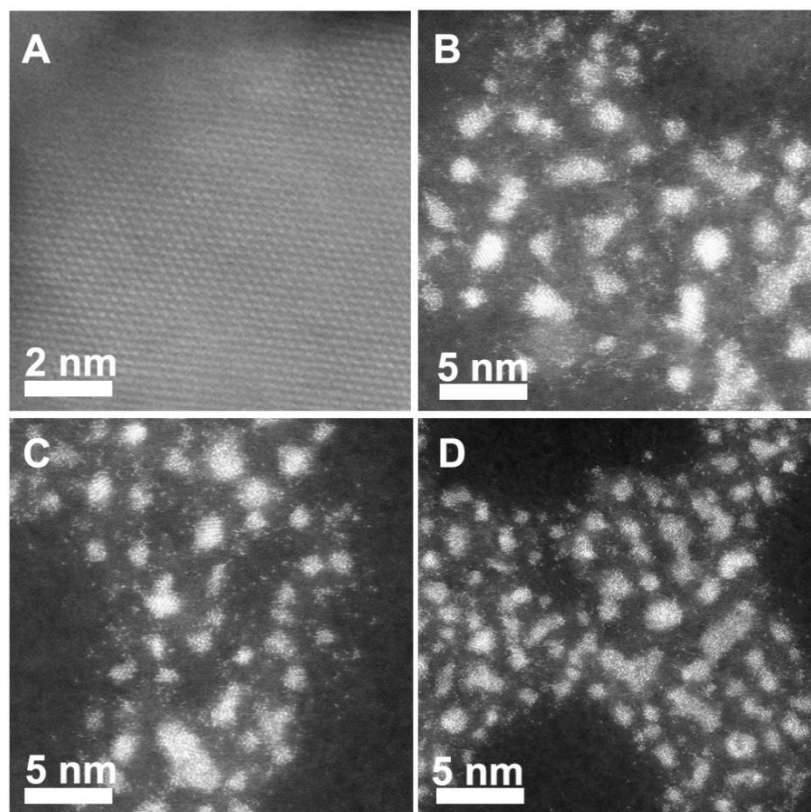


Figure 3.6. AC-HAADF-STEM images of the catalysts. (A) Cu and (B-D) PdCu SAA.

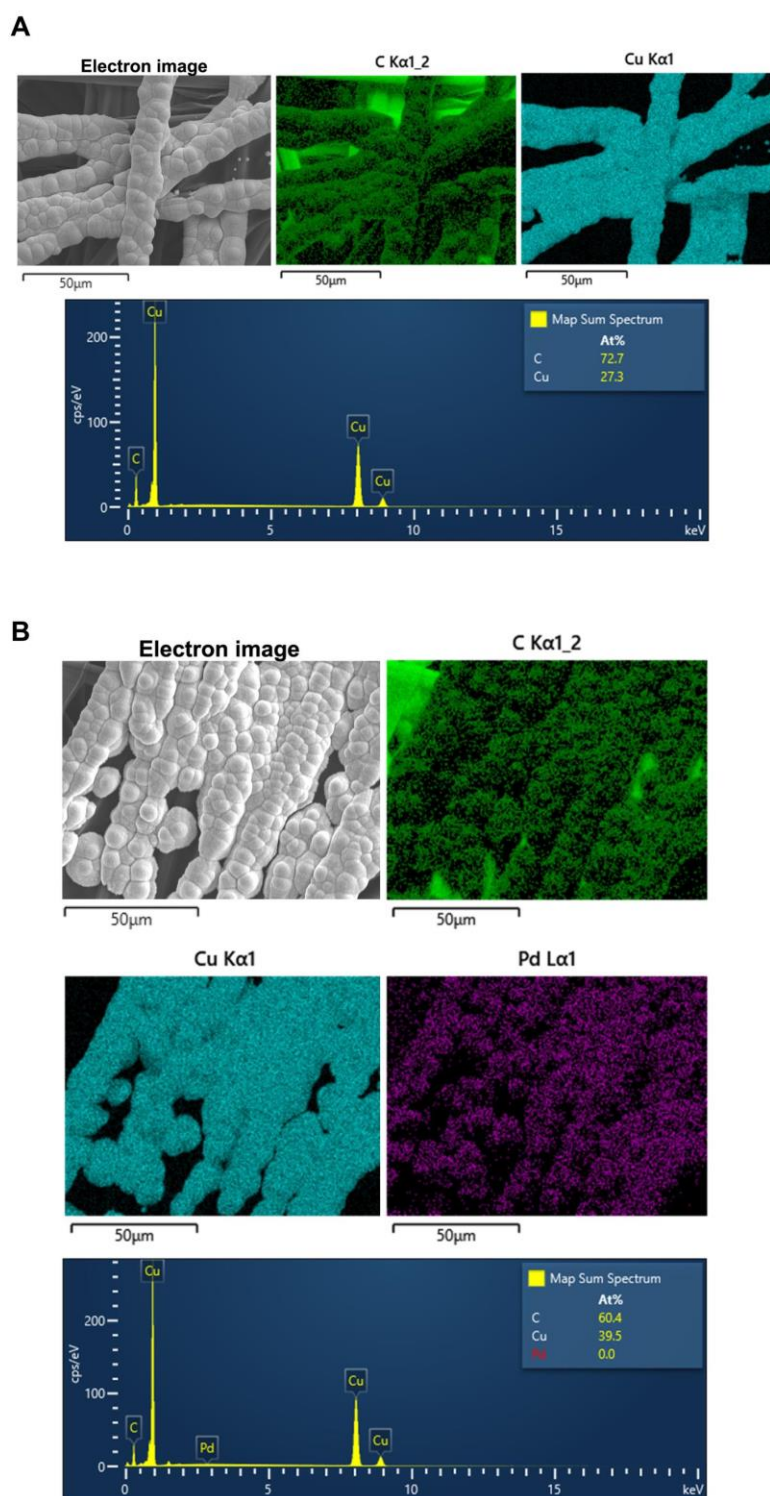


Figure 3.7. SEM-EDX maps. (a) Cu on CP. (b) PdCu SAA on CP. Please note that EDX is not good at quantity Pd single atoms.

3.3.2 Structural characterization and Bader charge analysis

To study the crystal structure, the grazing incidence X-ray diffraction (GI-XRD) test was measured for both the PdCu SAA and Cu samples. Both samples show obvious diffraction peaks of Cu (111) (200) and (220) planes (**Figure 3.8A**). No Pd peak appeared in the GI-XRD spectrum of PdCu SAA, indicating no Pd crystalline phase formed in the sample which agrees with the AC-HAADF-STEM results. Core-level X-ray absorption spectroscopy (XAS) was further used to study the local coordination structure of Pd and Cu in PdCu SAA. As shown in the Pd K-edge X-ray absorption near-edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) (**Figure 3.8B**), the white line of PdCu SAA shows a slight shift to lower energy for the adsorption edge (E_0) compared to that of Pd foil, indicating that Pd in PdCu SAA has a charge transfer with Cu support and carries a negative charge. The Bader charge analysis of PdCu SAA with Cu (100) reveals that the isolated Pd atoms carry substantially negative charges (**Figure 3.8C**), confirming the experimental observations.

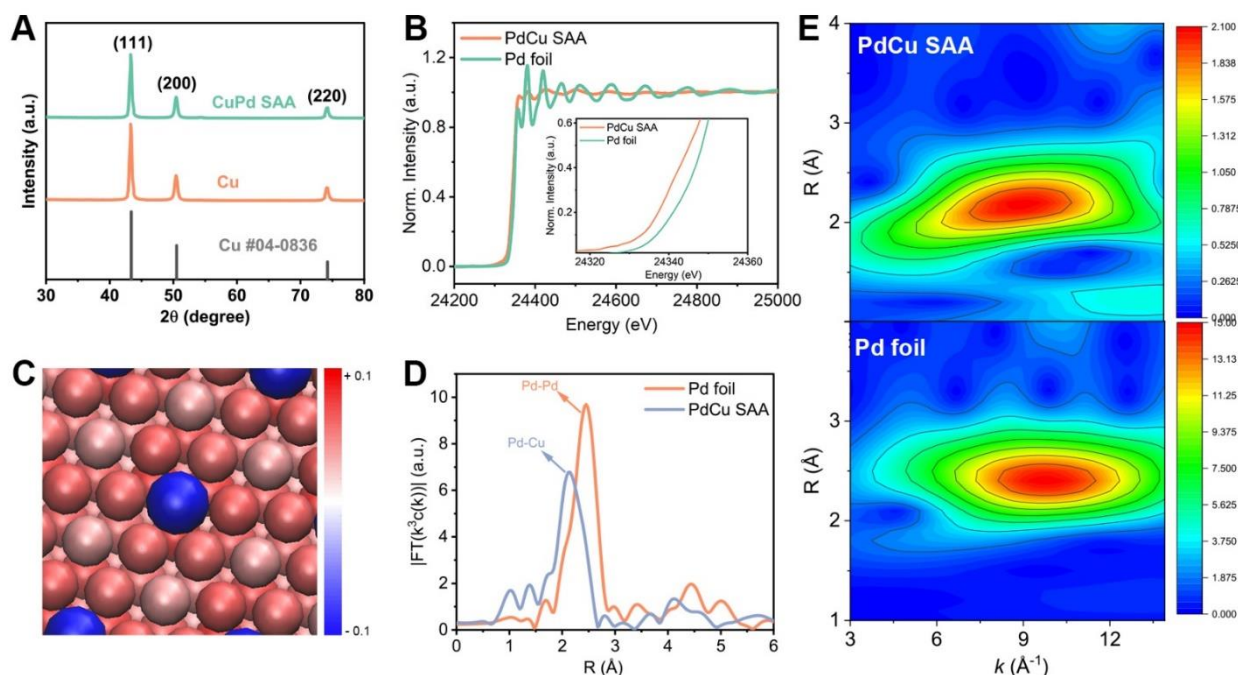


Figure 3.8. Structural characterization and Bader charge analysis. (A) GIXRD spectra of PdCu SAA and Cu; (B) Pd L-edge XANES and EXAFS of PdCu SAA and Pd foil reference, insert image is the enlarged spectra; (C) Bader charge analysis of PdCu SAA with Cu (100), red sphere represents Cu and blue sphere represents Pd atoms; (D) Pd L-edge Fourier-transform EXAFS spectra of PdCu SAA and Pd foil reference; (E) Wavelet transforms for the k^3 -weighted EXAFS signals of PdCu SAA and Pd foil reference.

Moreover, the Fourier transform (FT) of the k^3 -weighted EXAFS curve of the Pd K-edge of PdCu SAA shows only one main peak at 2.1 Å, indicating that the Pd atoms possess only one coordination (Pd-Cu), which is different from the Pd-Pd coordination in Pd foil at 2.4 Å (**Figure 3.8D**, **Figure 3.9** and **Table 3.1**). These results indicate that the Pd exists in PdCu SAA in single-atom form with Pd-Cu local coordination.^[121,122] In addition, high-resolution wavelet-transform EXAFS (WT-EXAFS) in k and R spaces were also presented to reveal the dispersion state of Pd atoms in PdCu SAA and Pd foil (**Figure 3.8E**). The WT-EXAFS oscillations show the main peak at about 8.9 Å⁻¹ which can be attributed to the Pd-Cu coordination for PdCu SAA, while the main peak at around 9.8 Å⁻¹ belongs to the Pd-Pd coordination in Pd foil. Combined with the EXAFS analysis and AC-HAADF-STEM images, the single-atom dispersion of Pd atoms in the PdCu SAA could be synergistically confirmed.

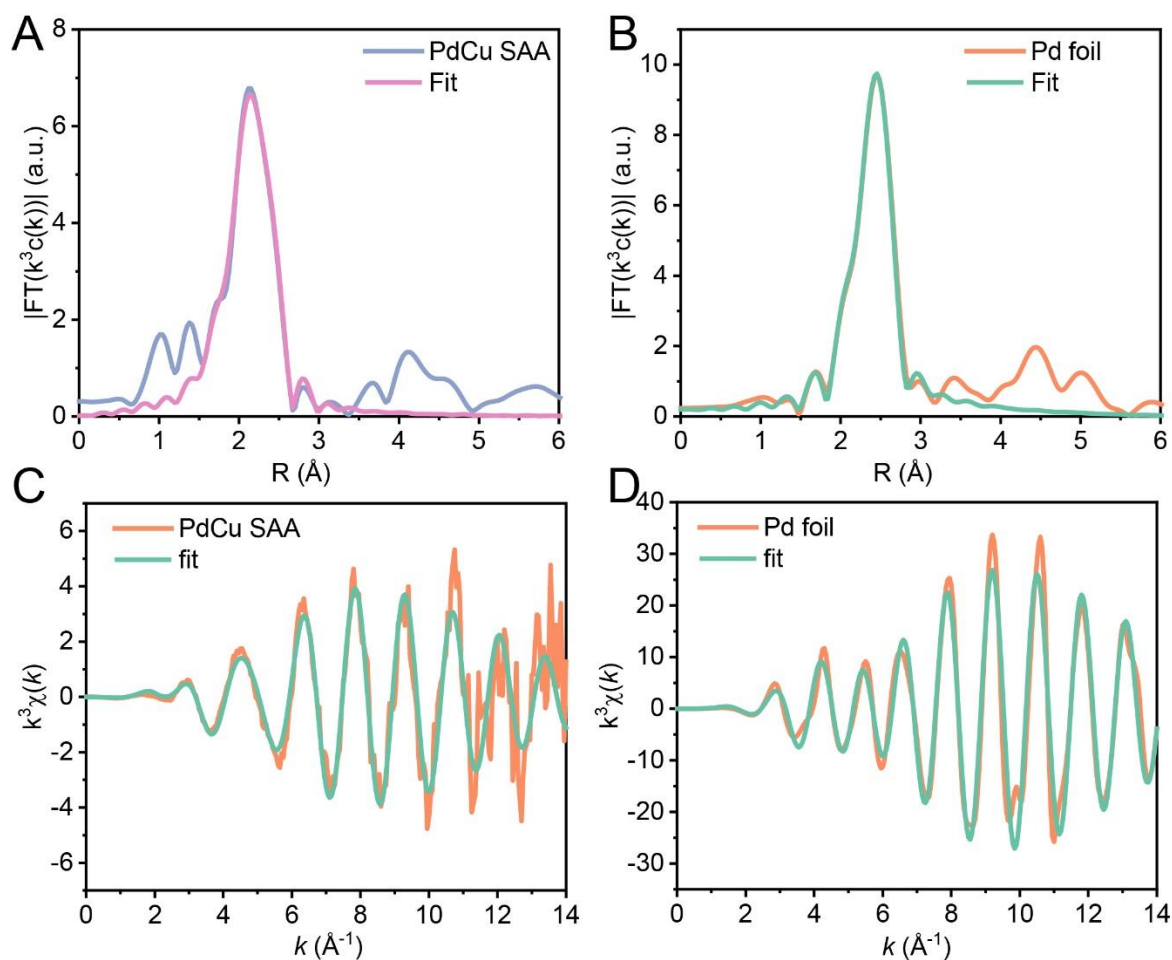


Figure 3.9. EXAFS fitting results of Pd L-edge in PdCu SAA and Pd foil. (A-B) Fourier-transformed (FT) Pd L-edge EXAFS spectra in R space and corresponding FT-EXAFS fitted curves of PdCu SAA (A) and Pd foil reference (B); (C-D) Pd L-edge EXAFS spectra in k space and corresponding FT-EXAFS fitted curves of PdCu SAA (C) and Pd foil reference (D).

Table 3.1. Fitted EXAFS parameters at the Pd K-edge for PdCu SAA based on Cu nanoparticles and Pd foil

	Shell	CN	R (Å)	$\delta^2 (10^{-3})$	ΔE	R factor
Pd foil	Pd-Pd	12	2.74 ± 0.03	6.1 ± 0.3	7.0 ± 0.3	0.003
PdCu SAA	Pd-Cu	10.5 ± 1.1	2.65 ± 0.05	9.2 ± 0.7	8.3 ± 1.7	0.01

CN: coordination numbers of identical atoms; R : interatomic distance; δ^2 : Debye-Waller factors; ΔE : energy shift. R factor: goodness of fit.

3.3.3 Electrocatalytic nitrate reduction

To evaluate the electrocatalytic NO_3^- RR performance of the PdCu SAA, linear sweep voltammetry (LSV) was firstly measured in an H-cell with 0.5 M Na_2SO_4 as the neutral electrolyte (**Methods**). The current density of PdCu SAA greatly increased after the addition of 600 ppm NO_3^- , indicating its high activity toward NO_3^- RR (**Figure 3.10**).

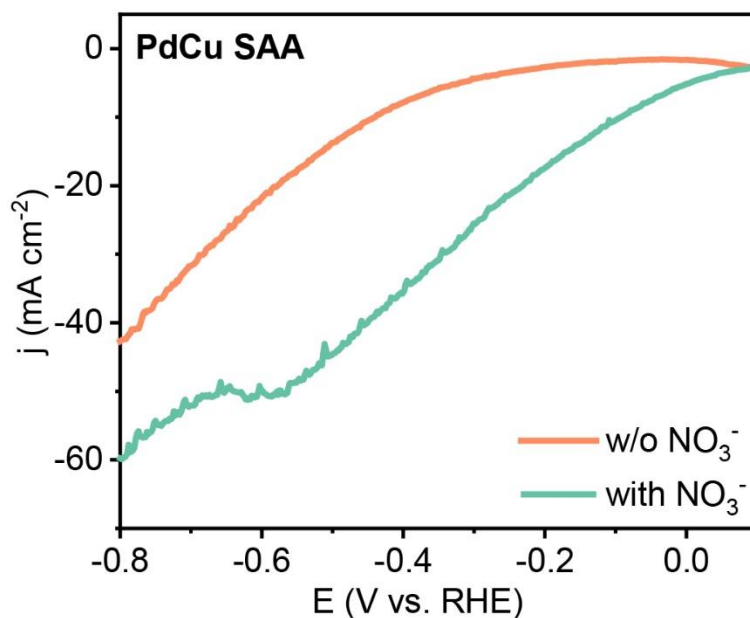


Figure 3.10. LSV measurement. LSV curves of PdCu SAA in 0.5M Na_2SO_4 with or without 600 ppm NO_3^- electrolyte, scan rate: 10 mV s^{-1} .

To further quantify the activity of electrocatalytic NO_3^- RR, chronoamperometry was measured for NO_3^- RR under different applied potentials and the produced ammonia was confirmed by both UV-visible (UV-

Vis) and nuclear magnetic resonance spectroscopy (NMR) (**Figure 3.11**). Given the high solubility of NH_3 in water, the electrolyte after electrolysis was taken out and measured to quantify the NH_3 production.

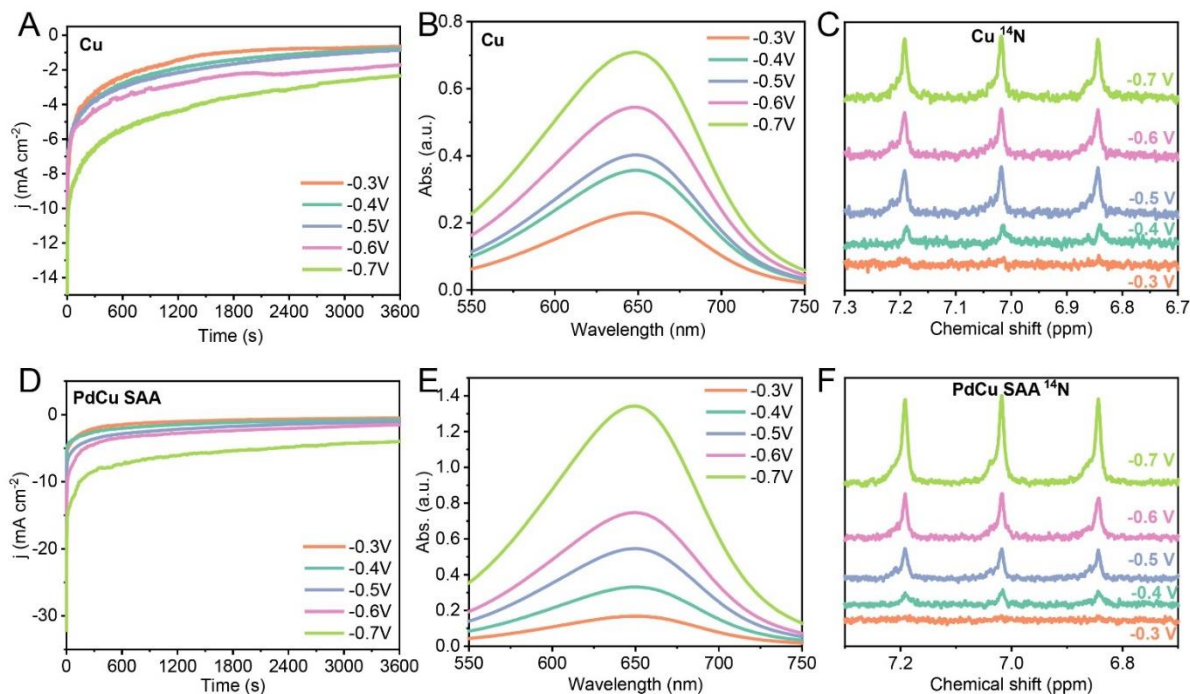


Figure 3.11. Electrochemical, UV and NMR data of the NO_3^- reduction data of Cu and PdCu SAA catalysts. (A-C) I-t curves (A), UV spectra (B), and NMR spectra (C) from Cu catalyst; (D-F) I-t curves (D), UV spectra (E), and NMR spectra (F) from PdCu SAA catalyst, all the electrolytes were diluted 5 times before UV test.

Indophenol blue colorimetry was first adopted to quantify the NH_3 concentration in the electrolyte with the assistance of UV-Vis spectroscopy (**Figure 3.1 A-B**). The yields of both PdCu SAA and Cu increased with the increase of applied negative potentials (**Figure 3.12A**) while the FE reached a maximum at -0.6V (**Figure 3.12B**). Specifically, the PdCu SAA exhibits the highest FE of 97.1% with a yield of $15.4 \mu\text{mol cm}^{-2} \text{h}^{-1}$ under -0.6V, which is much better than that of Cu (FE of 81.2% with a yield of $11.0 \mu\text{mol cm}^{-2} \text{h}^{-1}$) (**Figure 3.12B**). Specifically, the selectivity of this work not only outperforms most of the reported NO_3^- RR electrocatalysts in the neutral electrolyte (**Table 3.2**). To make cross-verification of the performance of the PdCu SAA, NMR was used to determine the NH_3 production. PdCu SAA and Cu show a similar performance-potential trend, namely, that yield increases with the increasing applied potential while FE reaches a maximum at -0.6V (**Figure 3.12C-D**, **Figure 3.11C and F**). In detail, the highest FE for PdCu SAA is 94.9% with a yield of $12.1 \mu\text{mol cm}^{-2} \text{h}^{-1}$, which is still much better than that of Cu (FE of 71.7% with a yield of $9.7 \mu\text{mol cm}^{-2} \text{h}^{-1}$) based on the NMR quantification method. Considering the possible

influence of NH_3 from the atmospheric environment and confirming the source of nitrogen in the reaction, a ^{15}N isotope experiment was also conducted with a $\text{Na}^{15}\text{NO}_3$ feed to confirm the source of NH_3 production (**Figure 3.12E-F**).

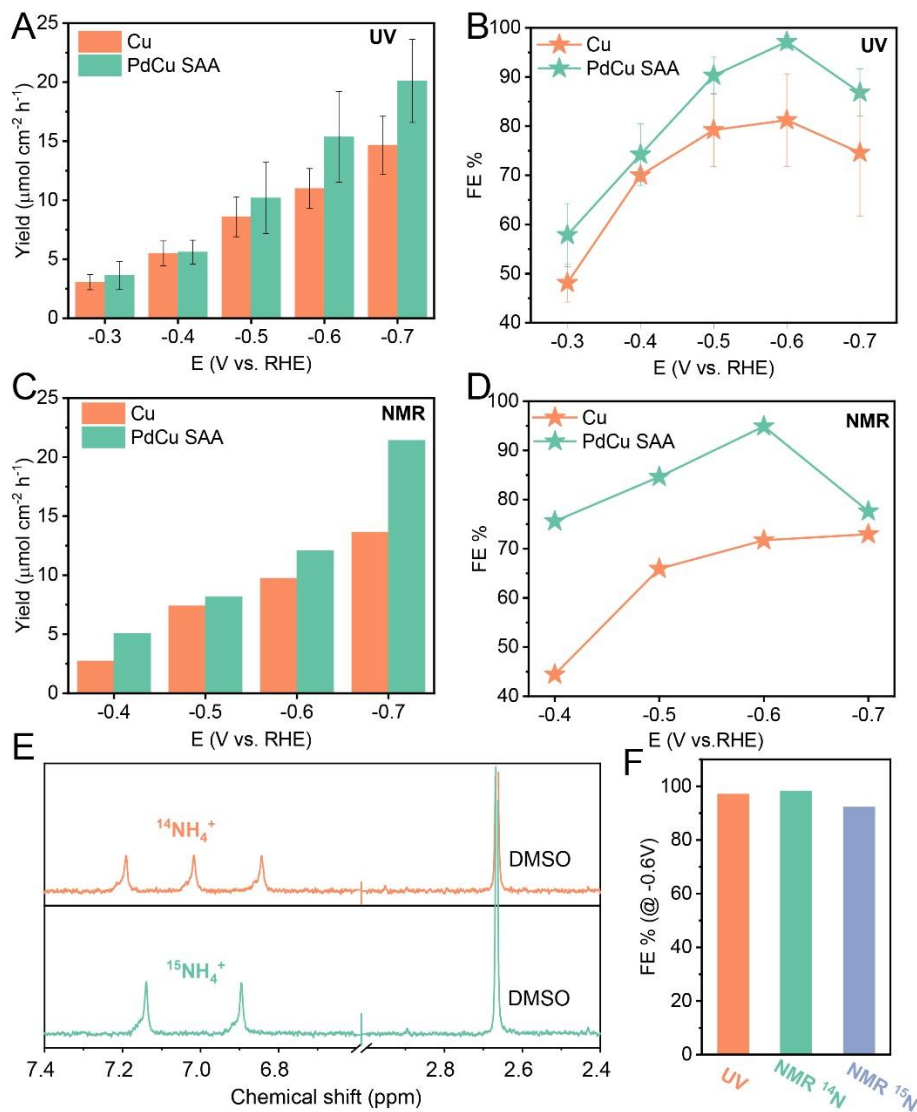


Figure 3.12. Electrocatalytic nitrate reduction performance characterizations. (A-B) Yield (A) and FE (B) results of PdCu SAA and Cu based on the UV detection method for NH_3 ; (C-D) Yield (C) and FE (D) results of PdCu SAA and Cu based on the NMR detection method for NH_3 ; (E) NMR spectra of produced NH_3 from $^{14}\text{NO}_3^-$ and $^{15}\text{NO}_3^-$ feeding; (F) Comparison of FE from different NH_3 detection methods under -0.6V over PdCu SAA.

The electrolyte after electrolysis of $\text{Na}^{15}\text{NO}_3$ shows the apparent doublet peaks in the range of 7.2 ppm to 6.8 ppm, which is due to H atoms binding to ^{15}N atoms with spin-spin coupling. In contrast, $\text{Na}^{14}\text{NO}_3$ electrolysis produces triplet peaks due to the symmetric distribution of H atoms binding with ^{14}N atoms

(Figure 3.12E). Hence, there is minimal disturbance from the atmospheric environment. Besides this qualitative evidence, it is also worth noting that the PdCu SAA shows a very similar FE value (92.3%) in $\text{Na}^{15}\text{NO}_3$ electrolysis compared to that of $\text{Na}^{14}\text{NO}_3$ electrolysis (97.1%) (Figure 3.12F). The PdCu SAA also shows good stability, maintaining a FE above 95% during a 10 h test (Figure 3.13). We also measured the Faradic efficiency (FE) and yield of NO_2^- (Methods, Figure 3.2). The PdCu SAA shows lower FE and yield of converting NO_3^- to NO_2^- comparing with Cu (Figure 3.14). This is consistent with the high FE of converting NO_3^- to NH_3 using PdCu SAA (Figure 3.12).

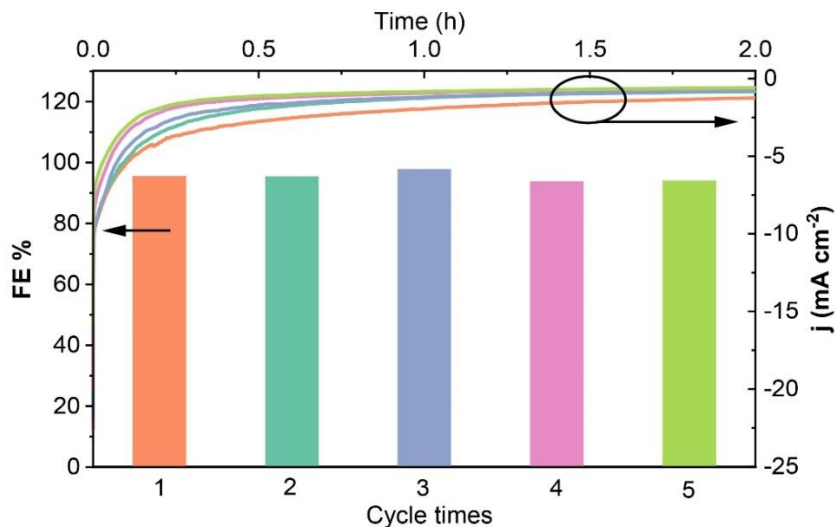


Figure 3.13. I-t curves and NH_3 FE results of 10 h stability test of PdCu SAA catalyst. The electrolyte was changed after each cycle test to 2h for each cycle and 5 cycles in total.

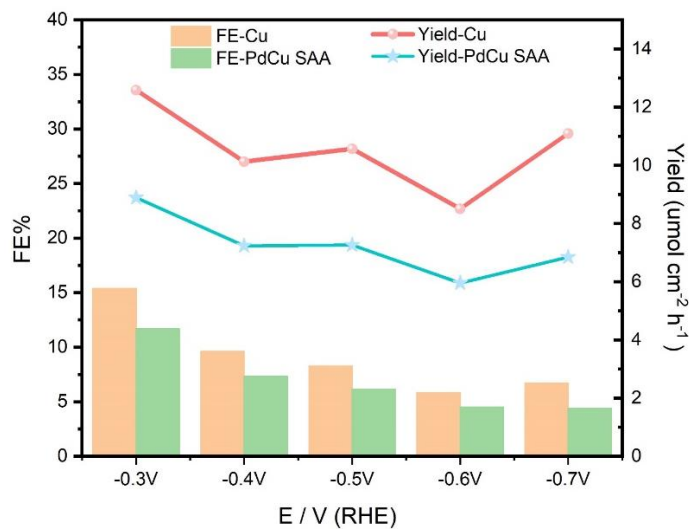


Figure 3.14. The Faradic efficiency and yield of NO_2^- products in PdCu SAA and Cu. The PdCu SAA shows lower FE and yield of converting NO_3^- to NO_2^- comparing with Cu.

Table 3.2 Comparison with recently reported catalysts under neutral media.

Catalysts materials	Electrolyte	FE of NH ₃	Reference
PdCu SAA	0.5 M Na₂SO₄	97.1%±1.2%	This work
Pd/TiO ₂	1 M LiCl	92%	Energy Environ. Sci., 2021 , 14, 3938–3944
Co-Fe@Fe ₂ O ₃	0.1 M Na ₂ SO ₄	85.2 ± 0.6%	PNAS 2022 Vol. 119 No. 6 e2115504119
polycrystalline copper	0.5 M Na ₂ SO ₄	94%	Nano Energy 97 (2022) 107124
Cu ⁰ /GDYNA	0.5 M Na ₂ SO ₄	81%	Nano Today 43 (2022) 101431
NbO _x	0.5 M K ₂ SO ₄	95%	Green Chem., 2022 , 24,1090–1095
RuNi-MOFs	0.1 M Na ₂ SO ₄	73%	J. Mater. Chem. A, 2022 ,10, 3963-3969
Co ₂ AlO ₄ /CC	0.1 M PBS	93%	Chem. Eng. J., 2022 , 435: 135104.
Fe/Ni ₂ P	0.2 M K ₂ SO ₄	94%	Adv. Energy Mater., 2022 , 12(13): 2103872.
Pd-NDs/Zr-MOF	0.1 M Na ₂ SO ₄	58%	Nano Lett. 2022 , 22, 6, 2529–2537
Fe ₂ TiO ₅ Nanofibers	PBS solution	88 %	Angew. Chem.Int. Ed. 2023 , e202215782
Cu-cis-N ₂ O ₂ SAC	0.5 M Na ₂ SO ₄	88%	Adv.Mater. 2022 , 34, 2205767
SN Co-Li ⁺ /PCNF	0.5 M Na ₂ SO ₄	73%	Adv. Energy Mater. 2022 , 12, 2202247
Cu/Cu ₂ O NWAs	0.5 M Na ₂ SO ₄	81%	Angew. Chem. 2020 , 132, 5388 –5392
CuFe	0.1 M K ₂ SO ₄	87 %	ChemSusChem, 2021 , 10.1002/cssc.202100127
CuPd aerogels	0.5 M K ₂ SO ₄	90%	Chem. Commun., 2021 , 57, 7525–7528
copper nanoplates	0.5 M K ₂ SO ₄	82%	J. Mater. Chem. A, 2021 ,9,16411–16417

What should be noted is that only neutral media system are compared here, since alkaline electrolyte can well suppress the competitive HER and resulting high selectivity of NO₃[−] reduction. But the alkaline electrolyte may cause severe equipment corrosion and largely increase the total cost. So, we investigated the neutral system and only compared to those reports in neutral system.

In order to investigate the effect of the amount of Pd loading, we synthesized PdCu alloy NP and Pd NP on Cu through increasing the Pd content (**Methods**). XRD patterns show the formation of Pd-Pd and Pd-Cu bond was observed with the increasing of Pd loading (**Figure 3.15**).

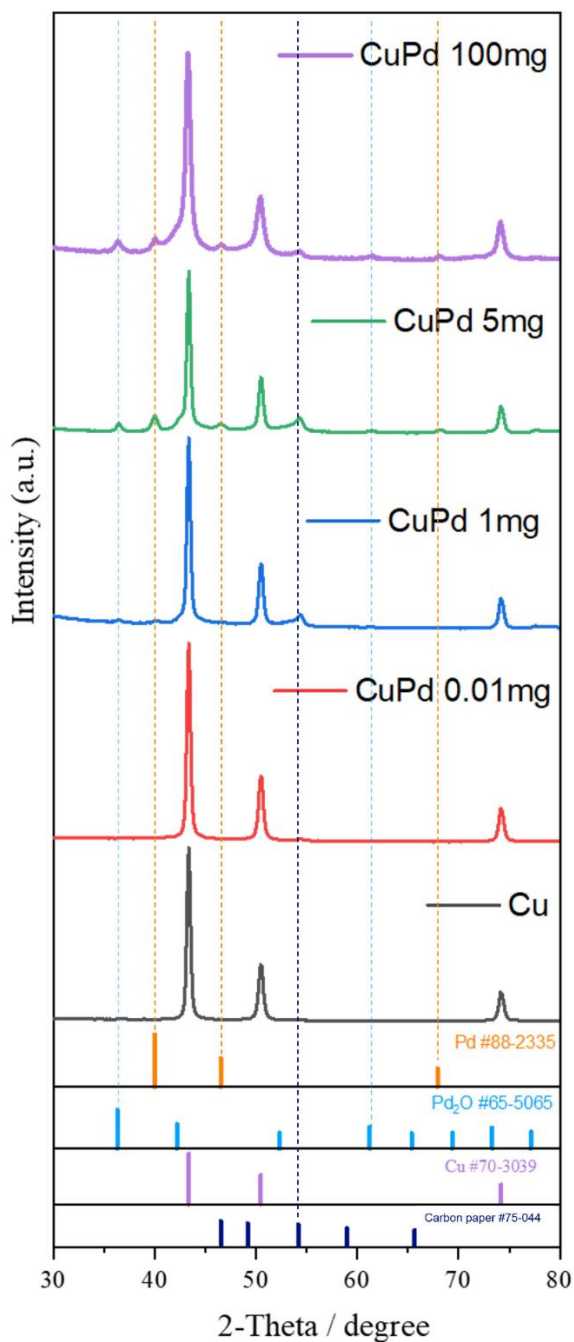


Figure 3.15. GIXRD patterns for increasing the Pd loading amount.

Although the NH_3 yield increased after the increase of Pd content in the PdCu materials, the FE apparently decreased (**Figure 3.16**). These results indicate that the highly atomic dispersion of Pd in the Cu nanoparticles is necessary for the high NH_3 selectivity. What should be noted is that the Pd is an expensive noble metal, which the high content of Pd may increase the total cost of catalyst. Thus, minimizing the usage of Pd is necessary.

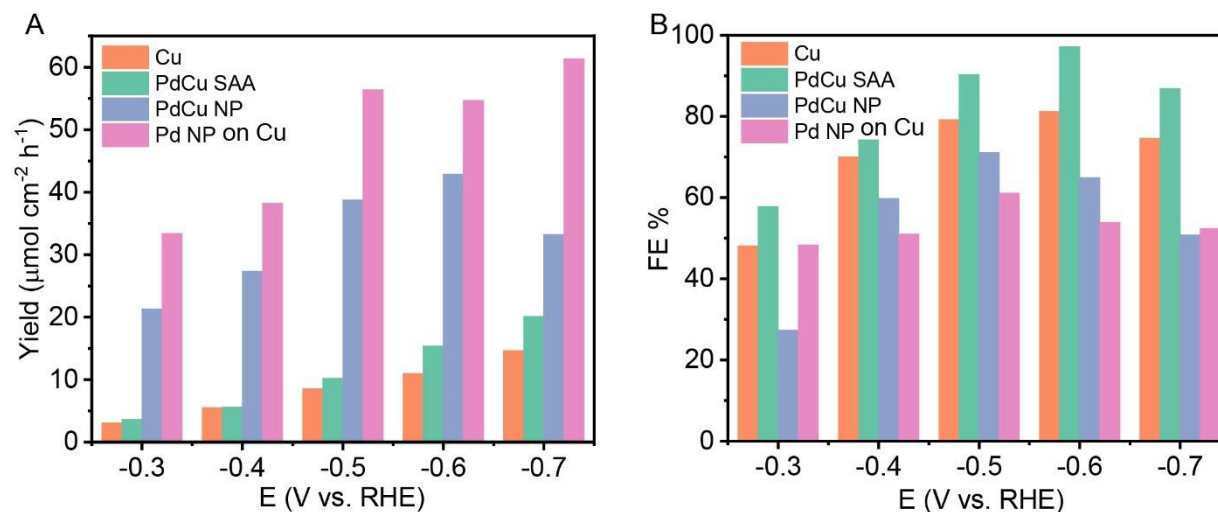


Figure 3.16. Effect of increasing amount of Pd loading on Cu. (A) Yield and (B) FE results of PdCu-based catalysts on the UV detection method for NH_3 . Although the NH_3 yield increased after the increase of Pd content in the PdCu materials, the FE apparently decreased.

In order to investigate the electronic state changes, we performed *ex-situ* X-ray photoemission spectroscopy (XPS) (**Figure 3.17**) and *operando* Raman spectroscopy (**Figure 3.18**). The *ex-situ* XPS analysis indicate Cu get oxidized after the reaction (**Figure 3.17**). In order to verify that, *operando* Raman spectroscopy (**Methods, Figure 3.18**) was performed under the given potentials. Cu species showed no signal in Raman spectroscopy. With the increase of the applied voltage, characteristic peaks of CuO, Cu_2O and PdO gradually appeared (**Figure 3.18**). The following characteristic peaks were observed for the PdCu SAA samples: (1) CuO at 298 cm^{-1} and 629 cm^{-1} , (2) Cu_2O stretching at 436 cm^{-1} (3) PdO at 725 cm^{-1} and 929 cm^{-1} .^[123-128] This indicates both the oxidation state of Cu and Pd increases during the reaction. This may due to the producing of OH^* radical from H_2O .^[129]

We also measured the electrochemical surface area (ECSA) of Cu and PdCu SAA based on the electrochemical double-layer capacitance. As presented (**Figure 3.19**), the ECSA of Cu and PdCu SAA are 1.7 cm^2 and 11.7 cm^2 , respectively. The yields based on ECSA of Cu are much larger than that of PdCu SAA under various potentials. It's reasonable to suppose that the increase of ECSA improves the

yield. The focus of this work is the selectivity, and the promoting effect of ECSA on the yield doesn't affect the conclusion that the PdCu SAA active site structure benefits the high selectivity of NH_3 product.

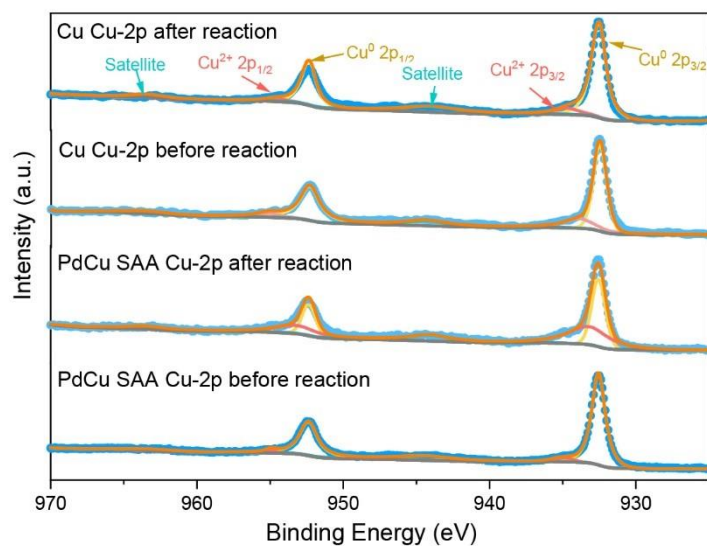


Figure 3.17. *Ex situ* XPS analysis.

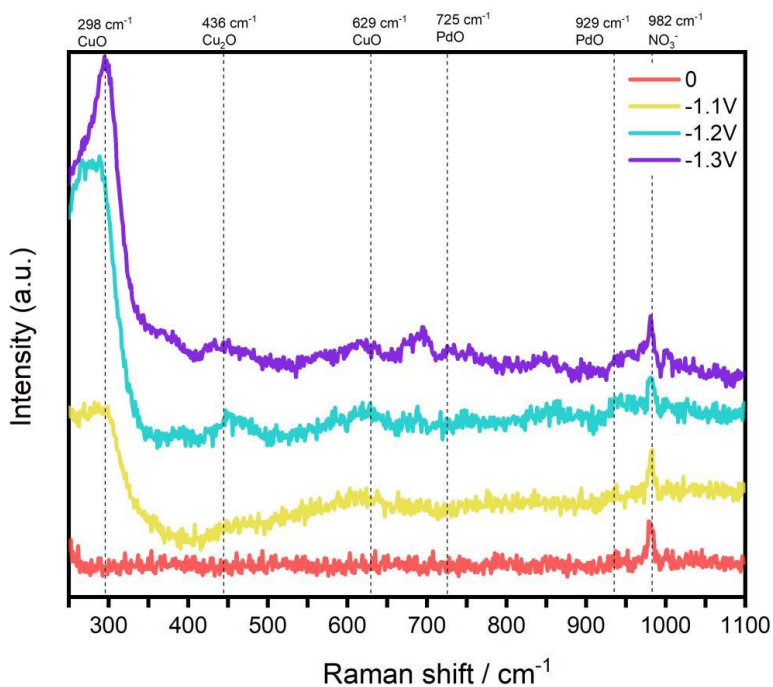


Figure 3.18. *Operando* Raman Spectroscopy during the electrocatalytic NO_3^- reduction reaction.

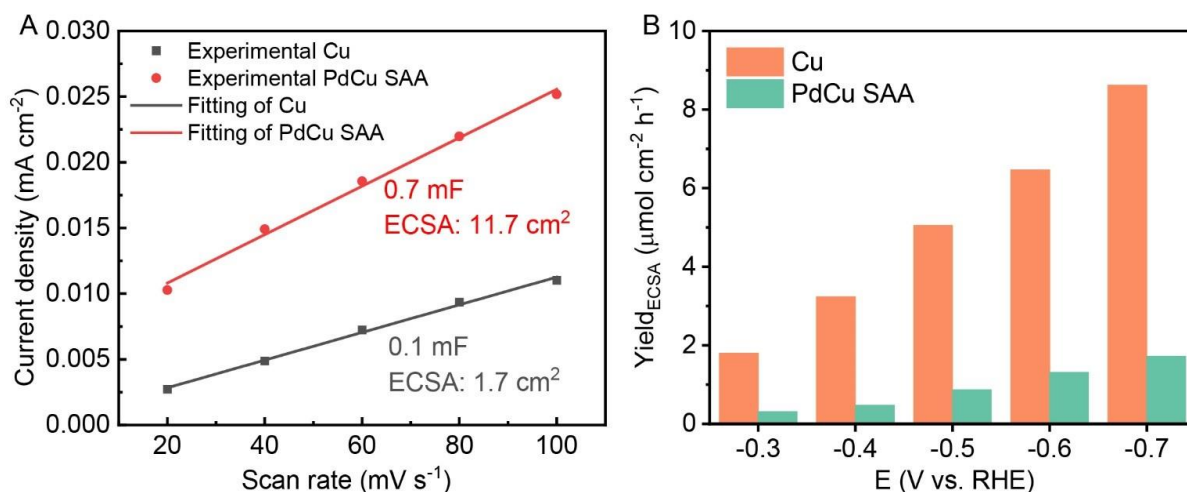


Figure 3.19. ECSA and yield measurement. (a) ECSA measurement of Cu and PdCu SAA. (b) the yield normalized by the ECSA.

3.3.4 Single crystal electrocatalytic performance and DFT calculations

The materials characterization and electrochemical results above demonstrate the advantages of PdCu SAA with Pd single atoms in improving the NO₃⁻RR performance. To explore the active sites of the reaction and whether it has a facet-dependent behavior, single-crystal experiments were carried out. The GIXRD spectrum of PdCu SAA (**Figure 3.8A**) shows the polycrystalline nature, including Cu (100), (110), and (111) Bragg reflections. To confirm the most active facet with the Pd single-atom, the Pd single-atom was doped on single-crystal Cu with different crystal facets, namely Cu (100), Cu (110), and Cu (111). XRD results show that the Pd doping does not produce a new crystal peak, indicating that no Pd crystals were formed (**Figure 3.20A** and **Figure 3.21A**). EXAFS results further demonstrate the single-atom dispersion of Pd atoms in the single-crystal Cu (**Figure 3.20B** and **Figure 3.21 B-I**). The white line of all PdCu single crystal samples shows a shift to lower energy for the adsorption edge (E_0) compared to that of Pd foil (**Figure 3.21 B and C**), suggesting electron transfer from Cu to Pd due to the formation of Pd-Cu bond, which agrees well with the results of Bader charge analysis in **Figure 2C**. It is worth noting that the smallest shift of PdCu (100) shifts among all PdCu single crystal samples means the lowest negative charge of Pd in PdCu (100) (**Figure 3.21 C**), indicating the Pd atoms on the Cu(100) surface will not strongly adsorb *H and hinder the following hydrogenation step on neighboring Cu sites. The detailed fitting results are shown in **Table 3.3**. The PdCu (100) SAA single crystal exhibits the highest NH₃ production FE of 99%, which is much higher than that of PdCu (110) SAA and PdCu (111) SAA (**Figure 3.20C** and **3.22 A-B**). Those results indicate that Cu (100) should be the most active crystal facet for Pd single-atom support for the NO₃⁻RR reaction. Then, DFT calculations were conducted to investigate the reaction mechanism based on the PdCu (100) model (**Figure 3.23**). In the reaction pathway (**Figure**

3.20D), NO_3^- was adsorbed on the single-atom Pd site and formed $^*\text{NO}_3$ with an energy decrease. The N-O bond in $^*\text{NO}_3$ was then cleaved to produce $^*\text{NOO}$. Next, two H atoms bound with O to form $^*\text{NOOH}$ and $^*\text{NOHOH}$ successively. With two further hydrogenation steps, the $^*\text{NOHOH}$ was transformed into $^*\text{NHOH}$. After losing one H_2O molecule, the active $^*\text{N}$ was formed. Subsequently, the $^*\text{NH}_3$ was formed through a series of hydrogenation steps from $^*\text{N}$ and then finally desorbed from the catalyst. Notably, the rate-determined step (RDS) for Cu (100) is the hydrogenation of $^*\text{NOO}$ with an energy barrier of 0.39 eV, while the RDS for PdCu (100) is the formation of $^*\text{NHOH}$ with an energy barrier of only 0.10 eV. As a result, the reaction was facilitated over PdCu (100), which is consistent with the experimental observation.

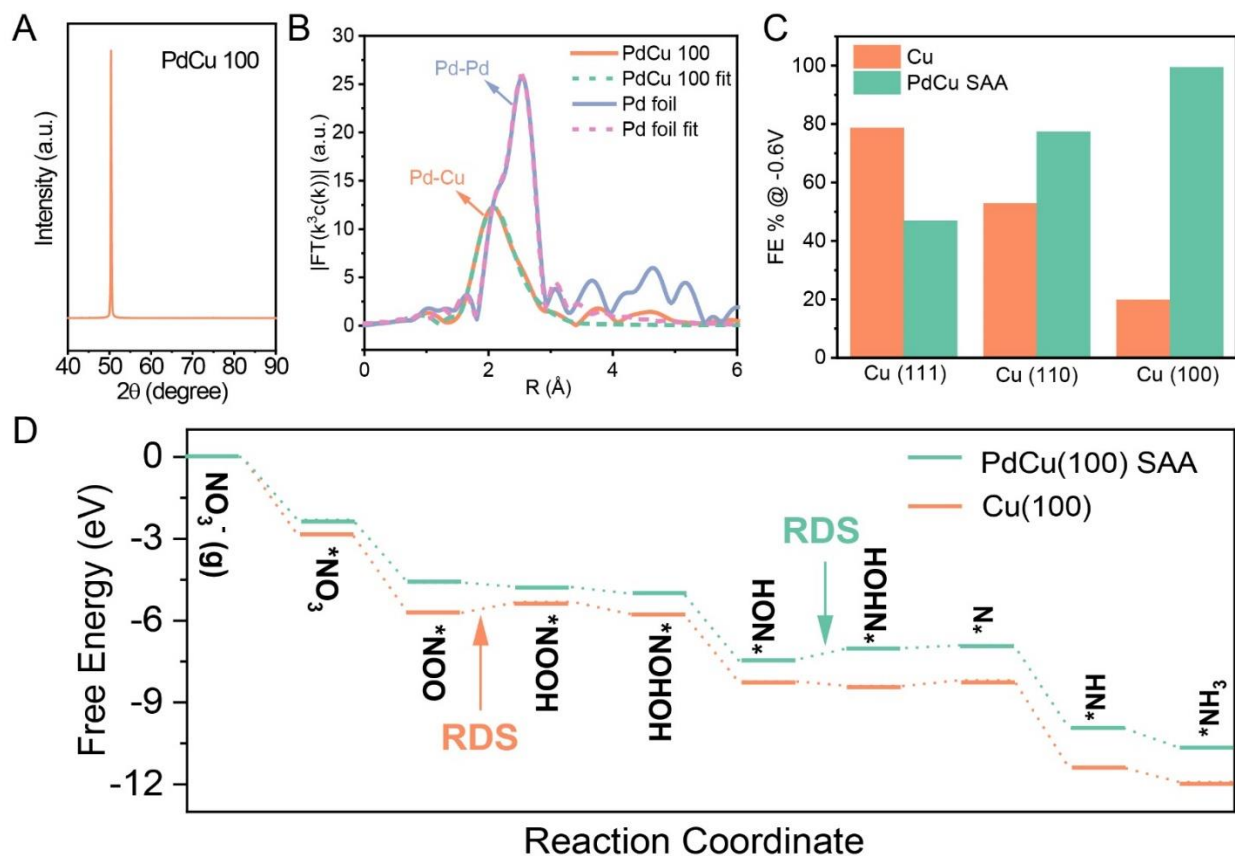


Figure 3.20. Single crystal electrocatalytic performance and DFT calculations. (A) GIXRD spectra of PdCu SAA based on single-crystal Cu 100; (B) Pd K-edge Fourier-transform EXAFS spectra of single-crystal based PdCu SAA based on single-crystal Cu 100 and Pd foil reference; (C) NH_3 FE results of single-crystal Cu and relative PdCu SAA; (D) Gibbs free energy diagram and reaction pathway of various intermediates generated during electrocatalytic NO_3^- RR over Cu (100) and PdCu(100) SAA.

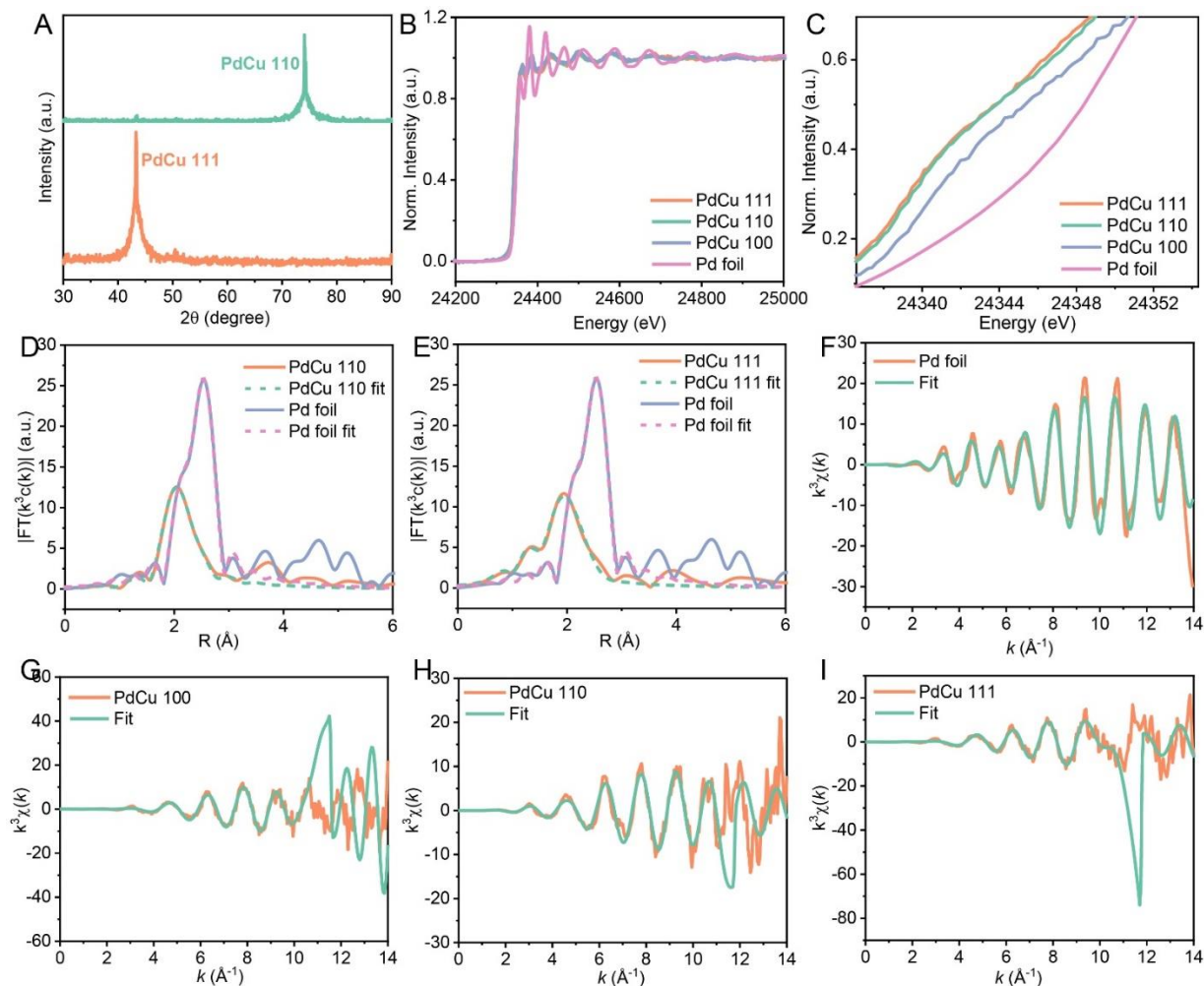


Figure 3.21. Characterization of PdCu SAA based on Cu single crystals. (A) GIXRD spectra of PdCu SAA based on single-crystal Cu (110) and Cu (111); (B) Pd L-edge XANES of PdCu SAA based on Cu single crystals and Pd foil reference; (C) Enlarged spectra from figure B; (D) Pd L-edge Fourier-transform EXAFS spectra of single-crystal based PdCu SAA based on single-crystal Cu (110) and Pd foil reference; (E) Pd L-edge Fourier-transform EXAFS spectra of single-crystal based PdCu SAA based on single-crystal Cu (111) and Pd foil reference; (F-I) Pd L-edge EXAFS spectra in k space and corresponding FT-EXAFS fitted curves of Pd foil reference (F) and PdCu SAA based on single-crystal Cu (100) (G), Cu (110) (H) and Cu (111) (I).

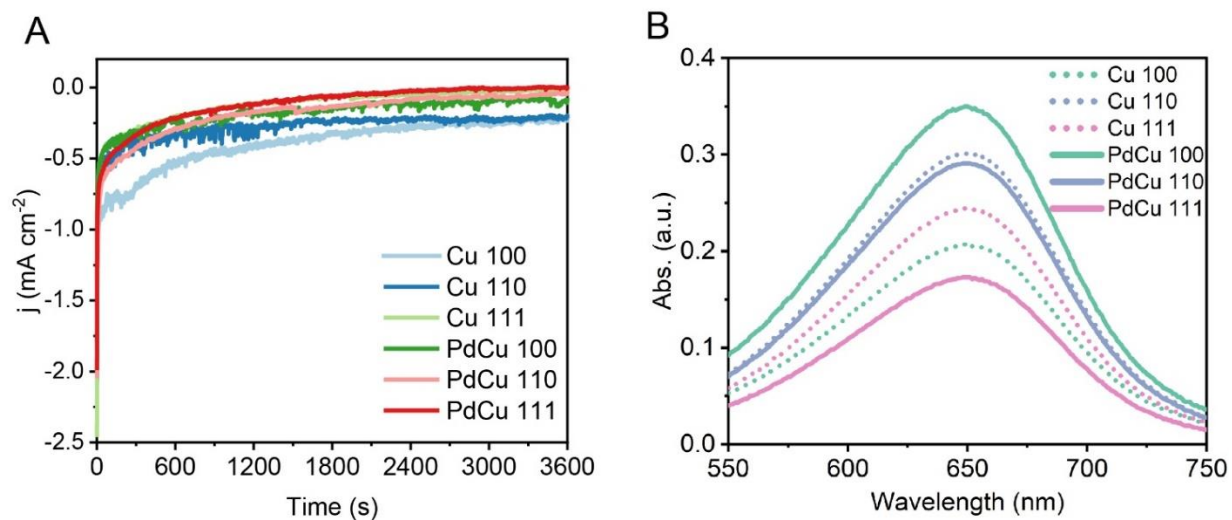


Figure 3.22. Electrochemical and UV data of the single-crystal samples. (A) I-t curves of Cu single-crystal and corresponding PdCu SAA samples under -0.6 V; (B) Corresponding UV curves of the I-t tests.

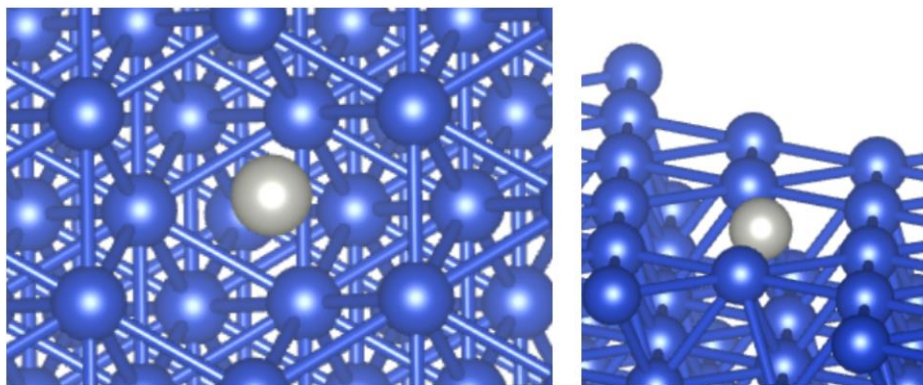


Figure 3.23. DFT model of PdCu (100)

Table 3.3. Fitted EXAFS parameters at the Pd K-edge for PdCu SAA based on Cu single crystals

	Shell	CN	R (Å)	$\delta^2(10^{-3})$	ΔE	R factor
PdCu 100	Pd-Cu	8.8 ± 0.8	2.54 ± 0.1	4.5 ± 0.4	9.7 ± 0.6	0.02
PdCu 110	Pd-Cu	8.4 ± 0.7	2.53 ± 0.1	3.6 ± 0.8	9.2 ± 0.8	0.01
PdCu 111	Pd-Cu	8.1 ± 1.0	2.49 ± 0.2	6.5 ± 0.7	9.3 ± 0.5	0.02

CN: coordination numbers of identical atoms; *R*: interatomic distance; δ^2 : Debye-Waller factors; ΔE : energy shift. *R* factor: goodness of fit.

3.4. Conclusion

In conclusion, a novel PdCu SAA was fabricated based on a facile galvanic replacement reaction and exhibited an ultrahigh FE of 97.1% with a yield of $15.4 \mu\text{mol cm}^{-2} \text{ h}^{-1}$ toward NH_3 production in the NO_3^- RR under mild neutral media. Single crystal experiments and DFT calculations reveal that the atomic Pd sites on Cu (100) facets are the most likely active sites. The Pd sites exhibit a facet-dependent behavior. Typically, with the introduction of single-atom Pd, the RDS on Cu changed from $^*\text{NOO} \rightarrow ^*\text{NOOH}$ with an energy barrier of 0.39 eV to $^*\text{NOH} \rightarrow ^*\text{NHOH}$ with an energy barrier of 0.10 eV on PdCu SAA. This work not only develops an effective catalyst for NH_3 production from nitrate reduction in mild neutral media but also demonstrates the promising application of single-atom alloys in NO_3^- RR for nitrate nutrition recovery from wastewater and other selective electrocatalytic applications.

3.5 Acknowledgement

I want to thank Dr. Cheng Du for providing valuable suggestions during my research. I'm willing to appreciate Dr. Xiyang Wang for EXAFS fitting and Jiaao Wang for DFT calculations. I also want to thank Wei Wei, Joel Philip Mills for experiment build up and Baizhou Zhang for SEM test.

Chapter 4 Ultra-stable Ru doped IrO_x catalyst for oxygen evolution reaction paired with CO₂ reduction under large industrial current density

4.1. Introduction

In the current energy consumption structure of human beings, traditional fossil energy such as coal, oil and natural gas still occupy a dominant position, which leads to the soaring anthropogenic CO₂ emissions, and the resulting environmental crisis has seriously threatened the living environment of human beings^[130]. The resource utilization of CO₂ is one of the most ideal solutions. Currently, there are various direct or indirect utilization methods of CO₂, among which the conversion and utilization of CO₂ by means of electrocatalytic conversion has been widely concerned by researchers due to its advantages of simple equipment, controllable reaction and mild reaction conditions. However, one of the main bottlenecks in the development of electrocatalytic CO₂ reduction technology is the high cost caused by high energy consumption. As a half reaction of electrocatalytic CO₂ reduction in membrane electrode assembly (MEA), the multi-electron transfer process and slow reaction kinetics of anodized oxygen evolution reaction result in high reaction overpotential, which is one of the main sources of high total reaction energy consumption. Specifically, the poor stability of OER catalysts under large industrial current density gradually increases the whole applied voltage, lowering the energy efficiency. Therefore, an efficient OER catalyst is a prerequisite to advance the technology towards eventual industrialization. In particular, catalysts that can achieve efficient catalysis in neutral electrolyte environment can not only further reduce the reaction cost and avoid "alkalinity problem", but also be applied to hydrogen production by sea water electrolysis, which has very important research value.

Considering the catalytic performance, carbon utilization and system stability, CO₂ reduction in neutral electrolyte (KHCO₃) seems most promising for industrial applications with high carbon utilization efficiency, low hydrogen evolution reaction, and low corrosion rate. But its long-term stability under industrial current density (>200mA cm⁻²) are severely limited by the counter reaction, oxygen evolution reaction (OER). Specifically, the poor stability of OER catalysts under large industrial current density gradually increases the whole applied voltage, lowering the energy efficiency. Thus, it's of particular importance to improve the stability of OER catalyst under large industrial current density in KHCO₃ electrolyte. Currently, IrO_x catalyst is widely used as the standard OER catalyst for CO₂ reduction reaction processes^[131].

IrO₂ and RuO₂ are both rutile type noble metal oxides. The metal Ir and Ru atoms are located in the center of the octahedron with oxygen atoms as the vertices, and each octahedron is connected by oxygen

at the common vertices ^[132]. Both RuO₂ and IrO₂ exhibit excellent OER catalytic activity in acidic and alkaline electrolytes (RuO₂ is slightly higher than IrO₂) and are generally considered the benchmark for OER catalysts. ^[133,134] However, the catalytic activity of RuO₂ and IrO₂ is highly dependent on the preparation method. For example, the membrane of IrO₂ in an acidic electrolyte requires 275 mV overpotential to achieve a current density of 0.1 mA·cm⁻², but RuO₂ particles can only achieve a current density of 0.01 mA·cm⁻² at the same voltage. ^[135] The stability of these catalyst is another issue to be solved practical applications. Cherevko *et al.* ^[136] demonstrated that both RuO₂ and IrO₂ experience dissolution and activity decay at high anodic potentials, with RuO₂ exhibiting a faster dissolution rate than IrO₂. During the Oxygen Evolution Reaction (OER) process, (Ru⁴⁺)O₂ transforms into RuO₂(OH)₂ and then undergoes protonation to form highly oxidized species ((Ru⁸⁺)O₄) ^[137]. However, these highly oxidized species are unstable and easily dissolve from the electrode, leading to a decline in catalytic activity. Similarly, IrO₂ also experiences a similar phenomenon during the OER process, forming unstable high oxidation state species (Ir⁶⁺)O₃ ^[138]. Several studies have confirmed that although the activity of IrO₂ may be slightly lower than that of RuO₂, IrO₂ exhibits significantly higher stability than RuO₂. To enhance the stability of RuO₂, a doped bimetallic oxide system (Ru_xIr_{1-x}O₂) has been explored ^[139-141]. The addition of a small amount of Ir substantially improves the stability of RuO₂ without sacrificing its OER catalytic activity. Another effective approach involves the construction of a core-shell structure (IrO₂@RuO₂) to prepare highly stable catalysts. Studies have shown that this core-shell structure not only reduces the overpotential but also enhances stability, with only a 3.3% activity decay after 1000 cycles of cyclic voltammetry testing ^[142]. However, the stability of IrO_x in KHCO₃ electrolyte has rarely been studied, especially under large industrial current density (>100 mA/cm²).

The anodic oxygen evolution reaction of carbon dioxide reduction in a neutral electrolyte environment with large industrial current density is yet to come. To address this challenge, we demonstrate a simple chemical method in this study, where Ru³⁺ ions are introduced as single-atom active sites into IrO_x-based catalysts to modulate their activity and stability. This chapter focuses on a series of investigations concerning the preparation, characterization, and performance testing of Ru/IrO_x catalysts to explore the relationship between changes in IrO_x electronic structure, the surface reconstruction and their performance after Ru doping. The Ru doped IrO_x catalyst (Ru/IrO_x), supported on a Ti mesh surface, exhibits excellent OER activity and long-term stability (>480 hours) in a neutral electrolyte of 0.5 M KHCO₃ at pH= 7.3, even at high current densities of 200, 500, and 1000 mA·cm⁻².

4.2. Method

4.2.1 Chemicals

Titanium Fiber Felt (Ti mesh) approximately 53-56% was purchased from Fuel cell store. Acetone, hydrochloric acid, oxalic acid dihydrate iridium (III) chloride hydrate, potassium carbonate, ruthenium (III) chloride hydrate, Iridium(IV) oxide, Ruthenium(IV) oxide, ethylene glycol, potassium bicarbonate, potassium hydroxide were purchased from Sigma with ACS grade. Gas Diffusion Layers Sigracet 39BB and Anion Exchange Membrane Sustainion® X37-50 Grade RT were purchased from Dioxide materials. Argon LaserStar 5.0 (99.9995%) and Carbon dioxide LaserStar 5.0 (99.999%) were from Praxair and Linde. Deionized water was used in the experiments. All reagents were used without further purification.

4.2.2 Fabrication of IrO_x/Ti electrodes by anodic electrodeposition

Before the electrodeposition process, Titanium Fiber Felt was firstly cut into 1 cm * 2 cm or 3 cm * 3 cm size and then fully washed with acetone, dilute HCl solution, and water, respectively. The IrO_x electrodeposition solution adopted the recipe reported by Zhang *et.al.* ^[143]: Oxalic acid dihydrate (1 mmol) was combined with 30 ml of water containing 0.2 mmol of IrCl₃. The mixture was stirred for 10 minutes, and then K₂CO₃ (5 mmol) was added to raise the pH to 10-10.5. Next, the solution was diluted to a total volume of 50 ml, resulting in a final concentration of iridium ions of 4 mmol L⁻¹. This solution was maintained at a temperature of 40°C for approximately 5 days or longer to achieve stabilization. Subsequently, it was stored as a stock solution at a temperature of 4°C. The electrodeposition was conducted using a three-electrode system, in which the Ti Fiber Felt served as the working electrode with a 1*1 cm² or 3*3 cm² working area. The reference electrode and counter electrodes were an Ag/AgCl electrode and a platinum wire, respectively. The electrochemical technique used for electrodeposition was the potentiometry method. The potentiometry electrodeposition was conducted in 25 mL electrodeposition solution with the Ti Fiber Felt as substrate under the potential of 0.0016A (vs. Ag/AgCl) for 15, 30, 60, 120 min, respectively. Finally, the samples were heat-treated in tube furnace for 1 h at 500°C under air.

4.2.3 Synthesis of Ru/IrO_x OER catalyst

Ru/IrO_x was synthesized by the galvanic replacement reaction. Typically, 2 or 40 mL x mg mL⁻¹ (x=0, 0.005, 0.01, 0.05, 1) RuCl₃ solution was first prepared using ethylene glycol (EG) as solvent. EG acts as a reducing agent in the synthesis to reduce Ru³⁺ ions. Then Ti Fiber Felt with IrO_x nanoparticles was immersed into the solution under 80°C for 15min. After washing with isopropanol and water, the Ti Fiber Felt with IrO_x was dried by air flow. Ti mesh acts as a conductive electrode and does not participate in OER reaction.

4.2.4 Preparation of gas diffusion electrode (GDE)

The silver was deposited on the 2.5*2.5 cm² GDL (Sigracet 39 BB) by AJA magnetic sputtering with a background pressure of 5x10⁻⁷ Torr. Ag metal was used as a bottom electrode which was deposited by direct current (DC) magnetic sputtering with the target Ag. The sputtering power was 100 W, the deposition pressure was 5 mTorr and the working gas was pure Ar of 12 sccm.

4.2.5 Electrochemical measurements

All electrochemical tests were measured on Metrohm Autolab PGSTAT 204 electrochemical workstations at room temperature with IR corrected. The OER stability and activity performance of the IrO_x and Ru/IrO_x catalyst with different Ru loading amount in neutral conditions (0.5M KHCO₃ electrolytes) systematically studied in a single compartment electrolytic cell. A three-electrode system was fabricated with the prepared IrO_x -based materials, platinum wire, and Ag/AgCl (in saturated KCl) electrode severing as the working electrode, the counter electrode, and the reference electrode, respectively. The synthesized Ti Fiber Felt with Ru/IrO_x catalyst directly served as the working electrode with an electrode holder. The surface area of the working electrode was controlled with 1 cm² in 25ml 0.5M KHCO₃ solution under an Ar gas environment. The Linear sweep voltammetry (LSV) under select potential range with 0.4V iR compensation were used for overpotential and activity measurement of Ru/IrO_x catalytic OER reaction. After that, the chronoamperometry (I-T) test were used for stability under the over potential at 10mA and 100mA for 30min or 60min. The Ru/IrO_x catalytic OER performance were evaluated using Chronopotentiometry (P-T) test under selective potential for 12, 100, 200 hours. Before OER test, linear sweep voltammetry (LSV) curves are performed until that the polarization curves achieve steady state. The electrochemically active surface area (ECSA) measurements were conducted using cyclic voltammetry (CV) scans at different rates from 10 to 50 mV s⁻¹ with a 10 mVs⁻¹ increment speed from 0.5 V_{RHE} to 0.7 V_{RHE}; within this potential range, the Faradic process is excluded. All the potential values are presented in RHE unless otherwise stated using the following equation^[144] (3.1):

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197\text{V} + 0.059 \times \text{pH} \quad (3.1)$$

The ESCA is calculated by the following equation ^[144] (3.2):

$$A_{\text{ECSA}} = \frac{\text{Specific capacitance}}{40 \mu\text{Fcm}^{-2}\text{cm}^{-2}_{\text{ECSA}}} \quad (3.2)$$

The specific capacitance of the sample was obtained by CV. It was carried out at different scan rates in the range of 0.5 V_{RHE} to 0.7 V_{RHE}. 40 mF cm⁻² is the specific capacitance of a flat surface for metallic and semiconducting materials with 1 cm² of the real surface area in the aqueous electrolyte ^[144].

4.2.6 OER performance measurement in MEA electrolyzers

The OER performance of Ru/IrO_x catalysts was evaluated in MEA electrolyzers coupling with CO₂ reduction reaction. A potentiostat with a current booster (Metrohm Autolab, 10 A) was used to apply the current. To facilitate the electrochemical reactions, a commercially available CO₂ MEA electrolyzer from Dioxide Materials was utilized. The MEA electrolyzer consisted of flow field plates with a serpentine-shaped flow field of 5 cm², serving as the anode and cathode, enabling a continuous supply of 0.5 M KHCO₃ anolyte and humidified CO₂ to their respective electrodes. As for the specific components, the cathode utilized an Ag gas diffusion electrode (GDE), the anode employed a Ti Fiber Felt with Ru/IrO_x catalyst, and a physically separated anion exchange membrane (AEM) (Sustainion X37-50 membrane) separated the anode and cathode. To ensure even distribution of electrical current, the cathode electrodes were securely taped to the stainless-steel flow field plate using a copper frame. The electrolyzer bolts were appropriately tightened with equal compression torque. Prior to conducting the electrochemical testing, the AEM was activated in 1 M KOH solution for more than 24 hours. Once the electrolyzer assembly was completed, the anolyte (0.5 M KHCO₃) flowed through the anode at a constant rate of 18 mL/min using a peristaltic pump with silicone tubing to circulate the anolyte, while the humidified CO₂ was supplied from the gas diffusion electrode (GDL) at a constant flow rate of 50 standard cubic centimeters per minute (sccm). The OER was then initiated by applying a constant current density (100, 200, and 500 mA cm⁻²) for long term stability test. The corresponding cell potentials for the current densities of interest were recorded with continuous monitoring. The full-cell potentials were reported without IR correction. Gas products were analyzed using GC (Agilent 6890) to determine the gas product yield. For each current density tested, the gas products were collected upon complete stabilization of the cell voltage at least three times.

4.2.7 Material characterization

Scanning electron microscopy (SEM) images were captured on a Hitachi S4800 with a working accelerating voltage of 10 kV. Glancing-incidence X-ray diffraction (GIXRD) was measured on a PANalytical X'Pert Pro MRD diffractometer with Cu K α radiation (1.54 Å) at an incidence angle of 0.3°. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo-VG Scientific ESCALab 250 microprobes with a monochromatic Al K α X-ray source (1486.6 eV). The obtained spectra were calibrated using the C 1s line. The catalyst was soniated from the carbon paper in IPA solution. Then the solvent was dropped casting onto ultrathin lacey carbon TEM grids for imaging. Some residue carbon paper is hard to separate from the samples. Aberration-corrected high-angle annular dark field scanning transmission electron microscope (AC-HAADF-STEM) tests were carried out on an FEI Titan 80-300 HB TEM equipped with energy-dispersive X-ray spectroscopy (EDX) at 80 kV. The HAADF-STEM images

were recorded by FEI Titan 80-300 HB TEM/STEM with double aberration correctors operating at 80 kV at the Canadian Center for Electron Microscopy (CCEM). Inductively coupled plasma mass spectrometry (ICP-MS) analyses were carried out on an Agilent 8800 triple quadrupole, using He as a collision cell gas, Ge and In as internal standards to correct for instrument drift, and ICP element standards (secondary standards from Delta Scientific Inorganic Ventures; primary calibration standards from Alfa Aesar and Aristar VWR Chemicals BDH) to confirm instrument accuracy (within 3%; relative standard deviation for individual sample analyses was $\leq 12\%$). Gas chromatography (GC) tests were conducted on an Agilent 6890 machine with Carboxen (TCD) and Carbonplot (FID) columns. Scanning transmission Soft X-ray microscopy (STXM) measurements were carried out at provides, beamline (10ID-1) at Canadian Light Source. XAS measurements were carried out at the 20-BM and 20-ID-C beamline of Advanced Photon Source (APS), Argonne National Laboratory. The measurements at the Ir L-edge and Ru K-edge were performed in fluorescence mode using a Lytle detector. The Ir L-edge and Ru K-edge XANES and EXAFS data were analyzed and treated using the software package Athena. The EXAFS data is fitted using the software package Artemis. Ir and Ru foil is applied for reference and calibration samples. In this fitting data, CN represents the coordination numbers of identical atoms; R is assigned as the interatomic distance; δ^2 is considered as Debye-Waller factors; R factor: goodness of fit. The fitting parameters strictly comply with all experimental requirements.

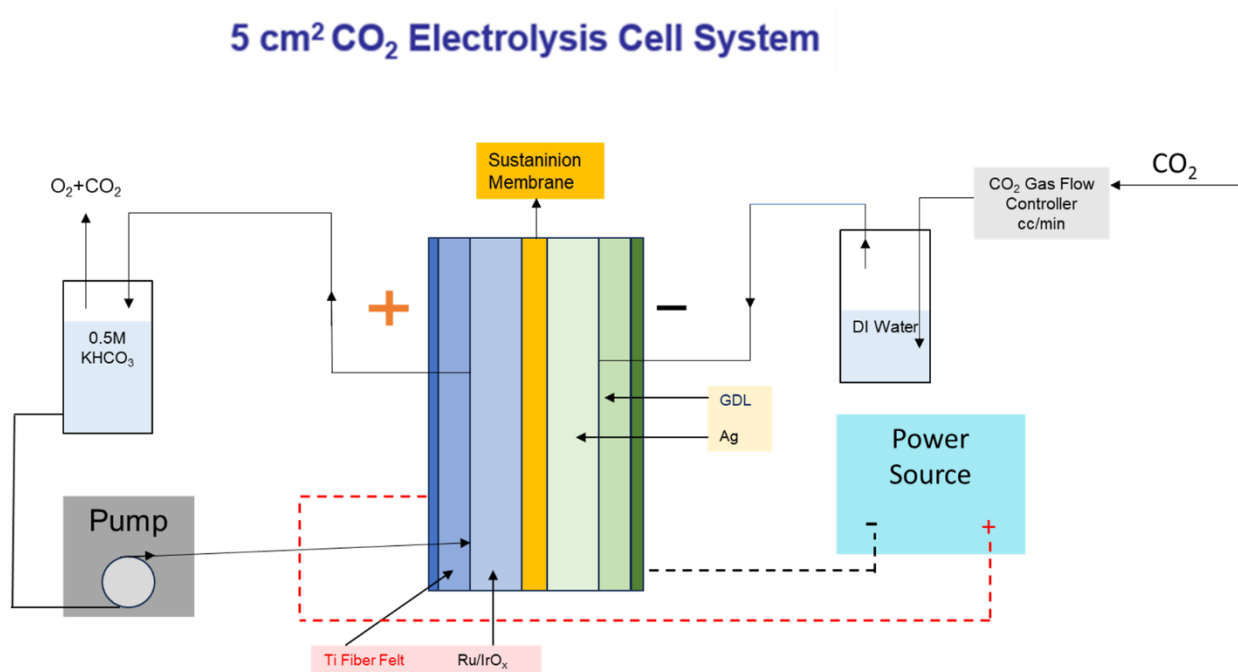


Figure 4.1. The electrolyzer setup

4.2.8 Determination of gas products using GC method

The product of the silver-catalyzed reduction of CO₂ is CO, so a standard curve for CO gas is first established using a standard gas. In detail, different concentrations were prepared by diluting the CO with CO₂ using mass flow controllers (Alicat Scientific). The produced standard curves are shown in **Figure 4.2**. During the electrocatalytic CO₂ reduction, the gas products flow into the GC with the input CO₂ gas in the online tube. In experiments, CO was detected by the thermal conductivity detector (TCD).

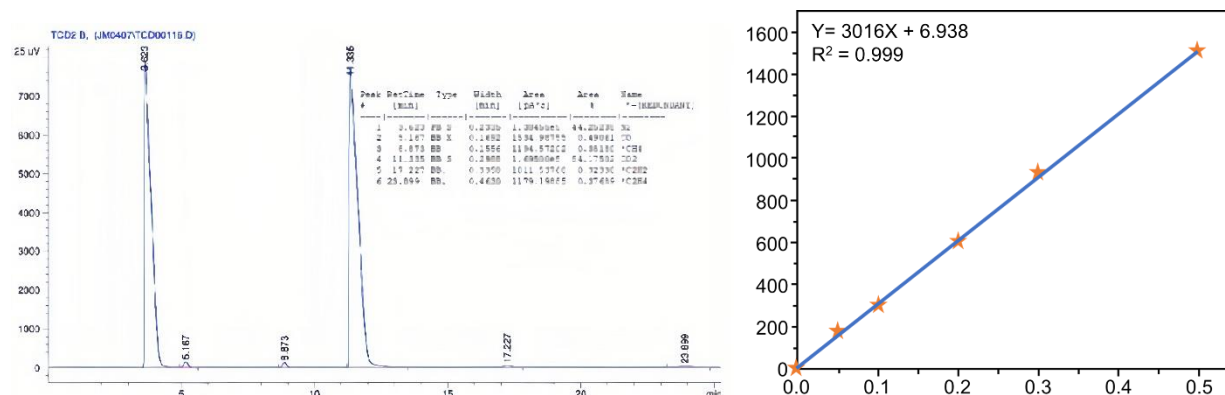


Figure 4.2. Representative GC thermal conductivity detector (TCD) spectrum for CO₂RR products; Standard curves of CO.

4.3. Result and discussion

4.3.1 Electrocatalytic OER performance

4.3.1.1 OER performance of different electrodeposited loading IrO_x

To determine the catalytic performance of different electrodeposited IrO_x, the OER performance of IrO_x (900s, 1800s, 3600s, 7200s) catalyst was recorded in Ar saturated 0.5 M KHCO₃ electrolyte. As shown by the LSV curves in **Figure 4.3A and B**, the catalysts subjected to IrO_x deposition for 3600 and 7200 seconds exhibit a smaller η value, measuring only 1.4V. This value is lower than that of the catalysts with deposition times of 900 and 1800 seconds. It indicates that the catalysts with deposition times of 3600 and 7200 seconds perform better. Furthermore, these catalysts also exhibit a smaller overpotential at 100 mA cm⁻², specifically $\eta_{100} = 2.1V$. To evaluate the performance of the three catalysts, chronoamperometry was conducted at deposition times of 1800, 3600, and 7200 seconds, with corresponding overpotentials of 10 mA cm⁻² and 100 mA cm⁻². The three catalysts exhibited favorable stability and activity throughout the 30-minute test, as shown in **Figure 4.3C and D**. In summary, both

the catalysts deposited for 2 hours and 1 hour demonstrate satisfactory performance. However, given that Ir is a noble metal and the deposition amount is relatively high within two hours, the 1-hour-deposited IrO_x catalyst was selected for subsequent experiments.

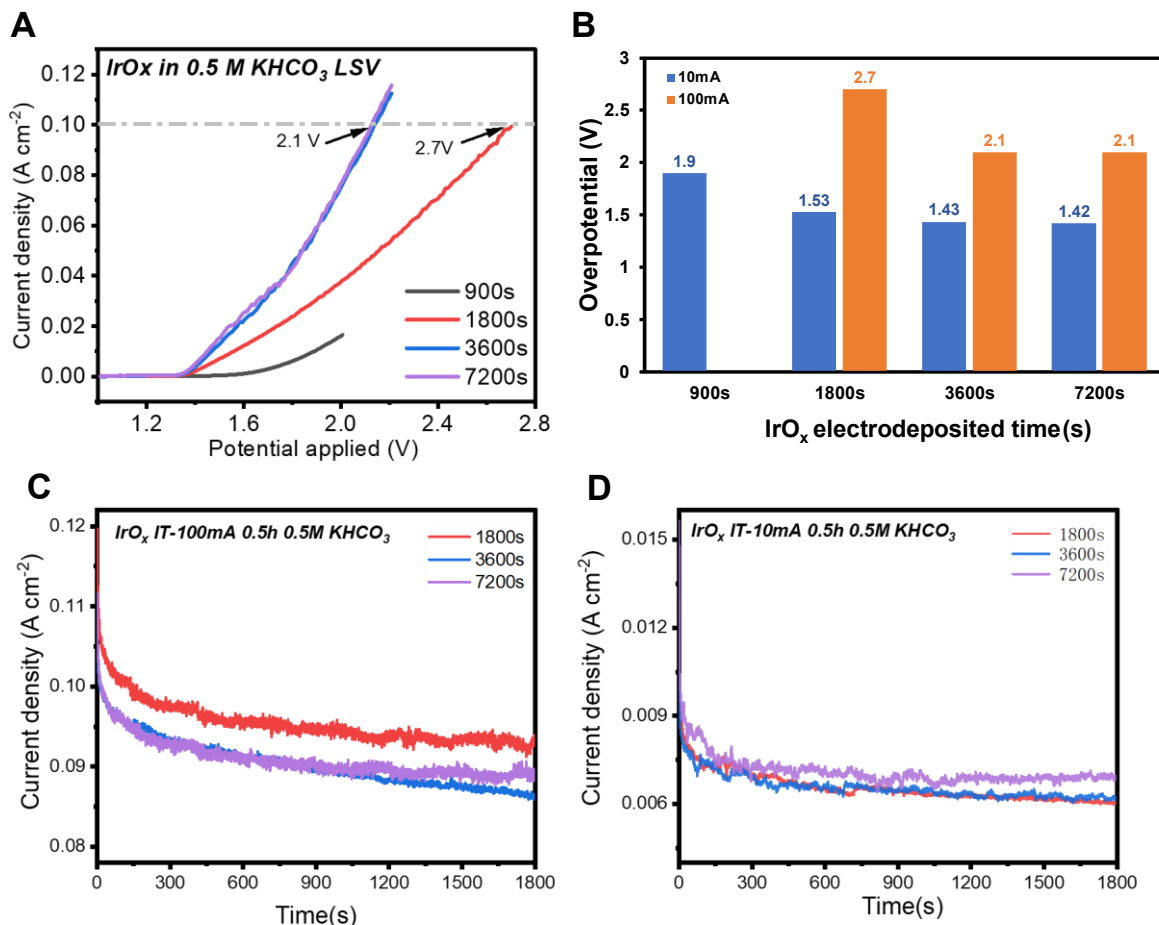


Figure 4.3. Different Electrodeposited IrO_x (A) LSV polarization curves (B) Overpotentials at a current density of 10 mA cm^{-2} and 100 mA cm^{-2} (C-D) I-T chronoamperometry curves with corresponding overpotentials at 100 mA cm^{-2} and 10 mA cm^{-2} .

4.3.1.2 OER performance of IrO_x with the effect of ethylene glycol (EG) treatment

Since we use 1h IrO_x immerse in xmg/ml EG ($x=0, 0.005, 0.01, 0.05, 1$) for 15min to dope Ru atoms, to unify the variables and exclude the effect of EG on the samples the IrO_x immerse in EG after deposition and then calcined it. The LSV curves (**Figure 4.4A and B**) show that the IrO_x catalyst exhibits a reduced overpotential at 200 mA cm^{-2} from 3.6V to 3.2V following EG treatment, suggesting an enhancement in catalyst performance through EG soaking. The results of Chronopotentiometry and ECSA also prove this point. As shown in the Chronopotentiometry test results of running for 12h at high current

densities of 10 mA cm^{-2} , 200 mA cm^{-2} , and 500 mA cm^{-2} (**Figure 4.4C-D**), it is observed that at a constant current density of 10 mA cm^{-2} and both catalysts demonstrate relative stability. ECSA did not change significantly before and after the reaction (**Figure 4.5**). However, as the current density increases to 200 and 500 mA cm^{-2} , the stability and ECSA performance of both catalysts deteriorates rapidly (**Figure 4.5**). Notably, the IrO_x catalyst treated with EG exhibits a significantly slower decay rate compared to the catalyst without EG treatment (**Figure 4.5**).

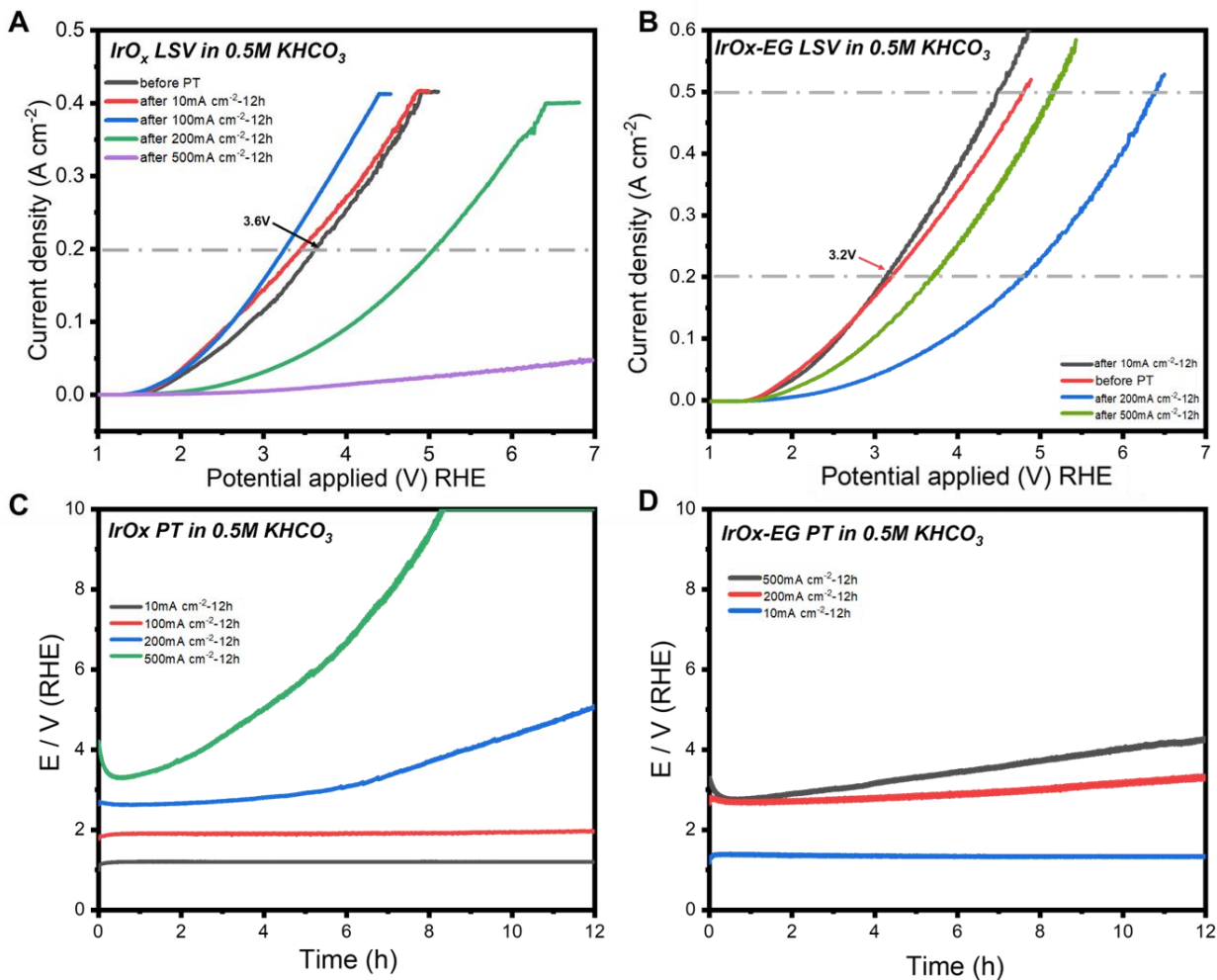


Figure 4.4 LSV and PT result for IrO_x with/without EG treatment

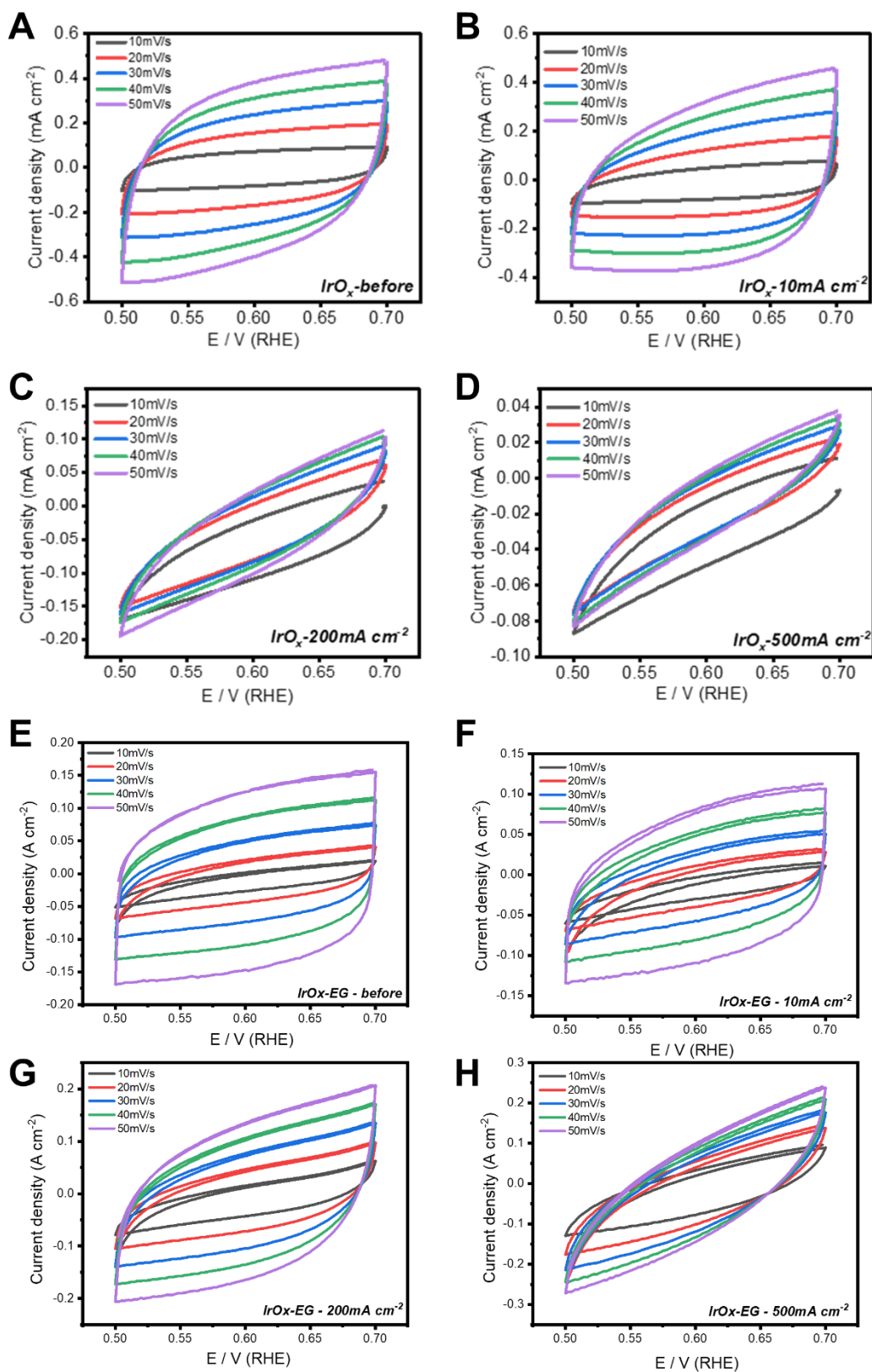


Figure 4.5 ECSA for IrO_x without (A-D) /with (E-H) EG treatment

4.3.1.3 OER performance of different loading amount of Ru in Ru/IrO_x

According to **Figure 4.6A**, the increase of incorporation of ruthenium (Ru) doping does not significantly enhance the initial OER performance of IrO_x regarding the overpotential. The overpotential (η) at 100 mA cm⁻² improves slightly from 2.6V to 2.5V (**Figure 4.6A**). However, Ru doping does improve the stability of IrO_x. This is evident in the chronopotentiometry curves presented in **Figure 4.6B**, where the IrO_x-Ru catalyst's activity remains stable after 1 hour of operation at I-T chronoamperometry test with corresponding overpotentials at 100mA cm⁻². As seen in the following **Figure 4.4** and **Figure 4.7**, Chronopotentiometry curves of IrO_x performs very well under the 10mA cm⁻² in the 12h stability test. However, its potential apparently increases during the stability test under 200 and 500 mA cm⁻², indicating its poor stability under large current density. To improve its stability under large current density, some Ru atoms are doped into the IrO_x. As seen in **Figure 4.6C-F** and **Figure 4.7**, the results of Chronopotentiometry curves of different doping amount of Ru/IrO_x at 10 mA cm⁻², 200 mA cm⁻², and 500 mA cm⁻² for 12h run at high current densities, which can be significantly observed that all samples are stable under 10 mA cm⁻² during 12h test; IrO_x is unstable under 200 mA cm⁻² during 12h test and only IrO_x-Ru 0.05mg and IrO_x-Ru1mg exhibits no apparent potential increase during the 12h stability test under all current densities, which suggesting its excellent stability.

What should be noted that, the Ru doping not only improve the stability, but also the activity. Activity for different loadings of IrO_x-Ru and IrO_x was determined in **Figure 4.8**. The IrO_x/Ru shows better initial activity than that of IrO_x (**Figure 4.8**). Especially, the OER activity of IrO_x-Ru 0.05mg even increases a little after the 12h stability test under 500 mA cm⁻², activity of IrO_x-Ru 1mg decreases a little, while other samples degrade severely after the stability test (**Figure 4.8**). Electrochemically active surface areas analysis (ECSA) shows in **Figure 4.9 to 4.13** indicate that ECSA of IrO_x decreases after the stability test; Ru0.005mg and Ru0.01mg almost keep the same; IrO_x-Ru0.05mg and IrO_x-Ru1mg increases after the stability test. Activity analysis (**Figure 4.14**) lends support to this observation. IrO_x-Ru 1mg sample showed highest specific activity, while the IrO_x's activity decreases.

Although it seems reasonable to attribute the stability change to the ECSA, the reason why the ECSA change differently in these two set of samples (IrO_x vs Ru/IrO_x) is still unknown. There are two main OER mechanisms, i.e., lattice oxygen mechanism (LOM) and adsorbate evolution mechanism (AEM) [146]. Usually, the catalysts working under LOM shows better activity but poorer stability than the catalysts working under AEM. For IrO_x-based catalyst, LOM may be the main reason for its poor stability. To be specific, the lattice oxygen of IrO_x participates in the OER reaction and exchange with the oxygen from water, resulting its poor long-term stability. This can be confirmed by ¹⁸O isotope experiment and will be done later. It's reasonable to attribute the decrease of ECSA of IrO_x to the LOM, but the reason for the

increase of ECSA of IrO_x/Ru before vs after reaction (**Figure 4.13**) is still unclear. Another question is that whether ECSA is the only reason for the activity change and difference in stability. To answer this question, the geometrical activity was normalized to ESCA. As seen in **Figure 4.14E-H**, the specific activity of IrO_x/Ru after stability test is much higher than that of IrO_x after stability test. This means that the difference of ECSA is not the only reason for the different activity between IrO_x and IrO_x/Ru after the stability test. This means the intrinsic active sites structure in IrO_x and IrO_x/Ru after the stability test are different.

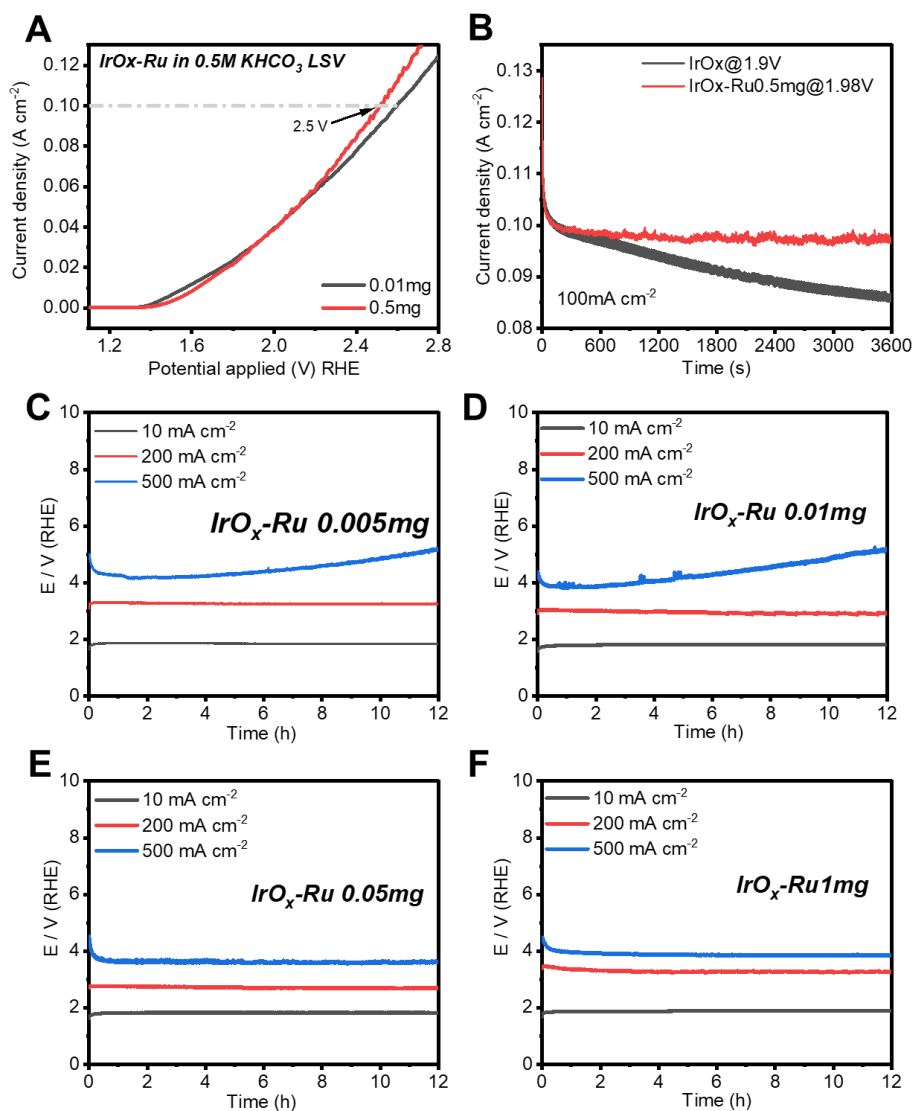


Figure 4.6. OER performance of Ru doped IrO_x (A) LSV polarization curves (B) I-T chronoamperometry curves at 100mA cm⁻²; (C-F) Chronopotentiometry curves during 12h of different doping Ru/IrO_x at 10 mA cm⁻², 200 mA cm⁻², and 500 mA cm⁻²

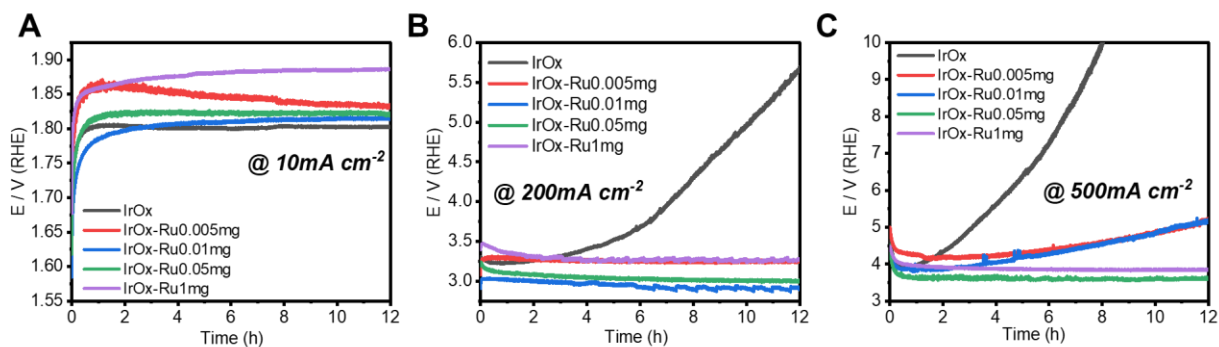


Figure 4.7. Chronopotentiometry (PT) curves during 12h of different doping Ru/IrO_x at 10 mA cm⁻², 200 mA cm⁻², and 500 mA cm⁻²

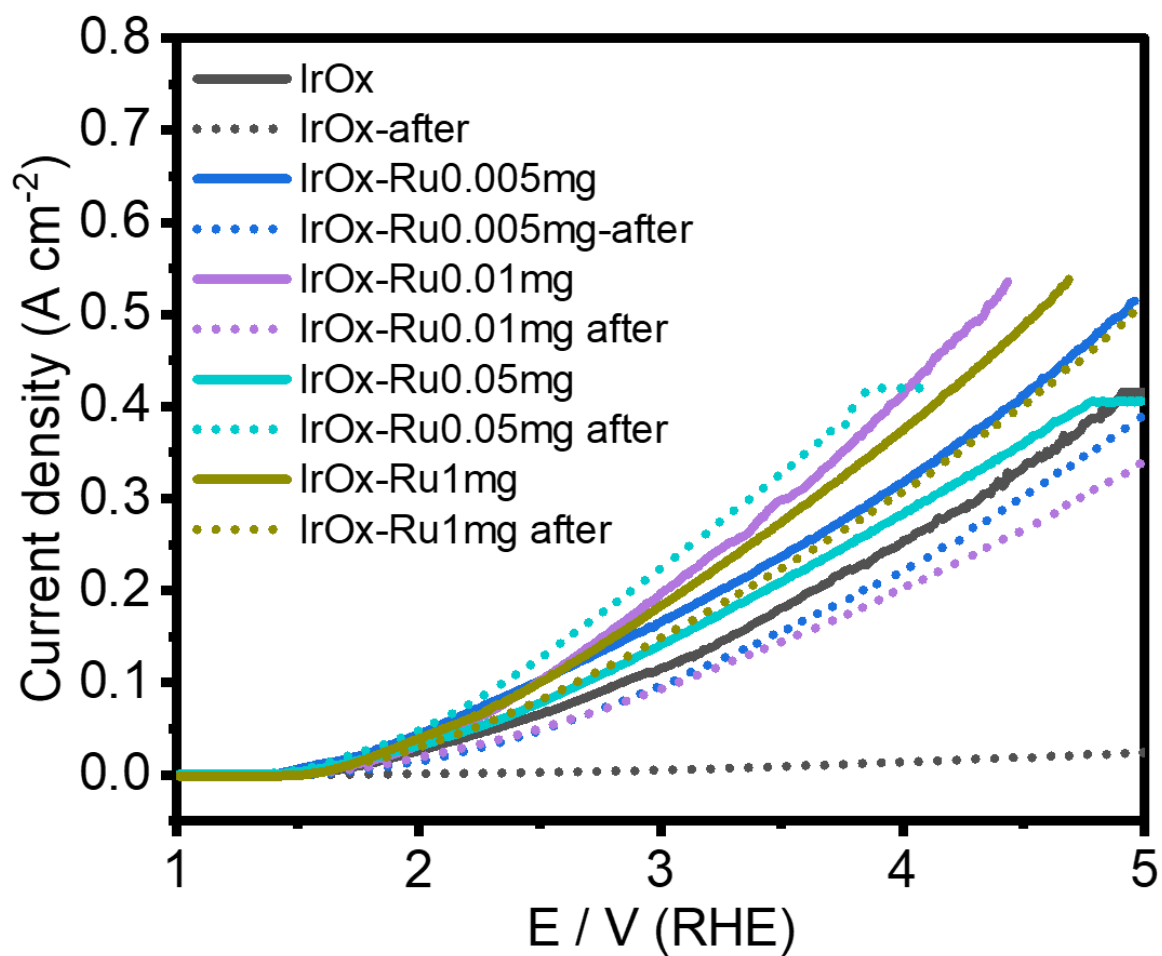


Figure 4.8. LSV curves normalized by geometric area with different doping samples before and after the 12h stability test under 500 mA cm⁻².

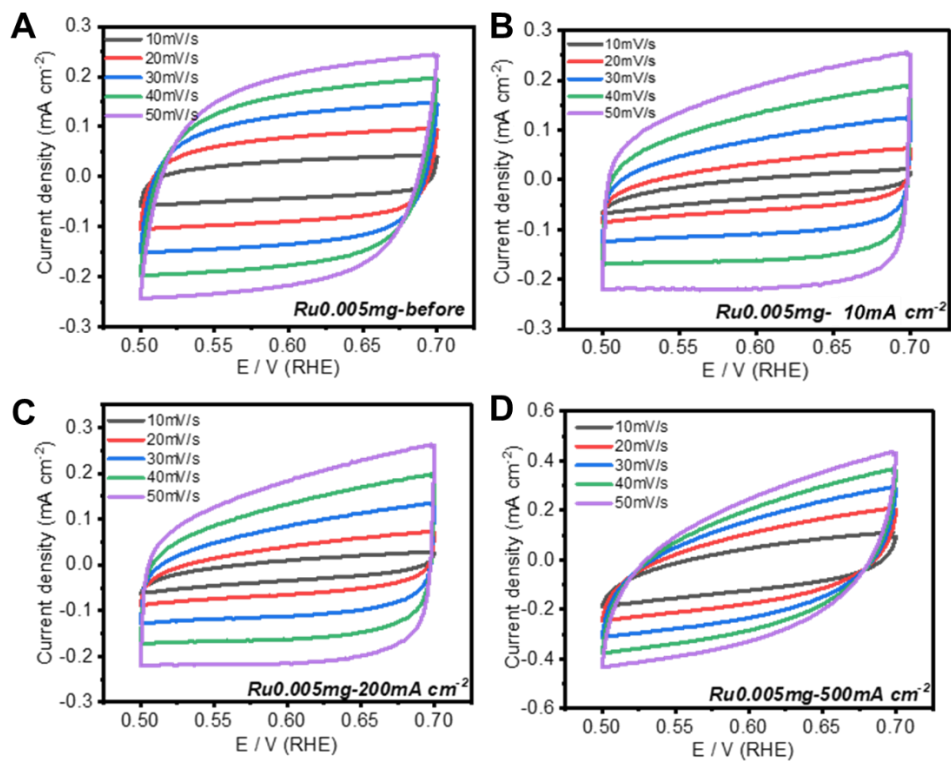


Figure 4.9. CV curves of IrO_x-Ru 0.005mg

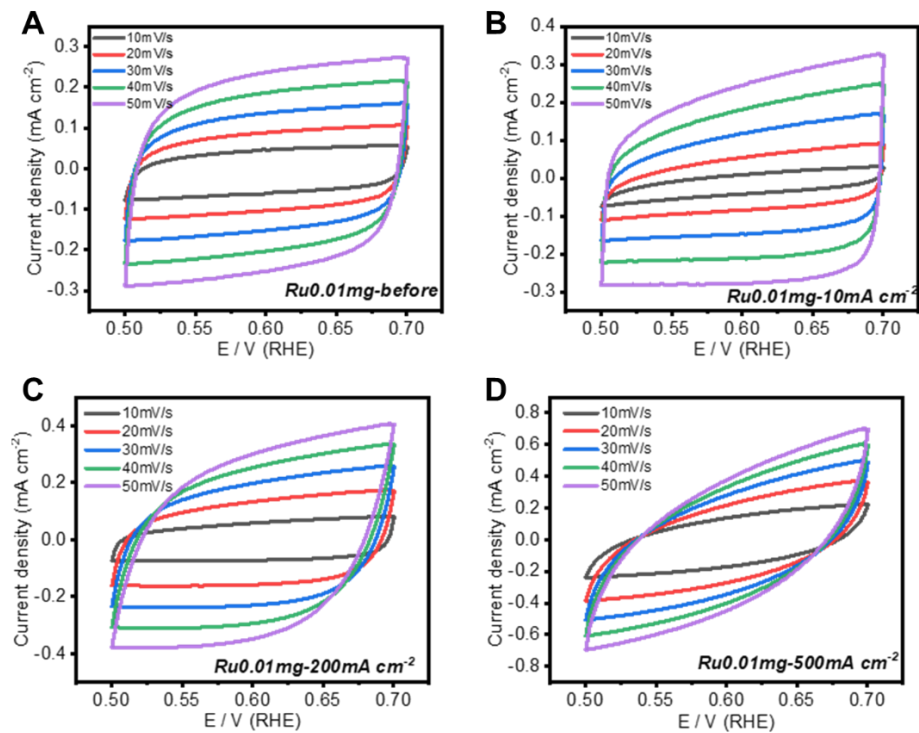


Figure 4.10. CV curves of IrO_x-Ru 0.01mg

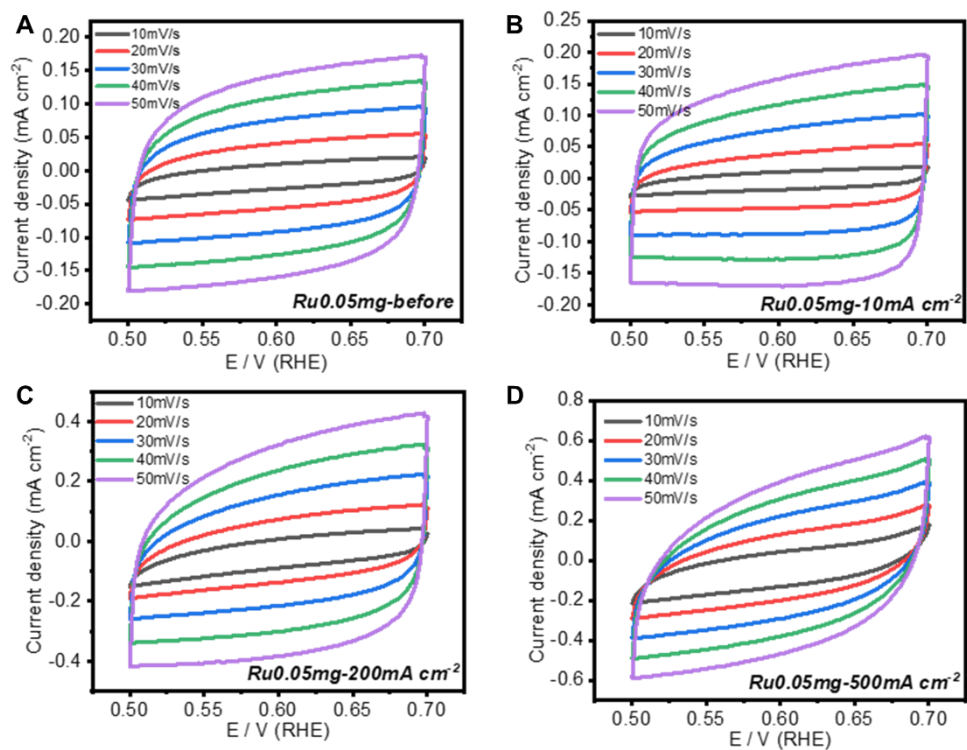


Figure 4.11. CV curves of IrO_x-Ru 0.05mg

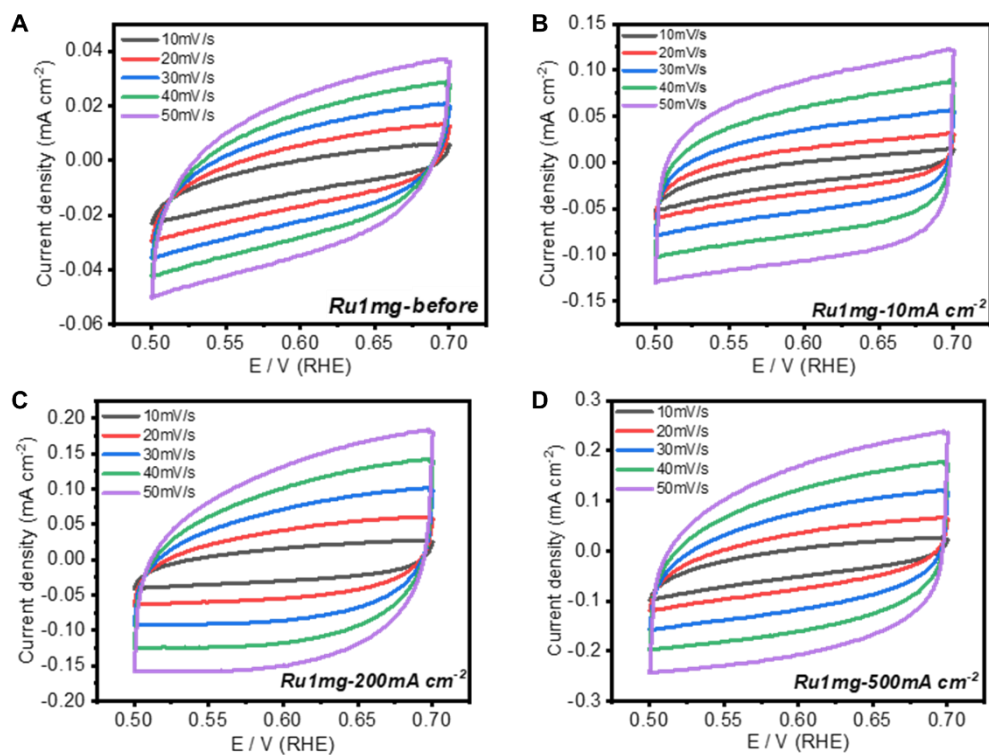


Figure 4.12. CV curves of IrO_x-Ru 1mg

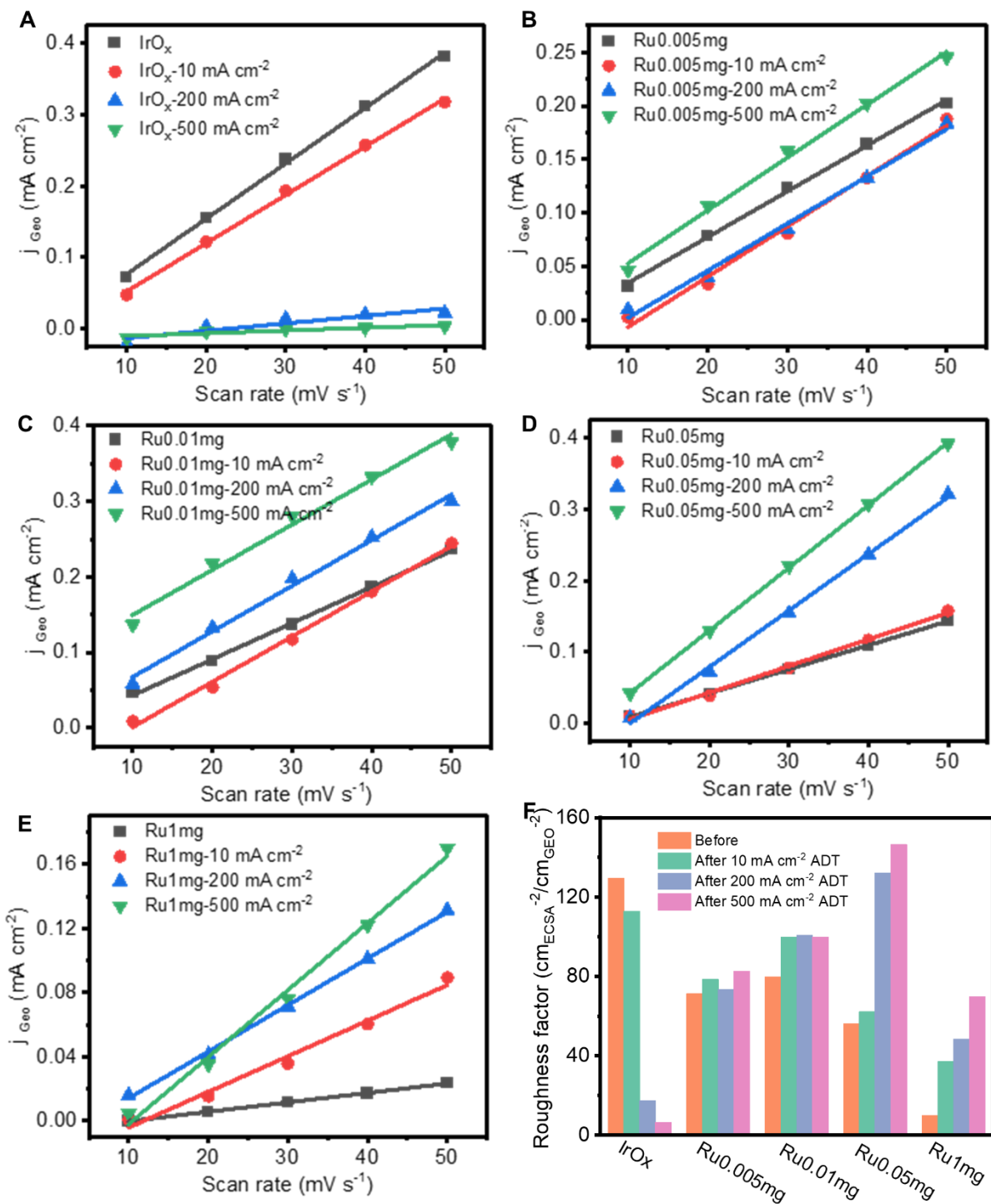


Figure 4.13. Double-layer capacitance (C_{dl}) represented by curve slope.

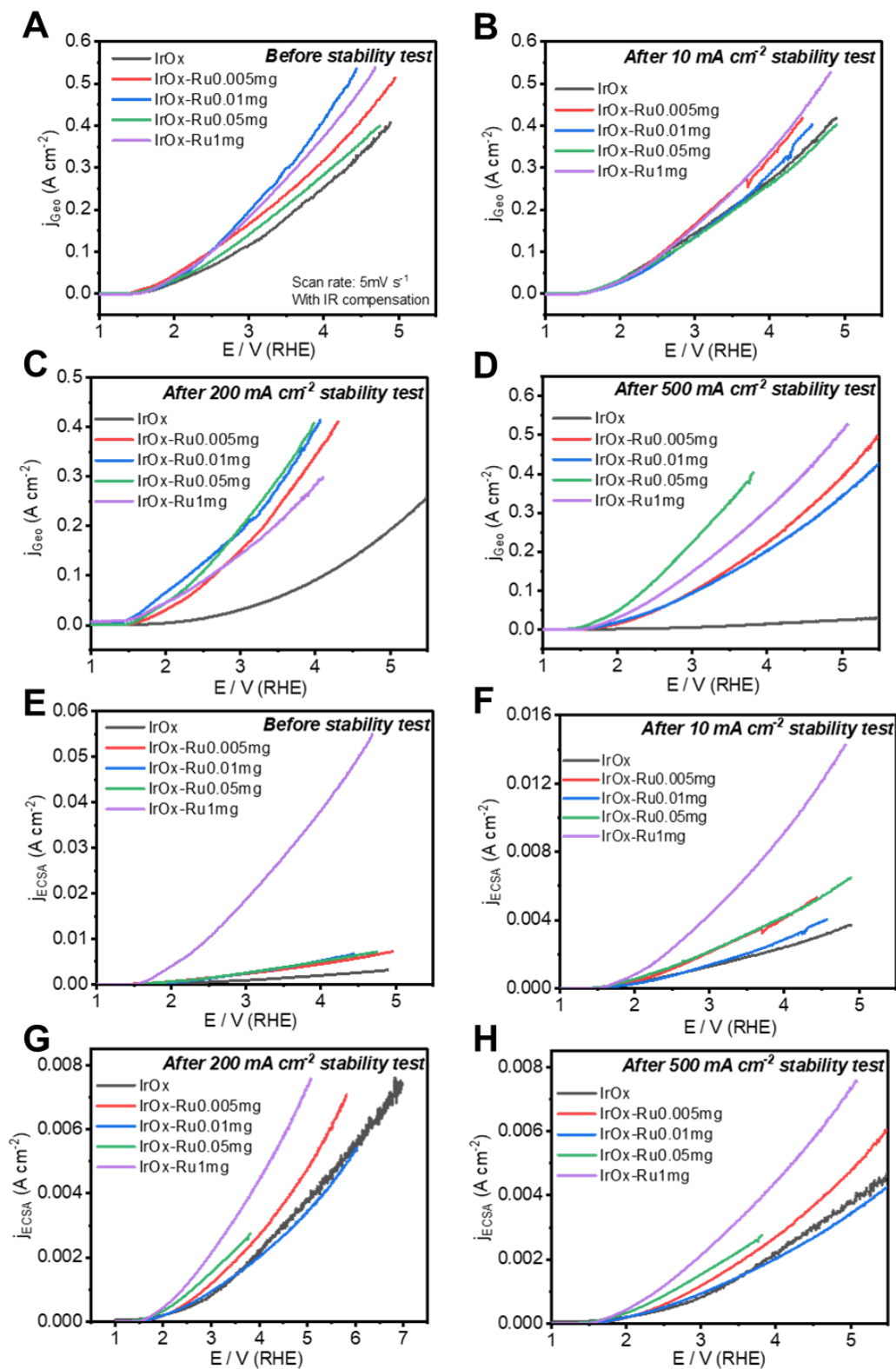


Figure 4.14. (A-D) LSV curves normalized by geometric area; (E-H) and LSV curves (A-D) normalized by ECSA for specific activity.

4.3.1.4 OER performance of Ru/IrO_x long term stability

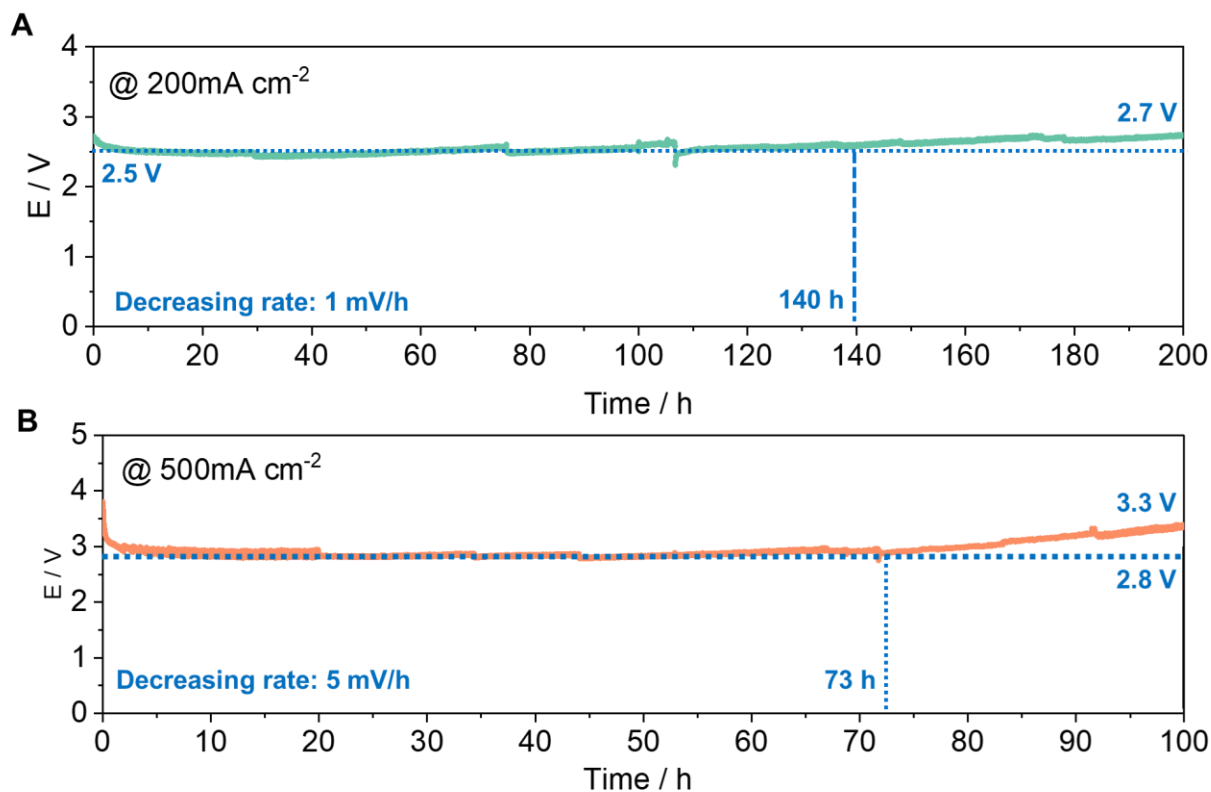


Figure 4.15. Electrochemical stability evaluation for neutral OER. The galvanostatic curves of Ru-0.05mg /IrO_x at a current density of 200 and 500 mA cm⁻²

From **Figures 4.6 and 4.7**, it is evident that both Ru-0.05mg-IrO_x and Ru-1mg/IrO_x exhibit good stability and activity, with a minor discrepancy at 200 mA/cm² and 500 mA/cm². Given the precious metal nature of Ru, we opted for the lower addition amount, Ru-0.05mg-IrO_x, for conducting the long-term stability experiments. **Figure 4.15** shows the electrochemical stability evaluation for neutral OER. The galvanostatic curves of Ru-0.05mg /IrO_x at a current density of 200 and 500 mA cm⁻². Obviously, Ru-0.05mg/IrO_x maintains almost unchanged performance to the initial state for 200 h at a constant current density of 200 mA cm⁻², and about 100h at a constant current density of 500 mA cm⁻². Furthermore, the novel OER catalyst in this work exhibits overpotentials of only 2.5V and 2.8V for current densities of 200 mA cm⁻² and 500 mA cm⁻², respectively.

4.3.1.5 Electrocatalysis of OER performance paired with CO₂ reduction in MEA systems

From **Figure 4.15**, it can be observed that Ru-0.05mg-IrO_x exhibits better long-term stability at a current density of 200 mA cm⁻² instead of 500 mA cm⁻². Thus, we have chosen a current density of 200 mA cm⁻² for the MEA testing. The OER performance of Ru-0.05mg/IrO_x catalyst for CO₂ reduction was validated in a commercial MEA electrolyzer, following the configuration described in **Method 2.6**. Anion exchange membrane (AEM) was employed to assess the MEA performance. A commercial MEA was set with an anodic 3 cm² Ru-0.05mg/IrO_x catalyst and 2.5 cm² Ag GDE as the cathode. The MEA exhibits a cell voltage of 3.9 V at 200 mA cm⁻². Ru-0.05mg/IrO_x exhibits highly substantial stability in CO₂ reduction MEA applications, with no apparent increase in cell voltage at 200 mA cm⁻² following 500 hours to produce CO [at standard temperature and pressure (STP)] as is seen from **Figure 4.16**. CO is the exclusive product of silver-catalyzed CO₂ reduction^[147], and the generated CO product in this study was monitored using online GC analysis (**Figure 4.17**). Further calculations are required to determine the Faradaic efficiency of the products. These findings combined confirm excellent OER activity and remarkable stability under neutral conditions and industrial-scale current densities.

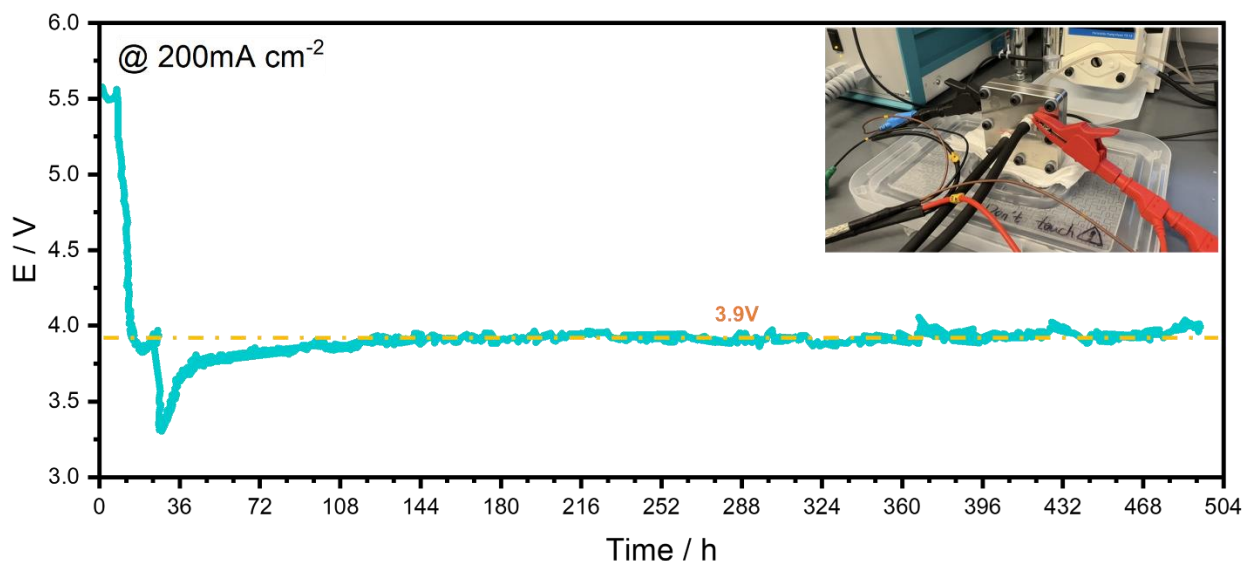


Figure 4.16. Chronopotentiometric curve of the CO₂ reduction MEA electrolyzer using Ru-0.05mg/IrO_x with digital photographs of MEA device.

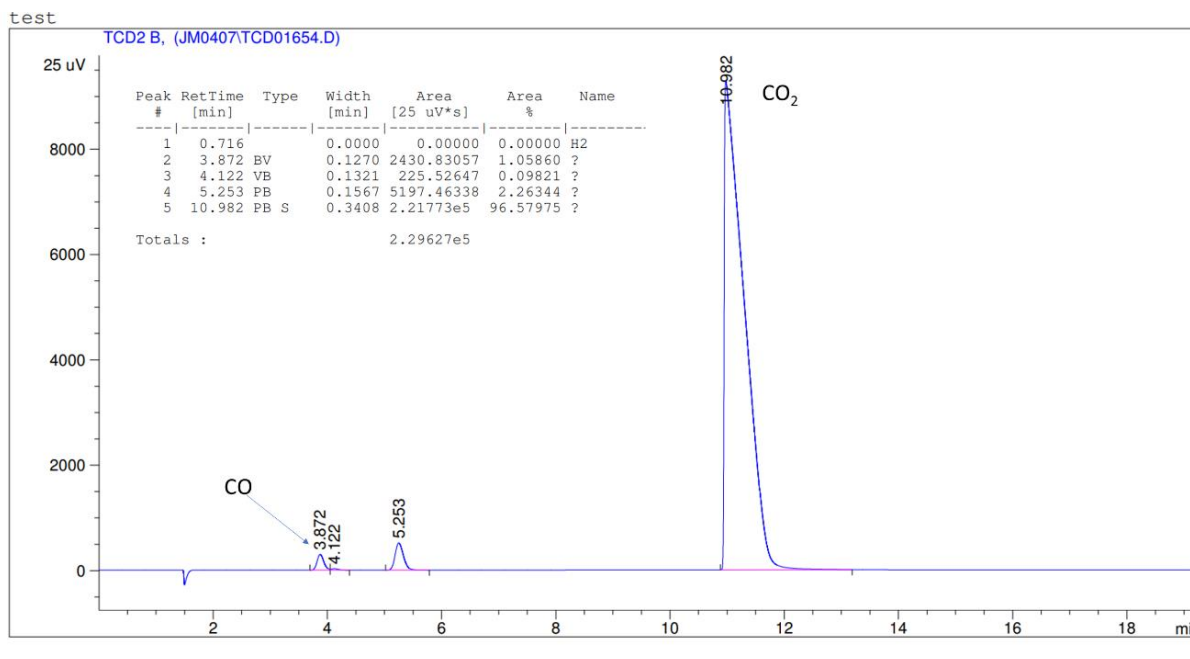


Figure 4.17. GC result of CO product

4.3.2 Materials characterization

In order to understand the mechanism of Ru/IrO_x and IrO_x in OER, a variety of materials characterisation was performed. Ru/IrO_x nanoparticles was prepared through the spontaneous galvanic replacement reaction, which was driven by the reduction potential difference between RuCl₃ and Ir.^[117,118] The grazing incidence X-ray diffraction (GI-XRD) measurement was first carried out to verify the crystalline structures of the synthesized for both the Ru/IrO_x and IrO_x samples. The characteristic peaks in the XRD pattern of Ru/IrO_x (**Figure 4.18**) can be ascribed to IrO₂ (PDF card No.43-1029) in rutile phase. No Ru peak appeared in the GI-XRD spectrum of IrO_x/Ru, indicating no Ru crystalline phase formed in the sample. The crystal phase remains largely unchanged before/after reaction in Ru-0.05mg/IrO_x and IrO_x. As shown in **Figure 4.20E-G** the energy dispersive spectroscopy (EDS) images and spectrum of Ru/IrO_x sample reveal a homogeneous distribution of Ru, Ir, and O elements, prove the co-existence and homogenous distribution of Ru and Ir elements in the Ru/IrO_x. The aberration corrected scanning transmission electron microscopy (AC-HAADF-STEM) images in **Figure 4.20C and D** shows that Ru/IrO_x and IrO_x sample features surface reconstruction before and after reaction. As seen from the scanning electron microscope (SEM) images (**Figure 4.19A and C**), no obvious morphology change was observed in the morphology of Ir after its galvanic replacement reaction with RuCl₃. SEM also test to observe the morphology of the catalysts before and after stability test. As shown in **Figure 4.19**, the Ru/IrO_x nanoparticles almost kept their initial morphology, while many nanoparticles of IrO_x peeled off

from the substrate after the stability test. This may be the reason of the decreasing activity of IrO_x . It was reported that the electrocatalyst would suffer irreversible oxidation and reconstruction during the OER process.^[148-151] The transmission electron microscopy (AC-HAADF-STEM) images (**Figure 4.20C and D**) was also observed that Ru/IrO_x electrocatalyst suffer reconstruction during the OER process from 4 fold symmetry to 6 fold symmetry, which would be the reasons for enhanced catalyst activity and stability. After the OER reaction, the surface structure of the IrO_x sample undergoes distortion, which might be a potential cause for the decrease in stability. (**Figure 4.20A and B**)

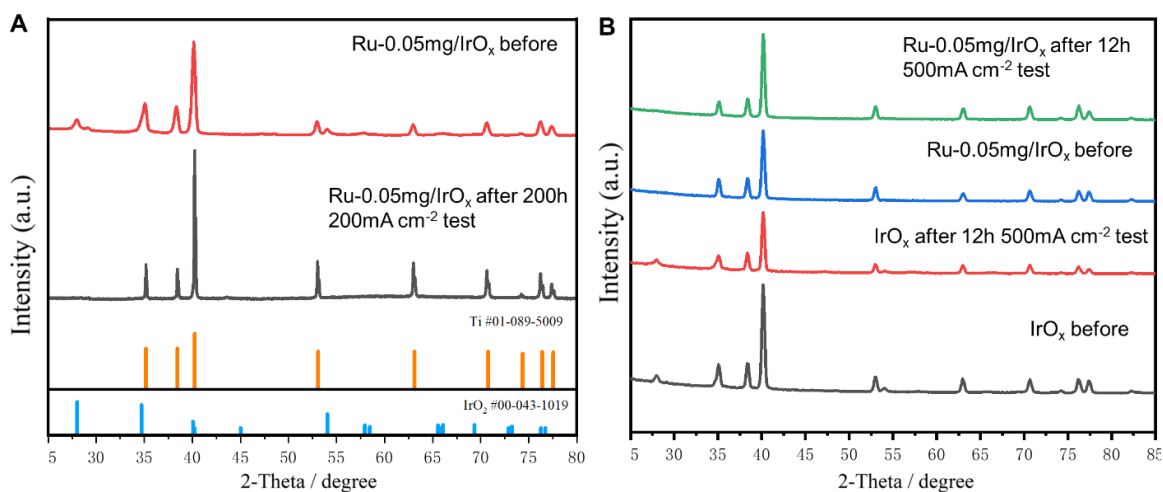


Figure 4.18. GIXRD patterns for of IrO_x and IrO_x/Ru before and after the stability test.

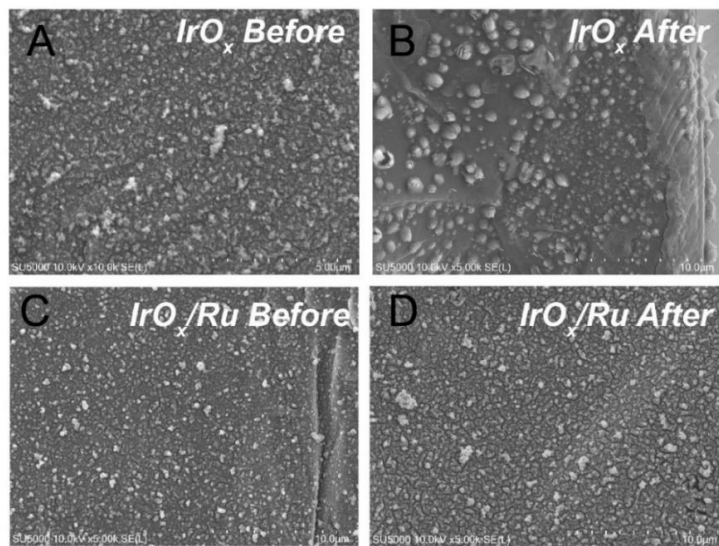


Figure 4.19. SEM images of IrO_x (A-B) and IrO_x/Ru (C-D) before and after the stability test under 500 mA cm^{-2} .

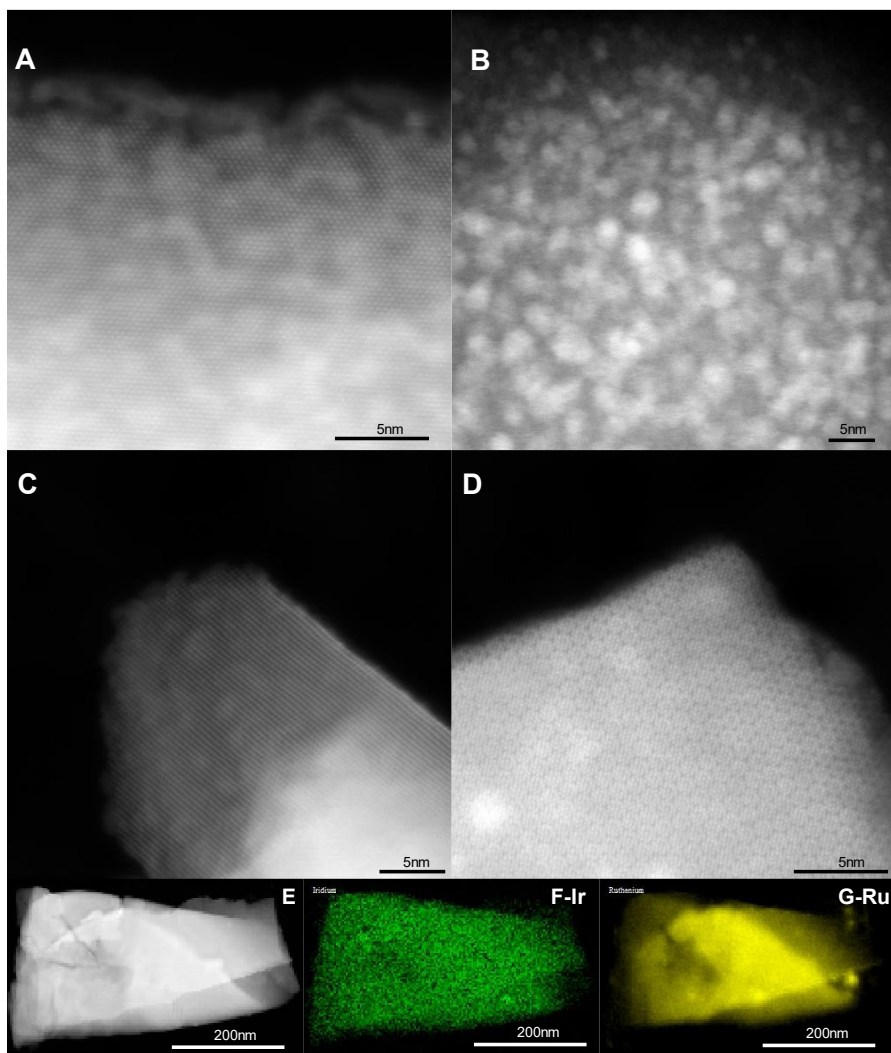
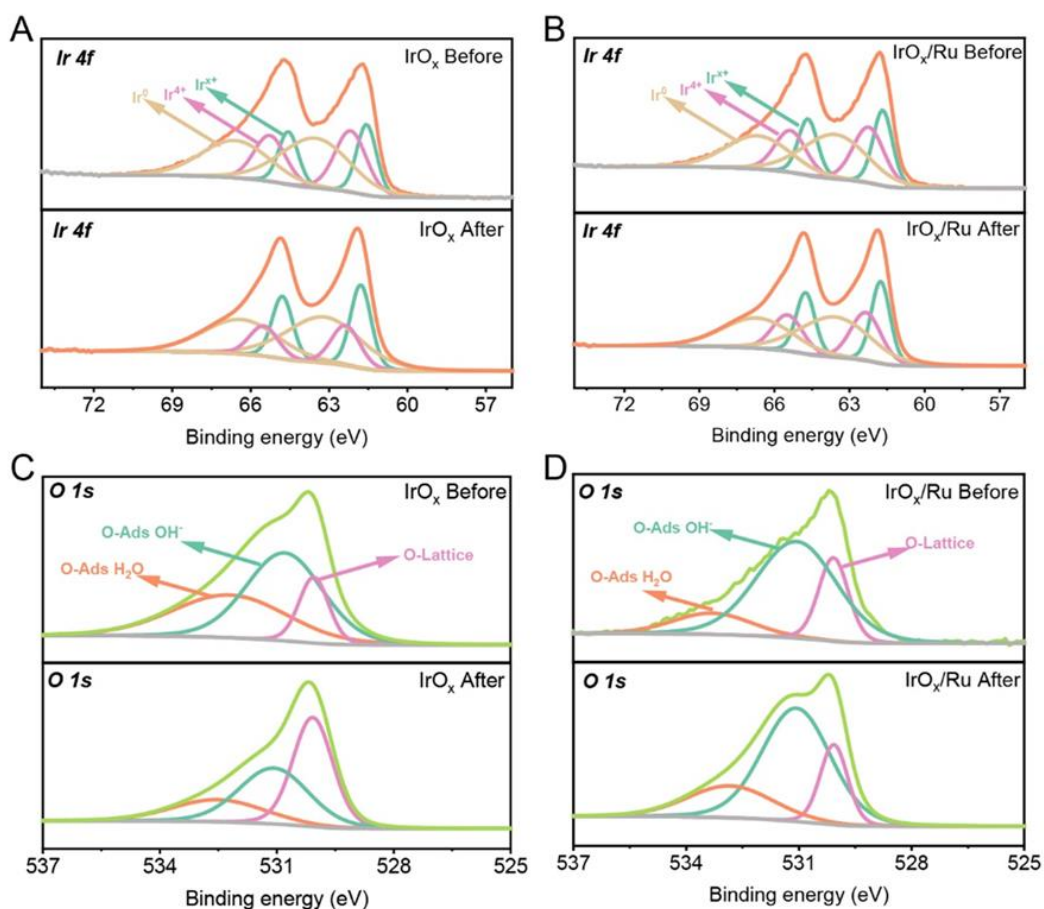


Figure 4.20. AC-HAADF-STEM image of IrO_x(A) before reaction and (B) after 12h 500mA cm⁻² neutral conditions reaction; IrO_x -Ru 0.05mg (C) before reaction and (D) after 12h 500mA cm⁻² neutral conditions reaction (E-G) STEM-EDS mapping of Ir and Ru elements in IrO_x -Ru 0.05mg

X-ray photoelectron spectroscopy (XPS) was measured for both samples before and after the stability test. As shown in **Figure 4.21**, for instability catalysts (IrO_x & Ru0.005mg/IrO_x) Ir⁰ decreased, high valence Ir⁴⁺ and lattice oxygen increased greatly increased after the stability test; for stability catalysts (Ru0.05mg/IrO_x & Ru1mg/IrO_x) Ir⁰ increased, high valence Ir⁴⁺ and lattice oxygen almost unchanged. This agrees well with the electrochemical results, since the high valence Ir and lattice O are responsible for the high activity of IrO_x. The lattice oxygen increase leads to the unstability in IrO_x. In contrast, there is a little decrease of the high valence Ir⁴⁺ from 29% to 24% in IrO_x/Ru catalyst after the stability test, while the lattice oxygen almost unchanged (**Figure 4.21B,D,E and F**). Usually, the ratio of lattice oxygen tends to increase during the stability test and causing activity degradation. But the lattice oxygen ratio

remains almost unchanged after stability test in Ru/IrO_x sample. The STXM oxygen K-edge X-ray absorption spectra are shown in **Figure 4.22**. Oxygen K-edge spectra measures the transition from oxygen 1s orbitals to unoccupied orbitals formed by the interactions between oxygen 2p and metal d orbitals. Thus, these oxygen K-edge spectra reflects the covalency in the metal-oxygen bond. The change of 1,2,3 peaks intensity may reflect a higher Ir-O covalency in Ru/IrO_x after the reaction relative to that in Ru/IrO_x before the reaction (**Figure 4.22**). The higher Ir-O covalency in Ru/IrO_x after the reaction suggests the decreasing amount of unoccupied 3d electrons in Ir. This indicates the valence state of Ir decreases in Ru-0.05mg/IrO_x after the reaction. A lower Ir-O covalency in IrO_x-after than that in IrO_x-before was also observed (**Figure 4.22**). A lower Ir-O covalency in IrO_x after the reaction indicates the increasing amount of unoccupied 3d electrons in Ir. This suggest the valence state of Ir increases in IrO_x after the reaction. This different trend may be relevant to Ru induced difference mechanism in OER vs bare IrO_x. This is consistent with the XPS analysis in **Figure 4.21**. Both Ru/IrO_x and IrO_x shows different oxygen K-edge peak than commercial IrO₂ (**Figure 4.22**). This indicates oxygen vacancies in Ru/IrO_x and IrO_x samples. The Ru extremely low content of 0.1wt%, as determined by the inductively coupled plasma mass spectrometry (ICP-MS) analysis.



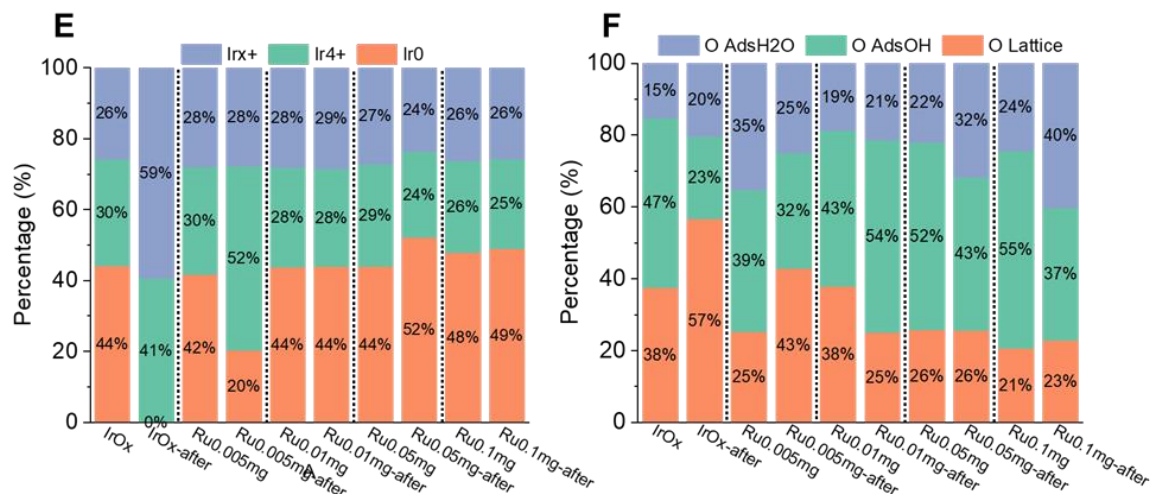


Figure 4.21. (A) Ir 4f XPS results of IrO_x before and after stability test under 500 mA cm⁻²; (B) Ir 4f XPS results of IrO_x/Ru before and after stability test under 500 mA cm⁻²; (C) O 1s XPS results of IrO_x before and after stability test under 500 mA cm⁻²; (D) O1s XPS results of Ru/IrO_x before and after stability test under 500 mA cm⁻² (E-F) XPS percentage results.

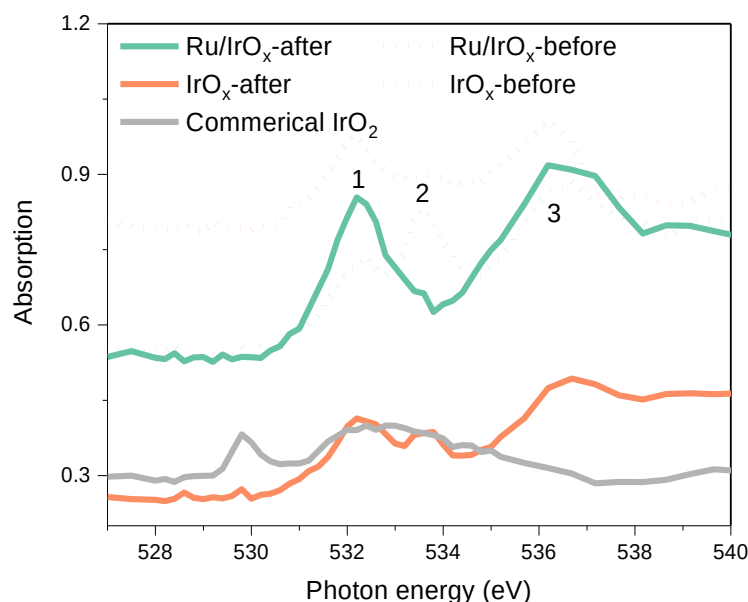


Figure 4.22. STXM oxygen K-edge X-ray absorption spectra of Ru-0.05mg/IrO_x-EG before/after reaction, and IrO_x-EG before/after reaction

To further reveal the coordination structure and bond configurations, investigation of changes in bulk structure and chemical environment of Ir and Ru in IrO_x and Ru-0.05mg/IrO_x, X-ray absorption spectroscopy (XAS) were carried out to provide information on the oxidation state and local structure of Ir and Ru. The X-ray absorption near edge structure (XANES) of Ir L₃-edge and Ru K-edge

region (**Figure 4.23**) and the extended X-ray absorption fine structure (EXAFS) measurements of Ir L₃-edge and Ru K-edge Fourier transformation (FT-EXAFS) are conducted with Ir and Ru foil (**Figure 4.24**). The k -range used in the Fourier transform was chosen in order to exclude the regions of noise at high- k ^[152]. The corresponding R-space profiles (without phase correction) was also analyzed. As shown in **Figure 4.23A**, XANES spectra at Ir L₃-edge of IrO_x and Ru-0.05mg/IrO_x before/after reaction catalysts are compared with the standard Ir foil, illustrating the changes in bulk structure and chemical environment of Ir in different catalysts. The energy of the Ir white-line peak is correlated with the symmetry of the bulk structure's central atom (O coordination); higher symmetry leads to an energy right shift, while lower symmetry causes a shift to the left^[153,154]. STEM results indicate that the Ru/IrO_x electrocatalyst undergoes reconstruction during the OER process, transitioning from 4-fold symmetry to 6-fold symmetry (**Figure 4.20C and D**). Increased symmetry results in a stabilized bulk structure and increased active sites, aligning with the observed rightward shift in the white-line peak for Ru/IrO_x after the reaction. On the other hand, the post-reaction IrO_x structure experiences distortion and decreasing the symmetry, exhibiting an unstable structure (**Figure 4.20A and B**), consistent with the leftward shift in the white-line peak for IrO_x after the reaction.

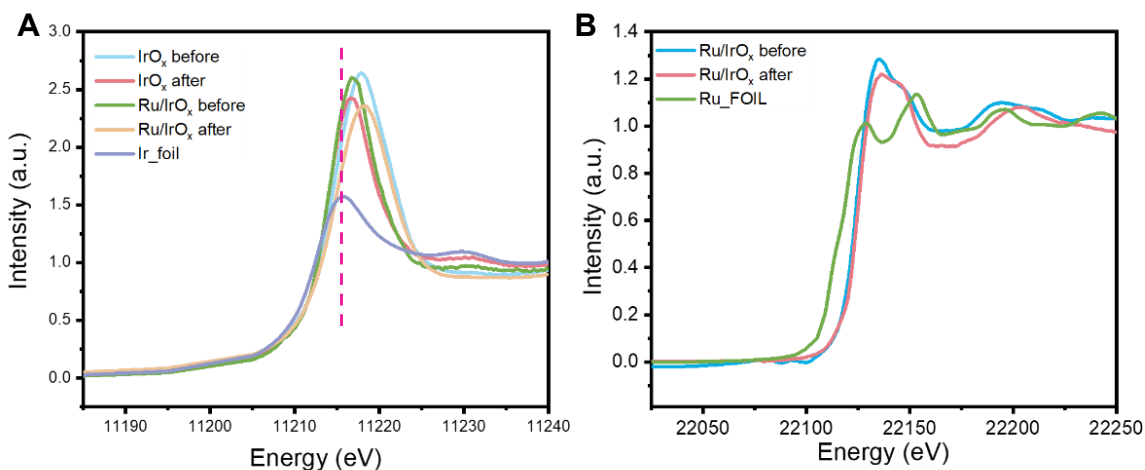


Figure 4.23. (A) Ir L₃-edge XANES of Ir foil reference, IrO_x before/after reaction and Ru/IrO_x before/after reaction; (B) Ru K-edge XANES of Ru foil reference and Ru/IrO_x before/after reaction

The oxidation state of Ir in IrO_x before and after the reaction at 500 mA cm⁻² for 12 hours was examined using EXAFS analysis. The fitting of the Ir L₃-edge was performed to assess the changes in Ir-O bonds and Ir-Ir bonds (**Figure 4.25**). The FT-EXAFS fitting results of the Ir L₃-edge in IrO_x before the reaction reveal a primary peak located at approximately 1.9 Å (**Figure 4.25B, Table 4.1**). This peak exhibits greater vibrational amplitudes compared to Ir foil. This phenomenon is attributed to the reverse scattering

of Ir-O in the first shell.^[155] Additionally, the coordination number of Ir-O is relatively low at 1.85 (**Table 4.1**). These findings provide evidence of the Ir-O structure in IrO_x. While the Ir-Ir bond at ~ 2.7 Å, displaying reduced vibrational amplitudes compared to Ir foil (**Figure 4.25B**), can be attributed to a decrease in Ir-Ir coordination and the relatively small size of nanoparticles.^[156] In comparison with the initial state of IrO_x with Ir-O bond at ~ 1.9 Å (**Figure 4.25B, Table 4.1**), the Ir-O bond in the after 12h 500mA cm⁻² reaction IrO_x exhibits a slight "elongation" to ~ 2.1 Å (**Figure 4.25D, Table 4.1**), accompanied by an increased coordination number of 5.7 (**Table 4.1**). The intensity of the Ir-Ir bond at around 2.7 Å also increases (**Figure 4.25D Table 4.1**), with a coordination number of 9.9 (**Table 4.1**). In comparison with IrO_x samples, the FT-EXAFS fitting results of the Ir L₃-edge for the Ru-0.05mg/IrO_x samples before and after the reaction reveal (**Figure 4.25E-H and Table 4.1**) that the Ir-O bond remains nearly unchanged at ~ 2.0 Å, along with a slight increase of coordination number ~ 5.9 (**Table 4.1**). These findings may indicate that the rise in lattice oxygen contributes to the instability in IrO_x and in agreement with the XPS analysis that for Ru/IrO_x sample, the lattice oxygen almost unchanged, validate the stability of the Ru/IrO_x samples in the context of OER.

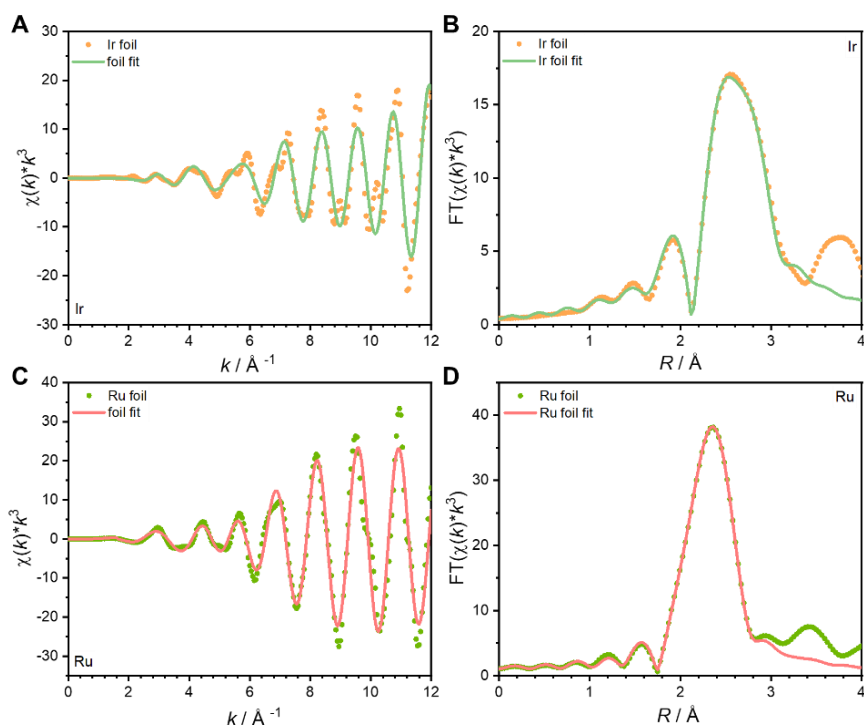


Figure 4.24. EXAFS result of: Ir foil reference L-edge EXAFS (points) and the curvefit (line), shown in k^3 weighted (A) k -space; (B) R -space (Fourier-transform magnitude); Ru foil reference K-edge EXAFS (points) and the curvefit (line), shown in k^3 weighted (C) k -space (D) R -space (Fourier-transform magnitude)

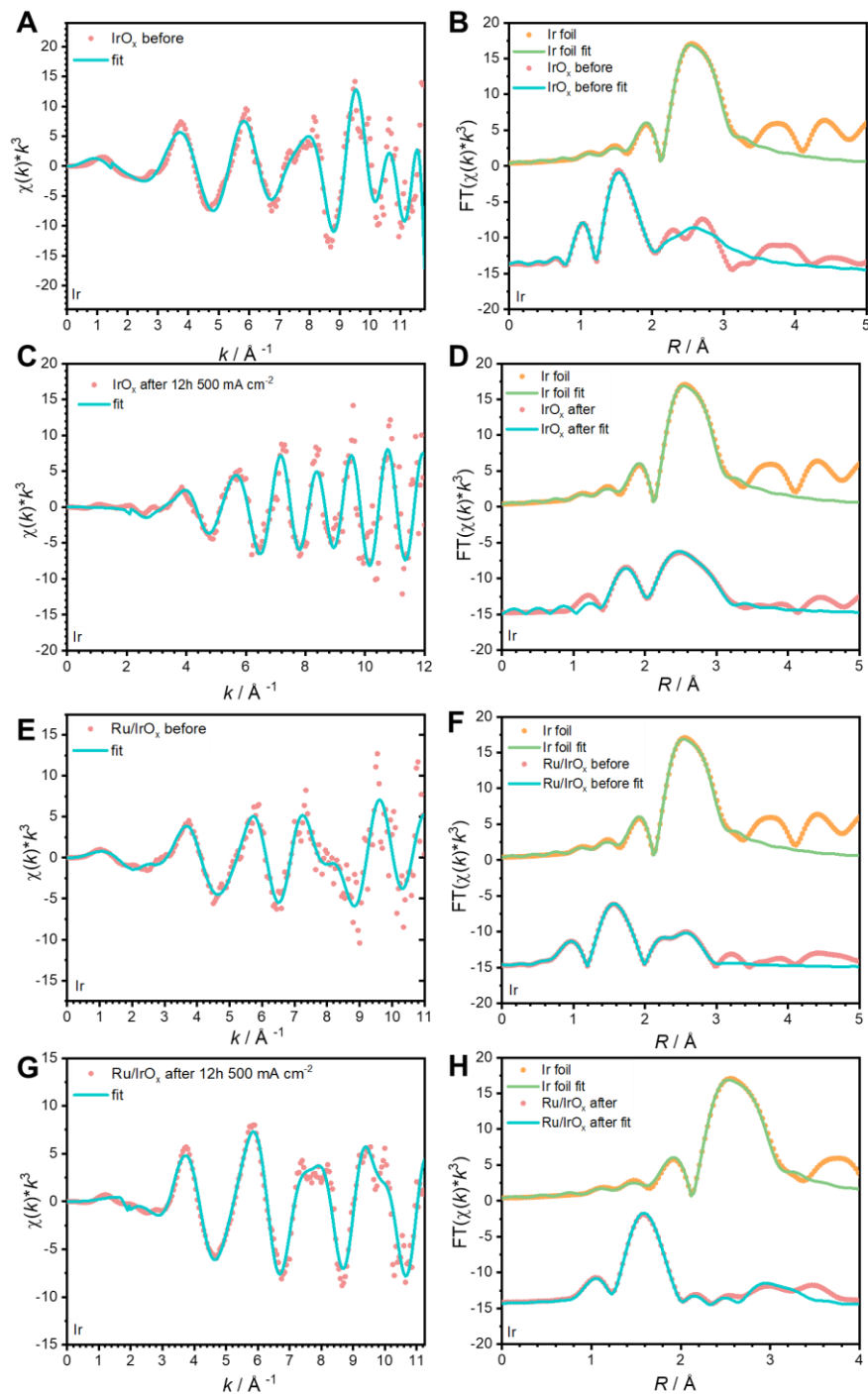


Figure 4.25. EXAFS result of: Ir L-edge EXAFS (points) and the curvefit (line) for (A) IrO_x before reaction (C) IrO_x after reaction (E) Ru/IrO_x before reaction (G) Ru/IrO_x after reaction, shown in k^3 weighted k -space; Ir foil reference and Ir L-edge EXAFS (points) and the curvefit (line) (B) IrO_x before reaction (D) IrO_x after reaction (F) Ru/IrO_x before reaction (H) Ru/IrO_x after reaction, shown in k^3 weighted R -space (Fourier-transform magnitude)

Table 4.1. Fitted EXAFS parameters at the Ir L-edge for IrO_x and Ru-0.05mg/IrO_x

	Shell	CN	R (Å)	$\delta^2 (10^{-3})$	ΔE	R-factor
Ir foil	Ir-Ir	12*	2.71(0.01)	4.2 (0.3)	8.9 (0.7)	0.014
IrO_x before	Ir-O	1.85(0.09)	1.87(0.03)	3.4 (0.2)	8.6 (0.6)	0.019
IrO_x after	Ir-O	5.66(0.12)	2.06(0.04)	5.4 (0.3)	8.2 (0.8)	0.018
	Ir-Ir	9.89(0.09)	2.71(0.05)	5.2 (0.4)	7.7 (0.6)	
Ru/IrO_x before	Ir-O	5.87(0.11)	2.04(0.03)	8.7 (0.5)	6.6 (0.4)	0.005
Ru/IrO_x after	Ir-O	5.95(0.04)	2.00(0.02)	4.0 (0.3)	9.5 (0.3)	0.023

CN: coordination numbers of identical atoms; R: interatomic distance; δ^2 : Debye-Waller factors; ΔE : energy shift. R factor: goodness of fit.

Figure 4.23B shows the Ru K-edge X-ray absorption near-edge structure (XANES) spectra of Ru-0.05mg/IrO_x before/after reaction catalysts and Ru foil for reference. The Ru/IrO_x catalysts show apparent shift to higher energy for the adsorption edge (E_0) and white-line peak intensity compared to that of Ru foil, suggesting that Ru^{x+} remains the dominant oxidation state in Ru/IrO_x catalysts. In addition, the white-line peak of also shows little decreasing intensity after the reaction relative to that in Ru/IrO_x before the reaction, indicates the valence state of Ru decreases. Through EXAFS analysis, the oxidation state of Ru in the Ru-0.05mg/IrO_x samples before and after the 12-hour 500mA cm⁻² reaction was examined (**Figure 4.26**). The evaluation of the Ru-O bonds and Ru-Ir bonds changes was performed by fitting the Ru K-edge. The Fourier transform (FT) of the k³-weighted EXAFS curve for the Ru K-edge of the Ru/IrO_x exhibited distinctive characteristics. Prior to the reaction, the FT-EXAFS curve showed Ru-O (2.15 Å) and Ru-Ir (2.67 Å) coordination (**Figure 4.26B**, **Table 4.2**). The distance between absorber and backscatter atoms for Ru/IrO_x before reaction sample is different from the standard Ru foil sample (**Table 4.2**). The Ru-O (2.15 Å) peak for the Ru/IrO_x before reaction could be corresponded to the formation of Ru–Ir bond^[157], which is shorter than that for Ru–Ru bond in Ru foil (2.67 Å), but longer than Ru–O bond (1.97 Å) in standard RuO₂ oxide^[158]. The proximity between the Ru-Ir (2.65 Å) peak and the Ru-Ru (2.67 Å) reference is attributed to the similar atomic properties of Ir and Ru.^[159] However, after the 12-hour 500mA cm⁻² reaction, the Ru/IrO_x sample displayed a single dominant peak Ru-O at 1.87 Å in the Fourier-transformed EXAFS curve. This could be suggesting the electrocatalyst would suffer irreversible oxidation and reconstruction during the OER process.^[148-151] These suggests that Ru atoms have only one coordination (Ru-O), which contrasts with the Ru-Ru coordination observed in Ru foil at 2.7 Å

(Figure 4.26 and Table 4.2). These findings collectively indicate that Ru in the Ru/IrO_x samples exists in a single-atom form with localized coordination.^[122]

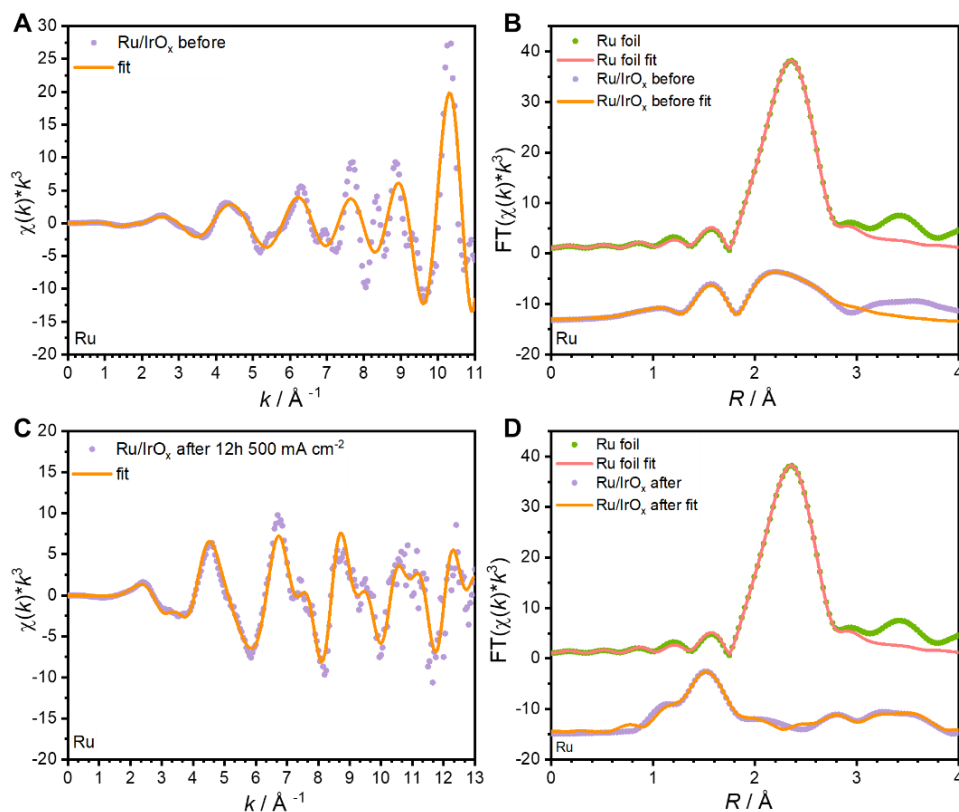


Figure 4.26. EXAFS result of: Ru K-edge EXAFS (points) and the curvefit (line) for (A) Ru/IrO_x before reaction (C) Ru/IrO_x after reaction, shown in k^3 weighted k -space; Ru foil reference and Ru K-edge EXAFS (points) and the curvefit (line) (B) Ru/IrO_x before reaction (D) Ru/IrO_x after reaction, shown in k^3 weighted R -space (Fourier-transform magnitude)

Table 4.2. Fitted EXAFS parameters at the Ru K-edge for Ru-0.05mg/IrO_x

	Shell	CN	R (Å)	$\delta^2 (10^{-3})$	ΔE	R-factor
Ru foil	Ru-Ru	6*	2.67(0.03)	4.3 (0.5)	7.5 (0.3)	0.0006
Ru/IrO_x before	Ru-O	5.85 (0.5)	2.15(0.04)	5.7 (0.6)	9.4 (0.4)	0.0026
	Ru-Ir	6.53 (0.8)	2.65(0.05)	9.4 (0.5)	8.7 (0.7)	
Ru/IrO_x after	Ru-O	1.82 (0.4)	1.87(0.04)	4.9 (0.3)	5.6 (0.7)	0.0098

CN: coordination numbers of identical atoms; R: interatomic distance; δ^2 : Debye-Waller factors; ΔE : energy shift. *R* factor: goodness of fit.

4.4 Conclusion

In summary, we demonstrate a novel design of efficient OER catalysts in neutral electrolyte by incorporating Ru signal atom into IrO_x, and the resultant Ru/IrO_x catalyst exhibits overpotentials of only 2.5V and 2.8V for current densities of 200 mA cm⁻² and 500 mA cm⁻², respectively, and at 200 mA cm⁻² maintained large than 480 hours. Which confirm excellent OER activity and remarkable stability under neutral conditions and industrial-scale current densities. Our research results would provide a new understanding for the OER catalysts in KHCO₃ electrolyte under large industrial current density. To investigate the mechanism, it's of particular importance to investigate the oxygen structure evolution process in the catalyst during OER. These mechanisms require further characterization and analysis.

4.5 Acknowledgement

I want to thank Dr. Cheng Du for providing valuable suggestions during my research. I'm willing to appreciate Dr. Xiyang Wang for EXAFS fitting, I also want to thank Wei Wei, Joel Philip Mills for experiment build up and Baizhou Zhang for SEM test.

Chapter 5 Conclusions and Future Work

5.1 Conclusions

With the growth of the global population, rapid urbanization, and the expansion of industrial production, the demand for water resources is continuously increasing. Excessive water resource development and irrational water usage practices have led to unsustainable utilization of water resources. Extensive water resources are being overexploited, resulting in declining groundwater levels, reduced water volumes in lakes and rivers, and even their drying up. This situation has brought about significant impacts on both the ecological environment and socioeconomic development. Therefore, the treatment of water pollution and the recycling of water resources are of paramount importance.

Over the past few decades, with the development of industrial and agricultural production, varying degrees of nitrogen pollution have been observed in both rural and urban groundwater. Excessive use of agricultural fertilizers, particularly nitrogen-based fertilizers, and improper disposal of animal waste have led to an increase in nitrate nitrogen content in surface water and groundwater in many parts of the world. This phenomenon poses a significant threat to the quality and safety of the unsaturated zone soil and groundwater, resulting in an increasingly severe nitrate pollution problem. Consequently, conducting research on approaches to control soil nitrates is of utmost importance. Such research aims to decrease the nitrate content in crops and vegetables, which is crucial for producing environmentally-friendly food products with reduced nitrate levels.

The Oxygen Evolution Reaction (OER) is a process where, in the presence of a catalyst, water is oxidized to oxygen gas using electrical energy. It serves as a crucial half-reaction in water electrolysis and also plays a significant role in various energy conversion and storage technologies. For instance, it is involved in CO₂ electrocatalytic reduction, metal-air batteries, fuel cells, and more. The multi-electron transfer process and sluggish reaction kinetics result in elevated reaction overpotentials, which constitute a significant contributor to the overall energy consumption. Efficient OER catalysts are a prerequisite for driving this technology towards industrialization.

To tackle these questions, this thesis focuses on studying the electrocatalytic processes of water electrolysis and nitrate reduction. It primarily aims to develop cost-effective and efficient catalysts and electrodes while comprehending the relationship between catalyst structures and electrode structures with catalytic activity. The main conclusions obtained are as follows:

(1) A novel PdCu single-atom alloy (SAA) was synthesized through a simple galvanic replacement reaction. This SAA exhibited an exceptionally high faradaic efficiency (FE) of 97.1% and achieved a

remarkable NH_3 production rate of $15.4 \mu\text{mol cm}^{-2} \text{ h}^{-1}$ in the NO_3^- RR under mild neutral conditions. Through single crystal experiments and density functional theory (DFT) calculations, it was elucidated that the atomic Pd sites located on Cu (100) facets served as the primary active sites. Notably, the Pd sites exhibited facet-specific behavior. Specifically, the introduction of single-atom Pd resulted in a transition from the rate-determining step (RDS) of $*\text{NOO} \rightarrow *\text{NOOH}$ with an energy barrier of 0.39 eV on Cu to $*\text{NOH} \rightarrow *\text{NHOH}$ with a significantly lower energy barrier of 0.10 eV on the PdCu SAA. This research not only introduces an efficient catalyst for NH_3 production via nitrate reduction in mild neutral conditions but also highlights the potential application of single-atom alloys in selective electrocatalytic processes like NO_3^- RR, aiding nitrate recovery from wastewater and other relevant electrocatalytic applications.

(2) Introduces an innovative approach to designing efficient oxygen evolution reaction (OER) catalysts in a neutral electrolyte by incorporating a Ru signal atom into IrO_x . The resulting Ru/IrO_x catalyst showcases impressive performance, with remarkably low overpotentials of just 2.5V and 2.8V for current densities of 200 mA cm^{-2} and 500 mA cm^{-2} , respectively. Moreover, this remarkable performance is maintained for an extensive duration of 480 hours at 200 mA cm^{-2} , attesting to the exceptional OER activity and stability of the Ru/IrO_x catalyst under both neutral conditions and industrial-scale current densities. These findings contribute to a fresh perspective on OER catalysts in KHCO_3 electrolyte operating at large industrial current densities. For a comprehensive understanding of the mechanism, it is of paramount importance to delve into the oxygen structure evolution process within the catalyst during the OER process. These intricate mechanisms warrant further investigation through comprehensive characterization and in-depth analysis.

5.2 Future Work

As a crucial component of electrocatalytic devices, catalytic electrodes play a pivotal role in determining the efficiency of electrocatalytic processes. The development of high-performance catalysts and electrodes has become a central issue in current research on energy conversion technologies. However, the conventional catalysts predominantly employed in electrocatalytic processes are still noble metals or noble metal oxides, which are characterized by their high cost, sluggish kinetic processes, and issues with catalytic activity stability. These factors severely impede the rapid advancement of the field of electrocatalysis. Therefore, in order to address the existing challenges in electrocatalytic development, it is imperative to investigate the following questions: How can the activity of current catalysts be improved? How can the cost of catalysts be reduced? How can electrodes be designed to better serve electrocatalytic processes? In view of the above problems, the future will be based on the two electrocatalytic processes of electrolytic water and carbon dioxide reduction to do related research, committed to the development

of cheap and efficient catalysts and electrodes, understanding the catalyst structure and the relationship between the electrode structure and catalytic activity, in order to achieve the industrial application of electrocatalytic CO₂ reduction as the goal to further improve the catalytic activity of the catalyst.

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