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DEVELOPPEMENT D'INTERFACES ELECTRO- PLASMONIQUES INNOVANTES - APPLICATION DANS DES REACTIONS D'OXYDOREDUCTION

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ABSTRACT:

Plasmon-driven chemical transformations have become promising approaches for enhancing sluggish electrocatalytic reactions such as the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). The complex four-electron transfer process taking place in ORR has been recognized as barrier for the construction of high-quality fuel cells and metal-air batteries. The same is true for the oxidation of water. Any improvement in the performance of the ORR and OER kinetics is highly sought after.

In this thesis, two different strategies based on the generation of plasmon-induced hot electrons were investigated. In the case of ORR, the intertwined plasmon-catalytic-electrochemical properties of a nanoporated gold thin film electrodes allowed to significantly enhance the ORR under alkaline conditions. Irradiation with light at 980 nm and 2 W cm^{-2} resulted in maximal current densities of $j = -6.0 \text{ A cm}^{-2}$ at 0.95 V vs. RHE, under hydrodynamic conditions, comparable to that of commercial Pt/C (40 wt. %) catalysts, with good long-term stability. The wavelength-dependent electrochemical reduction confirmed that the hot carriers formed during plasmon decay are responsible for the improved electrocatalytic performance. In the case of OER, a gold electrode modified with plasmonic nanohybrids based on gold nanoparticle decorated Cu_2O nanocrystals efficiently enhanced the transformation of water to oxygen. It could be shown that the morphology of Cu_2O nanocrystals has a strong influence on the electrocatalytic behavior for OER in basic medium, with cubic Cu_2O being more efficient for plasmon-enhanced electrocatalysis than octahedral Cu_2O : 10 mAcm^{-2} with a Tafel constant 97 mVdec^{-1} were achieved at overpotential of only 200 mV

Keys words: Localized surface plasmon resonance (LSPR), Cu_2O , gold nanoporated, ORR, OER.

RESUME:

Les transformations chimiques assistées par plasmon sont devenues des approches prometteuses pour l'amélioration des réactions électrocatalytiques lentes telles que la réaction de réduction de l'oxygène (ORR) et la réaction d'évolution de l'oxygène (OER). La construction des piles à combustible et des batteries métal-air de hautes qualités, nécessitent un processus de transfert à quatre électrons ($4 e^-$), ce dernier est reconnu par sa complexité ce qui le rend comme un obstacle pour L'ORR. Ceci s'applique de même à l'oxydation de l'eau. Ainsi, l'amélioration des performances catalytiques et cinétiques de l'ORR et l'OER est très recherchée.

Lors de ce travail de thèse, deux différentes stratégies basées sur la génération d'électrons chauds induits par plasmon ont été envisagées pour améliorer les processus électrocatalytiques. La combinaison des propriétés électrochimiques, plasmoniques et catalytiques d'une électrode d'or nanoperforées a permis d'améliorer considérablement la réaction de réduction de l'oxygène (ORR) au milieu basique. L'irradiation par la lumière à 980 nm et $2 W cm^{-2}$ conduit à une densité de courant maximale de $j = -6,0 A cm^{-2}$ à 0,95 V (par rapport au RHE), dans des conditions hydrodynamiques, comparable à ceux du catalyseur commercial Pt/C (40 wt. %), avec une bonne stabilité. L'influence de la longueur d'onde sur cette réaction électrochimique confirme la contribution de l'effet plasmonique dans l'activité électrocatalytiques.

Dans le cas de l'OER, une électrode en or modifiée par des nano-hybrides plasmoniques, à base de nanocristaux de Cu_2O décorés de nanoparticules d'or, a montré son efficacité dans la transformation de l'eau en oxygène, le comportement électrocatalytique de cette réaction d'oxydation est influencé par la morphologie des nanocristaux de Cu_2O . En effet les Cu_2O cubiques sont plus efficaces que les Cu_2O octaédriques pour l'électrocatalyse plasmonique. Dans les meilleures conditions testées une densité du courant $10 mA cm^{-2}$ avec une constante de Tafel de $97 mV dec^{-1}$ ont été obtenus à une surtension de seulement 200 mV ont été obtenue pour la forme cubique.

Mots clés: Plasmon de surface localisé (LSPR), Les nanoperforées d'or, Cu_2O , ORR, OER.

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This thesis, I dedicated to the memory of my dear grandmother

"NAIT Megdoud Zouina"

Tamazouzt
NAIT SAADA

ABBREVIATIONS

E _a	Activation Energy
AFC	Alkaline Fuel Cell
AWE	Alkaline Water Electrolysis
CB	Conduction Band
CV	Cyclic Voltammetry
EDX	Energy-Dispersive X-Ray Spectroscopy
EASA	Electrochemical Active Surface Area
GC	Glassy Carbon
Au NHs	Gold nanoholes electrode
HAADF-STEM	High-Angle Annular Dark Field Scanning TEM
HRTEM	High Resolution Transmission Electron Microscopy
HOMO	Highest Occupied Molecule Orbital
HER	Hydrogen Evolution Reaction
ICP-OES	Inductively Coupled Plasmon Optical Emission Spectroscopy
ITO	Indium Tin Oxide
K/ Au NHs	Kapton/ Gold Nanoholes
LSV	Linear Sweep Voltammetry
LOMO	Lowest Un-Occupied Molecular Orbital
LSPR	Localized Surface Plasmon Resonance
MOR	Methanol Oxidation Reaction
M-N	Metal Doped Nitrogen
M-N-C	Metal Nitrogen Carbon Support
M/C	Metal Carbon Support
NPs	Nanoparticles
NIR	Near Infrared
ORR	Oxygen Reduction reaction
OER	Oxygen Evolution Reaction
PEM	Polymer Electrolyte Membrane
Pt/C	Platinum /Carbon

PBS	Phosphate Buffered Saline
RDE	Rotating Disk Electrode
RHE	Reversible Hydrogen Electrode
SEM	Scanning Electron Microscopy
SERS	Surface Enhanced Raman Spectroscopy
TEM	Transmission Electron Microscopy
UV/ Vis	Ultraviolet-Visible Spectroscopy
VB	Valence Band
XRD	X-Ray Diffraction
XPS	X-Ray Photoelectron Spectroscopy

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OBJECTIVES:

In this work thesis, we want to show the role of plasmonic proprieties in the improvement of electrocatalytic reactions. We chose to study two reactions, which are Oxygen reduction reaction and oxygen evolution reaction known by their low kinetics and multi electron process. The interest for this two reaction reside in their important role in the construction of fuel cells and metal-Air batteries. The main object of this thesis is searching for low cost catalyst with plasmonic effect capable of improving catalytic activities of some reactions, especially ORR and OER .

The chapter I of this thesis was devoted to the state of the art and the knowledge of the works already done. We described information about: Oxygen reduction reaction, oxygen evolution, fuel cell, hydrogen evolution, Localized surface plasmon resonance, plasmon enhanced electrocatalysis and LSPR enhanced ORR and OER. Then come the experimental part in the chapter II and III.

The chapter II, is dedicated to the fabrication and characterization of plasmonic Au NPs Au electrode and it's application to oxygen reduction reaction (ORR).

The chapter III, include the preparation and characterization of hybrid nanostructures Cu₂O and Cu₂O-Au electrode with different shape cubic and octahedral application to water oxidation reaction (OER).

CHAPTER I: STATE OF THE ART

1.1. GENERAL INTRODUCTION TO ELECTROCATALYSIS

Electrocatalysis represent the study of electrode reactions in which the kinetics depend strongly on the physico-chemical properties of electrochemical interfaces, encompassing both the nature of electrode materials and the rarely discussed structure of the double layer.¹ The purpose of integrating catalyst onto electrochemical reactions is to provide alternate reaction pathways with a lower activation energy of any electrochemical rate limiting steps. Electrocatalysis is considered as a key component in the development of a sustainable energy economy, playing vital roles in the clean generation and consumption of fuels and in secondary battery charge and discharge cycles (**Figure 1.1**). Reactions such as oxygen reduction reaction (ORR), oxygen evolution reaction (OER), hydrogen evolution reaction (HER), CO₂ reduction reaction (CO₂RR), carbon fuels oxidation reaction, nitrogen reduction reaction (NRR) etc. Could be lately improve due to electrocatalytic considerations due to either enhancement of the rate or current density of the redox reaction under consideration at a given overpotential, or a reduction in the overpotential for the reactions. However, the extensive scale application of electrocatalysis is constrained by the lack of suitable catalysts. Ideal catalysts should meet demand of high activity, long durability, and low cost.

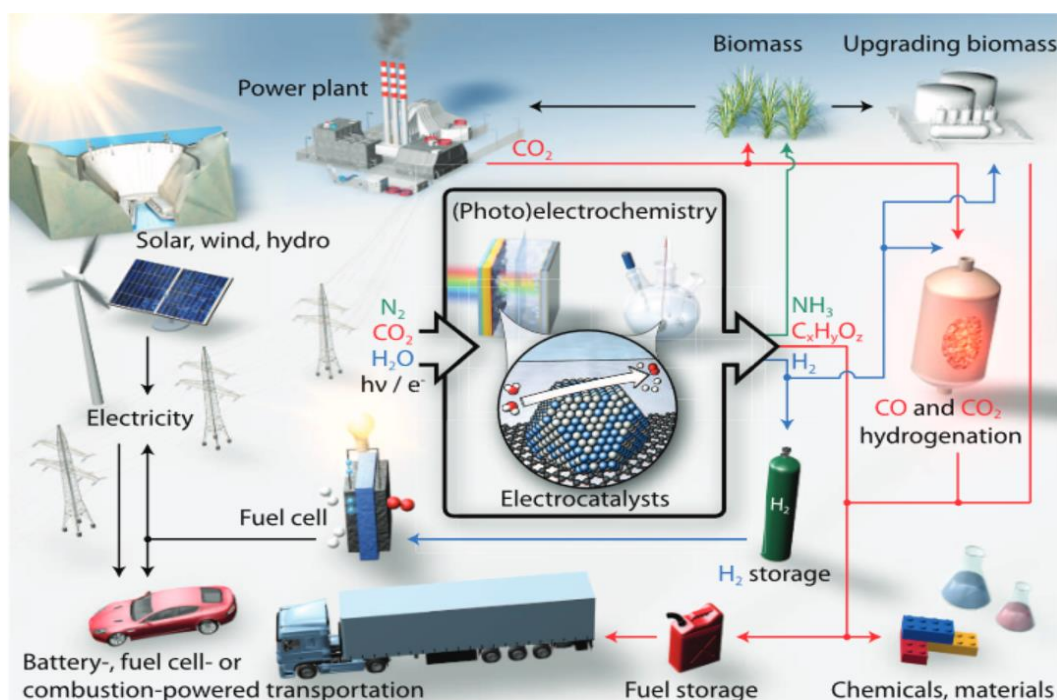


Figure 1.1. Schematic of a sustainable energy landscape based on electrocatalysis.²

The oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are ideal examples for the importance of electrocatalysis due to possible multielectron processes and sluggish redox kinetics. Noble metal-based electrocatalyst such as Pt, Ru, Ir, Rh, Pd and Au are considered the most powerful electrode materials for both reactions due to their high activity and durability. However, high price and low natural abundance limits their utilization. Many studies have been reported to settle these obstructions and various alternative catalysts are introduced. The different approaches are based on

1. **Reducing the amount of Pt by changing size/morphology**, when the Pt is Cut into NPs the surface ration become higher, since formerly internal atoms are introduced to surfaces where the catalysis reaction occurs. In addition, the small particles are more likely to possess dense, low-coordinated species such as steps, edges, and kinks, which are more capable of achieving high catalytic performance. In this concept, Liang et al. prepared Pt nanowires witch exhibited both higher mass activity 0.016 A/mg_{Pt} and better durability than the bulk Pt catalyst and commercial Pt/C.³ Generally, the size effect was attributed to the change on the morphology, because the relative amount of surface atoms in different crystal facets changes with size, the small particles should behave like a (110) single crystal since they feature more edge and corner sites. While, the large particles should similarities to (111) and (100).

2. **Integration of other catalytic elements being less expensive and more abundant,** adding second, even third metals to Pt catalyst to generate nanocrystals with structure in form alloys or core shells. The combination of proprieties of each distinct metal and appearance of new proprieties due to energetic effect between the two metals usually enhanced the catalytic activity. The transition metal such as Co, Fe, Ni and others are the most used for this approach. For example, Wu et al. prepared Pt₃Ni truncated-octahedral nano catalysts, these structures display 4 higher ORR mass activity than Pt/C catalyst and normal octahedral Pt₃Ni.⁴ In addition, doping Pt with carbon material like carbon black, graphene or carbon nanotube (CNT), these support materials provides a high surface area, excellent conductivity, chemical stability and corrosion resistivity. On the other hand, completely replacing Pt with non-precious metal such as metal oxide, carbon based non noble metal composite or N doped carbon material, show better activity. Fe–Co–P alloy fabricated by Kewei et al. exhibits excellent OER activity with a specific current density of 10 mA/cm² being achieved at an overpotential as low as 252 mV. The current density at 1.5 V (vs reversible hydrogen electrode) of the Fe–Co–P catalyst is 30.7 mA/cm², 100 times more active than that of FeP, and 45 times more active than that of CoP.⁵ Huang et al. fabricated Mo-Pt₃Ni/C shows the best ORR performance, with a specific activity of 10.3 mA/cm² and mass activity of 6.98 A/mg_{Pt}, which are 81- and 73-fold enhancements compared with the commercial Pt/C catalyst (0.127 mA/cm² and 0.096 A/mg_{Pt}).⁶

Photocatalysis based on the use of semiconductors which absorb photons and create electrons and holes (**Figure 1.2**) in the matrix is considered as one promising approaches to initiate ORR and OER. The electrons arriving at the surface of semiconductor particles can be transferred to various organic or inorganic species resulting in their reduction. The holes can play the role of oxidizer by subtracting the electrons from the species localized on the particle surface. One of the most common photocatalysts is titanium dioxide (TiO₂) due to its high activity, strong oxidation capability, chemical stability and low cost. Using pure TiO₂ for ORR proceeds by a series of sequential single-electron reduction reactions and led to the formation of various reactive oxygen species such O₂⁻, OH[·], and H₂O₂ which are able to strongly influence the reaction mechanism and make the 4 e⁻ process very difficult.⁷ In general, most photocatalysts are characterized by low photocatalytic efficiency and the lack of satisfactory visible-light-

responsive photocatalytic materials, together with problem of electron holes recombination has attracted attention for other considerations.

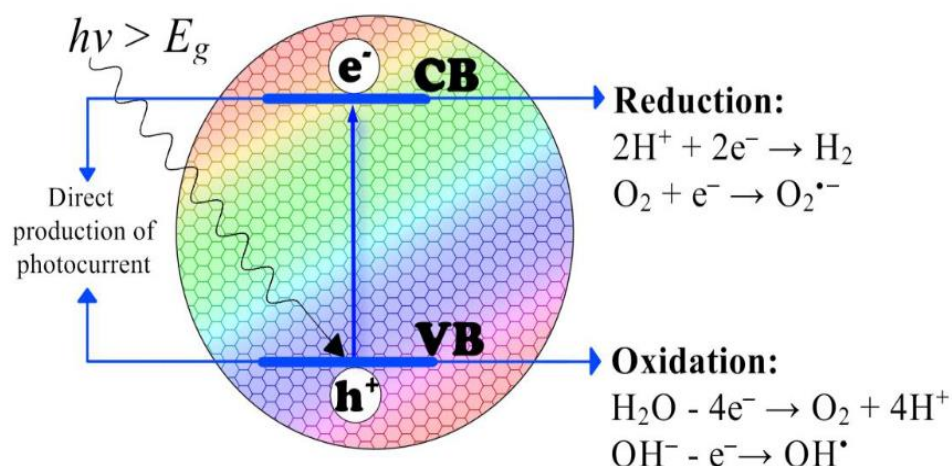


Figure 1.2. Schematic presentation of photocatalytic action on a semiconductor with the formation of electrons and holes in the conduction band (CB) and valence band (VB) respectively. The use of photogenerated electrons will be used for reduction processes, while the formed holes can be used in oxidation processes.

The use of metallic nanoparticles with a diameter smaller than the wavelength of light supporting coherent collective oscillations of delocalized electrons in response to electromagnetic radiation, known as localized surface plasmons (LSPR) enhancement, have become a promising way for improving electrocatalytic processes (**Figure 1.3a-b**). Chen and collaborators proposed a gold (Au) nanofiber based electrode for plasmon-induced methanol and ethanol oxidation, this structure demonstrate higher performance and stability and enhanced electrocatalysis 61% and 107% fold, respectively (**Figure 1.3a**).⁸

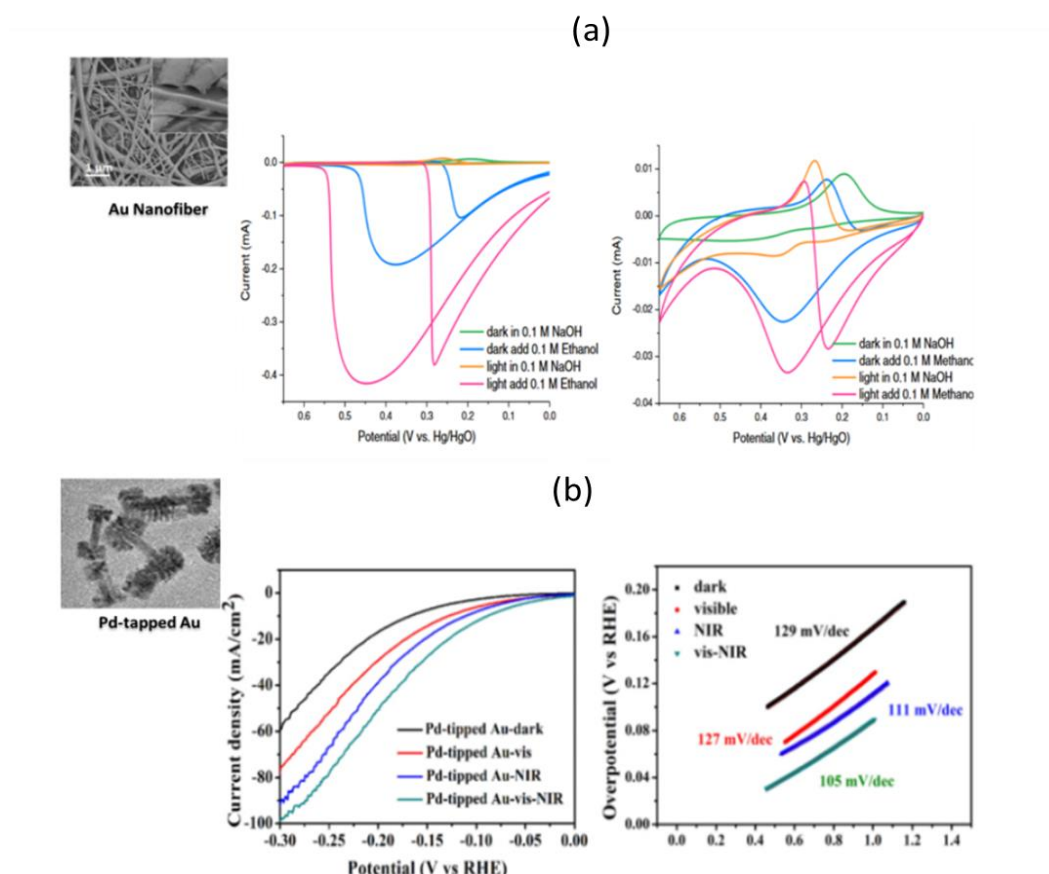


Figure 1.3. (a) SEM image of Au nanofiber plasmonic electrode, cyclic voltammograms of Au nanofiber electrode under light or in the dark recorded in NaOH (0.1M) in the presence or absence of methanol (0.1 M), cyclic voltammograms of Au nanofiber electrode under light or in the dark recorded in NaOH (0.1M) in the presence or absence of ethanol (0.1 M).⁸ (b) TEM images of Pd-tipped Au NRs, HER polarization curves of the Pd-tipped Au NRs electrodes under dark, visible light, near-infrared light, and Vis-NIR light irradiation with a scan rate of 5 mVs⁻¹; Tafel plot of the Pd-tipped Au NRs derived from the HER polarization curves.⁹

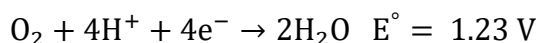
In addition, bimetallic or metal-semiconductor nanocomposites increase the performance of a catalytic system. For example, Wei et al. proposed plasmonic bimetallic structures based on Pd-tipped Au which exhibited larger electrochemically active surface area and more active sites, possessed promising hydrogen evolution performance with lower onset overpotential, higher exchange current density, and good stability in comparison with the fully covered ones under the vis-NIR light irradiation (**Figure 1.3b**).⁹ In the case of metal semi-conductor nanocomposite Xu et al. decorated a highly ordered TiO₂ nanotube arrays with Au NPs (1.9 at.%) for enhanced ethanol oxidation.

The LSPR properties of the nanostructures, mostly gold, and silver nanoparticles, are strongly dependent on morphology, size, shape, composition. Recently, coupling LSPRs effect to redox reactions shows an improvement in catalytic performance. However, few works have been done in this context, searching for new plasmonic materials is still current.

1.2. Oxygen reduction reaction (ORR)

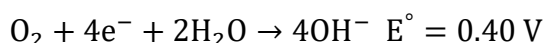
The oxygen reduction reaction (ORR) is one of the large studied topics in the fields of electrochemistry and catalysis due to its importance for electrochemical energy conversion and storage devices (fuel cells and metal-air batteries).¹⁰⁻¹² ORR is a multielectron process where the cathodic reduction reaction that can occur either by a four-electron ‘direct pathway’, where an oxygen molecule adsorbs onto the catalyst surface and gets reduced to water or by a two-electron pathway, which involves H_2O_2 as the intermediate, called a ‘peroxide pathway’,¹³ which can be further reduced to water or can chemically decompose to form water and oxygen. ORR pathways depend on the type of electro catalyst and the experimental conditions. The direct $4e^-$ oxygen reduction path is considered much more efficient than the $2e^-$ reduction pathway. The direct four electron pathway is written as

In acid medium:¹⁴



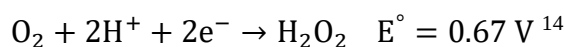
Eq 1.2.1

In basic medium:¹⁵



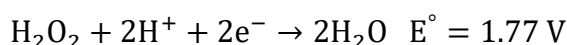
Eq 1.2.2

While the peroxidase pathway is as follow¹⁴

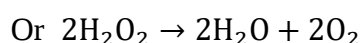


Eq 1.2.3

In acid solution, the peroxidase can further reduced or decomposed, according to this equation bellow¹⁴

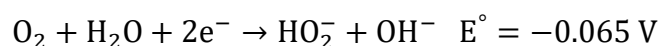


Eq 1.2.4



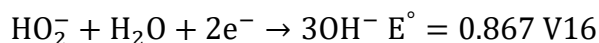
Eq 1.2.5

In basic condition the reaction is¹⁵



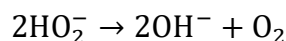
Eq 1.2.6

Followed by either further reduction¹⁵



Eq 1.2.7

Or disproportionation



Eq 1.2.8

The ORR consists of several adsorption / desorption and reaction phases involving oxygen-containing species such as O, OH, O₂⁻, HO₂⁻ and H₂O.¹⁷ The sluggish kinetics of the ORR and the complex four electron transfer process have been recognized as barriers to the construction of high performing fuel cells and metal air batteries.¹⁸ Indeed, oxygen reduction via a four-electron pathway competes with the production of undesired hydrogen peroxide in a two-electron transfer pathway.

The rotating disc electrode RDE method is the best tool used to evaluate the activity of the oxygen reduction reaction and to determine the extent of these reactions by applying the Koutecky-Levich equation $\frac{1}{j_{Lim}} = \frac{1}{j_k} + \frac{1}{B\omega^{\frac{1}{2}}}$. Yongye and co-workers used rotating-disk electrode (RDE) measurements to reveal the ORR kinetics of Co₃O₄/graphene (Co₃O₄/rmGO) and Co₃O₄/N-doped graphene (Co₃O₄/N-rmGO) hybrid catalysts in 0.1 MKOH, from the slopes of Koutecky–Levich plots the electron transfer number was 3.9 and 4, respectively (**Figure 1.4a-b**), suggesting that the two hybrid catalysts favors a 4e- oxygen reduction process.¹⁹

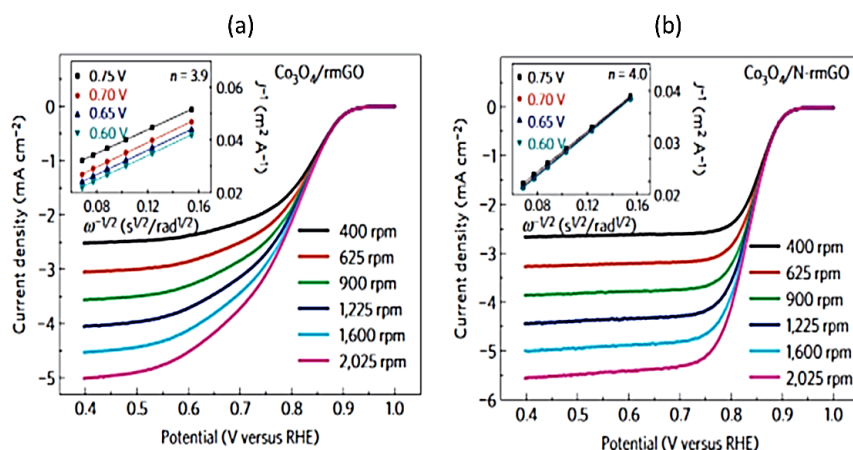


Figure 1.4. (a) Rotating-disk voltammograms of $\text{Co}_3\text{O}_4/\text{rmGO}$ hybrid (loading $\sim 0.1 \text{ mg cm}^{-2}$), (b) $\text{Co}_3\text{O}_4/\text{N-rmGO}$ hybrid (loading $\sim 0.1 \text{ mg cm}^{-2}$) in O_2 -saturated 0.1 M KOH with a sweep rate of 5 mV s^{-1} at the different rotation rates indicated. The insets in (a) and (b) show corresponding Koutecky–Levich plots (J^{-1} versus $\omega^{-0.5}$) at different potentials.¹⁹

Any improvements in suppressing the undesired intermediate H_2O_2 along with the improvement in the performance of the ORR kinetics are highly sought after.¹¹ When H_2O_2 is formed (**Figure 1.5**) $\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2\text{O}_2$, it can be re-oxidized to oxygen or reduced to water $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \leftrightarrow 2\text{H}_2\text{O}$. In addition, it can also be transported to the bulk or disproportionate into water and oxygen in a non-electrochemical reaction $\text{H}_2\text{O}_2 \leftrightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O}$.

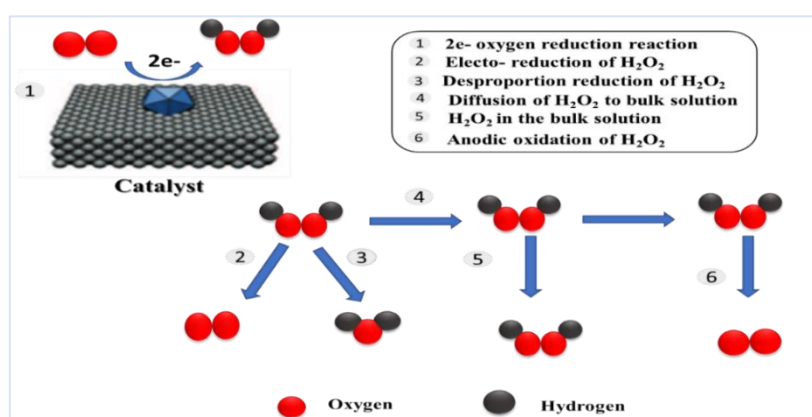


Figure 1.5. Oxygen reduction reaction 2e- pathway.

The ORR reaction begins with the adsorption of O_2 on the catalyst surface. Three adsorption modes for oxygen on the surface of the catalyst exist, The Griffiths model (single site) and Bridge model (dual site) are suitable for 4 electron reactions, and the Pauling model (single site) is suitable for 2-electron reactions (**Figure 1.6**). Then comes the O_2 activation, which

usually includes a proton and electron transfer to form adsorbed OOH before the O–O bond is broken, the catalyst must therefore reasonably be able to stabilize OOH. After dissociation, adsorbed O and OH are formed on the surface of the catalyst, and the catalyst must not bind these species too strongly to ensure H₂O desorption is fast.²⁰

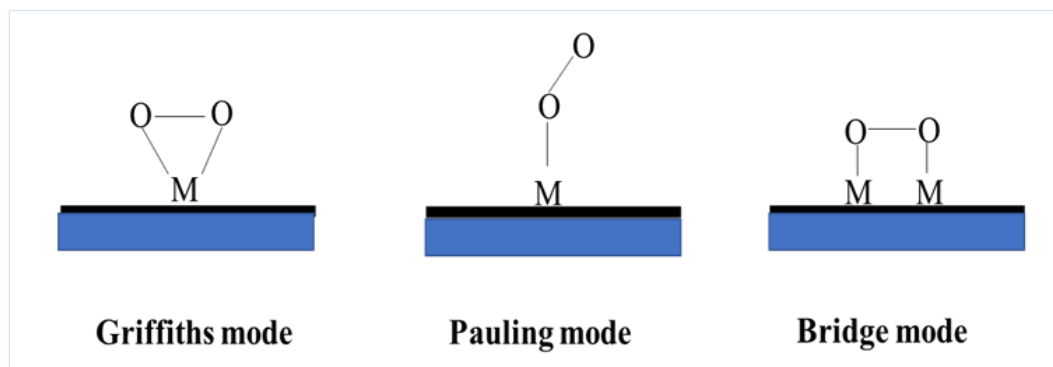


Figure 1.6. Three adsorption modes for oxygen on the surface of the catalyst.

ORR reaction has been widely studied at many electrode materials in different media (acidic and basic).²¹⁻²² However, alkaline media offer a less corrosive environment to the catalysts, and the ORR kinetics are faster in alkaline media than in acidic media.²³ In ORR it is desirable to use catalysts with an overpotential close to zero. High overpotential, resulting in low performance.

To date, the state-of-art catalysts for ORR consist of platinum-based materials (Pt).²⁰ A variety of Pt based nanostructures have been reported to exhibit significantly enhanced ORR (**Table 1.1**). At the beginning, Pt pure was used as a catalyst, with controlling his shape and size. It was shown that the ORR activity of Pt depends on the facet arrangement. For example, in H₂SO₄ solution, this activity increases in the order (111) < (100). However, when it is tested in a HClO₄ solution, the ORR activity increases in the order of Pt (100) << Pt (110) ≈ Pt (111).²⁴ These studies indicate that a Pt NP catalyst with a cubic shape are more active for ORR in H₂SO₄ and those with an octahedral shape are ideal for ORR in HClO₄. Concerning the size, the catalytic performance is enhanced with size reducing^{11, 25} since the small NPs have a large surface ration. The high cost of Pt, also increasing the concentration Pt leads to its agglomeration, therefore, a decrease in the surface area, hindering the catalytic performance. These limits called to reduce the Pt amount. For that, a number of strategies have been reported and several nanostructures were introduced.

Table 1.1. ORR activity of Pt based catalysts.

Catalyst	E _{onset} (vs. RHE) V	Tafel slope mV/decade	Electrolyte	Ref
Pt vulcan	0.93 0.79	60 81	0.1M NaOH	26
Pt 20 wt% C	1.07 0.91	57 120	0.1M NaOH	12
Pt-Fe/CNFs	0.99	62	0.1M NaOH	27
CuPt/NC	0.90	213	0.1M HClO ₄	28
Pt nanodendrites	0.86	52	0.1M HClO ₄	29
Pt /C-S	0.90	67	0.1M HClO ₄	30
Pt/CaMnO₃	0.95 0.81	65 109	0.1M NaOH	31
Pt / ITO	0.96 0.82	69 129	0.1 M NaOH	12
PtCu/C	1.05 0.97	51 102	0.1M NaOH	32
Ru@Co@Pt-skin	0.98	79	0.1M NaOH	33
Pt/NG-TiON	0.91	63	0.5H ₂ SO ₄	34
NiPdPt/C	0.73	69	0.1M HClO ₄	35
Ag@Pt@Ag	0.89 0.69	80 109	0.1 M NaOH	12

Alloying Pt with two or three 3d bloc metals are considered the best approach. A wide variety of metals have been used as the alloying components, including (M= Pd, ³⁶Co, ³⁷ Ni, and Cr,³⁸). These catalysts are less loaded with Pt, but their activity and durability for ORR are enhanced at least two to four times, due to the modification in the surface electronic structure of Pt. The activities of MPt alloys are in function of oxygen adsorption energy, and form a volcano-like plot.²⁰ The surface catalyst that has 0.0-0.4 eV weaker oxygen binding energy than that of Pt(111) should have better ORR activity.³⁹ As shown in the **Figure 1.7a**, the Pt₃Co, Pt₃Ni, and Pt₃Fe alloys dominate the top of the volcano and thus are supposed to display higher ORR activity than that of other PtM alloys or pure Pt materials.⁴⁰

The bimetallic catalysts are mostly employed as alloys, they can be grouped to: (i) PtM alloys⁴¹⁻⁴² (ii) Pt-monolayers on non-noble / noble core,⁴³⁻⁴⁴ and (iii) M@Pt or PtM@Pt core @shell, nanostructures.⁴⁵⁻⁴⁶ The catalytic activity for the ORR on such alloys dependent on the size, geometry (ratio of exposed facets (**Figure 1.7b**), eg: the ORR active Ni₃Pt increases in order: Pt₃Ni (100) < Pt₃Ni (110) < Pt₃Ni (111)⁴⁷), composition (ratio of Pt to base metal eg:

Pt₃Co, Pt₃Ni, Pt₁Co₁, Pt₁Ni₁, it was found that PtM alloys with a 3:1 Pt:M ratio exhibited much higher activity and better stability⁴⁸⁻⁴⁹) and nature of d band center .

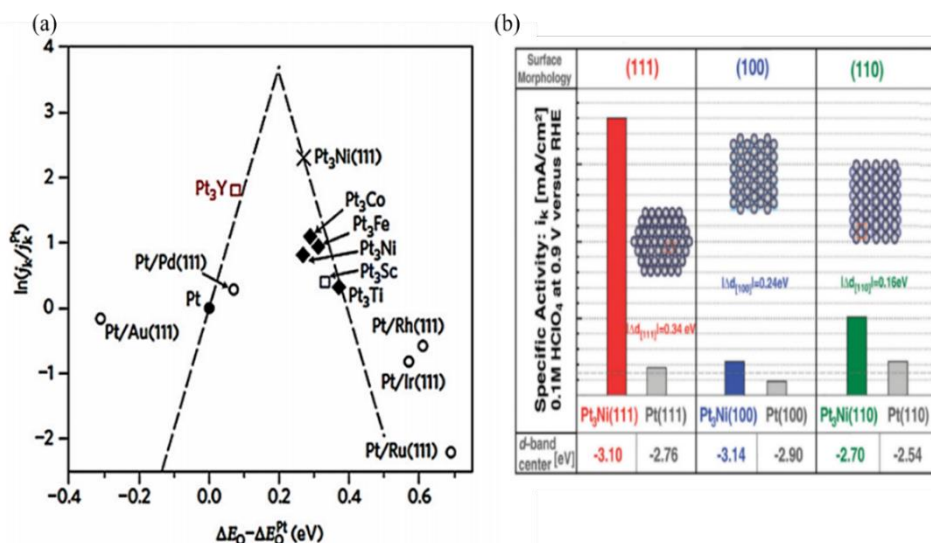


Figure 1.7. (a) Volcano plots for the oxygen reduction reaction on Pt based transition-metal alloys, (b) Influence of the surface morphology and electronic surface properties on ORR.⁴⁰

Non-Pt catalysts

The inconvenient of bimetallic ORR catalyst firstly resides on the strong affinity of the transition metal towards oxygen, what makes elimination of intermediate formed O and OH species difficult, secondly dissolution of base metal continent in Pt alloys in the reaction media, also core-shell and nanoparticle catalyst designs regularly need very intensive synthesis processes and /or temperatures exceeding 800 °C. These problems can be addressed by using non-precious material catalysts that are stable and less expensive. Materials that show appreciable ORR activity are:

1. **Transition metal oxides**-these types of catalyst have onset potentials as ≈ 0.94 V vs RHE. Several nonprecious-metal oxides have also been found to be catalytically active for ORR such as TiO₂, NbO₂, ZrO_xN_y, TaO_xN_y, and CoSe₂, but they suffer from poor durability in acid medium and limits their widespread adoption in PEMFCs, low conductivity and dispersion leads to other solution like doping transition metal with nitrogen (M-N) and deposition on a carbon support (M-N/C or M/C where M is the transition metal) ²⁴.
2. **Noble metal** , in particular gold with controllable size and geometry⁵⁰⁻⁵¹ The origin of his strong activity for ORR is due his unique electronic structure for reactant / intermediate adsorption, easy synthesis, high surface density of low coordination

number Au atoms and less electron density and high number of site active. Gold (100) plane shows better activity than other surface plane⁵². In this thesis we prepared gold interface efficient for ORR activity.

Table 1.2. ORR based non-precious catalysts

Catalyst	E_{onset} (vs. RHE) / V	Electrolyte	Ref
Co-N/C	0.93	0.1M NaOH	53
FeN/C	0.93	0.1M NaOH	53
NiN/C	0.88	0.1M NaOH	53
MoSe/NG-4	0.92	0.1M NaOH	54
25%Cu-N/C	0.91	0.1M NaOH	55
Co/nitrogen-doped Porous carbon composite	0.91	0.1 M NaOH	56
NC-FeCoNi	0.94	0.1 M NaOH	57
Mo-N/C@MoS₂	0.90	0.1M NaOH	58

Table 1.3. Gold based oxygen reduction reaction

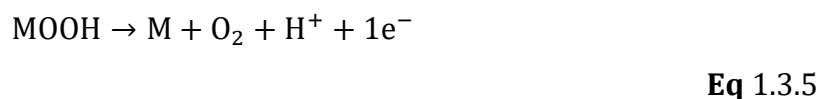
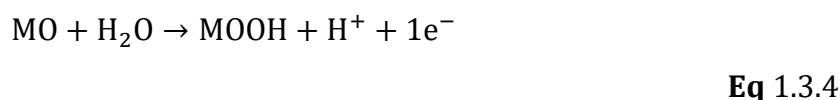
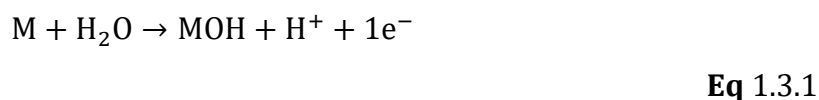
Catalyst	Comments	Electrolyte	Ref.
AuPC nonocopmosites	Number of electron (3.6-3.92), E_{onset} = 0.95V, catalytic activity comparable to that of 20wt% Pt/C	0.1M NaOH	59
Au@C	Onset potential=0.98 V, high stability compared to Pt/C	01M NaOH	60
AuNDs-GO	high electrocatalytic activity and a dominant four-electron pathway toward ORR	0.1M NaOH	61
AuPdCo/C Core-shell	comparable ORR activity with commercial Pt/C but much better long-term stability in alkaline medium	0.1M NaOH 0.1M HClO ₄	62
Pd@Au PNSs	high performance in terms of Pt group metals mass-specific activity, electrochemically active surface area ($ECSA$), specific $ECSA$, and specific activity, with high half-wave potential values (0.93–0.96 V	0.1M NaOH	63

1.3. Oxygen evolution reaction (OER)

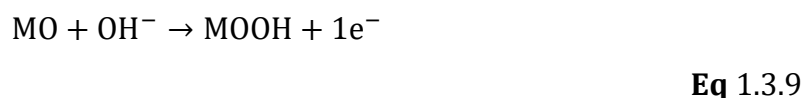
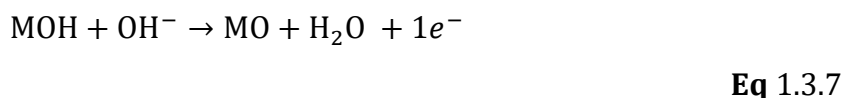
The OER is considered as the key process that governs the overall efficiency of electrochemical water splitting. The oxygen evolution reaction (OER) takes place in the anodic electrode. Where molecular oxygen is produced via several proton/electron coupled. Two water molecules (H_2O) are oxidized into four protons (H^+) and oxygen molecule (O_2). In basic electrolyte the hydroxyl groups OH^- are converted to H_2O and O_2 .

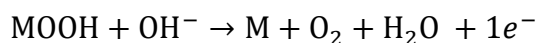
The mechanism of the OER is very complex, the OER occur in multi-step reactions with single-electron transfer at each. Many mechanisms for oxygen evolution reaction are proposed for either acid and alkaline electrolyte, usually the mechanism involve MOH and MO as intermediate, two different approaches to form oxygen from a MO intermediate exist. The first one is a direct combination of 2MO to produce O_2 the second one is the formation of the MOOH intermediate which decomposes to O_2 .

Under acidic media :



Under basic media :





Eq 1.3.10

The OER performance of an electrocatalyst depends on the number of active sites and the activity of the active site. the best catalysts require >320 mV overpotential to reach 10 mA/cm².⁶⁴ Ruthenium (Ru₂O) and iridium (IrO₂) oxides are highly active catalysts for OER in both acidic and alkaline media. They are the lone known materials that can reach ~5 mA/cm² with overpotentials less than 750 mV in acidic electrolyte.⁶⁴ However, under high anodic potential, these precious materials suffers from instability, and dissolves in the electrolyte. Ru₂O oxidized to RuO₄ and IrO₂ to IrO₃. In addition the high price of this Nobel metal leads to modification in their composition and morphology.

Coating metal oxide catalysts with transition metals such as cobalt (Co), iron (Fe), manganese (Mn), nickel (Ni), have been revealed to exhibit remarkable activity toward OER, since they are stable over a long period of electrolysis and are relatively abundant. Several families of metal oxides appeared, perovskite oxide whose the formula written as ABO₃ where A is alkaline or rare-earth metals, B is the transition metals, spinel oxide AB₂O₄ where A and B atoms usually are made up of group 2, group 13 and first-row transition metal elements, Great spinel oxides for OER are iron-based (ferrite) and cobalt-based composites with other transition/alkaline metals dopants (e.g; Mn, Ni, Cu, and Zn), However the fabrication of these transition metal based oxides are often complicated and also result in low electrical conductivity. Layer structure include metal hydroxides M(OH)₂ and metal oxyhydroxides MOOH,⁶⁵ where M represents the transition metals, have been reported as better alternatives to the rare earth noble metal oxides.

Copper-based catalysts are considered competitive candidates for OER, because copper is an abundant element, which is presents in Earth's crust in a proportion of 50 ppm. It is also much cheaper than noble metals. In addition, copper shows a large panel of redox properties, with a variety of valence states Cu(0), Cu(I) and Cu(2⁺) form.⁶⁶ Cuprous oxide (Cu₂O) has proven to be well-adapted for electrocatalytic redox reactions,⁶⁷⁻⁷⁰ including OER.⁷⁰⁻⁷¹ However, Cu₂O catalyst suffer from low activity and stability due to less available catalytic active sites, poor electrical conductivity and ease of aggregation during electrochemical process.⁷²

1.3.1. Fuel cell

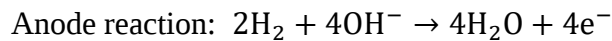
A fuel cell is an electrochemical device that transforms chemical energy of a fuel directly into electricity, it is one of the most important clean energy sources. Generally, each fuel cell is composed on two electrodes, the reductant (fuel) electrode (anode) and the oxidant electrode (cathode), immersed in an electrolyte. Several types of electrolytes can be used in fuel cells such as acids, bases, solid and polymer electrolytes. Hydrogen, methanol, and hydrocarbons are various fuels commonly used in fuel cells. Oxidants used are mostly air or oxygen O_2 .⁷³ Fuel cells can be classified on: Alkaline fuel cell (AFC), proton exchange membrane (PEMFC), direct methanol (DMFC), phosphoric acid (PAFC), molten carbonate (MCFC), and solid oxide (SOFC). As shown in the (Table 1.4)⁷⁴ these fuel cells are differentiated by their electrolyte and operating temperature. The electrolyte should be chemically resistant, conductive, and concentrated 84 wt.% from for cell operated high temperature ($\approx 250^\circ\text{C}$) or less concentrated (35-50 wt. %) for lower temperature ($< 120^\circ\text{C}$).

A fuel cell is similar to a battery as it based on the electrochemical energy conversion system, but there is a vital difference, a fuel cell does not stock fuel like a battery, but performs on a continuous fuel supply.

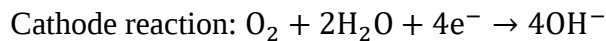
Table 1.4: Classification and characteristics of fuel cell systems

Fuel cell	Ion	T / °C	Fuel	Applications and notes	Efficiency/ %
Alkaline (AFC)	OH^-	20-200	Pure H_2	Space vehicles	60-70
Proton exchange membrane (PEMFC)	H^+	30-100	Pure H_2 , tolerates CO_2	Vehicles and mobile application	40-60
Direct methanol (DMFC)	H^+	20-90	Methanol	Portable electronic systems of low power	Up to 40
Phosphoric acid (PAFC)	H^+	200	Pure H_2 , tolerates CO_2	Large number of 200 kW combined heat and power system	36-42%
molten carbonate (MCFC)	CO_3^{2-}	650	H_2, CO, CH_4 , tolerates CO_2	Medium to large scale heat and power combined system, up to MW capacity	50-60%
Solid oxide (SOFC)	O^{2-}	500-1000	H_2, CO, CH_4 , tolerates CO_2	All sizes of heat and power combined system, 2kW to multi-MW	50-60%

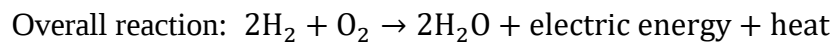
Alkaline fuel cell (AFC) offers high-energy conversion efficiency (~ 70%) with long lifetime performance. AFC Appeared in the 1950s with a farm tractor, then used in the 1960s for Apollo and space shuttle programs by NASA. AFC provides electricity power between 2-16 kW, and voltage of 28-32V. The operation time of the AFC is around 8 000 hours. In this system an aqueous solution of potassium hydroxide KOH is used as an electrolyte, NaOH also can be used , but regarding the conductivity and resistance (KOH is more expensive but more conductive (about 1.3 times) less aggressive than NaOH). The hydrogen H_2 is electrochemically oxidized at the anode, electrons generated from this reaction, travel towards the cathode where oxygen becomes reduced. At the end water and heat are produced. In AFC hydrogen charged on the anode react with hydroxyl anions generating water and electron. The electrons are transferred through an external circuit to the cathode, where the oxygen react with water to generate hydroxyl ions⁷⁵ (**Figure 1.8**). Basic electrode reactions in the AFC are



Eq 1.3.11



Eq 1.3.12



Eq 1.3.13

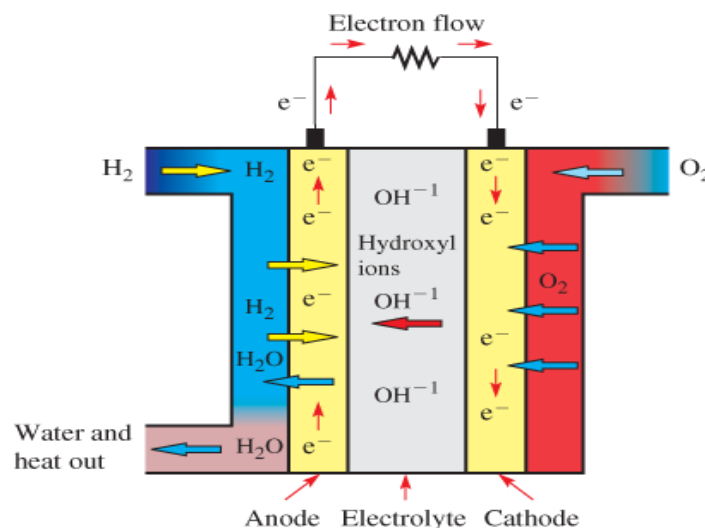


Figure 1.8. Schematic presentation of an alkaline fuel cell.

a) Alkaline fuel cell advantages/disadvantages

System	Alkaline fuel
Advantages	- Mechanically rechargeable - Low-cost considering the electrolyte used - Clean energy source, low environmental effect in terms of negligible air and noise pollution. - The heat and byproduct formed in the fuel cell are recovered by the thermal management system and water electrolyser
Disadvantages	- Slow kinetics of the oxygen reduction reaction (ORR) - The fuel needs to be treated and purified before using (fuel reformer) - Pure H₂ only - The fuel cell gets poisoned very easily in the presence of carbon dioxide CO₂ and CO. Carbonate formation decreases the ionic conductivity of the electrolyte solution thus leading to blockage of electrolyte pathways and / or electrode pores in the next reaction $\text{CO}_2 + 2\text{OH}^- \leftrightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$

1.3.2. Water splitting reaction

Hydrogen H₂ and oxygen O₂ produced from water splitting (electrolysis), is considered efficient, renewable and clean energy source that can be used in fuel cells and metal-Air batteries.^{17, 76} H₂ can store greater energy per unit weight or volume due to its high energy density. Water electrolysis can be generally divided into two half-reactions, oxygen evolution reaction (OER) in the anode and hydrogen evolution reaction (HER) in the cathode.

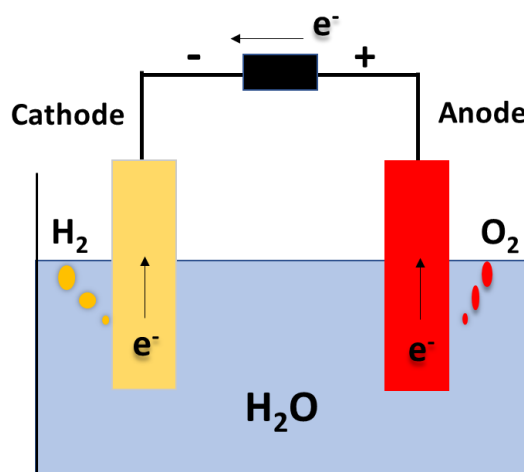
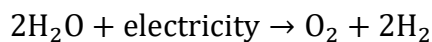


Figure 1.9. Schematic presentation of an electrochemical water splitting.

As shown in **Figure 1.9** the electrochemical water splitting system containing three components: cathode, anode, and electrolyte. Both the cathode and anode are coated with electrocatalysts to accelerate the water splitting reaction. When an external voltage is applied

to the electrodes, water molecules are decomposed into gaseous hydrogen and oxygen on the cathode and anode, respectively.⁷⁷ The overall water splitting reaction is as follows:



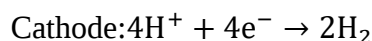
Eq 1.3.14

The standard oxidization potential of the OER is 1.23 V (RHE) and the standard reduction potential of HER is 0 V (RHE). The minimum energy required for electrolytic hydrogen production at standard conditions (293 K and 1 atm) is $\Delta G = 237.1$ kJ/mol. Water electrolysis depends on pH and temperature of an electrolyte used. The thermodynamic voltage of water splitting can be reduced by increasing the electrolyte temperature.

In acidic solution the redox reactions are⁷⁸:

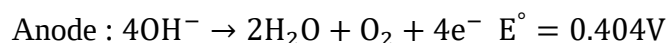


Eq 1.3.15

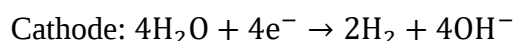


Eq 1.3.16

In basic solutions the redox reactions can be written as⁷⁹:



Eq 1.3.17



Eq 1.3.18

The production of hydrogen in the process of water splitting is severely restricted by the complex and the sluggish kinetics of the oxidation of water to oxygen (OER) due to the required $4\text{e}^-/4\text{H}^+$ process, while HER is only a two electron-transfer reaction. However, in the water electrolysis process, a larger applied potential is always required (it must apply voltages equal or higher than the thermodynamic potential value).⁸⁰ Water splitting can be accomplished by using efficient electrocatalysts. The noble metal group such as (Pt), ruthenium (Ru) and iridium (Ir) and their corresponding oxides/ hydroxides (e.g. IrO_2 , RuO_2) are the best active electrocatalysts for the both reactions of water electrolysis. Overpotential and Tafel slop is the most important factors to evaluate the performance of target electrocatalysts. Lower overpotential with a faster increase in corresponding current density (j), with smaller tafel slop indicates the superior electrocatalytic activity of the catalyst.

Two types of water electrolysis technology are available, alkaline water electrolysis (AWE) technology and polymer electrolyte membrane (PEM) technology (**Figure 1.10**). In AWE The cell involves of two electrodes separated by a gas-tight diaphragm. This assembly is immersed in a liquid electrolyte that is usually a highly concentrated aqueous solution of KOH (25–30 wt.%), this system operating temperature range from 65 to 100°C.⁸¹ In PEM technology, solid polysulfonated membranes were used as an electrolyte, the functional groups of the sulfonic acid (SO₃H) provide high proton (H⁺) conductivity (0.1 ± 0.02 S cm⁻¹). PEM usually has larger current and power densities, shorter start-up times and wider operating temperatures (20–80°C) with a smaller stack areas than Alkaline water.⁸² In addition water electrolysis is one of the favorite methods for conversion of renewable energy to high pure hydrogen .

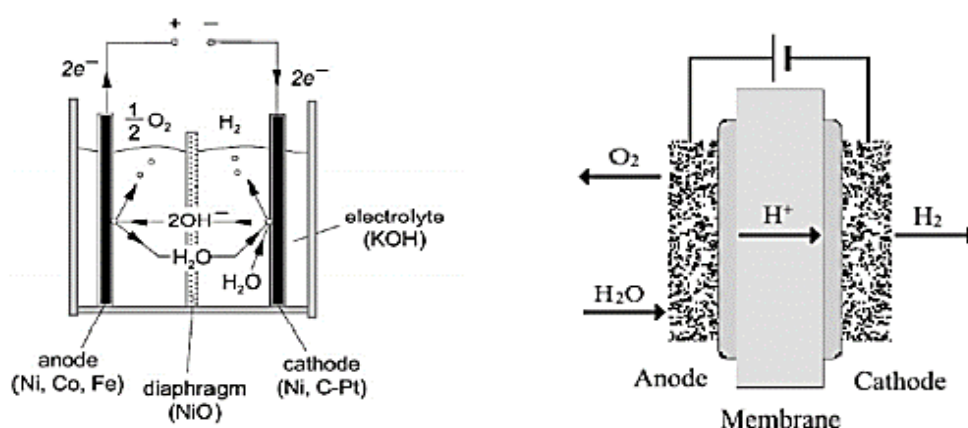
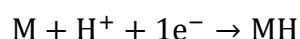


Figure 1.10. Schematic presentation of a) alkaline-water electrolysis, b) polymer electrolyte membrane.⁸³

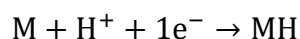
1.3.3. Hydrogen evolution reaction (HER)

Hydrogen evolution reaction (HER) is one of the two half reactions of the water splitting reaction. Take place at the electrode/electrolyte interface, H₂ produced via the reduction of either proton (H⁺) or H₂O. Mechanism of HER depend on the pH of an electrolyte. In acidic conditions HER involves two successive steps,⁸⁴⁻⁸⁵ Volmer step where H⁺ adsorbs on the catalyst surface , and the Heyrovsky step when the active site MH combines with a H⁺ and an electron (e⁻) to form an H₂ molecule. In addition H₂ can be formed directly by the combination of two MH on the catalyst surface (Tafel steps).⁸⁶ In alkaline conditions HER starts from dissociating H₂O molecules in protons (H⁺).

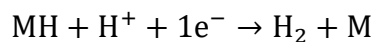
Under acidic media :



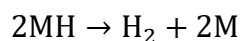
Eq 1.3.19



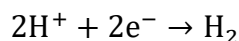
Eq 1.3.20



Eq 1.3.21

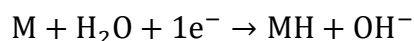


Eq 1.3.22

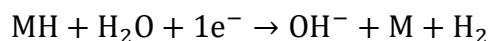


Eq 1.3.23

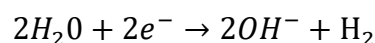
Under basic media :



Eq 1.3.24



Eq 1.3.25



Eq 1.3.25

From the reaction steps implicated in the HER it is clear that sufficient affinity for binding hydrogen atoms to the surface and the ability to release hydrogen gas by breaking “MH” bonds are the two essential characteristics for a perfect HER catalyst.⁸⁷ The best electrocatalysts used in HER are: Metal sulfides, Metal selenides, Metal carbides, Metal nitrides, Metal phosphides and Heteroatom-doped nanocarbons, these materials are characterized by their high activity similar to that of Pt, large durability, great chemical/catalytic stability over a wide pH range. Also, their low cost to ensure economical hydrogen production.⁸⁸

1.4. Plasmon enhanced electrocatalysis

Noble metal nanostructures are exceptional light absorbing systems, during which electron-hole pairs can be formed and used as “hot” charge carriers for catalytic applications. The main goal of the emerging field of plasmon-induced catalysis is to design a novel way for finely tuning the activity and selectivity of heterogeneous catalysts. The design strategies used for the preparation of the plasmonic nanomaterial for catalytic systems are highly crucial to achieve improvement in the performance of targeted catalytic reactions and processes.

Metallic nanoparticles of which the diameter is smaller than the wavelength of light are known to support coherent collective oscillations of delocalized electrons in response to electromagnetic radiation, known as localized surface plasmons (LSPs) (**Figure 1.11a**). Upon resonant excitation, the collective oscillations of the free electrons give rise to a local electric field enhancement near the surface of the nanoparticles, which strongly concentrates light intensities. The resonances where they occur are named ‘localized surface plasmon resonances’ (LSPR) to differentiate them from propagating surface plasmon polaritons of metal surfaces. A tremendous amount of efforts has been devoted to the design of plasmonic structures to adjust the LSPR frequency ($\lambda_{\max}$), and it is now possible to engineer nanostructures that show LSPR effects from the ultraviolet to the mid-infrared spectral zones (**Figure 1.11b**). This is possible as the LSPR properties of plasmonic nanomaterials are strongly dependent on their morphology, size, shape, composition, and even spacing between particle assemblies, allowing the use of several parameters for tuning their $\lambda_{\max}$. Since the LSPR frequency furthermore shifts upon changes of the refractive index of the medium surrounding the particles, embedding metallic nanostructures into other dielectric layers, or forming core-shell plasmonic structures are another means of tuning the LSPR effect.

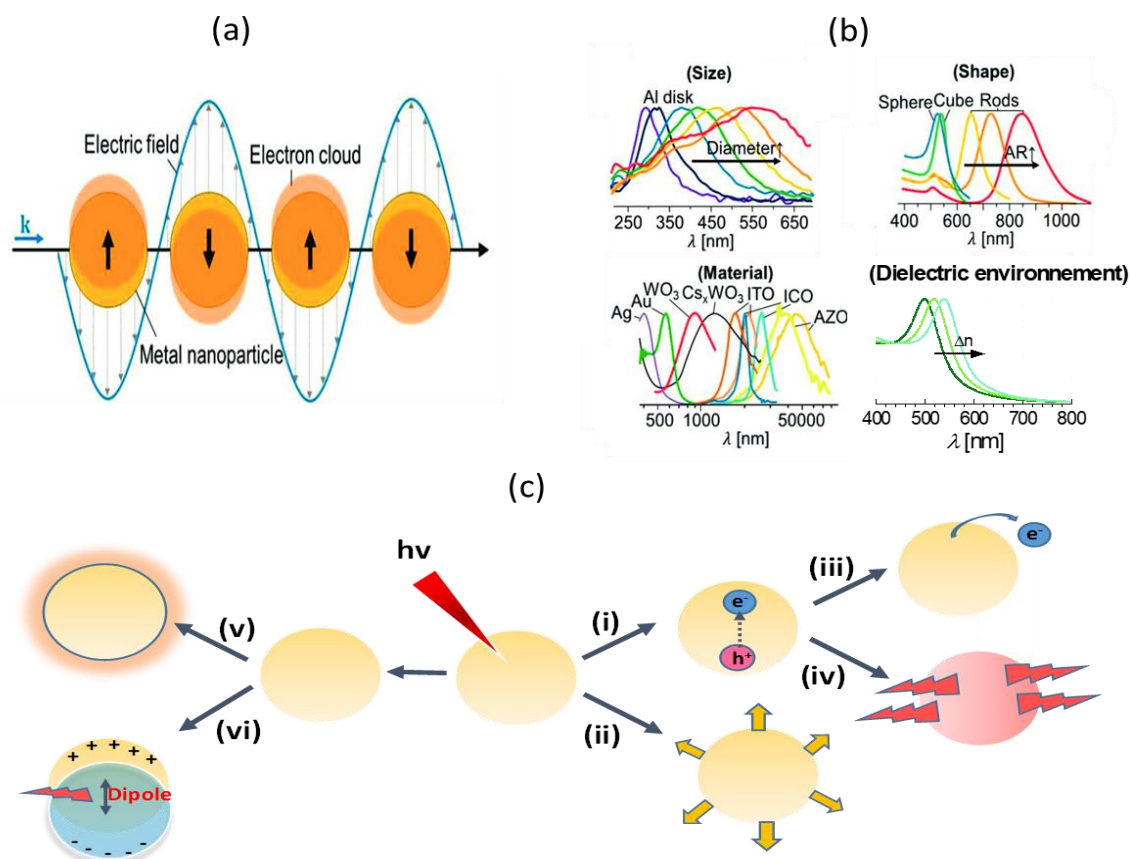


Figure 1.11. (a) Coherent collective oscillations of free electrons of metal nanoparticles in response to light when the diameter of the nanoparticle is smaller than the wavelength of light. (b) Plasmonic resonances engineered by size,⁹⁷ shape,⁹⁸ material composition of nanomaterials,⁹⁹ and dielectric environment ($n = 1.00$ to 1.50). (c) Decay processes of excited surface plasmon resonance waves: (i) non-radiative decay by excitations of charge carriers; (ii) radiative decay *via* scattering, (iii) transfer of hot charge carriers to the surrounding; (iv) relaxation *via* heat transfer, (v) electromagnetic field enhancement, (vi) dipole resonance energy transfer.¹⁰⁰

Following light absorption by nanoparticles and LSPR excitation in the nanoparticles, the plasmons can decay in several competitive pathways (**Figure 1. 11c**). One is the radiative decay, upon which the plasmon decays into photons resulting in strong light scattering effects. This phenomenon is often used for imaging applications and sensing⁸⁹⁻⁹⁰ and is at the heart of surface enhanced Raman spectroscopy (SERS).⁹¹⁻⁹² The other route is the non-radiative decay process, dominant for small metallic nanoparticles (< 40 nm) and leading to the generation of energetic electrons and holes in the plasmonic nanostructures. The excited surface plasmons can then decay by relaxation to generate localized heating effects, detrimental for thermal based applications such as photothermal therapy⁹³ as well as for plasmon-induced photocatalytic

chemical reductions.⁹⁴ In addition, excited surface plasmons can transfer “hot” charge carriers to the surrounding, primordial for light driven chemical transformations.⁹⁴ Indeed, hot-electron injections is the first mechanism reported for plasmon-enhanced photoactivity of wide-band gap semiconductors.⁹⁵⁻⁹⁶

Two situations have to be distinguished in the case of plasmon-mediated electrochemistry: (1) pure plasmonic metal nanostructures and (2) metal/semiconductor composites with underlying fundamentally different mechanisms.

Indirect mechanism using pure plasmonic nanostructures

Plasmon-accelerated electrochemical oxidation of glucose into gluconic was reported by Wang et al.¹⁰¹ (**Figure 1.12**). Enhanced electrochemical response of glucose oxidation was observed upon Au NPs LSPR excitation. Taking into account light intensity, heat effect and the influence of the LSPR wavelength, following reaction mechanism was proposed. Upon light absorption and LSPR excitation, the electrons of the Au NPs oscillate collectively and interband excitation occurs, which results in electrons at active states above the Fermi level energy of Au NPs. This excited charge is concentrated on the surface of the Au NPs, and have three possible transfer channels: (i) recombination with formed holes, (ii) electron transfer, (iii) being removed to external circuit. In this case, the positive applied potential drives the hot electrons to the external circuit, and the remaining hot holes are driven to the Au NPs surface and accelerate glucose oxidation. This corresponds to the generation and injection of hot charge carriers into molecules adsorbents, often identified as ‘indirect’ mechanism in the literature.

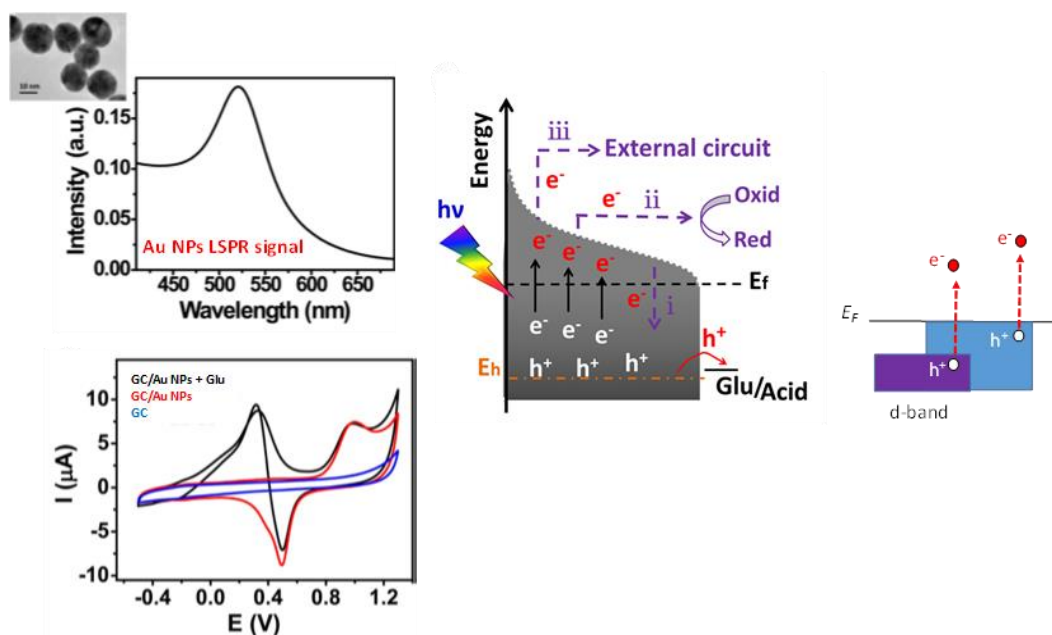


Figure 1.12. LSPR signal of Au NPs (inset TEM image) and cyclic voltammograms of GC/Au NPs in PBS (red) and in glucose (100 mM; black) as well as of GC in PBS (blue) together with mechanisms of direct plasmon-accelerated electrochemical reactions using the oxidation of glucose to gluconic acid as example.¹⁰¹

Direct mechanism by promotion of an electron from the metal to an empty molecular orbital on the adsorbate

In the case of using non-pure plasmonic substrate, but a metal/semiconductor composite, the situation is outlined in **Figure 1.13**. The hot electrons are injected from the metal nanoparticles to the conduction band of the semiconductors upon overcoming the Schottky barrier. This process enables the entrapment of hot electrons in the semiconductor particles, and, thereby, suppresses the electron-hole recombination, promoting redox reactions occurring on the semiconductor's nanoparticles. Yi et al. recently, demonstrated that plasmon-excited hot electrons generated on Au NRs can be injected to a MoS₂ layer due to the low Schottky barrier between Au NRs and MoS₂.¹⁰² This system exhibited enhanced electrocatalytic activity towards the hydrogen evolution reaction (HER) due to the increase in charge density on MoS₂ upon injection of hot-electrons. Three probable transfer pathways, namely: (i) recombination with holes in Au NRs, (ii) injection into the conduction band of the MoS₂, and (iii) direct electrochemical reduction of water on Au NRs by the generated hot electrons are described (**Figure 1.13**). Semiconductors are used as charge transfer mediators to efficiently collect the excited carriers and thereby promote electrochemical reactions.

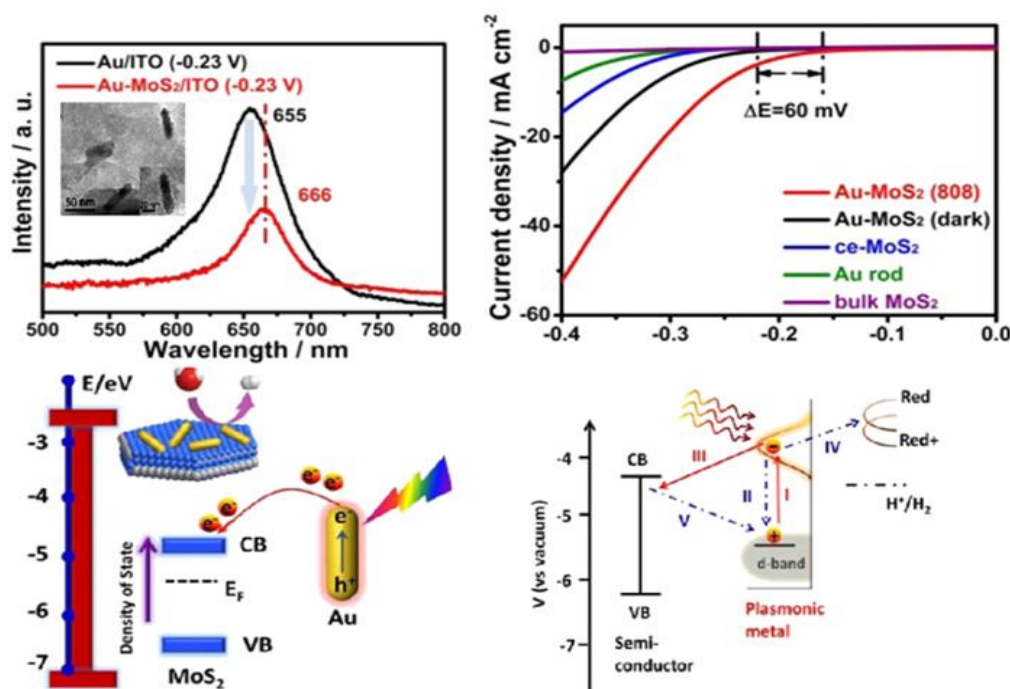


Figure 1.13. LSPR spectra of Au rods in Au/ITO and Au-MoS₂/ITO (inset: TEM image of Au-MoS₂ hybrids and Au NR), Polarization curves recorded on Au, MoS₂ and Au-MoS₂ hybrid (under illumination and dark) and energy level diagram.¹⁰²

Extensive efforts have been developed to create electrocatalytic materials with plasmonic effect. For variety of applications such as water-splitting reactions (oxygen evolution reaction OER and hydrogen evolution HER), oxygen reduction reaction (ORR), CO₂ reduction and alcohol oxidation. Plasmon-induced chemical processes have been gaining significantly increased attention due to their high throughput and low energy requirements. We can classify the plasmonic materials based electrocatalysis on two categories, Noble Metals Plasmonic Electrocatalysts (**Table 1.5**) and Metal-Semiconductor Composites (**Table 1.6**). In the first category Au and Ag with different shape, facets and size are widely explored as plasmonic nanostructures for electrocatalysis, Moreover, multi-metallic hetero-nanostructures such as alloy, and core-shell structures are used for enhancing electrocatalytic activity and selectivity, as well as stability/durability of this noble metal.¹⁰³ For example, Xu et al. prepared Pt₁-Ag₁ dendrites which display a great enhancement in catalytic activity towards ethylene glycol oxidation under visible light irradiation. Yang and his team found that the combination of plasmonic Au cores and catalytically active Pt shells (Au@2Pt NCs with a 55 nm Au core and 2 equivalent monolayers of Pt) provided synergistic effects for the enhancement of MOR¹⁰⁴. The Au@2Pt NCs showed about 2.6 times enhancement in the MOR activity after 530 nm illumination for 25 min. In the second category (metal/semi-conductor composite). Xu et al.

proposed TiO₂ nanotube with Au NPs for increased ethanol oxidation¹⁰⁵. Jin et al ,Developed Au nanoparticle (NP)-decorated bilayer TiO₂ nanotube (BTNT) heteronanostructure, enhanced the electrocatalytic activity and stability for the ethanol oxidation under visible light irradiation.

Table 1.5. Plasmonic Nobel metal enhanced electrocatalysis

Catalyst	Reaction	Comments	Ref.
Au nanofiber	Ethanol and methanol oxidation	Decreased passivation effect	⁸
Au NPs	Glucose oxidation	High alkaline condition to scavenge holes by OH ⁻	¹⁰¹
Au NPs, Au NRs, Au NSs	Ascorbic acid Oxidation	Au NPs have weakest effect	¹⁰⁶
Ag–Au NPs	Glycerol oxidation	100% fuel cell power output under visible light	¹⁰⁷
Pt–Ag dendrites	Ethylene glycol oxidation	1.7 fold increases in catalyst activity under light	¹⁰⁸
Ag–Pt nanocages	ORR	“Hot” electron transfer suppressed formation of H ₂ O ₂	¹⁰⁹
Au NPs, Au	Ethanol oxidation	2.6 effect enhancement	¹⁰⁴
Pd-tipped Au NRs	HER	High exchange current density of 1.585 mA/cm ²	⁹
PdAg hollow nanoflowers	Ethylene glycol oxidation	High active surface area of 25.8 m ² g ⁻¹ (Pt 9.8 m ² g ⁻¹)	¹¹⁰
Pt/Fe–Au NRs	HER	Photothermal effect results in electrocatalysis enhancement	⁵⁶
AuNP@rGO@Pd	OER HER	exhibited ≈1.9- and 1.1-fold activity in the HER and OER, respectively	¹¹¹
AuAg nanobowls	Ethylene glycol oxidation	2.3-fold enhancements of activity towards EGOR	¹¹²
Ag nanocubes Ag nanooctahedra	HER	AgNOs with (111) facet expressed higher current densities than those of AgNCs with (100) facet for electrocatalytic HER under laser irradiatio	¹¹³
Pt-Au/Graphen	MOR ORR	an efficient bifunctional electro-photo catalyst for catalyzing MOR and ORR.	¹¹⁵

Table 1.6. Metal /Semi-Conductor enhanced electrocatalysis

Catalyst	Reaction	Comments	Ref.
Au/CuI	Ethanol oxidation and organic pollutant degradation	Au/CuI showed ca. 5.6 and 13 times for the oxidation of ethanol and MB,	¹¹⁶
Au–TiO₂	ORR	Activity of 310 mA mg ⁻¹	¹¹⁷
Au–TiO₂ nanotubes	Ethanol oxidation	3.6-fold increase with low Au NPs (1.9 at.%)	¹¹⁸
Au–MnO₂ NPs	OER	60-mV overpotential	¹¹⁹
Ni(OH)₂–Au	OER	Four-fold enhancement, Tafel slope of 35 mV dec ⁻¹	¹²⁰
AuNHs onTi/TiO₂	HER	current density of -10 mA cm ⁻² can be attained at an overpotential of $\eta \approx -0.045$ V	¹²¹

1.5. Plasmon enhanced electrocatalysis for ORR and OER

In the case of plasmon enhanced ORR activity. Ag-Pt bimetallic nanocages able to suppress the peroxide intermediate through plasmonic effects from LSPR were prepared by Lin et al.¹⁰⁹ Limin et al. developed Au@TiO₂ plasmonic films exhibited significantly enhanced catalytic activities towards oxygen reduction reactions with an onset potential of 0.92 V (vs reversible hydrogen electrode), electron transfer number of 3.94, and limiting current density of 5.2 mA cm⁻².¹¹⁷ Wu and co-workers utilized Ag nanotriangles loaded on graphene as efficient ORR electrocatalyst under light illumination (**Figure 1.14**).¹²²

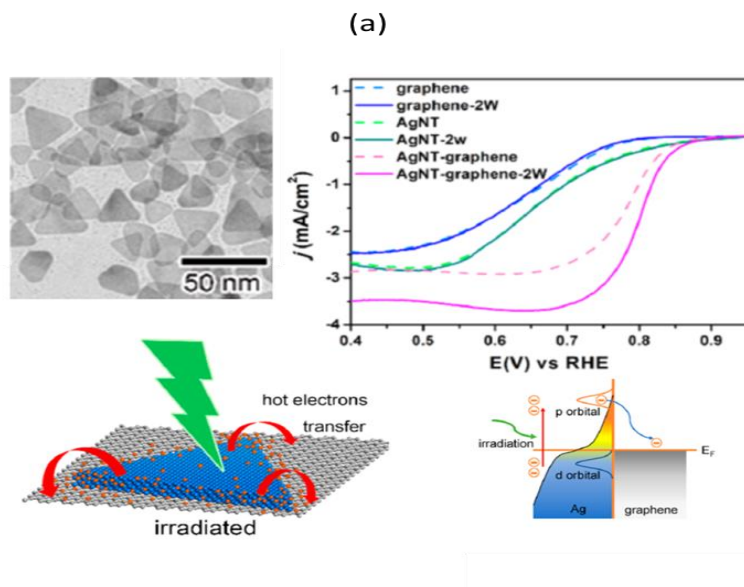


Figure 1.14. (a)TEM images, ORR properties of pure AgNTs, pure graphene, and theAgNT/graphene catalysts, Mechanism of plasmon-induced hot electrons enhancement for ORR and corresponding energy band diagrams.¹²²

For LSPR enhanced OER, Liu et al. demonstrated that Au NPs when decorated with transition-metal catalysts, such as Ni(OH)₂ nanosheets (**Figure 1.15**), form a plasmonic electrocatalyst, which, upon light illumination, enhances charge transfer from Ni(OH)₂ to Au NPs and greatly facilitate the oxidation of inactive Ni²⁺ to active Ni^{3+/4+} species, allowing more efficient water oxidation at lower onset potential.¹²⁰ Au NPs decorated MnO₂ nanosheets were reported by Xu et al. to be an ideal plasmonic electro-catalyst for the oxygen evolution reaction. The confinement of the outer electrons of the Mn cations by plasmonic “hot holes” generated in the Au NPs surface was largely promoted under green light illumination. These hot holes act as efficient electron traps to form active Mnⁿ⁺ species, providing active sites to extract electrons from OH⁻ and eventually facilitate OER catalysis.¹¹⁹

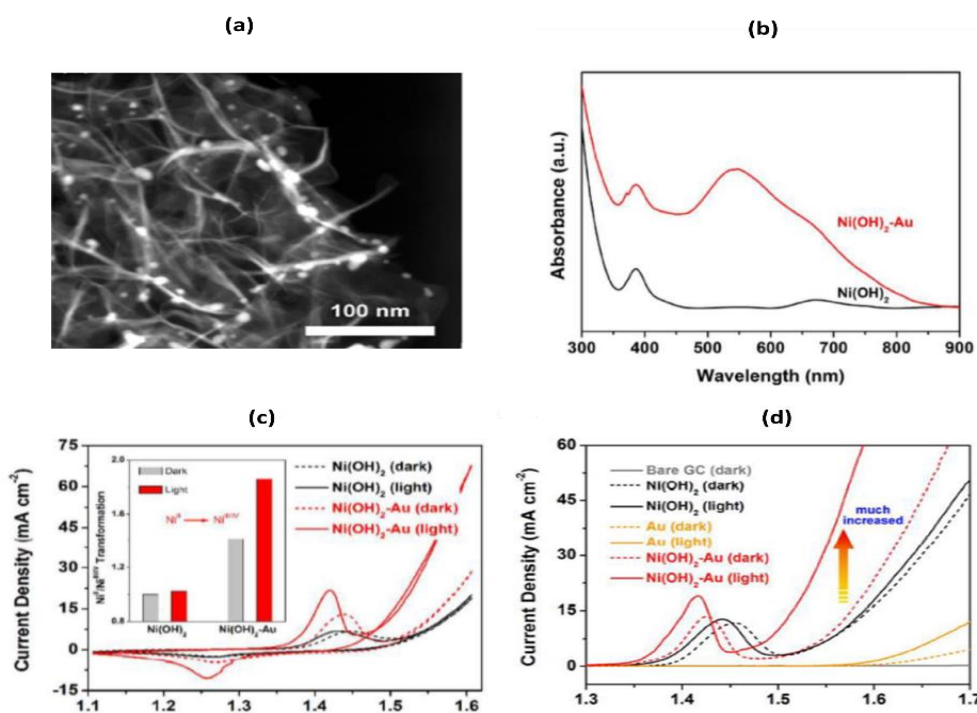


Figure 1.15. (a) HAADF-STEM image of Ni(OH)₂-Au hybridcatalyst; (b) UV/Vis absorption spectra of Ni(OH)₂nanosheets and Ni(OH)₂-Au hybrid catalyst,(c) cyclic voltammograms with and without light irradiation of Ni(OH)₂nanosheets and Ni(OH)₂-Auhybrid catalyst, and (d) oxygen evolution reaction (OER) polarization curves at 10 mV s⁻¹for differentelectrodes in dark and under light irradiation (532-nm laser, 1.2 W) in 1 M KOH; Ag/AgCl (SaturatedKCl) was used as reference electrode.¹²⁰

1.6. Conclusion

Localized Plasmon surface resonance enhanced activity, stability, and durability of electrochemical reactions. The LSPR response depends on the size, shape, material composition of material. Two situations distinguished plasmon-mediated electrochemistry: (ii) pure plasmonic metal nanostructures, and (iii) metal/semiconductor composites with underlying fundamentally different mechanisms. The complex four-electron transfer process taking place in ORR and ORR has been recognized as a barrier for the construction of high-quality fuel cells and metal-air batteries ORR. Pt is the best catalyst for this two reaction, but its sacristy and the high cost, pushes to find other alternative that shows similar or batter activity than Pt catalyst. LSPR is considered as the best alternative.

1.7. References

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CHAPTER II: Plasmon-enhanced Electrocatalytic Oxygen Reduction on Gold Nanohole Electrodes

2.1. INTRODUCTION

Gold nanoparticles have been widely applied in catalysis and electrocatalysis due to their wide variety of shape, size and composition. Gold based nanostructures are characterized by a strong light-matter interactions.¹⁻³ The generation of localized surface plasmon resonance (LSPR) excitations results in strong electromagnetic field enhancement and the generation of high concentration of energetic charge carriers at the surface of these nanostructures making them ideally suited to be considered for plasmon-accelerated chemical transformations.⁴

Next to being outstanding light absorbing materials with catalytic properties, their excellent conductive properties make gold nanostructures well suited in electrochemical based investigations. Surprisingly, there are still few reports on plasmon-enhanced electrochemical reactions using the triple (plasmon-catalytic-electrochemical) nature of gold nanostructures.⁵⁻⁷ Minter and co-workers fabricated Au nanofiber-based electrode and showed plasmonic enhanced electrocatalysis of ethanol and methanol in alkaline media.⁶ Wang et al. demonstrated the duality of gold nanoparticles deposited on glassy carbon electrodes (Au NPs/GCE) for plasmon accelerated electrochemical conversion of glucose to gluconic acid, and the excited charge concentrated on Au NPs surface has three possible transfer channel (**Figure 2.1a**).⁸ Chan et al. prepared Au nanostructures with different morphologies of nanospheres (NSPs), nanorods (NRs), nanostars (NSs), and triangular nanoplates (NPLs) toward the electrooxidation of ascorbic acid (AA), they found that the electrocatalytic activity on these Au nanostructures can be improved during light irradiation with the higher enhancing effect of NPL and NS Au than NSP and NR Au, This shape-dependent enhancement effect is suggested to be related to the number of “hot spots” in different NP surfaces generated from Au LSPR (**Figure 2.1b**).⁷

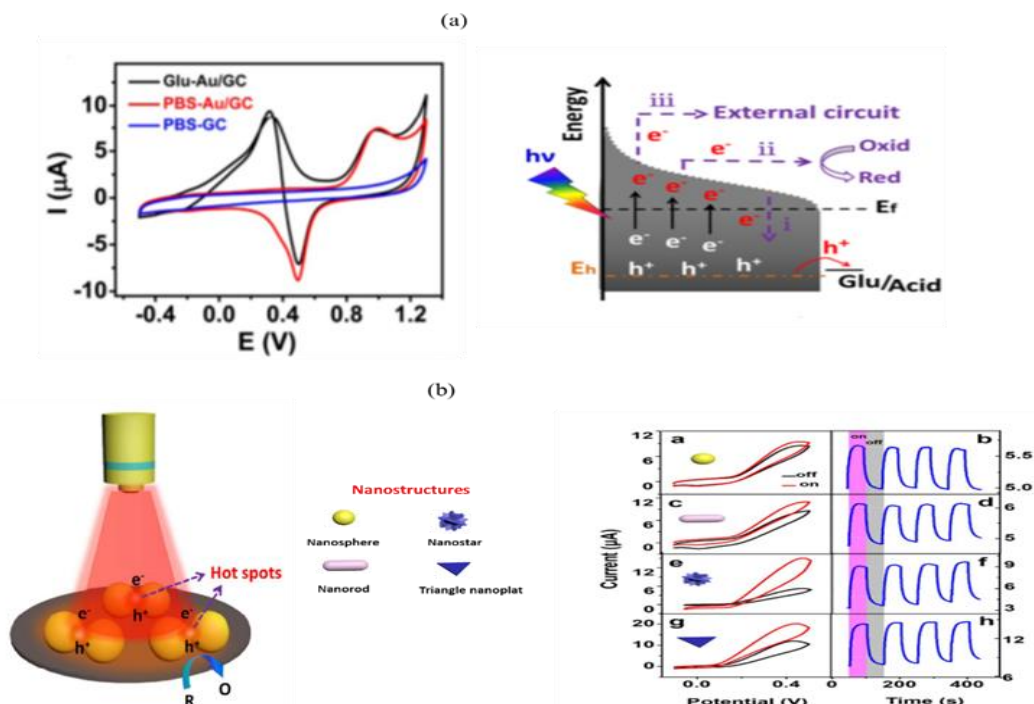


Figure 2.1. (a) CVs curves of GC/ Au NPs (Black: in PBS; Red: in glucose), and Mechanism of Plasmon accelerated electrochemical reaction on the Au NPs.⁸ (b) Generation of high energetic charge carriers for enhanced electrooxidation of ascorbic acid (AA) under light irradiation on different-shaped gold nanostructures, CVs of Au NSPs, NRs, NSs, NPLs modified GC electrodes, respectively (Black: in dark, Red : light on), and (b), (d), (f), (h) show the corresponding I-t curves of the Au NPs modified electrodes at 0.3 V (vs. Ag/AgCl) with light irradiation on and off in 1 mM AA solution.⁷

Recently, hybrid composites based plasmonic gold nanoparticles have been considered for the generation of hot electrons and holes. Guo et al. prepared a Au@Pt/Fe nanocomposite, which facilitates the transfer of photon-induced hot electrons from Au to Pt/Fe and promotes the electrocatalytic activity HER with a reduced overpotential at 10 mA cm^{-2} , a small Tafel slope (9.4 mV/dec), and the increased exchange current density.⁹ Xu et al. (**Figure 2.2**) fabricated Au-TiO₂ plasmonic structure enhance ORR activity, the effect of Au particle size on the plasmon-enhanced ORR demonstrated that 5 nm Au layer deposited on TiO₂ NCAs delivered a superior ORR performance with an onset potential of 0.92 V (vs RHE), with electron transfer number of 3.94, and limiting current density of 5.2 mA cm^{-2} .¹⁰ Also, plasmonic AuNP@rGO(1)@Pd enhanced 1.9- and 1.1-fold electrocatalytic activity of hydrogen evolution reaction and oxygen evolution reaction.¹¹

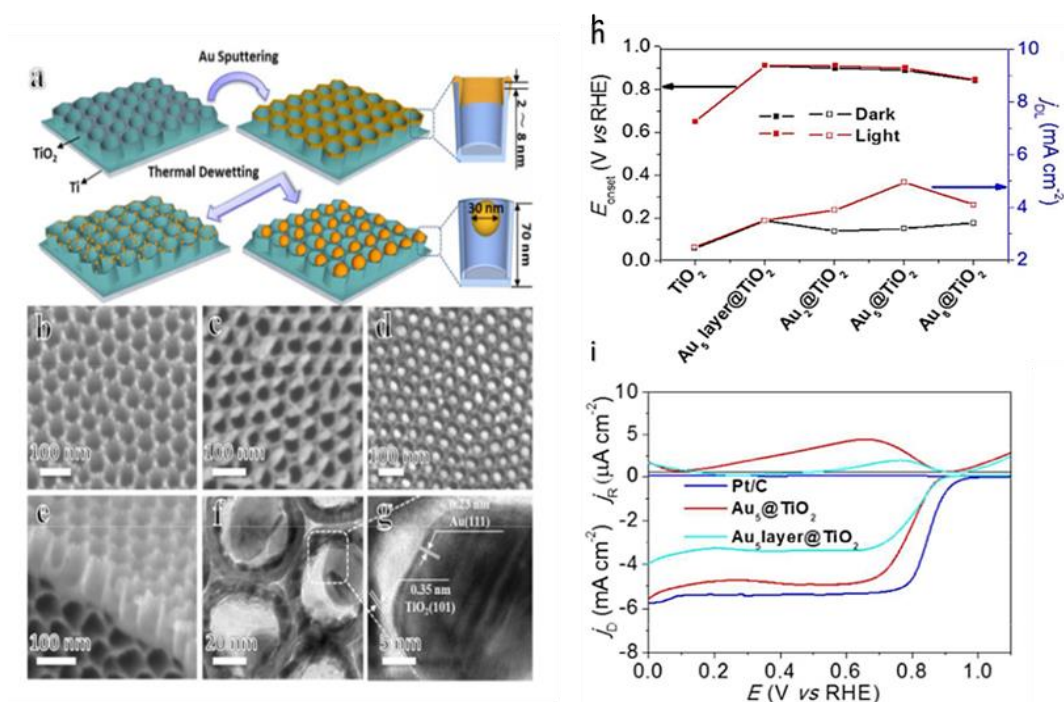


Figure 2.2. (a) Schematic illustration of fabrication steps for plasmonic Au@TiO₂ NCAs: Step 1, anodic formation of TiO₂ nanocavity arrays, Step 2, Au films deposition, Step 3, thermal dewetting treatment, (b-d) Top-view SEM images of Au₂@TiO₂, Au₅@TiO₂ and Au₈@TiO₂, respectively, (e) Cross-sectional view SEM image of Au₂@TiO₂ NCAs, (f-g) TEM images of isolated Au NPs inside TiO₂ nanocavities, (h) Onset potentials (left Y-axis) and limiting current densities (right Y-axis) of different samples in dark and simulated sunlight irradiation, (i) LSV curves of Au₅@TiO₂ NCAs. ¹⁰

In this chapter, we report the exceptional plasmon-promoted properties of an array of gold nanoholes (Au NHs) for the electrochemical reduction of oxygen in alkaline electrolytes (noted S1 in the following). This part of the work was in directly collaboration with Prof. Sorin Melinte from the Université catholique de Louvain, Belgium. Gold nanoparticle arrays attached to flexible substrates are essentially two-dimensional heating sources that can be operated uninterruptedly. Kapton, a highly aromatic polyimide resins, praised for its high thermal stability (> 300 °C), high tensile strength and bendability, was chosen due to the attractiveness of this material for a wide range of applications, including soft electronics and packaging. Electron beam or focused ion beam lithography are standard methods for the fabrication of well-ordered nanometric holes on various substrates. Next to these highly precise but expensive and time-consuming methods, colloidal lithography is a low cost and simple alternative (**Figure 2.3**) While the process is less perfect with local defects being present, this is not limiting given the final application targeted in this study, aiming at developing a flexible interface with

plasmonic features absorbing in the near infrared range. The hole diameter and the center-to-center spacing of the Au NHs array were adjusted to produce a strong absorption band close to 980 nm being adapted to plasmonic heating in the near-infrared with a 980 nm continuous wave laser. In such devices, more than 95 % of the photons from a light source can be absorbed by gold nanostructures and converted into heat *via* electron-phonon interactions that is subsequently transferred to the surrounding medium *via* phonon-phonon relaxation in a picosecond time scale.

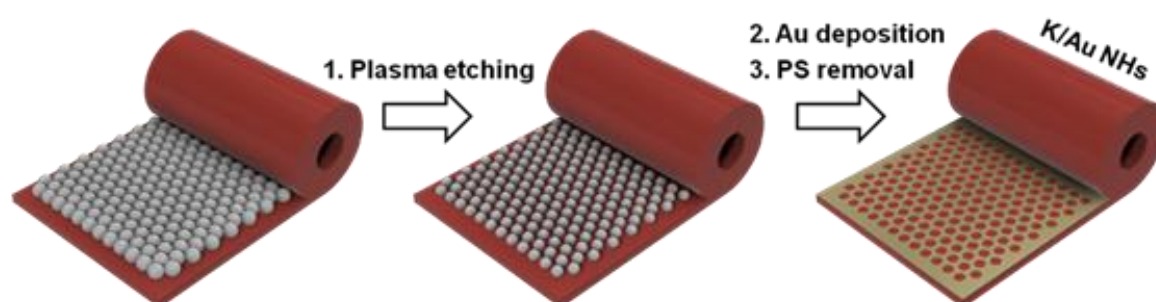


Figure 2.3. Flexible nanoholey photothermal heaters. Formation of the K/Au NHs interface.

2.2. Characterization of Au NHs Au electrode

The morphology and chemical composition of (Au NHs) electrode were characterized by Scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS). **Figure 2.4a-b.** The SEM image shows formation of holes with 630 ± 10 nm in diameter and center-to-center spacing $a = 980$ nm on the surface of Kapton. EDX mapping reveal the formation of a perforated gold thin film and affirm presence of gold (Au) nanoparticles. Which are uniformly distributed on Kapton surface.

The ultraviolet/visible (UV/vis) absorption spectrum was recorded (**Figure 2.4c**). This spectrum displays two obvious plasmon bands at 670 nm and 980 nm due to the excitation of surface plasmon waves, acting as two-dimensional diffraction gratings that convert incident photons into SP waves.¹² The increase in absorption < 500 nm is due to the underlying Kapton substrate showing strong absorption at this wavelength range.

To get insight into the surface plasmon modes of S1, the electric field distribution within the structure was determined using a finite element method. A sketch of the S1 cell used in the numerical computations is seen in **Figure 2.4d** and the corresponding results are shown in **Figure 2.4e-f**. The simulated electric field distribution within the structure for an incident light wave at 980 nm indicates the excitation of a surface plasmon mode of

S1. One notes, in particular, the enhancement of the electric field in the proximity of the nanoholes (**Figure 2.4e-f**), which is characteristic of a surface plasmon mode.

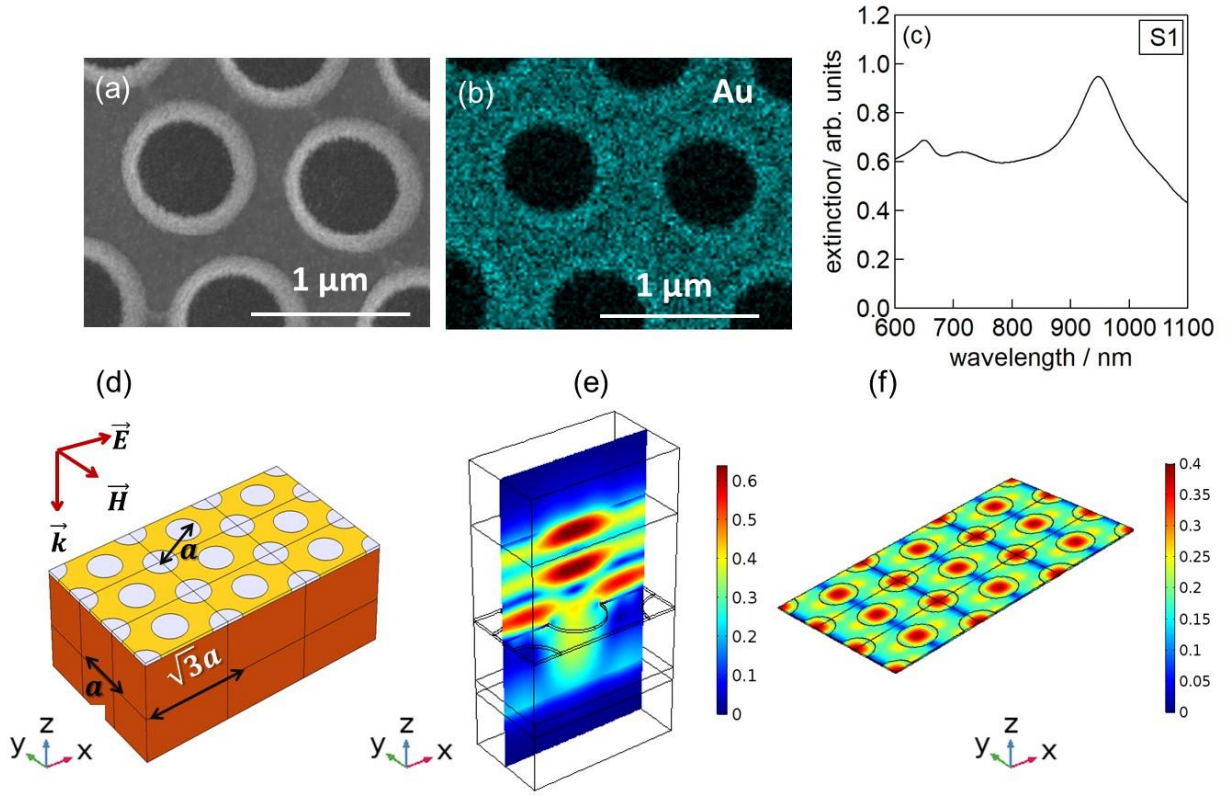


Figure 2.4. Plasmonic characteristics of the electrodes: (a) Scanning electron microscopy (SEM) image of a nano-perforated gold thin film electrode (S1), (b) EDS mapping of Au. (c) UV/vis absorption spectrum of S1, (d) Sketch of the simulated structure consisting of an Au NHs hexagonal grating deposited on a semi-infinite Kapton substrate. Incidence medium (air) is set on top of the Au NHs, (e) Computed electric field map depicted in the zx -cut plane, (f) Computed electric field map depicted in the xy -cut plane. The scale bars consider a normalized electric field in S1 with respect to the maximum value of the field in the system, corresponding to 980 nm incident light.

Figure 2.5a shows the temperature distribution map within a zx-cut plane (in the middle of the structure) at different instants of exposure time: $t = 1.7 \mu\text{s}$ (near $t = 0$), $t = 5 \mu\text{s}$ and $t = 20 \mu\text{s}$ (at equilibrium). Plasmon driven heating starts within the metal film part near and around the nanoholes where the localized plasmon is oscillating. The generated heat diffuses towards the upper boundary (water surface in contact with air) playing the role of a heat sink. Once equilibrium is reached, the heat remains at its maximum near the gold nanoholes in the metal part as well as in water near the upper surface, while it is, as expected, quite lower or null near the downward surface remaining at room temperature $T = T_r$. The change in temperature upon illumination S1 at 980 nm at 2 W cm^{-2} (**Figure 2.5b**), as measured by a photothermal-camera, shows a comparable temperature variation reaching 53°C . Illumination at 0.5 W cm^{-2} resulted in solution temperature of 30°C , while 40°C are reached at 1 W cm^{-2} .

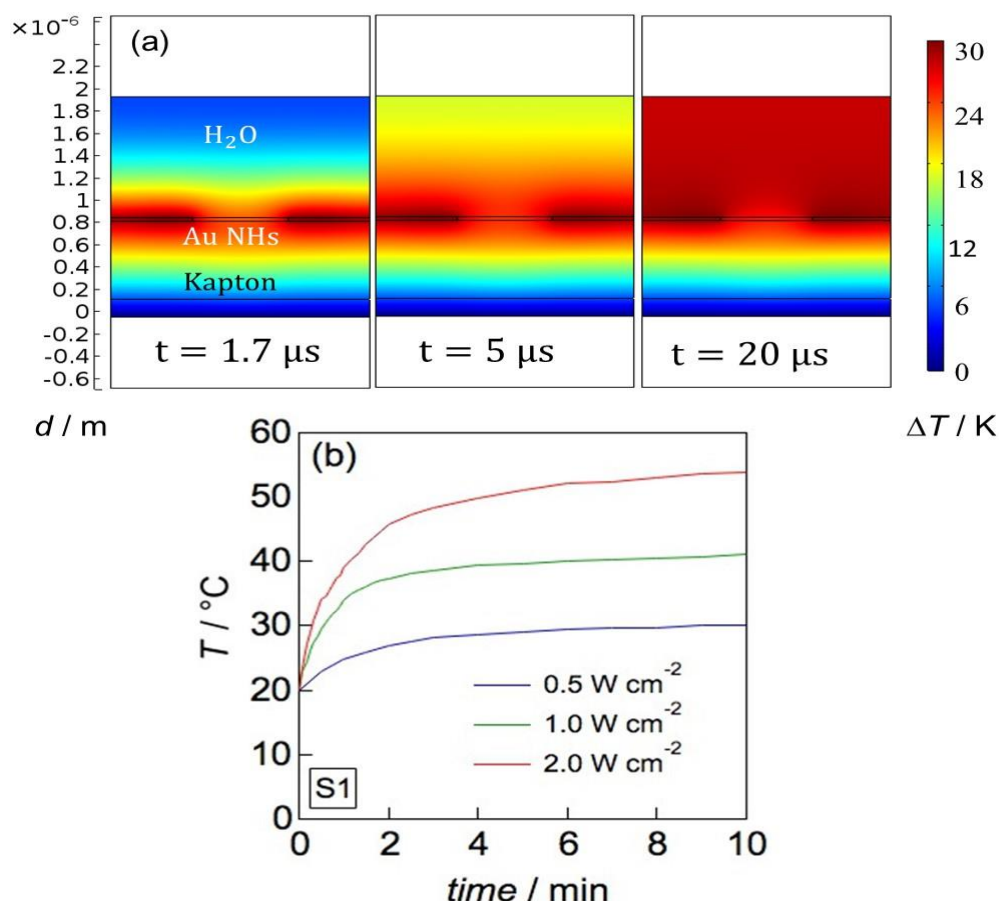


Figure 2.5. Plasmon driven temperature distribution map: (a) within the zx-cut plane (in the middle of the structure) at different instants of time, for an incident light intensity of 2 W cm^{-2} , (b) Photothermal heating curves of S1 immersed in 0.1 M NaOH solution and exposed to laser light of 980 nm at 0.5, 1.0 and 2.0 W cm^{-2} .

Electrochemical active surface Area

The electrochemically active surface area (A) in the electrochemical cell was derived from the linear plot of the peak current as a function of the of the scan rate (**Figure 2.6a-b**) according to Randles–Sevcik equation below :

$$i_p = 0.44nFAC_f \left(\frac{nFvD_f}{RT} \right)^{\frac{1}{2}}$$

Eq 2.1.1

$$A = \frac{S}{\left(268600 \times n^{\frac{3}{2}} \times D_f^{\frac{1}{2}} \times C_f \right)}$$

Eq 2.2.2

where n is the number of electrons transferred in the redox event ($n = 1$), D_f is the diffusion coefficient of ferrocenemethanol ($7.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$), C_f is the concentration of ferrocenemethanol ($0.0001 \text{ mol cm}^{-3}$), and S is the slope of the linear fit to the data. The exposed area of the working electrode was 0.75 cm^2 .

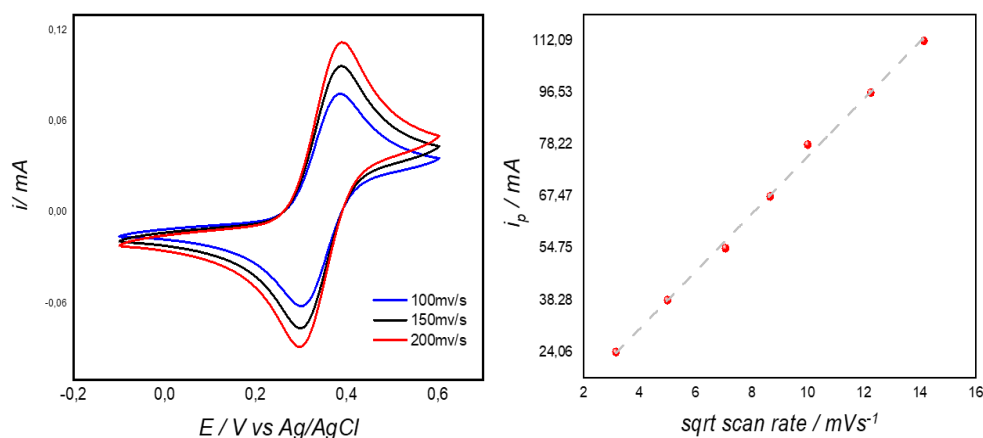


Figure 2.6. (a) Cyclic voltammograms (CVs) recorded in ferrocenemethanol (10 mM) / KCl (0.1 M) at different scan rate, (b) current density vs square root of the scan rate.

2.3. Electrochemistry under light illumination

Under light irradiation at 980 nm, the electrochemical charge transfer increases (**Figure 2.7a**). The current density rises linearly with light intensity (**Figure 2.7c**) and an activation energy (E_a) of $13.7 \pm 0.4 \text{ kJ mol}^{-1}$ was determined (**Figure 2.7b**). It has been recently postulated that illumination intensity-dependent photocatalytic activities lead to relevant mechanistic insights.¹³ While exponential relationships between photon-induced rates and illumination intensities have been assigned to mechanisms that are driven by a thermal process, a linear rate dependence on intensity is usually associated with an electron driven process, which corroborates our observations.

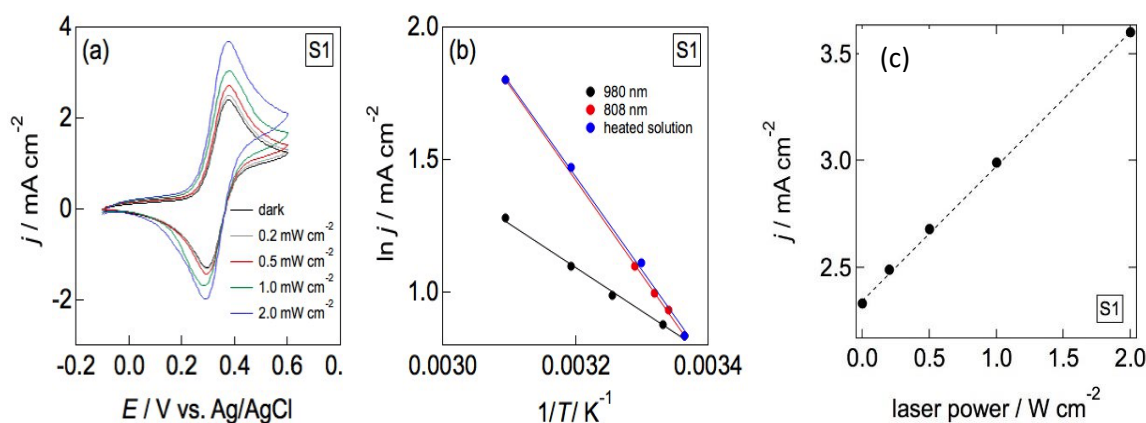


Figure 2.7. Plasmon-enhanced electrochemical activity of nanoperforated gold thin film electrodes(S1): (a) Cyclic voltammograms (CVs) recorded in ferrocenemethanol (10 mM) / KCl (0.1 M) with a scan rate of 100 mV s^{-1} under light irradiation for 5 min at 980 nm with varying intensity, (b) Arrhenius plots of the maximal current density derived from Figure 2.6a and Figure 2.7a-b, (c) Variation of the anodic peak current as a function of light intensity.

To account for possible temperature-related effects, cyclic voltammograms were recorded in thermostated solutions with temperatures up to 50°C (**Figure 2.8a**), providing an activation energy of $E_a = 29.4 \pm 0.9 \text{ kJ mol}^{-1}$ (**Figure 2.7b**) (E_a was calculated according to Arrhenius equation ($\ln j = \ln j_0 - E_a / RT$)). The difference of 15.7 kJ mol^{-1} in E_a is due to the plasmon-mediated effect and the generation of hot electrons, facilitating electron transfer and oxidation of ferrocenemethanol. In addition, a wavelength-dependent current is observed (**Figure 2.8b**). Irradiation of S1 with a laser at 808 nm resulted in $E_a = 29.0 \pm 0.9 \text{ kJ mol}^{-1}$, comparable to that of a heated solution

and lower when compared to illumination at 980 nm. This verifies experimentally the occurrence of plasmon mediated hot electron injection.

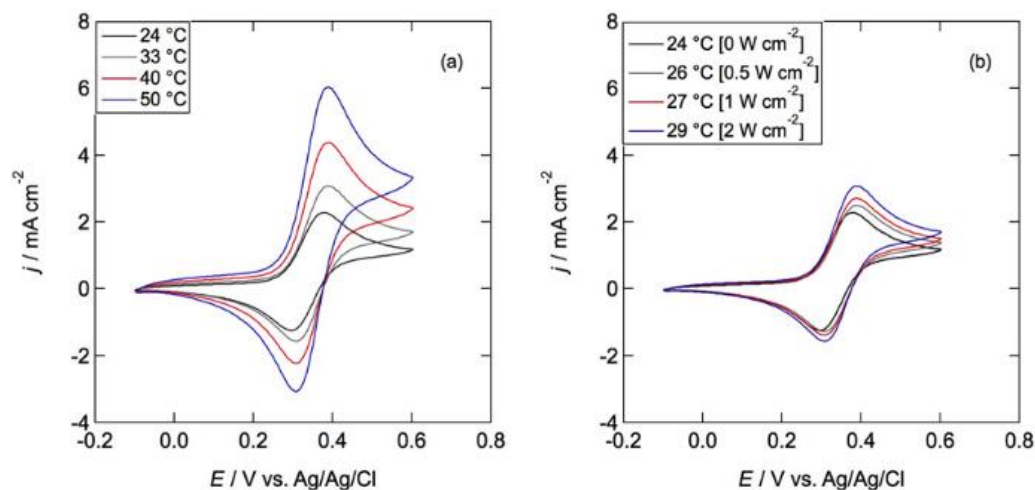


Figure 2.8. Cyclic voltammograms recorded in ferrocenemethanol(10 mM)/KCl (0.1 M) solutions at (a) different temperatures and (b) under 808 nm laser irradiation from 0 to 2 W cm⁻², Scan rate is 100 mV s⁻¹.

2.4. Application to oxygen reduction reaction

The electrocatalytic activity of S1 towards ORR in alkaline condition (0.1 M NaOH) was investigated in the following. Several studies indicate that the first electron transfer to O₂ determines the overall rate, being O₂ + e⁻ → O₂⁻ in basic electrolytes.¹⁴ Note that using gold as electrode, the reaction depends on the surface atomic arrangement, being faster on Au(100) due to a lower coverage with absorbed OH in the region where the ORR occurs.

Plasmon-enhanced ORR activity was assessed by voltammetric measurements. Linear sweep voltammetry curves of S1 in N₂-saturated and O₂-saturated 0.1 NaOH solution at an angular rotation rate of 1000 rpm and a scan rate of 25 mV s⁻¹ are presented in **Figure 2.9a**. An increase in the cathodic current is observed in the O₂-saturated solution, suggesting that S1 has electrocatalytic activity for reducing oxygen. Irradiation with a laser light of 980 nm increases the current density related to oxygen reduction as a function of light intensity. The ORR onset potential, determined at a current density of 10 μA cm⁻² is 0.98 V (vs. RHE) at 0.5 W cm⁻², 1.02 V (vs. RHE) at 1 W cm⁻² and 1.07 V (vs. RHE) at 2 W cm⁻². It is comparable to that of a Pt/C (40 wt. %) electrode,

experimentally determined as 1.07 V (vs. RHE) (**Figure 2.9b**), and in excellent agreement with the onset potential reported by Perez et al.¹⁵ $E_{\text{onset}} = 1.07$ V (vs. RHE). Moreover, the limiting current density upon irradiation at 2 W cm^{-2} ($j = -4.2 \text{ mA cm}^{-2}$) is comparable to that of Pt/C (40 wt.%) under irradiation ($j = -3.9 \text{ mA cm}^{-2}$) and largely increased compared to that of Pt/C (10 wt.%) ($j = -2.8 \text{ mA cm}^{-2}$) at $E = 0.80$ V (vs. RHE) bias. Performing ORR in a thermostated electrode (**Figure 2.9c**) results in lower ORR currents even at 50°C . The performance of S1 under light irradiation is competitive to other electrocatalysts reported in the literature (**Table 2.1**).¹⁶

Table 2.1. ORR performance of precious metal-based catalysts in O_2 -saturated NaOH (0.1 M)

Catalyst	E_{onset} vs RHE	Conditions	Ref.
Noble metal-based catalysts			
Pt/C	1.07V	Alkaline/Acidic	15
Au NHs (980nm)	1.07V	Alkaline	This work
Pd Nanocubes	1.00V	Alkaline/Acidic	17
Au (100)	0.96V	Alkaline	18
rGO/Au	0.88V	Alkaline	19
Au (111)	0.84V	Alkaline	17
Metal-free catalysts			
N doped graphene	0.89V	Alkaline	20
S- and N-Doped CNT	0.96V	Alkaline	21
Transition metal-carbon hybride			
Fe/N/C	0.92V	Alkaline	22
Co/N/rGO	0.93V	Alkaline	23

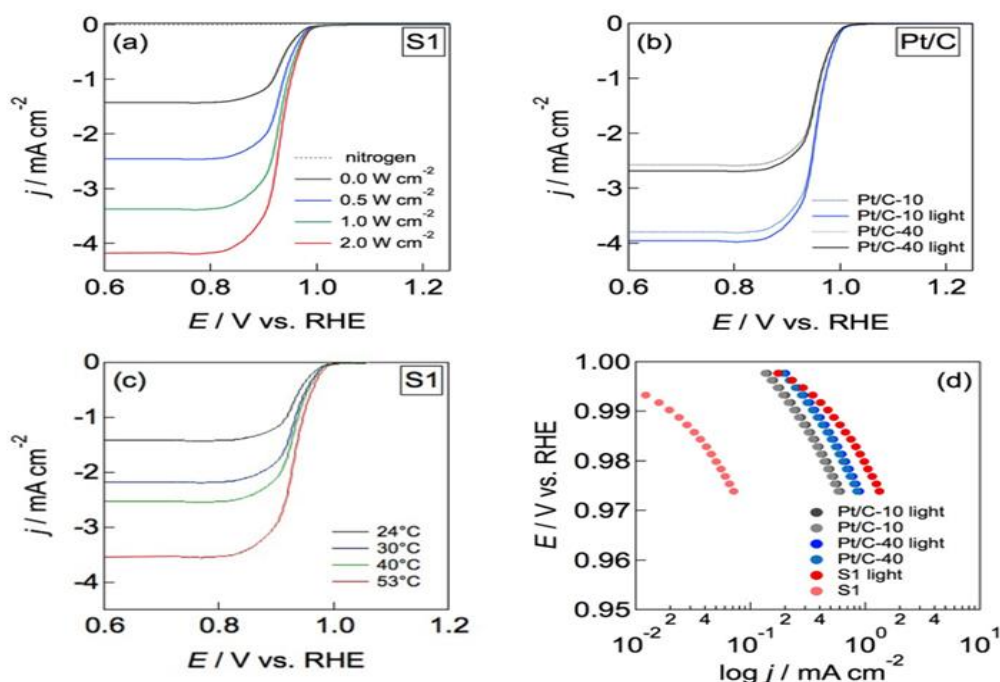


Figure 2.9. Linear sweep voltammetry (LSV) curves at constant rotation speed of 1000 rpm: (a) S1 in N₂- (grey) and O₂-saturated 0.1 M NaOH solution without (24 °C) and with laser illumination at 980 nm for 5 min at a power density of 0.5, 1 and 2 W cm⁻² corresponding to solution temperatures of 30 °C, 40 °C, 53 °C. The scan rate is 25 mV s⁻¹, (b) Pt/C (10 wt.%) and Pt/C (40 wt.%) in O₂-saturated 0.1 M NaOH solution without and with laser illumination at 980 nm for 5 min at 2 W cm⁻². Rotation speed is 1000 rpm and the scan rate is 25 mV s⁻¹. The temperatures of the solution correspond to 24 °C (no illumination) and 28 °C with illumination, (c) Linear sweep voltammograms of S1 in O₂-saturated 0.1 M NaOH solution thermostated at different temperatures, (d) Tafel slopes in O₂-saturated 0.1 M NaOH solution of the perforated Au NHs interface (S1) with and without irradiation at 2 W cm⁻² as well as the Pt/C (10 wt.%) and Pt/C (40 wt.%) interfaces.

Based on the polarization curves at 1000 rpm, the corresponding Tafel plots were estimated to evaluate the influence of light irradiation on the ORR kinetics (**Figure 2.9d**). The Tafel slopes for Pt/C (40 wt.%) are -72 mV/decade (in dark) in accordance with other reports¹⁵. Under light irradiation of Pt/C (40 wt.%) it drops to -54 mV/decade. In the case of Pt/C (10 wt.%) Tafel slopes of -100 mV/decade were obtained and did not change upon irradiation. When illuminated at 980 nm, S1 exhibits a Tafel slope of -44 mV/decade, while in the absence of illumination, a Tafel slope of -377 mV/decade was determined as expected to the low electrocatalytic activity of gold (**Table 2.2**). The

reduction in the Tafel slope suggests that the surface adsorption of oxygen is increasing and that oxygen bonds can be directly broken.

Table 2.2. Tafel slopes of S1 and Pt/C catalysts determined from LSV measurements in O₂-deaerated NaOH

Interface	Tafel slope mV/decade (Dark)	Tafel slope mV/decade (Light)
S1	-377	-44
Pt/C (40wt.%)	-72	-54
Pt/C (10wt.%)	-100	-100

2.5. Mechanism Au NHs enhanced ORR

To understand the origin of the current enhancement, the ORR reaction was performed at different solution temperatures up to 50°C (**Figure 2.10c**). The temperature corresponds to the surface temperature as determined with a thermocouple attached to the sample when immersed in 0.1 M NaOH and irradiated with a 980 nm laser at 2.0 W cm⁻² for 10 min. We observed that the thermal heating effect on the ORR was weaker than the plasmonic effect. To gain further evidence of the plasmon-mediated ORR, the activation energy (E_a) of ORR was determined under light illumination and compared to that of a thermostated solution. Plots of $\ln j$ vs. $1/T$ revealed a linear relationship in both cases (**Figure 2.10a**). Using the Arrhenius equation, E_a under light irradiation was estimated as 22.2 ± 0.2 kJ mol⁻¹, while in the dark, it was 33.5 ± 0.3 kJ mol⁻¹. Plasmon-induced processes generated a significantly higher ORR reactivity on S1 due to the formation of hot electrons.²⁴ According to these results, the mechanism for the enhanced activity towards ORR under laser irradiation is as following (**Figure 2.10b**): under laser excitation, localized surface plasmons are generated on the nanopatterned gold film electrode forming electron-hole pairs. The generated hot electrons can then follow different pathways: (i) recombination with the formed holes in the Au NHs layer, (ii) direct electrochemical oxygen reduction in alkaline solutions on the Au NHs surface, or (iii) injection into the conducting band of the Ti/TiO₂ semiconductor adhesion layer, followed by oxygen reduction. In our case, both direct electrochemical reduction of oxygen and the injection of hot electrons via the Mott-Schottky barrier into the thin Ti/TiO₂ layer might occur, assuming that the electron injection is faster than the electron-

hole recombination process. The fast generation and the injection of hot electrons at 980 nm affect the current density profile abruptly (**Figure 2.10c**); irradiation at 808 nm results in no change in the current density profile, underlying a plasmon-driven effect occurring at 980 nm.

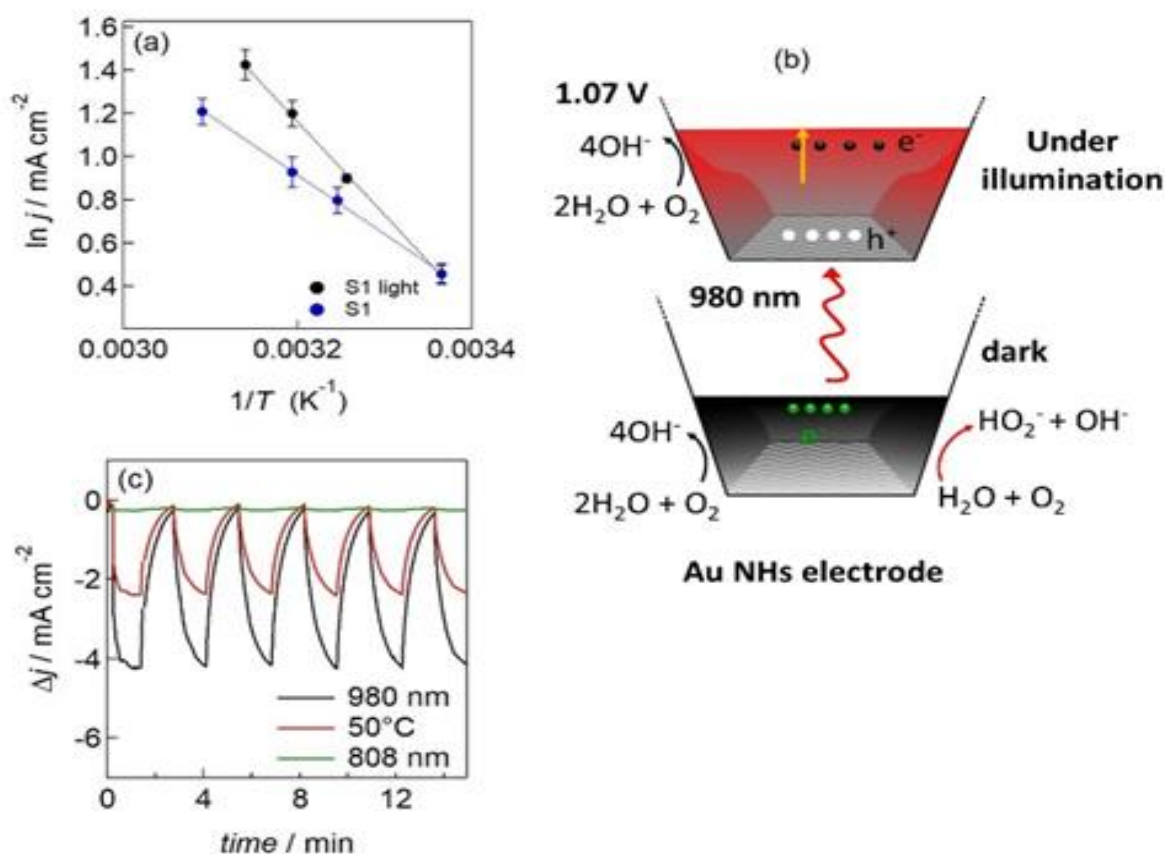


Figure 2.10. Mechanistic considerations: (a) Arrhenius plots under irradiation at 980 nm (black) and for a thermostated electrolyte (blue), (b) Schematics of the plasmon-enhanced ORR mechanism under basic conditions, (c) Current density - time curves with irradiation at 980 nm (black) at 2 W cm^{-2} , 808 nm at 2 W cm^{-2} (green) and with no illumination but thermostated at 50°C (red) when immersed in 0.1 M NaOH at $+0.92 \text{ V}$ (vs. RHE) bias.

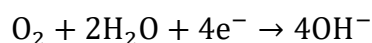
2.6. ORR under hydrodynamic conditions

The ORR is in addition studied under hydrodynamic conditions using a rotating disk electrode to induce forced convection. **Figure 2.11a** depicts the ORR voltammograms recorded at different rotation speeds under irradiation at 980 nm. The corresponding Koutecký-Levich plot ($1/j_{\text{lim}}$ vs. $\omega^{-1/2}$) is presented in **Figure 2.11b**. The number of electrons transferred in the ORR under light illumination was estimated as $n = 4.08 \pm 0.4$ according to

$$\frac{1}{j_{\text{Lim}}} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}$$

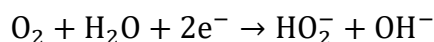
Eq 2.6.1

where j_{lim} is the diffusion-limiting current density (A cm^{-2}), j_k is the kinetic current density (A cm^{-2}), $B = 62nFCD^{2/3}\nu^{-1/6}$ is the Levich constant, ω is the angular velocity of the disk (rad s^{-1} , $1 \text{ rpm} = \pi/30 \text{ rad s}^{-1}$), F is the Faraday constant (96485 C mol^{-1}), c the bulk concentration of O_2 ($c = 1.2 \times 10^{-6} \text{ mol cm}^{-3}$), ν is the kinematic viscosity of the electrolyte ($\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$), and D is the diffusion coefficient of O_2 in 0.1 M KOH ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$). This underlines that the ORR reduction occurs in a direct four-electron pathway according to

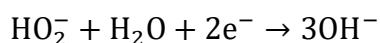


Eq 2.6.2

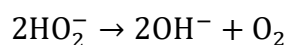
Interestingly, from measurements in dark (**Figure 2.11c**), $n = 3.5 \pm 0.3$ was determined. This indicates that a minor concentration of oxygen is reduced by the alternative two-electron pathway¹⁶ followed by either further reduction to OH^- or a disproportionation reaction as



Eq 2.6.3



Eq 2.6.4



Eq 2.6.5

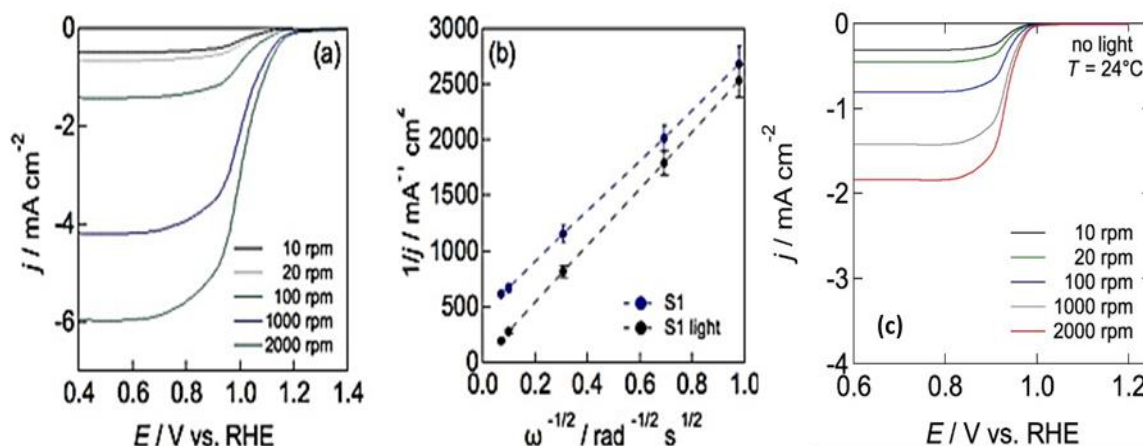


Figure 2. 11 . Hydrodynamic conditions: (a) Current density vs. potential curves in O₂-saturated 0.1 M NaOH solution recorded by angular rotation rates from 10 to 2000 rpm under light irradiation at 980 nm, (2 W cm⁻²) at a scan rate of 25 mV s⁻¹, (b) Koutecký-Levich plots under irradiation (data from panel a) and in dark (data from Figure 2.10c), (c) Linear sweep voltammograms of S1 in O₂-saturated 0.1 M NaOH solution in dark: Current density vs. potential curves of S1 in O₂-saturated 0.1 M NaOH solution under recorded angular rotation rates of 10, 20, 100, 1000 and 2000 rpm. Scan rate = 25 mV s⁻¹, no light irradiation (T = 24°C).

2.7. Stability

The ORR was found to be highly reproducible as seen in the overlapping LSV curves for 5 different electrodes (**Figure 2.12a**), while the long-time stability was assessed by current density - time plots (**Figure 2.12b**). No significant decrease in the oxygen reduction current was observed over a period of 30 h. Furthermore, the LSPR band as well as the morphology of the samples has not been altered after ORR stability tests. These results clearly confirm that nanoporated gold thin film interfaces are suitable electrodes for the ORR reaction (**Figure 2.12c-d**).

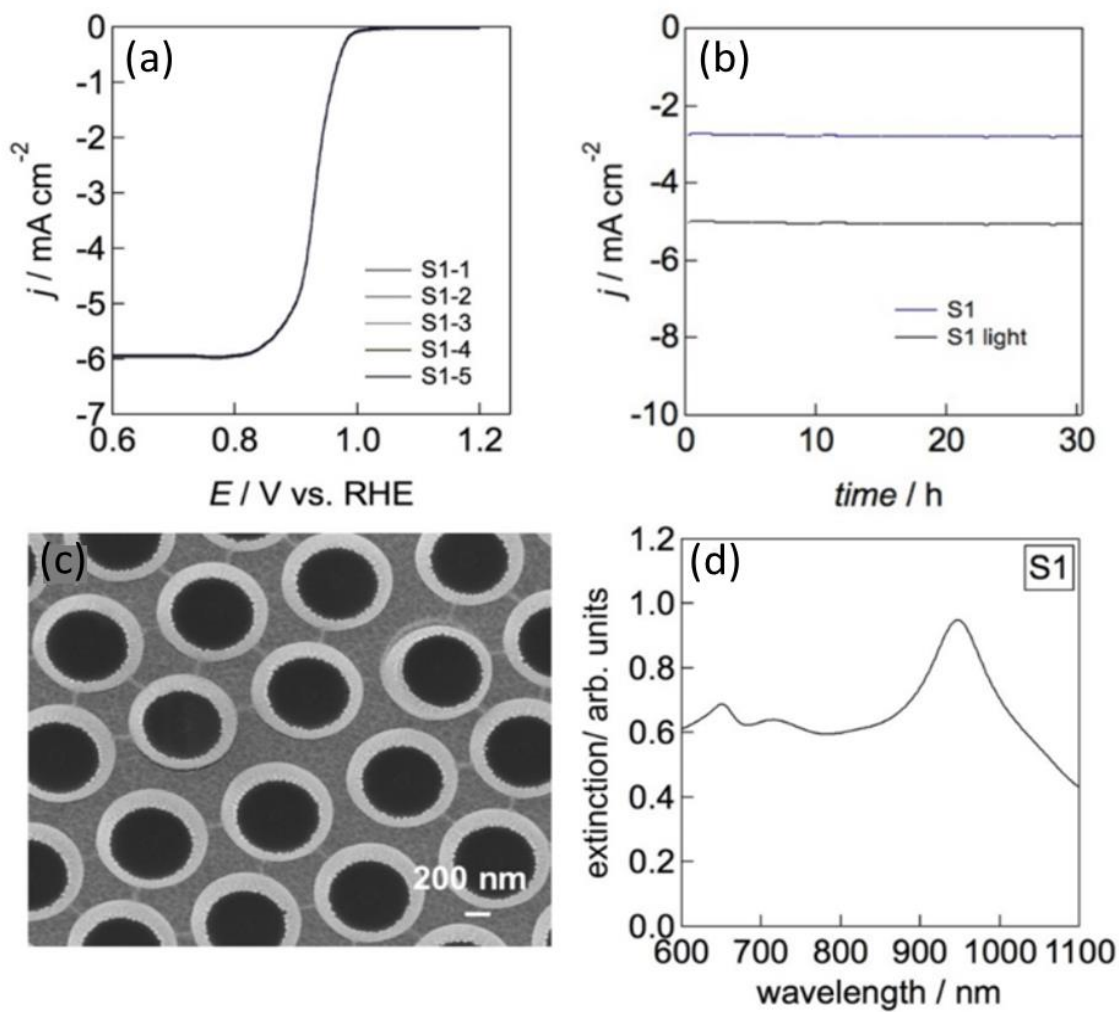


Figure 2.12. (a) ORR polarization curves of five specimens in O₂-saturated 0.1 M NaOH. (b) ORR stability tests at $E = + 0.90$ V without (blue) and with light irradiation at 2 W cm⁻² (black) by following the change of the current density with time, (c) SEM image after ORR stability tests, (d) UV/Vis after ORR testing.

2.8. Conclusion

The results indicated that hot electrons are generated from plasmon decay, which in turn facilitate the electrocatalytic oxygen reduction reaction. Using this experimental strategy, it was found that ORR under light irradiation proceeds via a $4e^-$ pathway, while in the dark it has a contribution from the $2e^-$ side reaction. Plasmon-enhanced electrochemical reduction of oxygen to water on perforated gold nanohole electrodes represents another application of triple - plasmonic, chemical and catalytic - functional gold nanostructures. In general, this highly practical plasmon-induced hot electron enhancement method will be beneficial to energy and environmental applications and may open up avenues for the optical control of (electro)chemical reactions.

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CHAPTER III: Plasmon-enhanced Electrocatalytic activity of Gold Nanoparticles/ Cu_2O Nanocrystals for Oxygen Evolution Reaction

3.1. INTRODUCTION

The oxygen evolution reaction (OER) is one of the important process in water splitting technologies. The OER's sluggish kinetics with a multistep electron transfer can produce an overpotential that is higher than the thermodynamic value of 1.23 V, thereby severely impeding the realization of efficient water splitting. An efficient electrocatalyst is required to accelerate its reaction rate and decrease the overpotential for OER.

Copper-based catalysts are considered ideally suited as they show a large panel of redox properties (Cu^0 , Cu^+ , Cu^{2+} and Cu^{3+}), are robust, of low-cost and low toxicity.¹ They have demonstrated superior electrocatalytic activity and stability and become the most promising alternative materials in OER. Next to Cu^0 and Cu^{2+} based materials, Cu^+ in the form of cuprous oxide (Cu_2O) has proven to be well-adapted for electrocatalytic redox reactions,²⁻⁵ including OER.⁵⁻⁶ Cu_2O is a p-type semiconductor with a narrow band gap of 2.1 eV (571 nm) and a relatively high absorption coefficient in the visible region. It crystalizes in a cubic with lattice parameter of 4.27 Å and can be viewed as two sublattices, a body-centered cubic (bcc) of oxygen anions (**Figure 3.1**) and a face-centered cubic (fcc) sublattice of copper cations. The oxygen atoms occupy tetrahedral interstitial positions relative to the copper. The distance between Cu-O atoms is 1.85 Å, O-O is 3.68 Å and Cu-Cu is 3.02 Å.

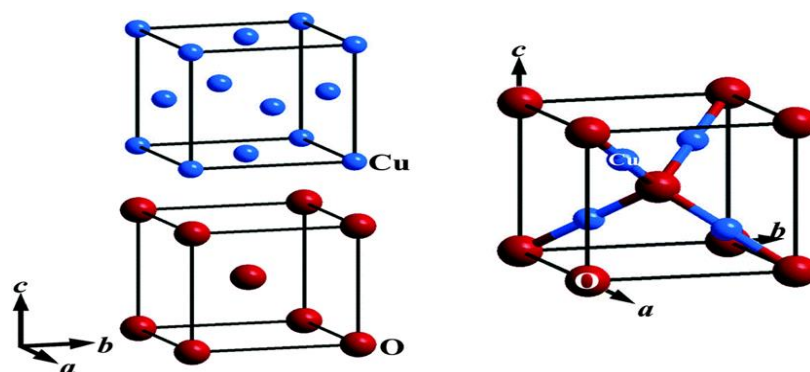


Figure 3.1. Crystallographic structure of Cu_2O with oxygen as the center of the bcc cell. oxygen represented in red and copper in blue.

Upon irradiation with photons with energy higher than the band gap, electrons in the valence band can be promoted to the conduction band, resulting in electrons and holes separation used as energetic carries for photocatalytic driven redox reactions. The fast recombination of the photogenerated charge carriers together with the low conductivity and limited stability restricts until now the wider use of Cu_2O in electrocatalysis however.

A general approach to increase the conductivity of electrocatalysts is to mix them with high conductive materials such as metals, conducting polymers, carbon structures etc. Xu et al. developed a three-dimensional Cu_2O -Cu hybrid electrode with an overpotential of 250 mV for OER and a Tafel slope of $67.52 \text{ mV dec}^{-1}$ in alkaline solution. A durability over 50 h at a current density of 10 mA cm^{-2} was recorded.⁵ Zhang et al. synthesized Cu_2O nanoparticles coated with carbon ($\text{Cu}_2\text{O}@\text{C}$) with an onset overpotential of 250 mV and a Tafel slope of $63 \text{ mV decade}^{-1}$ in 1 M KOH aqueous solution. This catalyst maintained its catalytic activity for at least 100 h and required only an overpotential of 330 mV to attain a current density 10 mA cm^{-2} .⁷

The fast recombination of the photogenerated charge carriers can be also decreased by integration of noble metal nanostructures onto the surface of semiconductor catalysts. Gold nanoparticle-decorated $\text{Ni}(\text{OH})_2$ nanosheets⁸ and Au nanorod-decorated MoS_2 nanosheets⁹ represent examples of plasmonic metal–semiconductor electrocatalysts for OER respectively. Pan et al. developed Cu_2O -Au hybrid materials,⁴ efficient for photodegradation of methylene blue under visible light irradiation (**Figure 3.2**). Photoexcited electrons can be transferred from Cu_2O to the noble metal nanostructures, acting as electron sink due to the formed Schottky barrier at the metal-semiconductor interface, while the holes in the valence band remain free. Moreover, Au nanoparticles (Au NPs) display unique optical properties in the visible range as a result of the excitation of their localized surface plasmon resonance (LSPR), enabling enhanced light absorption favorable for plasmon-enhanced photocatalysis.

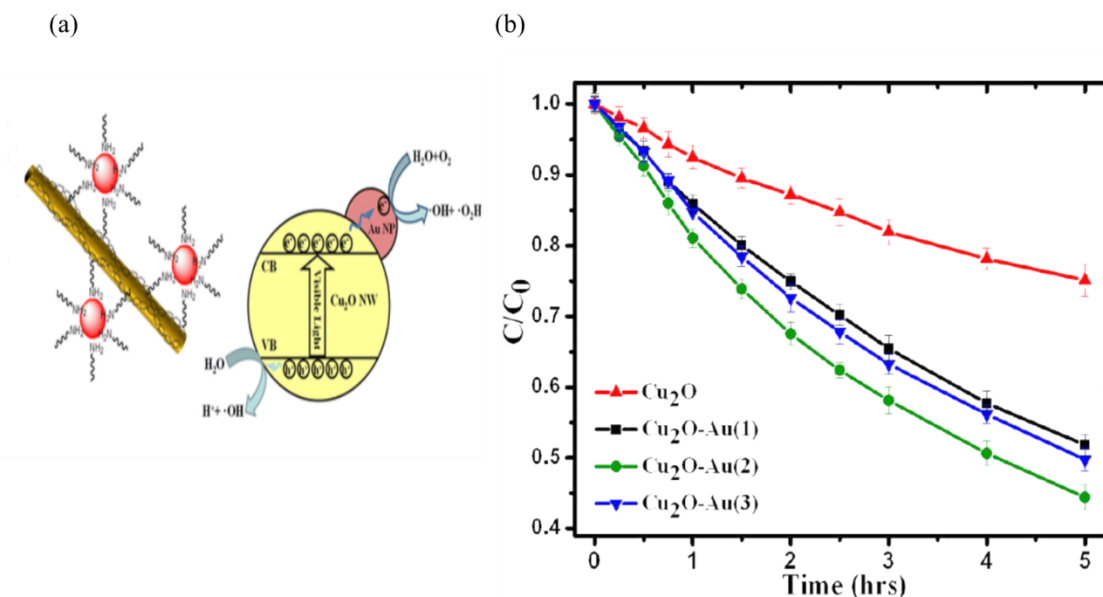


Figure 3.2. (a) Coupling between Cu₂O NWs and Au NPs and hot electron transfer from Au to Cu₂O in the presence of light. (b) The photodegradation of methylene blue in the presence of pure Cu₂O NWs and Cu₂O NWs attached to Au NPs with different coverage densities.⁴

Motivated by the work on Cu₂O-Au nanostructures, we investigated in the following of the morphology of Cu₂O nanocrystals has an influence on the electrocatalytic behavior for OER in basic medium. Although plasmon-enhanced electrocatalytic activities using Au nanostructures on Cu₂O have been reported,^{3-4, 10-14} these studies did not investigate the structure–performance relationships of Cu₂O-Au electrocatalysts. It is however well accepted that exposed crystal facets can strongly affect the catalytic activity of Cu₂O nanostructures.^{2, 15}

We investigated five different interfaces (**Figure 3.3**): gold electrodes (noted as S1 and used as control), S1 coated with Cu₂O cubes (S2) and octahedra (S3) as well as gold nanoparticle decorated Cu₂O cubes (S4, Cu₂O-Au cubes) Cu₂O octahedra (S4, Cu₂O-Au octahedra). The electrodes were formed by shape-directed solution synthesis of Cu₂O and Cu₂O-Au nanostructures followed by drop casting suspensions of the material onto gold thin film electrodes (see Annex for experimental details).

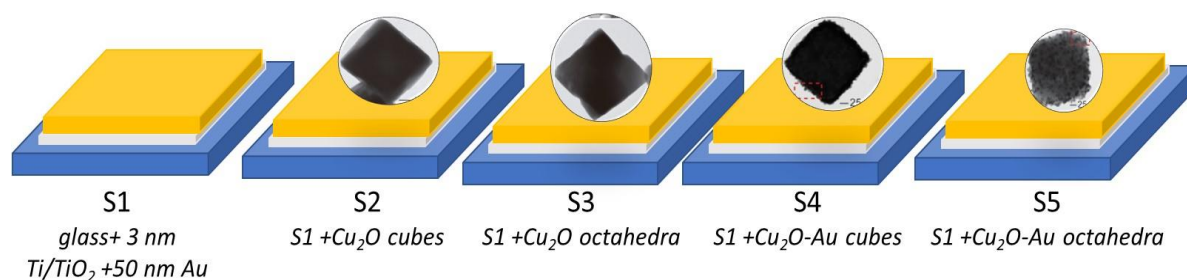
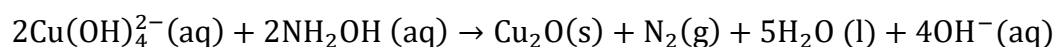


Figure 3.3. Schematic illustration of the five different electrode architectures employed for OER in this chapter.

3.2. Preparation of Cu₂O and Cu₂O-Au cubic and octahedral nanostructures

Cu₂O nanostructures with cubic and octahedral morphology were obtained using CuCl₂ precursor, sodium dodecyl sulfate (SDS) as surfactant and (NH₂OH·HCl) reducing agent under basic conditions. The synthesis of Cu₂O crystals was achieved by simply varying the amount of NH₂OH·HCl in the mixture as described in the following reaction:¹⁶



Eq 3.2.1

The formation of cubic and octahedral structures depends on the NH₂OH·HCl concentration, as this parameter influences the reaction kinetics and the growth rate along the [100] direction.

The synthesis of metal-semiconductor heterostructures may allow the combination of function of the corresponding components and/or enhanced performance resulting from the interactions between the different components. Previous reports on the synthesis of Au NPs decorated Cu₂O focused on using Au seeds to control the final shape of Cu₂O shell. Here, the Cu₂O cubes and octahedra were employed as templates for the nucleation and growth of Au NPs over their surface without the need of any surface modification/functionalization step, as depicted in **Figure 3.5a**. Our approach employed AuCl₄⁻(aq) as the Au precursor, PVP as the stabilizer, water as the solvent, and 90 °C as the reaction temperature.

The size of the cubic Cu_2O crystals was determined from the SEM and TEM images to be 298 ± 34 nm (**Figure 3.4a** and **4c**), which is comparable to 302 ± 38 nm for the octahedral Cu_2O crystals (**Figure 3.4b** and **4d**). The XRD diffractograms. (**Figure 3.4e**) of Cu_2O cubes and octahedra display peaks assigned to the (111), (200), and (220) crystallographic planes of the cubic structure of Cu_2O (JCPFS card number 05-0667). Interestingly, the relative intensity ratio between the (200) and the (111) peaks decreased as the shape varied from cubic to octahedral, which agrees with the formation of Cu_2O cubes and octahedra bounded by (200) and (111) facets, respectively. X-ray photoelectron spectroscopic (XPS) investigation of the Cu 2p region of both Cu_2O structures (**Figure 3.4f**) reveals bands at a binding energy of 932.5 and 952.4 eV corresponding to Cu(I) in Cu_2O , in accordance with literature reports¹⁷ and XRD analysis. The additional band at 934.2 eV (17 at.%) and 954.1 eV together with shake-up bands at 943.3 and 962.6 eV indicate the presence of some Cu^{2+} .¹⁷

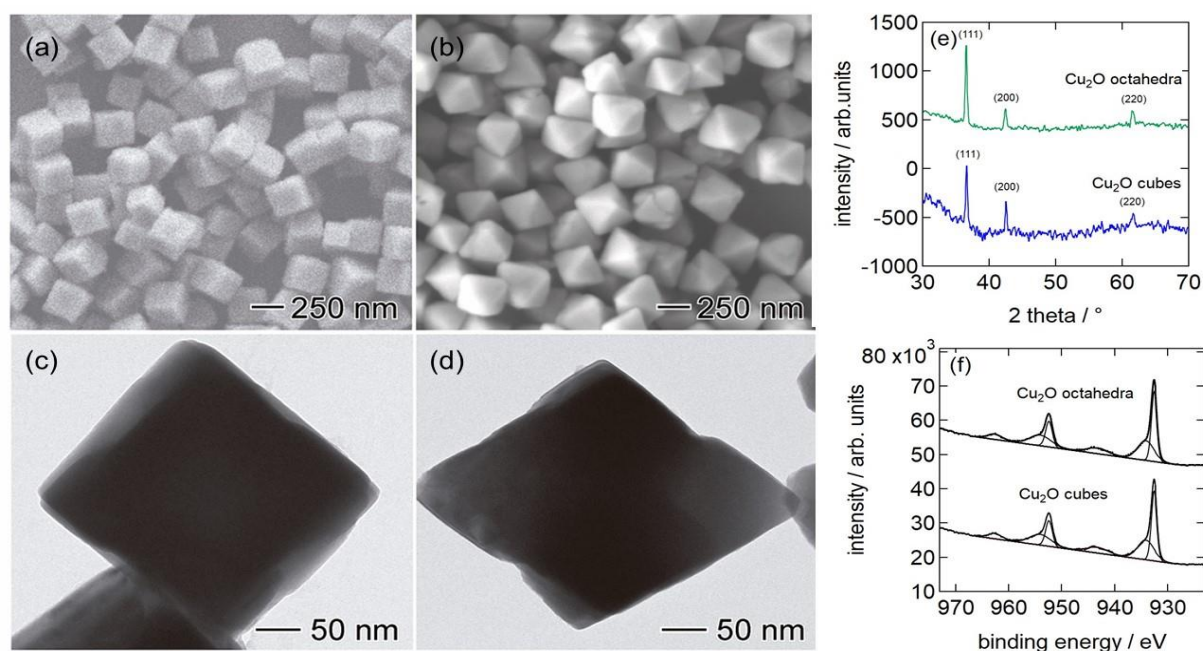


Figure 3.4. Characterization of Cu_2O cubes and octahedra. (a-b) Scanning electron microscopy (SEM) images of Cu_2O cubes (a) and Cu_2O octahedra (b). (c-d) High-resolution transmission electron microscopy (HRTEM) images of Cu_2O cubes and octahedra. (e) X-ray diffraction (XRD) patterns. (f) Cu 2p core level XPS spectra

Figure 3.5b-g depicts SEM, TEM and HRTEM images of the Cu₂O cubes and octahedra decorated with Au NPs obtained by this procedure. The uniform deposition (without agglomeration) of monodisperse, spherical, and ultrasmall (12 ± 3 nm) Au NPs over the entire surface of the Cu₂O can be clearly observed.

The XRD patterns of Cu₂O cubes and octahedra decorated with Au NPs (**Figure 3.5h**) agree with HRTEM results. While the peaks assigned to Cu₂O for both Cu₂O-Au cubes and octahedra remained unaffected after the deposition of Au NPs, the appearance of a low intense and broad peak assigned to Au (111) crystallographic planes of the fcc structure of gold could be clearly detected for both shapes.

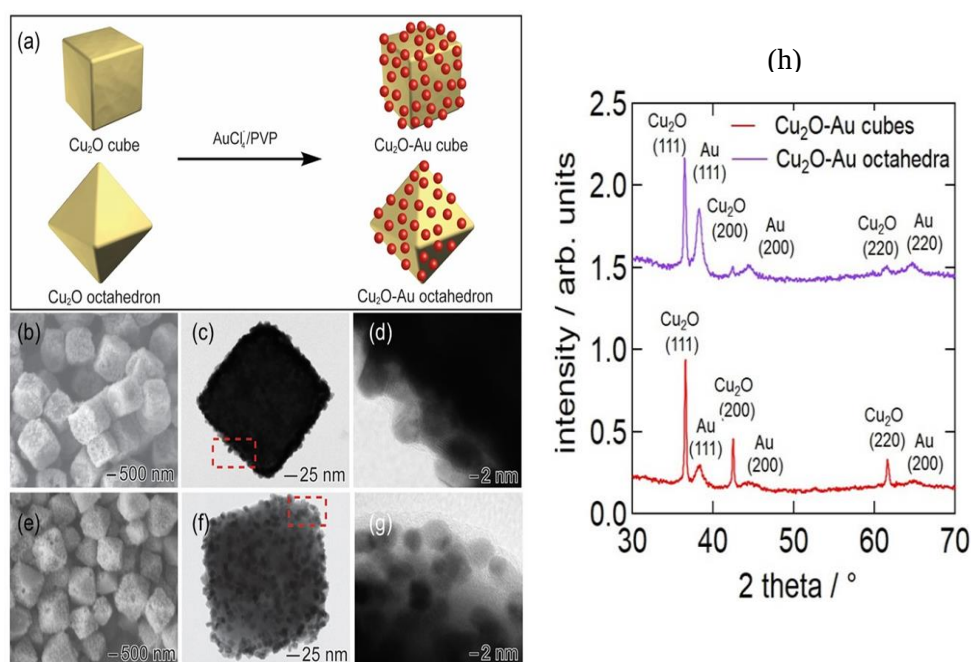


Figure 3.5. Cu₂O cubes and octahedra decorated with Au NPs on their surface. (a) Synthetic approach. (b, e) SEM images of Cu₂O-Au cubes and Cu₂O-Au octahedra. (c, f) TEM images of Cu₂O-Au cubes and Cu₂O-Au octahedra. (d, g) HRTEM images of Cu₂O-Au cubes and Cu₂O-Au octahedra. (h) X-ray diffraction (XRD) patterns for Cu₂O-Au cubes and Cu₂O-Au octahedra

3.3. Considerations about the electrochemical active surface area (EASA)

The activity of electrocatalysts is attributed to both intrinsic effects and surface area effects. In order to compare the intrinsic catalytic activity of various electrode materials, the electrochemically active surface area (EASA) of each electrode must be determined. Electrochemically active surface area (EASA) represents the area of the electrode material that is accessible to the electrolyte that is used for charge transfer and/or storage. In this work EASA were determined by recording cyclic voltammograms in the potential range between 0.15 and 0.20 V vs. RHE where no faradic processes are observed (**Figure 3.6**). From the slope of the current density (j) vs. scan rate dependence, the electrode capacitance C ($\mu\text{F cm}^{-2}$) and the EASA values of S1-S5 (**Table 3.1**) were determined and used in the following. The EASA is defined as $C_{\text{electrode}}/C_{\text{gold}}$.

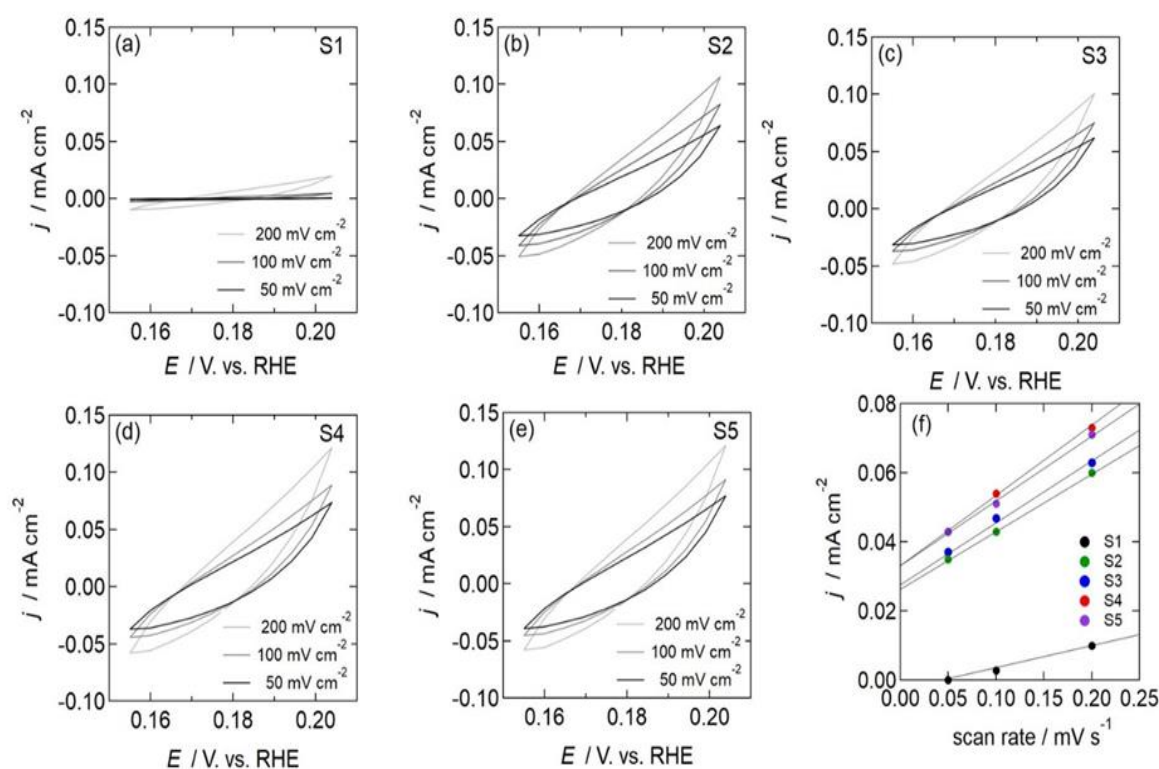


Figure 3.6. Determination of electrochemical active surface area (EASA). (a-e) Cyclic voltammograms in 0.1 M NaOH at different scan rates (50, 100, 200 mV s^{-1}) for S1-Au, S2-Au/ Cu_2O cubes, S3-Au/ Cu_2O octahedra, S4-Au/ Cu_2O -Au cubes, S5-Au/ Cu_2O -Au octahedra. (f) Current density vs. scan rate of S1-S5.

Table 3.1. Determined capacitance values for S1-S5 from Figure S2 together with calculated EASA values.

Electrode	Capacitance $\mu\text{F cm}^{-2}$	EASA) cm^2
S1	67	1.00
S2	170	2.50
S3	167	2.49
S4	198	2.95
S5	185	2.76

3.4. Application to Oxygen evolution reaction

The five different electrodes S1-S5 (**Figure 3.3**). Were investigated for their electrocatalytic activity in NaOH (0.1 M). In order to ensure correct and appropriate comparison among the electrodes, and in agreement with recommendations in recent literature¹⁸.

The electrocatalytic activities of S1-S5 for the oxygen evolution reaction (OER) in O₂-saturated 1 M NaOH are presented in **Figure 3.7a**. The gold electrode (S1) exhibits very limited OER activity within the measured potential range. The onset potential of oxygen evolution on S2 is 1.46 V (vs. RHE) corresponding to an overpotential of $\eta = 230$ mV, comparable to that of previously reported IrO₂ (230 mV)^{17, 19} and Cu₂O-Cu foam electrodes (250 nm).⁵ To reach 10 mA cm⁻², an overpotential of 350 mV is required. S3 has an OER onset potential at 1.61 V (vs. RHE) correlating to $\eta = 470$ mV at 10 mA cm⁻².

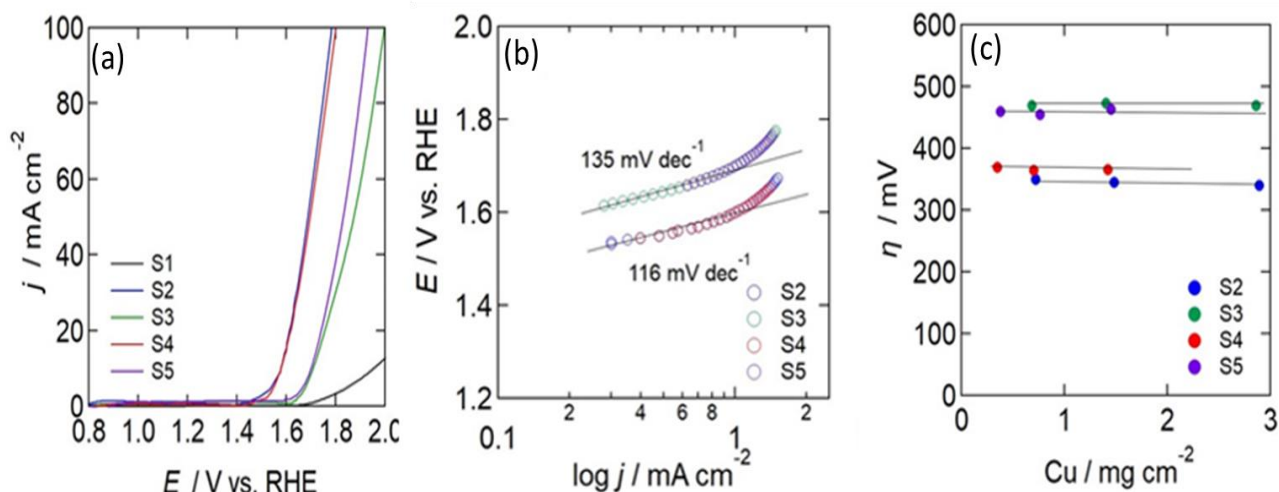


Figure 3.7 . Oxygen evolution reaction (OER) under basic conditions. (a) Linear sweep voltammograms (LSV) in O₂-deaerated NaOH (0.1 M) of S1 (black), S2 (blue), S3 (green), S4 (red) and S5 (violet), scan rate of 25 mV s⁻¹. (b) Tafel plots of S1 (black), S2 (blue), S3 (green), S4 (red) and S5 (violet). (c) influence of Cu mass on overpotential at 10 mA cm⁻²

The kinetics of the electrocatalytic OER reaction was evaluated by recording the corresponding Tafel plots (**Figure 3.7b**). Tafel slopes of 116 mV/decade (S2) and 135 mV/decade (S3) were determined respectively. Decoration of Au nanoparticles onto Cu₂O does not show any further improvement of the OER reaction (**Table 3.2**).

Table 3.2. OER activity: Overpotential and Tafel slopes of S2-S5 determined from LSV measurements in O₂-deaerated NaOH

Interface	η @10mA cm ⁻²	Tafel slope mV/decade
S2	350	116
S3	470	135
S4	370	116
S5	460	135

To investigate further the effect of the Cu concentration on the interfaces electrodes of different Cu loading as determined by ICP-OES (**Table 3.3**) were investigated. The OER activity showed to be independent on the mass of Cu₂O deposited (**Figure 3.7c**).

Table 3.3. ICP-OES (inductively coupled plasma - optical emission spectrometry) analysis of the material loading on S1.

Cu ₂ O deposited onto S1/mg	Cu ₂ O cubes/mgcm ⁻²	Cu ₂ O octahedra/mg cm ⁻²
1	0.72±0.4	0.68±0.4
2	1.48±0.5	1.40±0.4
4	2.89±0.3	2.86±0.3
Cu ₂ O-Au deposited onto S1/mg	Cu ₂ O cubes/mg cm ⁻²	Cu ₂ O octahedra/mg cm ⁻²
1	0.35±0.4	0.38±0.4
2	0.70±0.5	0.76±0.4
4	1.42±0.3	1.45±0.3

The results indicated that the cubic shaped Cu₂O nanostructures were more active than the octahedra ones. The Cu₂O and Cu₂O-Au cubes have OER activity comparable and even superior to a large range of other metallic and non-metallic OER catalysts (**Table 3.4**).

Table 3.4. Comparison of electrocatalytic activity of some reported Cu-based nonprecious OER electrocatalysts in alkaline media.

Catalyst	η /mV (10 mA cm ⁻²)	Tafel slope (mVdec ⁻¹)	Ref.
Cu-N-C/graphene	770	n.a.	²⁰
CuFe ₂ O ₄ spinel nanofibers	490	94	²¹
Cu ₂ O-Cu foams	350	67.5	⁵
Cu ₂ O and Cu ₂ O-Au nanocubes on gold electrodes	350	116	This work
N and S co-doped graphite foam	346	78	²²
Cu/Cu ₂ O/CuO	290	64	²³
Cu ₂ O-Au nanocubes under solar light irradiation	200	97	This work

The p-type Cu₂O semiconductor displays a broad absorption from 500-800 nm, a region which accounts for 42-43% of the total sun light irradiation. Gold-based nanoparticles, on the other hand, exhibit narrow absorption bands with spherical colloidal gold particles having absorbance

maxima between 515-570 nm.⁴ Integration of Au nanoparticles onto Cu₂O is expected to increase light absorption and form LSPR excited hot charge carriers. While these hot electrons cool very fast (picoseconds) by electron-phonon scattering within the noble metal lattice, the hot electrons can be injected into the conduction band of Cu₂O, stabilizing the holes in Cu₂O, assuming that the electron injection is faster than the electron-hole recombination process.

The UV-vis absorption spectra of S2-S5 (**Figure 3.8a**) show a broad absorption between 450-680 nm with a maximal absorption at around 561 nm. S4 exhibits a red shift in its maximum to 606 nm with an intense absorption between 450-760 nm. S3 and S5 display sharper UV-vis signatures with absorption maxima at about 566 nm (S3) and 570 nm (S5). The presence of Au NPs in S4 and S5 is largely overlapped by the Cu₂O absorption band. However closer inspection of the UV-vis spectra for S4 and S5 shows a shoulder at 518 nm, characteristics of Au nanospheres of 12 nm in diameter.

Figure 3.8b depicts the linear sweep voltammograms of S1-S5 when irradiated with a 150 W arc lamp at a power density of 1.3 sun (180 mW cm⁻²). No change in OER behavior was observed for S1-S3. This indicates most likely that the generated hole-electron pairs in Cu₂O are recombining faster, making unavailable the holes for water oxidation. The situation is different in the case of S4 and S5. Solar light illumination shifts the OER onset potential from 1.61 V (vs. RHE) to 1.39 V (vs. RHE) for S4 and from 1.65 V (vs. RHE) to 1.52 V (vs. RHE) for S5 (**Figure 3.8b**) corresponding to an overpotential of 200 mV to reach 10 mA cm⁻² for S4 and 350 mV for S5. The Tafel plots (**Figure 3.8c**) indicate an enhancement in the OER kinetics for both interfaces with Tafel slopes of 97 mV dec⁻¹. To be noted, such light density does not result in rise in the solution temperature even when illuminated for more than 30 min. Furthermore, illumination with a laser at 980 nm using the same power density does not yield any change of the catalytic activity due to the absence of LSPR effect (**Figure 3.8d**).

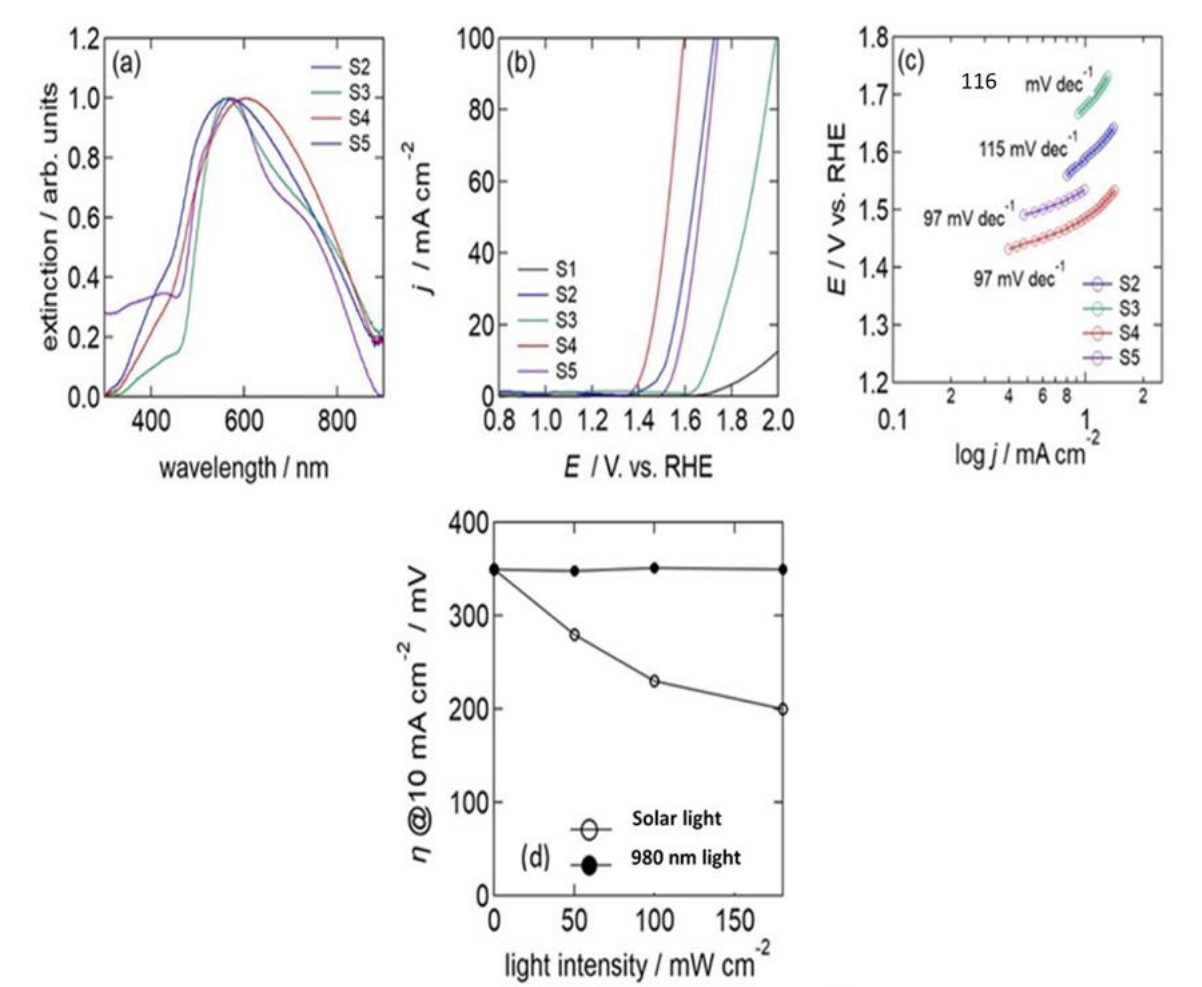


Figure 3.8. Oxygen evolution reaction (OER) under visible light irradiation. (a) UV-vis spectra of S2-S5. (b) Linear sweep voltammograms (LSV) in O₂-deaerated NaOH (0.1 M) of S1 (black), S2 (blue), S3 (green), S4 (red) and S5 (violet) under illumination (150 W arc lamp, power density 180 mW cm⁻², scan rate = 25 mV s⁻¹). (c) Tafel plots of S2 (blue), S3 (green), S4 (red) and S5 (violet) under illumination. (d) Influence of light wavelength and intensity on the OER overpotential determined on S4 in O₂-deaerated NaOH (0.1 M).

3.5. Mechanistic considerations for OER

On the basis of the above results, the expected mechanism of the enhanced activity toward OER under solar light irradiation is the following: under light excitation, surface plasmons are generated on the Au nanoparticles attached to Cu₂O forming electron-hole pairs (**Figure 3.9a**). The generated electrons are injected from the Au NPs into the conduction band of Cu₂O cubes. The generated hot electrons are then injected into Cu₂O via the formed Mott-Schottky barrier. The resultant electron-deficient Cu₂O cubes oxidize water under basic conditions to oxygen. The fast generation and injection of hot electrons affect the current density profile abruptly upon laser irradiation, as illustrated in **Figure 3.9b**, when S4 is biased at 1.44 V (vs. RHE).

The OER activities are highly reproducible as seen in the curves recorded on four different S4 specimens (**Figure 3.9c**). As the stability is one of the key factors in determining the usefulness of an electrocatalyst, the long-term stability of S4 was assessed by potential-time transients plots in basic environment (0.1 M NaOH). **Figure 3.9d** depicts the chronopotentiometric curves of S4 recorded at a current density $j = 10 \text{ mA cm}^{-2}$. The potential-time measurements indicate an almost steady overpotential without any significant decay during 20 h of continuous OER, revealing excellent durability of the interface.

The Faradic yields of O₂ production was in addition found to be quantitative within experimental errors (**Figure 3.9e**). Up to $14 \text{ } \mu\text{mol cm}^{-2}$ O₂ was formed after irradiation for 8 min. which represents a 3-fold enhancement compared to S4 without activation.

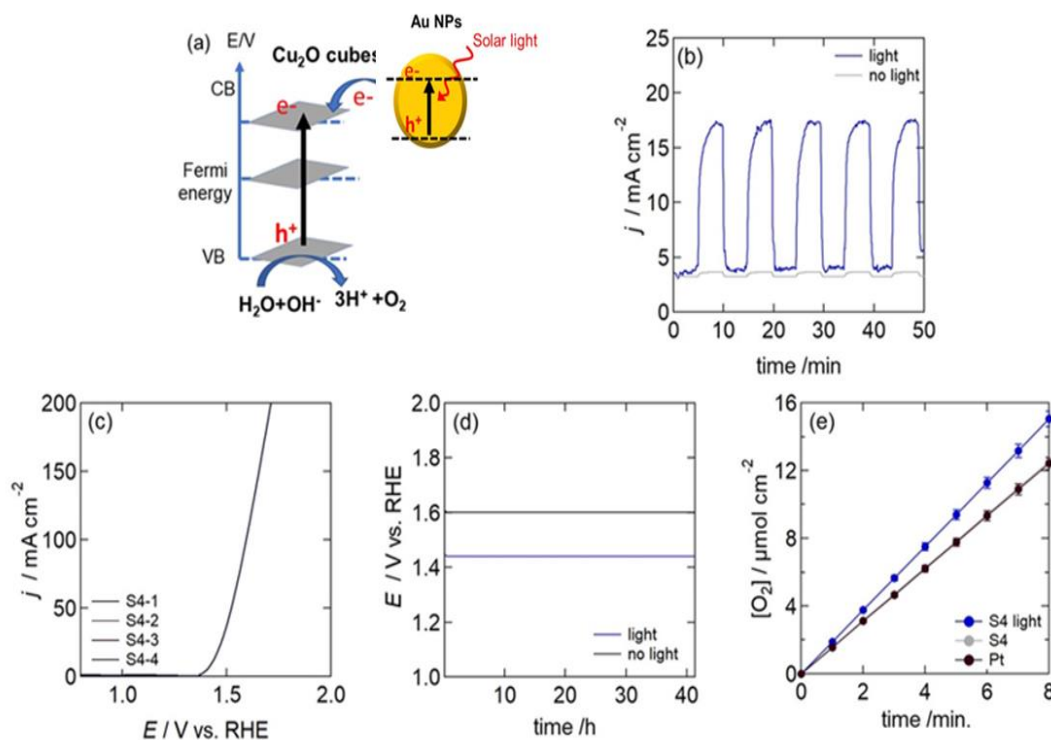


Figure 3.9. Mechanistic considerations for OER on S4. (a) Schematic presentation of the mechanism involved in OER. (b) Current density - time curves at $E = 1.44$ V (vs. RHE) under light illumination (black) and with no illumination (grey) for S4. (c) OER polarization curves of four S4 interfaces in 0.1 M NaOH at a scan rate of 25 mV s^{-1} in dark. (d) OER stability tests of S3 at $j = 10 \text{ mA cm}^{-2}$ under light illumination (black) and in dark (grey) by following the change of the overpotential with time. (e) O₂ production efficiency catalyzed by S4 at a potential of 1.50 V in 0.1 M NaOH with (blue) and without (grey) light irradiation (symbols). The theoretical efficiency (lines) was calculated according to the cumulative charge, assuming a 100% Faradic efficiency for O₂ production. The current density was $j = -10 \text{ mA cm}^{-2}$. Data for Pt is shown as well (black).

3.6. Conclusion

In conclusion, Cu₂O cubes decorated with gold nanostructures (Cu₂O-Au) show enhanced electrocatalytic activity for the oxygen evolution reaction (OER) in alkaline media under solar light illumination. The enhanced OER activity was ascribed to increased light absorption due to the plasmonic properties of Cu₂O-Au cubes. Indeed, illumination Cu₂O nanostructures with solar light did not enhance the electrocatalytic OER. The Cu₂O-Au nanostructures need an overpotential of 200 mV to reach 10 mA cm⁻² with a Tafel constant of 97 mV dec⁻¹. Furthermore, cubic Cu₂O structures were more active than octahedral ones.

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CHAPTER IV: CONCLUSION AND PERSPECTIVES

In conclusion, in this thesis two different possibilities for plasmon-enhanced electrocatalysis were investigated. One is based on the use of a gold nanohole array electrode, which was designed to show a strong localized surface plasmon behavior at 980 nm. It could be shown that these nanoporated gold thin films when irradiated at 980 nm (2 W cm^{-2}) show electrocatalytic oxygen reduction in basic conditions comparable to that of commercial Pt/C electrodes. To underpin the plasmonic enhancement effect the oxygen reduction reaction was performed in addition at different wavelengths and in electrolytes thermostated at different temperatures. The influence of the ORR on the wavelength and the indication that thermal effects are less efficient in acceleration the ORR made us to conclude that hot electrons are generated from plasmon decay, which in turn facilitate the electrocatalytic oxygen reduction reaction.

The other approach was based on the decoration of a thin gold film with cubic and octahedral Cu_2O nanostructures decorated with gold nanoparticles. In this case, the electrochemical activity of these nanostructures for the oxygen evolution reaction (OER) in alkaline media was assessed in the dark and under solar light irradiation. While illumination of Cu_2O nanostructures alone with solar light did not enhance the electrocatalytic OER, electrodes modified with cubic-shaped Cu_2O -Au nanostructures revealed enhanced electrocatalytic OER activity. Indeed, most interestingly it could be shown that the morphology of Cu_2O nanocrystals has a strong influence on the electrocatalytic behavior for OER in basic medium under solar light illumination with cubic Cu_2O being more efficient for plasmon-enhanced electrocatalysis than octahedral Cu_2O . This preference of the cubic over the octahedral-shaped nanostructures is believed to be linked to the hydroxylation of the (111) surfaces hindering the OER as supported by numerical computations carried out in collaboration with Guido Petretto and Gian-Marco Rignanese from the Université catholique de Louvain, Belgium.

More recently the use of perforated gold nanohole electrodes for plasmon-enhanced electrocatalytic oxidation of methanol and glucose was investigated. Plasmon-enhanced

oxidation process are more complicated to be performed on these interfaces as the generated hot electrons needed for these electrochemical conversions are not energetically efficient. This requires the use of additional catalysis such as PtRu for methanol oxidation and the use of Cu based nanomaterials for glucose oxidation. However, while the hurdle could be overcome for methanol oxidation, it proved to be not sufficient for glucose oxidation until now. More work remains to be done to achieve interesting glucose conversion yields for any practical application.

While indeed my work focused on energy related applications, plasmonic nanostructures can and have found wide application for biological sensing. In a review article “entitled “Magneto-Optical nanostructures for viral sensing” published in *Nanomaterials* 2020, the focus was on the interest of viral sensing using plasmonic enhanced magnetic nanostructures. While this topic was a bit far from my thesis topic, it allowed me during the Covid-19 confinement to gain theoretical knowledge in the construction and use of magneto-plasmonic nanostructures. These promising hybrid materials can be directly applicable for sensing and might be in the long run also of interest for electrocatalytic applications as those investigated in the thesis. The use of magnetic field is believed to have in addition advantages for electrocatalytic plasmon-enhanced applications and might result in tuning the selectivity of the product formed. Indeed, this concept would lead to a new research area around magneto-plasmonic enhanced electrocatalysis. The future of such research is thus bright and full of opportunities.

ANNEX:

1. Materials

All chemicals were reagent grade or higher and were used as received unless otherwise specified. Sodium hydroxide (NaOH), potassium hexacyanoferrate (II) ($[K_4Fe(CN)_6]$), hydrochloric acid (HCl), polyvinylpyrrolidone (PVP M.W. 55.000 g mol⁻¹), copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, $\geq 99\%$), tetrachloroauric acid ($HAuCl_4 \cdot 3H_2O$, $\geq 99\%$), sodium dodecyl sulfate (SDS, $\geq 90\%$), hydroxylamine hydrochloride ($NH_2OH \cdot HCl$, $\geq 99\%$) were purchased from Sigma-Aldrich.

Commercial E-TEK 10 wt.% or 40 wt.% Pt/C was used for making catalyst inks. The catalyst dispersion was prepared as follows: 5.0 mg of 10 wt.% Pt/C was dispersed in 400 μ L EtOH, 40 μ L 5 wt.% Nafion (Nafion® DE 520, Sigma-Aldrich) and 60 μ L deionized water by sonication for 15 min. Then 10 μ L catalyst dispersion was transferred onto the glassy carbon disk by using a pipette and dried at room temperature. The catalyst loading on the electrode was 50 μ g cm⁻² Pt (10 wt.% Pt/C) and 200 μ g cm⁻² Pt (40 wt.% Pt/C).

The water used throughout the experiments was purified with a Milli-Q system from Millipore Co. (resistivity = 18 M Ω .cm).

2. Instrumentation

2.1. Scanning electron microscopy (SEM)

The scanning electron microscopy (SEM) data of Cu₂O were obtained with a JEOL microscope FEG-SEM JSM 6330F operated at 5 kV. The samples were prepared by drop-casting an aqueous suspension of the nanostructures over a Si wafer, followed by drying under ambient conditions.

The scanning electron microscopy (SEM) images of nanoporeformed Au NHS interface were obtained using an electron microscope ULTRA 55 (Zeiss) equipped with a thermal field emission emitter, three different detectors (EsBdetector with filter grid, high efficiency in-lens

SE detector, Everhart-Thornley Secondary Electron detector), elemental analysis of NHs Au electrode, were developed using EDS equipped with SEM system ULTRA 55 (Zeiss).

2.2. Transmission electron microscopy (TEM)

Transmission and high-resolution transmission electron microscopy (TEM and HRTEM) images were acquired with a JEOL 1010 microscope operating at 80 kV and with a FEI Tecnai TF30 microscope operated at 200 kV. Samples were prepared for TEM and HRTEM imaging by drop-casting an aqueous suspension of the nanostructures over a carbon-coated copper grid, followed by drying under ambient conditions

2.3. UV-visible spectroscopy

The UV/vis absorption spectra were recorded using a Perkin Elmer LambdaUV-Vis 950 spectrophotometer.

2.4. X-Ray diffraction (XRD)

The X-ray diffraction (XRD) data of Cu₂O nanostructures were obtained using a Rigaku - Miniflex equipment, CuK α radiation. The diffraction patterns were measured in the 2θ range of 30–70° with a 1° min⁻¹ angular speed scan.

2.5. X-ray photoelectron spectroscopy (XPS)

The XPS analysis was performed with an SPECSLAB II (Phoibos-Hsa 3500 150, 9 channeltrons) SPECS spectrometer, with Al K α source ($E = 1486.6$ eV) operating at 12 kV, pass energy ($E_{\text{pass}} = 40$ eV, 0.1 eV energy step and acquisition time of 1 s per point. The residual pressure inside the analysis chamber was $\sim 1 \times 10^{-8}$ Torr. All XPS were referenced according to the adventitious C1s peak (284.5 eV).

2.6. ICP-AES measurements

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were performed on a single quadrupole ICP-MS (Varian, 820-MS). The samples were taken up in 1 mL of nitric acid and heated 30 min at 80 °C in an oven. A quantity of 9 mL of ultrapure water was added and the sample was diluted 50 times for analysis. The results correspond to the response at 327.395 nm wavelength (Cu).

2.7. Light sources

For plasmon-enhanced oxygen reduction reaction (ORR), the electrode was illuminated with light from a continuous wave laser (808 and 980 Gbox model, Fournier Medical Solution) with a laser power output between up to 2 W cm^{-2} . Irradiation at 808 nm was performed using a laser from Phototech. The incident photon-to-current efficiency was estimated according to literature and was $\leq 1\%$ for 808 nm and $\leq 2\%$ for 980 nm.²⁵ The temperature changes were captured by an infrared camera (Thermovision A40) and treated using ThermoCam Researcher Pro 2.9 software.

For plasmon-enhanced oxygen evolution reaction (OER), the electrode was illuminated with light from a 150 W arc light source (LSB 251, Lot Quantum Design, Belgium) with an irradiation density of 180 mW cm^{-2} corresponding to about 1.3 sun (1 sun = 137 mW cm^{-2}). In a control experiment, electrodes were illuminated with light from a continuous wave laser (980, Gbox model, Fournier Medical Solution) with a laser power output of 2 W cm^{-2} . The temperature changes were captured by an infrared camera (Thermovision A40) and treated using ThermoCam Researcher Pro 2.9 software.

3. Electrochemical measurements

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements were performed with a potentiostat/galvanostat (Metrohm Autolab) electrochemical test station in a standard three-electrode system with the plasmonic electrode (or Pt/C coated electrode) as the working electrode, a platinum plate as the counter electrode and an Ag/AgCl (3.5 M KCl) electrode as the reference electrode. In either $\text{K}_4\text{Fe}(\text{CN})_6$ 10 mM/0.1 M KCl or 0.1 M NaOH solution pH=13 at the scan rate of 25 or 100 mV s^{-1} .

Chronoamperometry were recorded in 0.1 NaOH electrolyte at scan rate equal to 25 mV s^{-1} under laser irradiation Onn/Off at a constant potential. All experiment were tested at room temperature.

The measured potentials were converted with respect to the reversible hydrogen electrode (RHE) according to:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E_{\text{Ag/AgCl}}^{\circ} \quad \text{With } E_{\text{Ag/AgCl}}^{\circ} = 0.205 \text{ V}$$

Eq A. 1

Rotating Disk Electrode (RDE) measurements were performed on an electrode holder of 0.8 cm in diameter and carried out in 0.1 M NaOH using a modulated speed rotator (Radiometer Analytical) at a scan rate of 25 mV s⁻¹. Oxygen was used to purge the solution to achieve an oxygen-saturated electrolyte. The laser light was directed onto the rotating disk part of the electrode. All measurements were repeated at least four times. The number of electrons transferred per O₂ molecule in the ORR for Pt/C and Au NHs with and without light irradiation was calculated by the Koutecký-Levich equation (**Eq 3.2**) applied to the ORR curves obtained at different rotation speeds (10, 20, 100, 1000, 2000 rpm).

$$\frac{1}{j_{\text{Lim}}} = \frac{1}{j_k} + \frac{1}{B\omega^{\frac{1}{2}}}$$

Eq A. 2

where j_{lim} is the diffusion-limiting current density (A cm⁻²), j_k is the kinetic current density (A cm⁻²), ω is the angular velocity of the disk (rad s⁻¹, 1 rpm = $\pi/30$ rad s⁻¹) and B is the Levich constant:

$$B = 62nFcD^{\frac{2}{3}}\nu^{\frac{1}{6}}$$

Eq A. 3

Where F is the Faraday constant (96485 C mol⁻¹), c the bulk concentration of O₂ ($c = 1.2 \times 10^{-6}$ mol cm⁻³), ν is the kinematic viscosity of the electrolyte ($\nu = 0.01$ cm² s⁻¹), and D is the diffusion coefficient of O₂ in 0.1 M KOH (1.9×10^{-5} cm² s⁻¹).

4. Preparation of electro-plasmonic electrodes

4.1. Preparation of Gold Nanoholes electrode (Au NHs)

Kapton interfaces of thickness d around 100 μ m were modified with gold nanoholes according to our previous work. with Ti (2nm) adhesion layer. In short, a monolayer of 1000 nm polystyrene beads (ThermoFisher Scientific) was deposited onto glass by self-assembly, followed by SF₆ and oxygen plasma etching for 8 min (gas flow 2 sccm and 30 sccm, respectively at 10 mTorr chamber pressure) to reduce the particle size. The samples were then coated with 50 nm Au at a constant deposition rate of 0.2 Å s⁻¹ using physical vapor deposition. The beads on top of Kapton were removed by peeling the surface with Blue Low Tack tape (Semiconductor

Equipment Corp.). The surfaces were copiously washed with acetone and dried under nitrogen flow. The arrays display holes of 630 nm average size and center-to center spacing of $a = 980$ nm.

4.2. Synthesis of Cu₂O cubes

1 g of sodium dodecyl sulfate (SDS) and 1 mL of CuCl₂(aq) (0.1 M) were added to 94 mL of water and mixed until the complete dissolution. Then, 2.5 mL of NH₂OH.HCl(aq) (0.2 M) and 2.5 mL NaOH(aq) (1 M) were added sequentially. The resulting mixture was mixed under magnetic stirring (200 rpm) for 2 h at room temperature. After this time, the supernatant was removed by centrifugation for 10 min at 7.800 rpm and the solid was suspended in 100 mL of PVP aqueous solution (0.1 wt.%) for the synthesis of bimetallic structures after addition of HAuCl₄(aq).

4.3. Synthesis of Cu₂O octahedra

1 g of sodium dodecyl sulfate (SDS) and 1 mL of CuCl₂(aq) (0.1 M) were added to 88 mL of water and mixed until the complete dissolution. Then, 8.5 mL of NH₂OH.HCl(aq) (0.2 M) and 2.5 mL NaOH(aq) (1 M) were added sequentially. The resulting mixture was mixed under magnetic stirring (200 rpm) for 2 h at room temperature. After this time, the supernatant was removed by centrifugation for 10 min at 7.800 rpm and the solid was suspended in 100 mL of PVP aqueous solution (0.1 wt.%) for the synthesis of bimetallic structures after addition of HAuCl₄(aq).

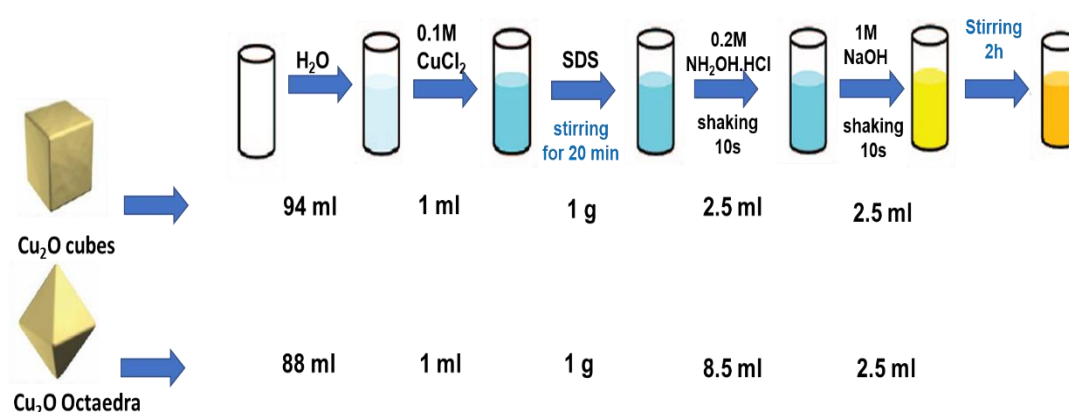


Figure A1. Schematic Illustration of the Procedure Used To Grow Cu₂O Crystals

4.3. Synthesis of Cu₂O-Au nanomaterials

A suspension of 50 mL of Cu₂O cubes or octahedra in PVP (0.1 wt.%) was stirred at 90 °C for 10 min in a 100 mL round-bottom flask. Then 7.5 mL of HAuCl₄ (0.375 M) was added dropwise and the resulting mixture was kept for 30 min at 90 °C. After cooling down to room temperature,

the suspension containing the bimetallic nanomaterial was washed twice with water and ethanol by successive rounds of centrifugation at 7.800 rpm for 10 min and removal of the supernatant. The particles were then suspended in 1 mL water and used for drop casting.

The gold electrode with surface area ($A=0.04 \text{ cm}^2$) was modified with the nanocomposite by drop-casting 80 μL of a 2 mg solution of Cu_2O , $\text{Cu}_2\text{O-Au}$ nanostructures or Pt/C followed by air drying for 3 h time.

5. Overview

5.1. Tafel slope

Oxidation/reduction (redox) reactions can be described by two principal concepts. The thermodynamic concept refers to the change in enthalpy (ΔH) and entropy (ΔS) throughout a reaction. The kinetic concept associates with the rate of a redox reaction. The first one is the study of different potentials at equilibrium. In general, when a faradic current flow through the electrode-solution interface, the potential of electro active species are different. This can be explained in terms of the energy levels of the reacting species and the electrode. For example if the electrode is a metal, electrons are transferred from the Fermi level of this metal to the lowest unoccupied molecular orbital (LUMO) of species present in the solution. In this case, the energy level of the electrode decreases whereas the energy level of the solution will increase, until an equilibrium is reached. Here the potential is described by the Nernst equation (**Eq A.4**) obtained from the relationship $\Delta G = -nFE$ (The Gibbs free energy).

$$E_{\text{equilibrium}} = E_{\text{Ox/Red}}^{\circ} + \frac{RT}{nF} \times \ln \frac{[\text{Ox}]^{\alpha}}{[\text{Red}]^{\beta}}$$

Eq A. 4

Where $E_{\text{ox/red}}^{\circ}$ is the standard potential is always measured relative to the hydrogen evolution reaction $2\text{H}^{+} + 2\text{e}^{-} = \text{H}_2$, the E° value is more positive, reduction reaction will be more favorable, whereas, the more negative value facilitates the oxidation, $R=3.3145 \text{ Jmol}^{-1} \text{ K}^{-1}$ ideal gas constant, T is the temperature in Kelvin, $F=96485 \text{ Cmol}^{-1}$ is faraday constant, and n is the number of electrons exchanged.

Usually, the potential of an electrode strongly affects the kinetics, which means that the rate of the electron transfer reaction at the electrode surface can be varied by changing the applied electrode potential. The kinetics of electrochemical processes were studied by Butler and Volmer, the expression of the charge transfer kinetics at the interfaces are explained below .

The reduction reaction illustrated above can be written as follows:



The rate of the forward reaction is:

$$v_f = k_f C_{\text{Ox}} = \frac{i_c}{nFS}$$

Eq A. 5

And the rate of the backward reaction can be written as:

$$v_b = k_b C_{\text{red}} = \frac{i_a}{nFS}$$

So the total current is:

$$i_{\text{total}} = i_c - i_a$$

$$i_t = nFS (k_{\text{red}} C_{\text{Ox}} - k_{\text{ox}} C_{\text{red}})$$

Eq A. 6

Also, Rate constants vary with temperature according to the Arrhenius rate equation

$$k = A \exp \left[-\frac{E_a}{RT} \right]$$

Eq A. 7

Where E_a is the activation energy of the reaction, R is the gas constant, T is the temperature in Kelvin, and A the pre-exponential factor

The final equation can be written as follows:

$$j = j_0 \left\{ \exp \left[\frac{\alpha n F}{R T} \eta \right] - \exp \left[-\frac{\beta n F}{R T} \eta \right] \right\}$$

Eq A. 8

Where η is overpotential, R is the universal gas constant, T is temperature, α and β are the transfer coefficients, $\beta + \alpha = 1$, F is the Faraday constant, n is the electron number, j is the current density and j_0 is the exchange current density.

At steady state (and at large overpotentials), the anodic current component is negligible, and the equation is given as :

$$j = j_0 \exp \left[\frac{-\alpha F}{RT} \eta \right]$$

Eq A. 9

This leads to the Tafel equation:

$$\eta = \frac{2.3 RT}{\alpha F} \log j_0 - \frac{2.3 RT}{\alpha F} \log j$$

Eq A. 10

If

$$a = \frac{2.3 RT}{\alpha F} \log j_0$$

And

$$b = \frac{-2.3 RT}{\alpha F}$$

At the end the Tafel equation will be :

$$\eta = a + b \log j_0$$

Eq A. 11

The Tafel analysis is used when the reaction is out of equilibrium, the sense that either the anodic or the cathodic current is dominating the current density measured. The logarithm of the current density $\log|i|$ can be plotted as a function of the overpotential, which is known as Tafel plot. The linear region of the Tafel plot can be used to evaluate the overpotential as a function of the current density.

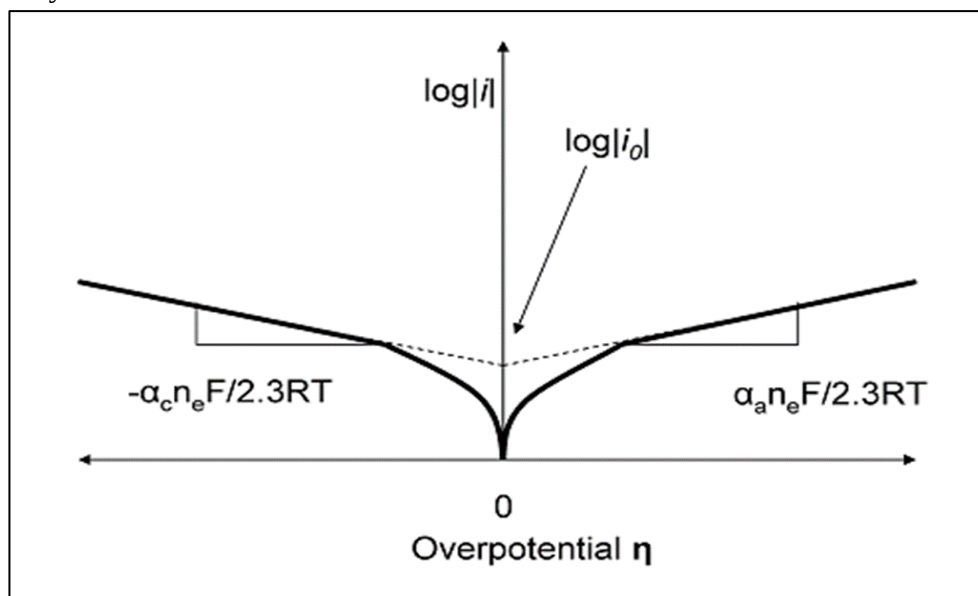


Figure A2. Tafel plot of anodic and cathodic branches of redox couple with α coefficient

5.2. Linear sweep voltammetry (LSV)

Linear sweep voltammetry (LSV) is the most straightforward voltammetric technique as it involves measuring the current produced by an electrode with respect to the potential applied between a working and reference electrode, $I = f(E)$. This potential is swiped between two values, the low potential E_1 to the high potential E_2 , at a constant scan rate. The resulting plot of current, (I) vs potential (E), is called a linear sweep voltammogram (**Figure A3**).

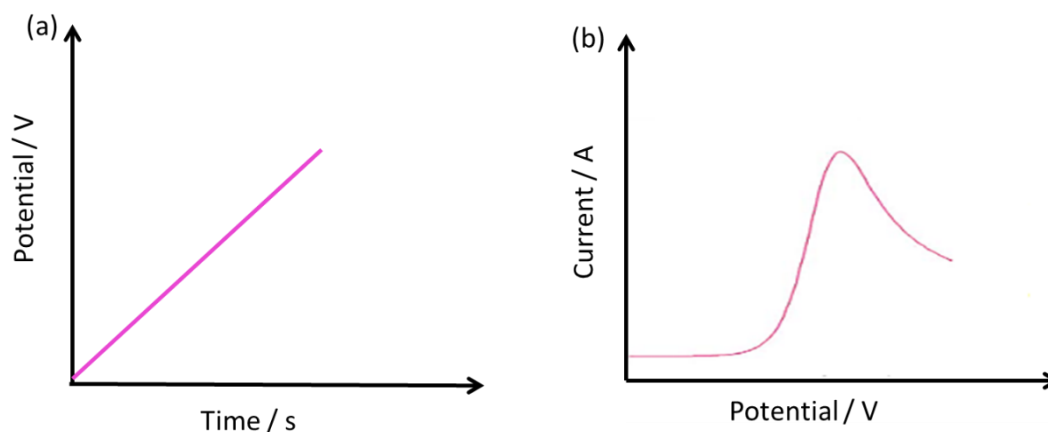


Figure A3. Linear sweep voltammetry, (a) Potential-time excitation, (b) current versus potential.

5.3. Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) is a powerful and popular electrochemical technique commonly employed to investigate the reduction and oxidation processes of molecular species. The CV technique helps to acquire qualitative and quantitative information about electrochemical reactions, including reaction kinetics, the reversibility of the reactions, reaction mechanisms, and electrocatalytic processes, this method is often used for investigating ORR, OER and HER performance of different catalysts. CV is an extension of LSV. Where the potential at the working electrode is cycled linearly between two potentials, low (E_{Initial}) and high value (E_{Final}), and then reversed to the E_{Initial} . The scan rate during the CV experiment is generally maintained in the order of mV s^{-1} to V s^{-1} , This technique produces a triangular potential waveform (**Figure A4**). CV gives the current (i/A) versus the potential (E/V) plot. The resulting curves are called cyclic voltammograms. The important components of CV are the anodic and cathodic peak currents ($i_{p,c}$ and $i_{p,a}$) and the corresponding peak potentials ($E_{p,c}$ and $E_{p,a}$). The anodic current is positive and the cathodic current is negative. The intensity of current through the working electrode in CV can be calculated according to the Randles sevcik equation :

$$i_p = 2.69 \times 10^5 n^{\frac{3}{2}} A C \sqrt{\nu D}$$

Eq A. 12

Where i_p (A) is the peak current, n is the number of electrons in the redox reaction, A (cm^2) is the area of the working electrode, C (mol cm^{-3}) is the concentration of the analyte at the

electrode, v (V s^{-1}) is the scan rate, and D ($\text{cm}^2 \text{s}^{-1}$) represents the diffusion coefficient of the electroactive species.

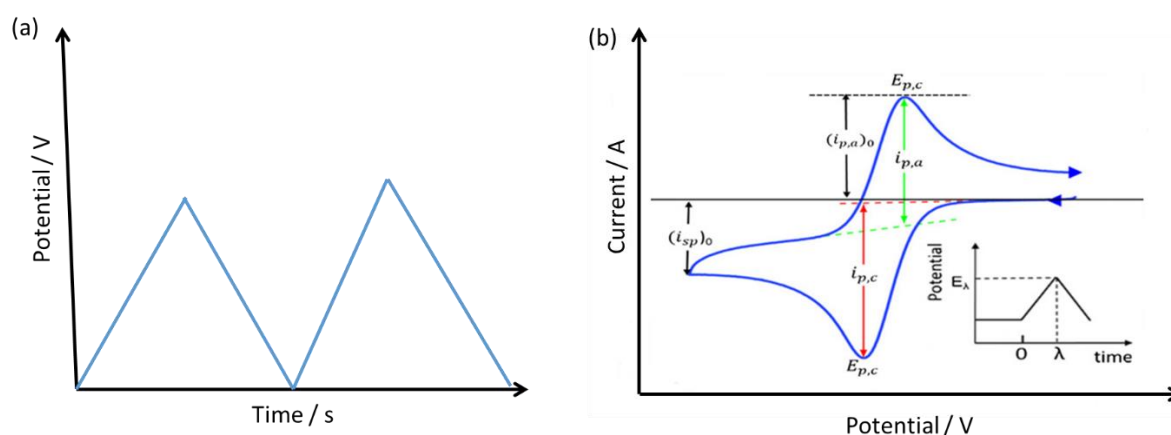


Figure A4. (a) Potential waveform applied to working electrode in cyclic voltammetry, (b) Diagram of cyclic voltammogram for a simple reversible redox couple.

In addition, CV provides Information about reversible, irreversible, or quasi-reversible nature of the system. If the ratio of the anodic and the cathodic peak currents is equal to 1, it means both the anodic and the cathodic peak currents are the same, the nature of the system is reversible. But if the ratio is not equal to 1, then the system is quasi-reversible. In contrast the system can be said to be irreversible when its oxidized or reduced product is not reversible. The Plotting current as a function of scan rate, helps to know if the electron transfer involves freely diffusion or adsorbed redox species. Also we can extract the details about capacitive behavior of a system and measure the capacitance values at different sweep rates. Using the following equations

$$C_s = \frac{\int I dV}{vm\Delta V}$$

5.4. Rotating disc electrode (RDE)

The rotating disc electrode (RDE) is the classical hydrodynamic electro- analytical technique, required for minimizing the diffusion layer thickness, and for studying the kinetic and mechanism of reactions in a three electrode cell. A rotating disc electrode consists of a conductive disc electrode which is made of Pt, Ni, Cu, Au, Fe, or Si, embedded in an insulating material such as Teflon. During the analysis, this disc electrode is attached to a motor. When the RDE is placed in the solution, rotation forces transported the electro active species near the electrode surface. The electrode is rotated about its vertical axis and the movement of the electrolyte is in a radial direction outward from the center of the electrode (**Figure A5**).

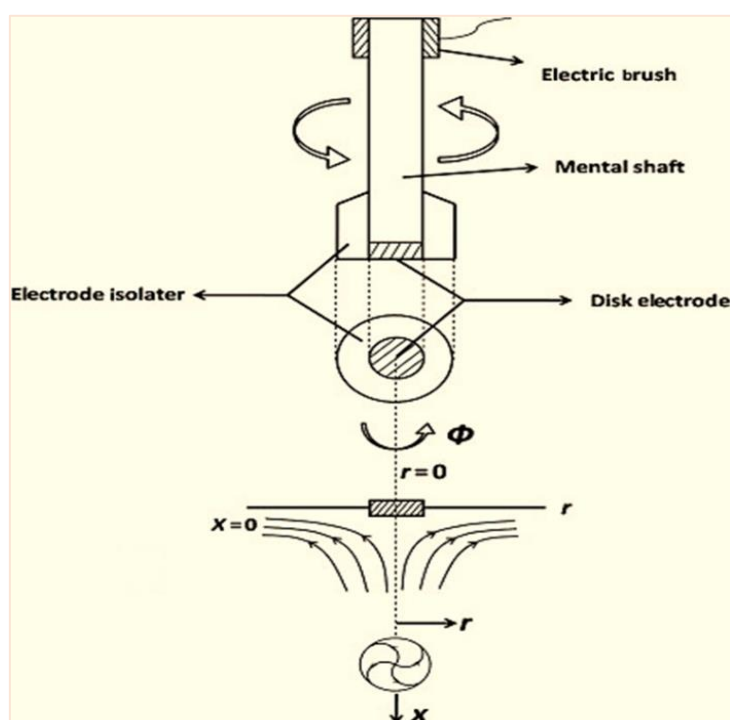


Figure A5. (a) Schematic representation of the rotating disc electrode (RDE), (b) solution flow pattern near the disk electrode surface.

Convective mass transport is particularly important if the concentration of the involved species is low. This is the case, when dissolved gases are used as reactants, such as in the oxygen reduction reaction, due to their low solubility. For processes where the kinetic reaction is faster than the mass transfer of the active site, the reaction rate is limited by diffusion. The thickness of the diffusion film can be adjusted by varying the rotational speed of the RDE, as defined in the equation below:

$$\delta = 0.211 D^{1/3} \nu^{1/6} \omega^{-1/2}$$

Eq A. 13

$$\omega = 2\pi f$$

Where δ is the diffusion layer thickness, D is the diffusion coefficient of the electroactive species; ν (m^2s^{-1}) is the electrolyte kinematic viscosity; ω (rpm) is the rotation speed of the disk and f (Hertz) is the rotation frequency. The diffusion -limited current density using for an RDE setup is proportional to the square root of the rotation rate and it can be defined by:

$$j_d = 0.62 n F C D^{2/3} \nu^{-1/6} \omega^{-1/2}$$

Eq A. 14

For reactions which are controlled by both diffusion of the reactants (mass transfer) and kinetics (charge transfer) at rotating disk electrodes, the total flux j_{lim} of the reacting electroactive species is described in Koutecky-Levich equation:

$$\frac{1}{j_{\text{lim}}} = \frac{1}{j_k} + \frac{1}{j_d}$$

Eq A. 15

$$\frac{1}{j_{\text{lim}}} = \frac{1}{j_k} + \frac{1}{0.62 n F C D^{2/3} \nu^{-1/6} \omega^{-1/2}}$$

Eq A. 16

5.5. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface technique, that analyses the atomic composition of chemical compounds and the oxidation states of the atoms present in the samples. The working principle of this technique is based on irradiating a sample with a strong monochromatic beam of X-rays, that knocks out the core electrons from the atoms present on the surface layer (<10nm) of the specimen. The kinetic energy (E_k) and the number of electrons

ejected from the sample can be quantified by the detector. When the energy of incident photons ($h\nu$), is higher than the electron binding energy (E_B). the (E_K) can be represented as:

$$E_K = h\nu - E_B - \phi_{\text{Spectrometer}}$$

Eq A. 17

Where $h\nu$ represents the energy of the absorbed photon (h is Plank's constant and ν the frequency of the photons), and $\phi_{\text{spectrometer}}$ is the function of the spectrometer.

XPS method is a non-destructive technique, it gives information about the chemical bonds between the element as well as the electronic structures, recording the kinetic energy makes possible to go back to the band energy of the elements (**Eq A 17**). All the elements of the periodic table are detected by XPS except hydrogen (H) and helium, since their electron core is not strongly attached to the nucleus.

5.6. X-Ray Diffraction (XRD)

The XRD diffraction is a non-destructive technique for characterizing the crystalline materials. The data extracted from the XRD analysis provide information about the crystalline phases present in the sample, the arrangement of the planes, the composition and the size of the crystallite. This analysis method is based on the scattering phenomenon of incident x-radiation, during its interaction with the valence electrons of an atom. Moreover the x-rays diffraction is an elastic scattering, where the energy of the reflective beam is similar to that of incident beam. The principle of x-ray diffraction is explained by Bragg law (**Figure A6**).

$$n \lambda = 2 d \sin \theta$$

Eq A. 18

Where $n=1,2,3,\dots$ is the diffraction number, λ is the wavelength of emitted X-ray, d is the inter planer distance, and θ is the angle between the incident ray and the reflecting surface, A diffractometers is an instrument used for obtaining the XRD pattern of various samples. From the diffraction angles and their intensities, it is possible to identify the crystal structure of the material.

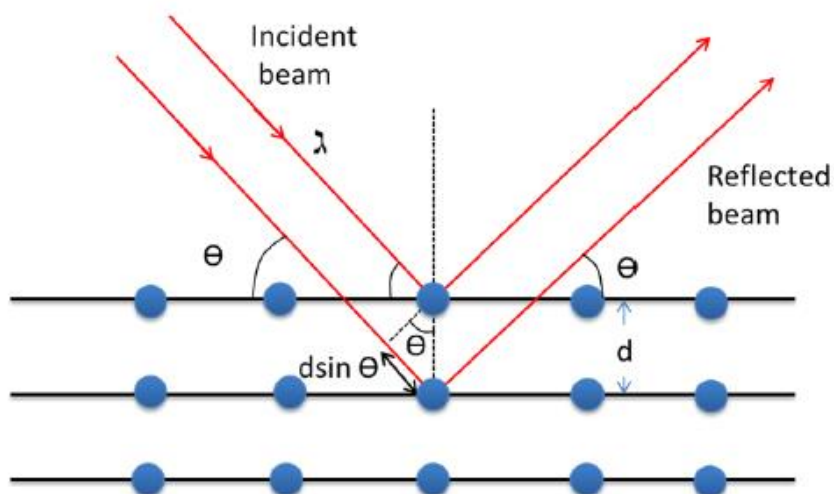


Figure A6. X-ray diffraction by a crystal to demonstrate Bragg's law

5.7. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is an imaging technique that provides information about the structural morphology, and chemical composition of materials. The interaction between an electron beam generated from the filament (electron energies are 1 -30 keV) and the surface atoms of the specimen, produces several signals: back-scattered electrons (BSE), Auger electron, secondary electron (SE), cathodoluminescence (CL) and characteristic X-rays (**Figure A7**). All these electrons are collected by the specific detectors installed inside the SEM instrument and transformed into the form of an image. The surface region where the interaction beam/sample occurs is called 'interaction volume'. The interaction volume increases with the energy of the incoming beam and decreases when the atomic number of the material goes higher. In SEM characterization, the most of the incident electrons are emitted as back-scattered and secondary electrons which possess relatively low energy (3-5 eV). The secondary electrons are the consequence of inelastic scattering, which create surface topography with high resolution (≥ 10 nm). The characteristic analysis of characteristic X-rays provides information on the chemical composition.

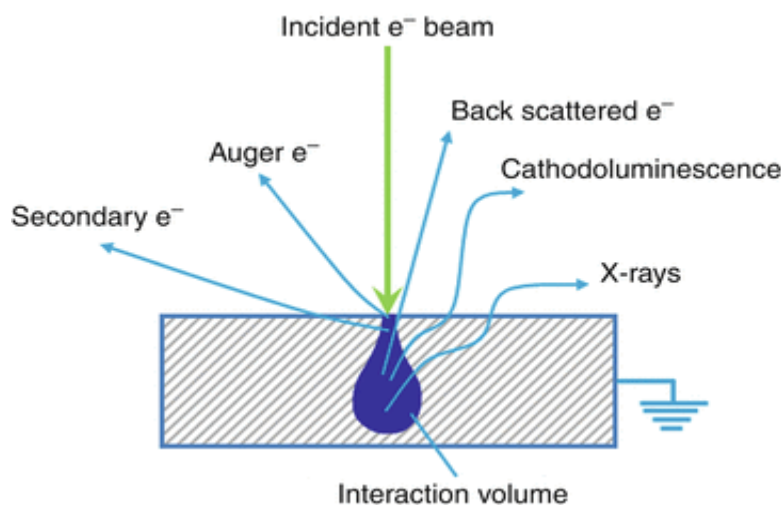


Figure A7. Illustration of several signals generated by the electron beam–sample interaction in the scanning electron microscope.

5.8. Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) technique is similar to scanning electron microscope (SEM). In TEM characterization, the energy of the incident electron beam is higher (80-300 keV) compared to that of the SEM technique. Moreover the analyzed sample is in the form of a thin layer, with a thickness less than 100 nm. The final resulting image obtained from a TEM instrument is of a high resolution (0.1- 0.2 nm).

As shown in the figure below (**Figure A8**), during SEM analysis, the electron beam is focused on a spot, and then scanned sequentially onto the analyst. For each illumination region, the detector records the emitted signals and transfers them into the image forms. In the case of TEM analysis, the incident electron beam is concentrated on a fixed area of the sample, these electrons penetrate the sample and reach the detector, which is placed in a parallel position inside the instrument and form images.

In addition to these two techniques, there is a machine called scanning transmission electron microscopy (STEM), which operates with the principles of both TEM and SEM. A scanning system similar to that of conventional SEM, but the detection system corresponds to that of TEM (figure11). The detector used is placed under the sample in order to collect the transmitted electrons. STEM is now one of the leading instruments for obtaining the morphology of samples at very high resolution.

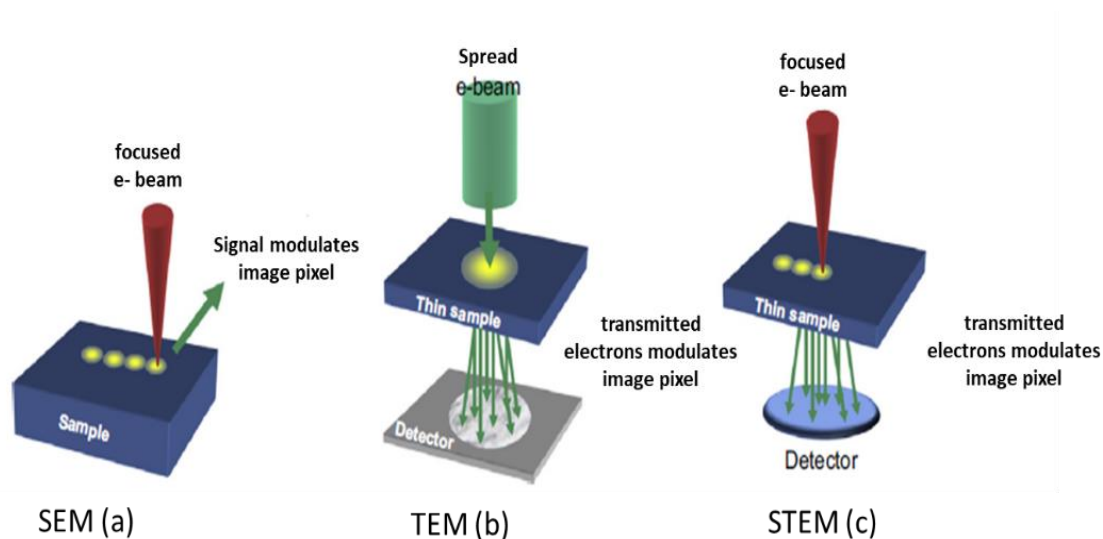


Figure A8. Schematic illustration of SEM, TEM, and STEM



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PUBLICATIONS

- 1. Plasmon Enhanced Electrocatalytic Oxygen Reduction Reaction In Alkaline Media On Gold Nanoholes Electrode.**
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- 2. Magneto-Optical Nanostructures For Sensing**
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- 3. Plasmon-enhanced Electrocatalytic Activity of Gold Nanoparticles/Cu₂O Nanocrystals for Oxygen Evolution Reaction in Alkaline Media**
Tamazouzt Nait Saada, Liuqing Pang, André H.B. Dourado, Lucas D. Germano, Eduardo D. Vicentini, Ana P.L. Batista, Antonio G.S. de Oliveira-Filho, Franck Dumeignil, Sébastien Paul, Robert Wojcieszak, Sorin Melinte, Georgiana Sandu, Guido Petretto, Gian-Marco Rignanese, Dalila Meziane, Rabah Boukherroub, Susana I. Córdoba de Torresi, Anderson G.M. da Silva et Sabine Szunerits.
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