TUNING THE SURFACE OF METAL OXIDE/OXYHYDROXIDE NANOCRYSTALS BY INORGANIC POLYANIONS FOR PHOTO(ELECTRO)CATALYTIC APPLICATIONS

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by

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Submitted

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Dedicated to my family

Certificate

This is to certify that the thesis entitled **"Tuning the Surface of Metal Oxide/Oxyhydroxide Nanocrystals by Inorganic Polyanions for Photo(electro)catalytic Applications",** submitted by Mr. Laxmikanta Mallick to the Indian Institute of Technology Delhi for the award of the degree of Doctor of Philosophy in Chemistry, is a record of the original, bonafide research work carried out by her under our supervision and guidance. The thesis has reached the standards fulfilling the requirements of the regulations related to the award of the degree.

The results of this thesis have not been submitted in part or in whole to any other university or institute for the awarding of any degree or diploma to the best of our knowledge.

Date:

Prof. Biswarup Chakraborty
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Abstract

The conversion of small molecules like H_2O, CO_2, N_2, and NO_x into essential chemical species like H_2, O_2, CH_4, and NH_3, respectively, is vital for numerous chemical and industrial applications. These conversions generally involve several processes, including redox reactions, catalytic mechanisms, and energy input from heat (thermochemical), light (photochemical), or electricity (electrochemical). Understanding and optimizing these conversions is important for sustainable energy solutions and addressing environmental problems. Among the various processes, photochemical and electrochemical processes are attracting due to their energy-intensive nature. Moreover, the advancement of electrocatalysts necessitates appropriate metal ions; if it functions as a redox catalyst, it must attain an appropriate valence state in line with the Sabatier principle. Furthermore, it should adsorb species with an intermediate strength—neither too strong nor too weak—while also exhibiting conductivity and being composed of earth-abundant materials, as earth-abundant elements. Further, the earth-abundant elements, such as transition metals (e.g., Fe, Co, Ni, Mn, Cu, etc.), have become a center point of research due to their availability, cost-effectiveness, and environmentally friendly properties. However, challenges such as low turnover number or frequency, insufficient activity, poor product selectivity, and lack of stability highlight the need for the development of a superior electrocatalyst. In a similar context, photocatalysts require a tunable bandgap, photon absorption efficiency, and suitable charge transfer dynamics, which encompass electron capture, migration, and the reduced recombination of electron-hole pairs for superior photochemical reaction. Additionally, tunable structural characteristics such as dimensions, aggregation, and electronic attributes—including defect states and band gaps—improve catalytic processes. Furthermore, the distinct size effect observed in nanomaterials leads to increased catalytic efficiency in catalysis. The confinement effect in catalysis modifies essential properties of a system, such as its structure and electronic state, by restricting a particular physical state, like a nano-state, thereby influencing the

catalytic performance of the system. Due to poor conductivity, inherent tendency towards coagulation of the bulk metal oxides and faster charge recombination under photo irradiation conditions, they are less likely to behave as active photo(electro)catalysts. In this context, the metal oxide nanoparticles (NPs) are widely used in catalytic processes. However, the nanoparticles of >100 nm size also have larger sizes, active sites get blocked during reaction due to aggregation, a wide band gap, poor reactivity, and conductivity, poor charge transport, and light absorption limit the catalytic activity. In this direction, quantum dots (QDs) attract attention among researchers these days due to their distinctive physical and optical properties. The preparation of metal oxide quantum dots (QDs) requires suitable surfactants, capping agents, reducing agents, and hazardous organic solvents, which limit the economic and environmental feasibility of the process. Moreover, hydrophilic organic ligands with side chains used to stabilize QDs can reduce the solubility of the QDs and make them unstable in aqueous environments. Given that, my doctoral research work focuses on the design of metal oxide quantum dots (QDs) stabilized by polyoxometalate (POMs) as a protecting ligand. The POMs have oxo groups and are hydrophilic, so adsorption of analyte and water is suitable in an aqueous phase. Moreover, in POM, the metal ions are in the highest valence state. Consequently, they are more stable in oxidative conditions and also show multi-electron redox properties, which make them suitable stabilizing ligands to protect QDs with tunable electronic and structural properties.

In my first doctoral work, we attempted to prepare different phases of FeO(OH) under surfactant-free conditions and aimed to understand the behaviour of different phases of FeO(OH) on the electrode surface towards catalysis, such as water oxidation. In addition, among the different phases, polycrystalline γ–FeO(OH) exhibits a better activity compared to the other phases. Further, when the γ-FeO(OH) was stabilized by polyoxomolybdate ($(NH_4)_6[Mo_7O_{24}]$) in the quantum regime, it exhibits better activity compared to bare γ-FeO(OH) due to higher surface area and ionic surface fosters the formation of an ordered electrical double layer, thereby improving charge transport at the electrode-electrolyte

interface. In the subsequent study, water-soluble polyoxometalate ($[Mo_7O_{24}]^{6-}$) stabilized oxygen vacancy-rich SnO_2 quantum dot nanoparticles are synthesized for electrochemical nitrate reduction to NH_3, which not only enhances the oxygen vacancy of SnO_2 QD core and provides an ionic surface to prevent aggregation but also enhance the activity due to a synergic effect between SnO_2 and $(NH_4)_6Mo_7O_{24}$. In the follow up work, $[Mo_7O_{24}]^-$ cluster anion is used to stabilize a vacancy-rich CeO_2 quantum core ($Mo_7@CeO_2$), which demonstrates a tunable band gap favors the absorption of visible light and enhancement of oxygen vacancy which not only facilitates the charge transfer dynamics between the CeO_2 QDs and $[Mo_7O_{24}]^{6-}$ though S-scheme heterostructure, but also promotes the photocatalytic nitrate reduction to ammonia due to spatially separate electron-hole. Further, the quantum confinement enhances the surface area, facilitating the catalytic activity. In the final chapter of my thesis, a polyoxometalate (POM) stabilized ionic TiO_2 nanostructure ($[POM]_x@TiO_2$) is synthesized, where sodium counter ions on the surface, which balance the charge of POMs, are replaced with copper(II) ions, resulting in $Cu_x[POM]@TiO_2$. The band alignment indicates that the TiO_2 core has a photo-harvesting efficiency for the photochemical CO_2R reaction. Further, the quasi-in-situ Raman investigation provides support for the adsorption of CO_2 on the $Cu_x[POM]@TiO_2$ surface via $\{Cu\text{-}[CO_2]^-\}$ adduct, which is the crucial step for photochemical CO_2 reduction. Moreover, distinct components such as TiO_2 acting as a photosensitizer, POM serving as a protective ligand for the TiO_2 nanocore, Cu^{II} functioning as a co-catalyst, and simultaneously serving as the active site to promote the CO_2R reaction through the creation of a stable metal-CO_2 adduct are highlighted. The thesis highlights the use of polyoxometalates (POMs) as stabilizers to stabilize bulk metal oxide to metal oxide quantum dots (QDs), which not only resists the aggregation, reduce the size with increase the active surface area which favors the stability and charge transport during catalysts and influences electrochemical process. It also enhances defect states, facilitates charge dynamics, and reduces band gaps, which favors visible light absorption and enhances photocatalytic application. Compared to bulk materials, the QD material stabilized by POM

anions designed in this thesis work shows better electrochemical water oxidation, nitrate reduction, and photochemical CO_2 reduction, and nitrate reduction to ammonia. These types of materials are a unique class of complete inorganic nanostructures which have never been studied in literature, and the detailed mechanistic study presented in the thesis will help further to discover new energy materials and their potential applications, such as photo(electro)chemical biomass or organic conversion to value-added products and optoelectronics study.

सारांश

H_2O, CO_2, N_2 और NO_x जैसे छोटे अणुओं का क्रमशः H_2, O_2, CH_4 और NH_3 जैसी आवश्यक रासायनिक प्रजातियों में रूपांतरण, कई रासायनिक और औद्योगिक अनुप्रयोगों के लिए महत्वपूर्ण है। इन रूपांतरणों में आम तौर पर कई प्रक्रियाएँ शामिल होती हैं, जिनमें रेडॉक्स प्रतिक्रियाएँ, उत्प्रेरक तंत्र और ऊष्मा (थर्मोकेमिकल), प्रकाश (फोटोकेमिकल), या बिजली (इलेक्ट्रोकेमिकल) से ऊर्जा इनपुट शामिल हैं। इन रूपांतरणों को समझना और उनका अनुकूलन करना स्थायी ऊर्जा समाधानों और पर्यावरणीय समस्याओं को संबोधित करने के लिए महत्वपूर्ण है। विभिन्न प्रक्रियाओं में से, फोटोकेमिकल और इलेक्ट्रोकेमिकल प्रक्रियाएँ अपनी ऊर्जा-गहन प्रकृति के कारण आकर्षित कर रही हैं। इसके अलावा, इलेक्ट्रोकैटेलिस्ट की उन्नति के लिए उपयुक्त धातु आयनों की आवश्यकता होती है; यदि यह रेडॉक्स उत्प्रेरक के रूप में कार्य करता है, तो इसे सबेटियर सिद्धांत के अनुरूप एक उपयुक्त वैलेंस अवस्था प्राप्त करनी चाहिए। इसके अलावा, इसे मध्यवर्ती शक्ति वाली प्रजातियों को अवशोषित करना चाहिए - न तो बहुत मजबूत और न ही बहुत कमजोर - जबकि चालकता भी प्रदर्शित करता है और पृथ्वी-प्रचुर तत्वों के रूप में पृथ्वी-प्रचुर पदार्थों से बना होता है। इसके अलावा, पृथ्वी पर प्रचुर मात्रा में पाए जाने वाले तत्व, जैसे संक्रमण धातु (जैसे, Fe, Co, Ni, Mn, Cu, आदि), अपनी उपलब्धता, लागत-प्रभावशीलता और पर्यावरण के अनुकूल गुणों के कारण शोध का केंद्र बिंदु बन गए हैं। हालांकि, कम टर्नओवर संख्या या आवृत्ति, अपर्याप्त गतिविधि, खराब उत्पाद चयनात्मकता और स्थिरता की कमी जैसी चुनौतियाँ एक बेहतर इलेक्ट्रोकैटेलिस्ट के विकास की आवश्यकता को उजागर करती हैं। इसी तरह के संदर्भ में, फोटोकैटेलिस्ट को एक ट्यूनेबल बैंडगैप, फोटॉन अवशोषण दक्षता और उपयुक्त चार्ज ट्रांसफर डायनेमिक्स की आवश्यकता होती है, जिसमें बेहतर फोटोकैमिकल प्रतिक्रिया के लिए इलेक्ट्रॉन कैप्चर, माइग्रेशन और इलेक्ट्रॉन-होल जोड़े के कम पुनर्संयोजन शामिल होते हैं। इसके अतिरिक्त, ट्यूनेबल संरचनात्मक विशेषताएँ जैसे आयाम, एकत्रीकरण और इलेक्ट्रॉनिक विशेषताएँ - जिसमें दोष अवस्थाएँ और बैंड गैप शामिल हैं - उत्प्रेरक प्रक्रियाओं में सुधार

करती हैं। इसके अलावा, नैनोमटेरियल में देखे जाने वाले विशिष्ट आकार के प्रभाव से कटैलिसीस में उत्प्रेरक दक्षता में वृद्धि होती है। कटैलिसीस में परिरोध प्रभाव एक प्रणाली के आवश्यक गुणों को संशोधित करता है, जैसे कि इसकी संरचना और इलेक्ट्रॉनिक स्थिति, एक विशेष भौतिक अवस्था, जैसे कि नैनो-स्थिति को प्रतिबंधित करके, जिससे प्रणाली के उत्प्रेरक प्रदर्शन पर असर पड़ता है। खराब चालकता, थोक धातु ऑक्साइड के जमाव की अंतर्निहित प्रवृत्ति और फोटो विकिरण की स्थितियों के तहत तेजी से चार्ज पुनर्संयोजन के कारण, वे सक्रिय फोटो (इलेक्ट्रो) उत्प्रेरक के रूप में व्यवहार करने की कम संभावना रखते हैं। इस संदर्भ में, धातु ऑक्साइड नैनोकणों (एनपी) का व्यापक रूप से उत्प्रेरक प्रक्रियाओं में उपयोग किया जाता है। हालांकि, >100 एनएम आकार के नैनोकणों का आकार भी बड़ा होता है, एकत्रीकरण के कारण प्रतिक्रिया के दौरान सक्रिय साइटें अवरुद्ध हो जाती हैं, एक विस्तृत बैंड गैप, खराब प्रतिक्रियाशीलता और चालकता, खराब चार्ज परिवहन और प्रकाश अवशोषण उत्प्रेरक गतिविधि को सीमित करते हैं। इस दिशा में, क्वांटम डॉट्स (QDs) इन दिनों अपने विशिष्ट भौतिक और ऑप्टिकल गुणों के कारण शोधकर्ताओं के बीच ध्यान आकर्षित करते हैं। धातु ऑक्साइड क्वांटम डॉट्स (QDs) की तैयारी के लिए उपयुक्त सर्फेक्टेंट, कैपिंग एजेंट, रिड्यूसिंग एजेंट और खतरनाक कार्बनिक सॉल्वैंट्स की आवश्यकता होती है, जो प्रक्रिया की आर्थिक और पर्यावरणीय व्यवहार्यता को सीमित करते हैं। इसके अलावा, QDs को स्थिर करने के लिए उपयोग किए जाने वाले साइड चेन वाले हाइड्रोफिलिक कार्बनिक लिगैंड QDs की घुलनशीलता को कम कर सकते हैं और उन्हें जलीय वातावरण में अस्थिर बना सकते हैं। यह देखते हुए, मेरा डॉक्टरेट शोध कार्य एक सुरक्षात्मक लिगैंड के रूप में पॉलीऑक्सोमेटलेट (POMs) द्वारा स्थिर किए गए धातु ऑक्साइड क्वांटम डॉट्स (QDs) के डिजाइन पर केंद्रित है। POMs में ऑक्सो समूह होते हैं और वे हाइड्रोफिलिक होते हैं, इसलिए जलीय चरण में एनालाइट और पानी का सोखना उपयुक्त होता है। इसके अलावा, POM में, धातु आयन उच्चतम वैलेंस अवस्था में होते हैं। नतीजतन, वे ऑक्सीडेटिव स्थितियों में अधिक स्थिर होते हैं और बहु-इलेक्ट्रॉन रेडॉक्स गुण भी दिखाते हैं, जो उन्हें ट्यूनेबल इलेक्ट्रॉनिक और संरचनात्मक गुणों के साथ QDs की रक्षा करने के लिए उपयुक्त स्थिरीकरण लिगैंड बनाते हैं।

मेरे पहले डॉक्टरेट कार्य में, हमने सर्फेक्टेंट-मुक्त परिस्थितियों में FeO(OH) के विभिन्न चरणों को तैयार करने का प्रयास किया और इलेक्ट्रोड सतह पर FeO(OH) के विभिन्न चरणों के व्यवहार को समझने का लक्ष्य रखा, जैसे कि जल ऑक्सीकरण। इसके अलावा, विभिन्न चरणों में, पॉलीक्रिस्टलाइन γ–FeO(OH) अन्य चरणों की तुलना में बेहतर गतिविधि प्रदर्शित करता है। इसके अलावा, जब γ–FeO(OH) को क्वांटम शासन में पॉलीऑक्सोमोलिब्डेट ((NH4)6[Mo7O24]) द्वारा स्थिर किया गया, तो यह उच्च सतह क्षेत्र और आयनिक सतह के कारण नंगे γ-FeO(OH) की तुलना में बेहतर गतिविधि प्रदर्शित करता है, जो एक व्यवस्थित विद्युत दोहरी परत के गठन को बढ़ावा देता है, जिससे इलेक्ट्रोड-इलेक्ट्रोलाइट इंटरफेस पर चार्ज ट्रांसपोर्ट में सुधार होता है। बाद के अध्ययन में, जल में घुलनशील पॉलीऑक्सोमेटलेट ($[Mo_7O_{24}]^{6-}$) स्थिर ऑक्सीजन रिक्ति-समृद्ध SnO_2 क्वांटम डॉट नैनोकणों को NH3 में इलेक्ट्रोकेमिकल नाइट्रेट कमी के लिए संश्लेषित किया जाता है, जो न केवल SnO_2 QD कोर की ऑक्सीजन रिक्ति को बढ़ाता है और एकत्रीकरण को रोकने के लिए एक आयनिक सतह प्रदान करता है, बल्कि SnO_2 और $(NH_4)_6Mo_7O_{24}$ के बीच एक सहक्रियात्मक प्रभाव के कारण गतिविधि को भी बढ़ाता है। अनुवर्ती कार्य में, $[Mo_7O_{24}]^-$ क्लस्टर आयन का उपयोग रिक्ति-समृद्ध CeO_2 क्वांटम कोर ($Mo_7@CeO_2$) को स्थिर करने के लिए किया जाता है, जो एक ट्यूनेबल बैंड गैप को प्रदर्शित करता है जो दृश्य प्रकाश के अवशोषण और ऑक्सीजन रिक्ति को बढ़ाने के लिए अनुकूल है जो न केवल CeO_2 QDs और $[Mo_7O_{24}]^{6-}$ के बीच चार्ज ट्रांसफर डायनेमिक्स को S-स्कीम हेटरोस्ट्रक्चर के माध्यम से सुविधाजनक बनाता है, बल्कि स्थानिक रूप से अलग इलेक्ट्रॉन-छेद के कारण अमोनिया में फोटोकैटलिटिक नाइट्रेट कमी को भी बढ़ावा देता है। इसके अलावा, क्वांटम परिरोध सतह क्षेत्र को बढ़ाता है, जिससे उत्प्रेरक गतिविधि को सुविधाजनक बनाया जाता है। मेरी थीसिस के अंतिम अध्याय में, एक पॉलीऑक्सोमेटालेट (POM) स्थिर आयनिक TiO_2 नैनोस्ट्रक्चर ($[POM]_x@TiO_2$) को संश्लेषित किया गया है, जहाँ सतह पर सोडियम काउंटर आयन, जो POMs के आवेश को संतुलित करते हैं, को कॉपर (II) आयनों से प्रतिस्थापित किया जाता है, जिसके परिणामस्वरूप $Cu_x[POM]@TiO_2$ बनता है। बैंड संरेखण इंगित करता है कि TiO_2 कोर में फोटोकैमिकल CO_2R प्रतिक्रिया के लिए फोटो-हार्वेस्टिंग दक्षता है। इसके अलावा,

अर्ध-इन-सीटू रमन जांच {Cu-[CO_2]-} एडक्ट के माध्यम से Cu_x[POM]@TiO_2 सतह पर CO_2 के सोखने के लिए समर्थन प्रदान करती है, जो फोटोकैमिकल CO_2 कमी के लिए महत्वपूर्ण कदम है। इसके अलावा, TiO_2 जैसे विशिष्ट घटक जो फोटोसेंसिटाइज़र के रूप में कार्य करते हैं, POM जो TiO_2 नैनोकोर के लिए सुरक्षात्मक लिगैंड के रूप में कार्य करता है, CuII जो सह-उत्प्रेरक के रूप में कार्य करता है, और साथ ही एक स्थिर धातु-CO_2 अभिक्रिया के निर्माण के माध्यम से CO_2R प्रतिक्रिया को बढ़ावा देने के लिए सक्रिय साइट के रूप में कार्य करता है, पर प्रकाश डाला गया है। थीसिस बल्क मेटल ऑक्साइड को मेटल ऑक्साइड क्वांटम डॉट्स (QDs) में स्थिर करने के लिए स्टेबलाइज़र के रूप में पॉलीऑक्सोमेटालेट्स (POMs) के उपयोग पर प्रकाश डालती है, जो न केवल एकत्रीकरण का प्रतिरोध करता है, बल्कि सक्रिय सतह क्षेत्र को बढ़ाने के साथ आकार को कम करता है जो उत्प्रेरक के दौरान स्थिरता और चार्ज परिवहन का पक्षधर है और इलेक्ट्रोकेमिकल प्रक्रिया को प्रभावित करता है। यह दोष स्थितियों को भी बढ़ाता है, चार्ज डायनेमिक्स को सुगम बनाता है, और बैंड गैप को कम करता है, जो दृश्य प्रकाश अवशोषण का पक्षधर है और फोटोकैटलिटिक अनुप्रयोग को बढ़ाता है। बल्क सामग्रियों की तुलना में, इस थीसिस कार्य में डिज़ाइन किए गए POM आयनों द्वारा स्थिर की गई QD सामग्री बेहतर इलेक्ट्रोकेमिकल जल ऑक्सीकरण, नाइट्रेट कमी और फोटोकैमिकल CO_2 कमी और अमोनिया में नाइट्रेट कमी दिखाती है। इस प्रकार की सामग्रियां पूर्ण अकार्बनिक नैनो संरचनाओं का एक अद्वितीय वर्ग है, जिसका साहित्य में कभी अध्ययन नहीं किया गया है, और थीसिस में प्रस्तुत विस्तृत यांत्रिक अध्ययन नई ऊर्जा सामग्रियों और उनके संभावित अनुप्रयोगों, जैसे कि फोटो (इलेक्ट्रो) रासायनिक बायोमास या मूल्यवर्धित उत्पादों और ऑप्टोइलेक्ट्रॉनिक्स अध्ययन में उनके संभावित अनुप्रयोगों की खोज करने में मदद करेगा।

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Abbreviations

AQY	**Apparent Quantum Yield**
BET	**Brunauer–Emmett–Teller**
CA	**Chronoamperometry**
CB	**Conduction Band**
CO_2RR	**CO_2 Reduction Reaction**
CC	**Carbon Cloth**
CBM	**Conduction Band Minima**
CE	**Counter Electrode**
CV	**Cyclic Voltammetry**
DFT	**Density Functional Theory**
DOS	**Density of States**
EDX	**Energy Dispersive X-ray**
EIS	**Electrochemical Impedance Spectroscopy**
ECSA	**Electrochemical Surface Area**
EPR	**Electron Paramagnetic Resonance**
EXAFS	**Extended X-ray Absorption Fine Structure**
E_f	**Fermi Level**
FE	**Faradaic Efficiency**
fs-TAS	**Femtosecond Transient Absorption Spectroscopy**
FESEM	**Field Emission Scanning Electron Microscopy**
FTIR	**Fourier Transform Infrared**

GC	**Glassy Carbon**
HER	**Hydrogen Evolution Reaction**
HRTEM	**High Resolution Transmission Electron Microscopy**
ICDD	**International Centre for Diffraction Data**
ICPMS	**Inductively Coupled Plasma Mass Spectrometry**
JCPDS	**Joint Committee on Powder Diffraction Standards**
KPFM	**Kelvin Probe Force Microscopy**
LSV	**Linear Sweep Voltammetry**
MS	**Mott–Schottky**
MONPs	**Metal Oxide Nanoparticles**
NF	**Nickel Ffoam**
NMR	**Nuclear Magnetic Resonance**
NCs	**Nanocrystals**
NO_3RR	**Nitrate Reduction Reaction**
NRR	**Nitrogen Reduction Reaction**
OER	**Oxygen Evolution Reaction**
OWS	**Overall Water Splitting**
POMs	**Polyoxometalates**
PXRD	**Powder X-ray Diffraction**
QDs	**Quantum dots**
RDS	**Rate Determining Step**
RRDE	**Rotating Ring Disk Electrode**

RE	**Reference Electrode**
RHE	**Reversible Hydrogen Electrode**
SAED	**Selected Area Electron Diffraction**
STA	**Solar to Ammonia**
SAXS	**Small Angel X-ray Spectroscopy**
SEM	**Scanning Electron Microscopy**
TEM	**Transmission Electron Microscopy**
TOF	**Turnover Frequency**
UV	**Ultraviolet**
VBM	**Valence Band Maxima**
VB	**Valence Band**
XPS	**X-ray Photoelectron Spectroscopy**
XANES	**X-ray Absorption Near Edge Structure**

Symbols

$\mathring{A}$	**armstrong**
S	**area**
A_i	**amplitude**
E	**applied potential**
k_B	**boltzmann constant**
A_0	**baseline correction**
℃	**celsius**
cm	**centimetre**
i_C	**current**
α	**charge transfer coefficient**
R_{ct}	**charge transfer resistance**
j	**current density**
C_{dl}	**double-layer capacitance**
D	**diffusion coefficient**
τ_i	**decay time**
ε	**dielectric constant**
μ	**dipole**
eV	**electron volt**
$j_\circ$	**exchange current density**
e	**electric charge**
E	**electric field**

F	**faraday constant**
fs	**femtosecond**
$\Delta G°$	**free energy**
h	**hour**
C_0	**initial concentration of electrolyte**
W	**input energy**
K	**kelvin**
keV	**kilo electron Volt**
v	**kinetic viscosity**
kV	**kilo Volt**
I	**light intensity**
μm	**micrometre**
mA	**milli-Ampere**
mL	**milliliter**
mol	**mole**
min	**minute**
B	**magnetic field**
nm	**nanometre**
n	**number of transferred electrons**
N_D	**Number of donor**
η	**overpotential**
ps	**picosecond**

α	**polarizabilty**
t	**probe time delay**
p	**planks constant**
ε_0	**permittivity of free space**
m	**reaction order**
ω	**rotating rates**
R_s	**solution resistance**
c	**speed of light**
A	**surface area**
C_s	**specific capacitance**
β	**symmetry factor**
Q	**charge**
b	**tafel slope**
T	**temperature**
λ	**wavelength**
Φ	**workfunction**