Modified Carbon Nanomaterials as Active Electrocatalysts

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Abstract

Water splitting (WS) has attracted increasing attention for producing highly pure hydrogen and oxygen. WS is also a promising technique to store intermittent electrical energy from renewable resources such as solar and wind energy in the form of H₂ fuel. WS consists of two half-reactions: hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). For HER, efficient non-precious catalysts are required to replace the rare and expensive Pt-based catalysts. For OER, more efficient low-cost catalysts should be designed to improve the sluggish reaction rate of OER and reduce the reaction overpotential. In this thesis, a few synthesis methods have been developed to introduce novel hybrid carbon nanomaterials with efficient catalytic activity toward HER and OER.

We have developed a one-step floating catalyst chemical vapor deposition synthesis process to grow carbon-encapsulated iron nanoparticles (CEINs) supported on carbon nanotubes (CNTs), as highly active electrocatalysts. In CEINs, the active metallic core is protected from atmospheric-oxygen-induced degradation and agglomeration with neighboring nanoparticles. Single-shell CEINs decorated on single-walled CNTs (SWNTs) exhibit a high catalytic activity for HER in acidic media comparable to that of platinum. Furthermore, the structure of the CEINs has been transformed to crystalline maghemite (γ-Fe₂O₃) nanoparticles using a simple electrochemical technique. The electrochemically modified CEINs decorated on CNTs have been introduced as active and durable electrocatalysts for alkaline OER. It has also been shown that CNTs are selectively opened during OER, suggesting a technique for selective opening of CNTs which is beneficial for endohedral functionalization of CNTs.

We have further introduced SWNTs as promising supports to stabilize individual atoms or subnano clusters of Pt. An atomic-scale Pt catalyst system allows minimizing the Pt loading. However, ultra-small structures of Pt are not stable unless they are immobilized on a suitable support. The SWNTs have been activated with pseudo-atomic scale Pt, including mostly the active surface atoms, using a simple electroplating method. These activated SWNTs exhibit a similar activity toward HER in acidic media to that of commercial Pt/C with a significantly higher Pt loading.

We have also investigated that immobilization of organometallic Ni complexes on the sidewalls of multi-walled CNTs (MWNTs) is a promising strategy to synthesize a new class of efficient non-precious electrocatalysts. A synthesis method has been developed to covalently functionalize MWNTs with Ni bipyridine complexes. The Ni-bipyridine-MWNT shows a high activity for alkaline OER, ranking the material among the most active OER electrocatalysts reported so far.

Keywords Carbon nanotubes, carbon-encapsulated iron nanoparticles, pseudo-atomic-scale Pt, functionalization, hydrogen evolution, oxygen evolution, electrocatalyst
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Helsinki, August 2017

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<th>Definition</th>
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<tbody>
<tr>
<td>At-Pt</td>
<td>Pseudo-atomic-scale Pt</td>
</tr>
<tr>
<td>BF</td>
<td>Bright-field</td>
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<tr>
<td>CE</td>
<td>Counter electrode</td>
</tr>
<tr>
<td>CEIN</td>
<td>Carbon-encapsulated iron nanoparticle</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DF</td>
<td>Dark-field</td>
</tr>
<tr>
<td>E</td>
<td>Electrode potential</td>
</tr>
<tr>
<td>$E_0$</td>
<td>Equilibrium (standard) potential</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray spectrometry</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
<tr>
<td>GR</td>
<td>Graphene</td>
</tr>
<tr>
<td>HAADF</td>
<td>High-angle annular dark-field</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen evolution reaction</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron microscopy</td>
</tr>
<tr>
<td>$j$</td>
<td>Current density</td>
</tr>
<tr>
<td>$j_o$</td>
<td>Exchange Current density</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear sweep voltammetry</td>
</tr>
<tr>
<td>MWNT</td>
<td>Multi-walled carbon nanotube metallic nanoparticle</td>
</tr>
<tr>
<td>MNP</td>
<td>Metallic nanoparticle</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
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</table>
\( n \)  Number of transferred electrons in the electrode reaction

OER  Oxygen evolution reaction

ORR  Oxygen reduction reaction

PEM  Polymer electrolyte membrane

RDE  Rotating disc electrode

\( R \)  Universal gas constant

RE  Reference electrode

RHE  Reversible hydrogen electrode

RRDE  Rotating ring disc electrode

SCEIN  Single-shell carbon-encapsulated iron nanoparticle

SEM  Scanning electron microscopy

STEM  Scanning transmission electron microscopy

SWNT  Single-walled carbon nanotube

\( T \)  Absolute temperature

TEM  Transmission electron microscopy

TM  Transition metal

WE  working electrode

XPS  X-ray photoelectron spectroscopy

\( Z \)  Atomic number

\( \alpha_a \)  Anodic transfer coefficient

\( \alpha_c \)  Cathodic transfer coefficients

\( \epsilon \)  Faradaic efficiency

\( \eta \)  Overpotential
This doctoral dissertation consists of a summary of the following publications which are referred to in the text by their numerals


Author’s Contribution

**Publication I:** Single-Shell Carbon-Encapsulated Iron Nanoparticles: Synthesis and High Electrocatalytic Activity for Hydrogen Evolution Reaction

M. Tavakkoli had a major role in defining the research plan together with the co-authors, characterized the materials, had a major role in interpretation of the results, designed and performed the electrochemical experiments, and wrote the manuscript. T. Kallio supervised the electrochemical analysis. O. Reynaud synthesized the material. E.I. Kauppinen and A.G. Nasibulin supervised the synthesis of the material. Ch. Johans supervised the electrochemical measurements. J. Sainio and H. Jiang performed XPS and HRTEM measurements, respectively. K. Laasonen supervised the research work.

**Publication II:** Maghemite nanoparticles decorated on carbon nanotubes as efficient electrocatalysts for the oxygen evolution reaction

M. Tavakkoli conceived and developed the idea, characterized the materials, had a major role in interpretation of the results, designed and performed the experiments, and wrote the manuscript. T. Kallio supervised the electrochemical analysis. O. Reynaud synthesized the pristine material. E.I. Kauppinen and A.G. Nasibulin supervised the synthesis of the pristine material. J. Sainio and H. Jiang performed XPS and HRTEM measurements, respectively. K. Laasonen supervised the research work.

**Publication III:** Electrochemical Activation of Single-Walled Carbon Nanotubes with Pseudo-Atomic-Scale Platinum for the Hydrogen Evolution Reaction

M. Tavakkoli conceived and developed the idea, characterized the materials, had a major role in interpretation of the results, designed and performed the experiments, and wrote the manuscript. N. Holmberg performed the DFT calculations and wrote the DFT section in the manuscript. R. Kronberg assisted in the electrochemical measurements. J. Sainio and H. Jiang performed XPS and HRTEM measurements, respectively. E.I. Kauppinen supervised the material analysis. T. Kallio supervised the electrochemical analysis. K. Laasonen developed the idea and supervised the research work.

**Publication IV:** Functionalized Carbon Nanotubes with Ni(II) Bipyridine Complexes as Efficient Catalysts for the Alkaline Oxygen Evolution Reaction

M. Tavakkoli developed the idea, characterized the materials, had a major role in interpretation of the results, designed and performed the electrochemical experiments, and wrote the manuscript. M. Nosek performed the synthesis of the materials and assisted in writing the synthesis section. J. Sainio performed the XPS analysis and assisted in writing the
XPS section. F. Davodi assisted in the electrochemical measurements. T. Kallio supervised the electrochemical measurements. P. Joensuu designed and supervised the synthesis process of the materials. K. Laasonen supervised the project and performed the DFT calculations on the structure of materials.
1. Introduction

Hydrogen, as an environmentally friendly fuel, has attracted increasing attention. Hydrogen can potentially address the issues of sustainability, environmental emissions, and energy security [1]. Although hydrogen is the most abundant element in the universe, pure hydrogen gas is scarce in earth’s atmosphere. Currently, up to 96% of hydrogen is produced by steam reforming natural gas or other fossil fuels [2-4]. However, this method requires non-renewable resources and produces low purity hydrogen with a high concentration of pollutant carbonaceous species [5]. Among current technologies for production of hydrogen, water splitting (electrochemical hydrogen production) is attracting increasing attention [6] and remarkable improvement has been achieved in this technology [5]. Nevertheless, only about 4% of H\(_2\) is produced by water electrolysis as a clean method which produces highly pure H\(_2\) [7]. Another promising advantage of water splitting (i.e., H\(_2\)O → H\(_2\) + 1/2O\(_2\)) is the ability to store intermittent electrical energy from renewable resources such as solar and wind energy in the form of H\(_2\) fuel [8-10].

Electrochemical water splitting can be divided into two half-reactions: the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) [11,12]. The efficiency of electrolyzers strongly depends on the performance of the catalyst materials for HER and OER and the electrode/electrolyte interfaces [5,9-11,13-15]. The price and efficiency of hydrogen produced by water electrolysis can be notably reduced by introducing more efficient and cheaper electrocatalysts. For instance, if the operating voltage of electrolyzers is reduced as little as 0.1 V by only using more efficient catalyst materials for the HER and OER, the current electricity expenses for electrolysis can be decreased by about 0.3 billion Euros [16].

Pt-based catalysts have shown the highest electrocatalytic activity for HER, however scarcity and the high price of platinum limit the widespread commercialization of electrolyzers [17,18]. Despite these limits of Pt, in the modern polymer electrolyte membrane (PEM) electrolyzers, a relatively large loading of Pt is required to efficiently catalyze the HER (~ 0.5–1.0 mg cm\(^{-2}\)) [16]. Therefore, the use of noble metals such as Pt in HER catalysts should be reduced. To synthesize alternatives to high loaded Pt catalysts, there are two strategies: i) replace Pt with efficient, stable, and earth-abundant low-cost catalyst materials or ii) reduce the loading of Pt in HER electrocatalysts by designing more efficient Pt nanocatalysts. The former and the latter strategies have been followed in Publications I and III, respectively.

OER is a critical reaction in electrochemical water splitting to generate and store clean energy. For OER, efficient, low-cost and stable electrocatalysts that can withstand the harsh conditions are required to replace active catalysts such as Ir or Ru-based materials, which are expensive and rare materials [19]. The OER (water oxidation) is a thermodynamically uphill
and kinetically sluggish reaction, which limits the efficiency of water electrolysis and causes a large cell voltage for hydrogen production. Therefore, the development of electrocatalysts for OER to reduce the overpotential and accelerate the sluggish kinetics has received considerable attention in the past decade [20].

Metal nanoparticles (NPs) have been widely used as active catalysts in the chemical industry. However, metal NPs have a tendency to agglomerate with neighboring NPs to form larger particles, decreasing the efficiency of the catalyst. To improve the performance and prevent the degradation of the metal NPs during catalysis, the metal NPs can be anchored onto high surface area and robust supports, preventing aggregation and increasing the number of active sites on the catalyst surface [21,22]. Therefore, the selection of a proper support can significantly improve the catalyst performance. Among the current candidates for catalyst supports, carbon nanotubes (CNTs) are excellent choices for heterogeneous catalysts due to their unique structure and intrinsic properties [23-27]. In this thesis, the metal active sites have been decorated on the CNTs to make active and stable hybrid nanocatalysts. In Publications I-III, we have also shown that metal active sites can even be decorated on CNTs which have not been functionalized or pre-treated.

In Publication I, a chemical vapor deposition (CVD) technique has been developed to synthesize single-walled carbon nanotubes (SWNTs), as the catalyst support, and single-shell carbon-encapsulated iron nanoparticles (SCEINs), as active catalysts, simultaneously. Transition metals (TMs) such as iron are utilized as earth-abundant and low-cost catalysts in a wide-range of catalytic reactions. Nonetheless, TMs are oxidized in air and dissolved in acidic electrolytes, limiting their application to non-acidic conditions. In this work, the encapsulation of active iron NPs inside a single graphene layer has been proposed as a promising strategy to protect active Fe NPs from oxidation in ambient air and from dissolution into acidic electrolytes. The single-shell carbon cage in SCEINs does not hinder access of reactants to iron and protects the metal core from oxidation in air and from agglomeration with neighboring Fe NPs during electrocatalysis. The SCEIN/SWNT functions as an active and durable hybrid nanocatalyst toward HER under acidic conditions, exhibiting a comparable HER activity to that of state-of-the-art Pt electrocatalysts.

In Publication II, we have electrochemically modified carbon encapsulated iron nanoparticles (CEINs) to activate them for OER in alkaline media. The CEINs decorated on the few-walled CNTs (CEIN/CNT) are synthesized by an aerosol CVD method in a one-step synthesis with a similar growth process to that of CNTs. Then, the structure of the CEIN/CNT nanohybrids is transformed to $\gamma$-Fe$_2$O$_3$/CNT through a fast and simple electrochemical modification technique. This modification technique might be also used for tuning the structure of other metal@C core-shell NPs. The $\gamma$-Fe$_2$O$_3$/CNT sample is reported as an active and durable catalyst for OER in alkaline media. Furthermore, it has been shown that this electrochemical modification method can also be used as a technique for selective opening of CNTs, which is critical for endohedral functionalization of CNTs.

In Publication III, we have developed a simple and readily upscalable electroplating method to immobilize pseudo-atomic-scale Pt, i.e. individual atoms or subnanometer clusters, on the sidewalls of the SWNTs (SWNT/at-Pt). The atomic-scale catalysts are not stable because of their high surface energy, unless they are decorated on supports providing strong
metal–support interactions to prevent agglomeration of atoms. In comparison to other carbon nanomaterials, SWNTs have been suggested as a promising support to stabilize Pt atoms and form atomic scale Pt catalysts. SWNT/at-Pt materials with a Pt loading of 0.19–0.75 atom % at the electrode surface can function as highly active catalysts. The activated SWNTs with a minimal amount of Pt exhibit a similar activity toward HER in acidic media to that of commercial Pt/C with a significantly higher (≈66–333-fold) Pt loading.

In Publication IV, we have developed a synthesis method to covalently functionalize multi-walled carbon nanotubes (MWNTs) with organometallic Ni complexes. Immobilisation of such complexes on MWNTs has been proposed as a promising strategy to introduce a new class of highly active electrocatalysts. We have shown that Ni bipyridine (bipy) complexes immobilized on MWNTs are highly active and stable catalysts toward OER in alkaline media. The high activity of the Ni-bipy-MWNT catalyst places this material among the most active OER electrocatalysts reported to date. Organometallic compounds include a wide range of the materials and this approach can open new avenues for the use of these compounds in electrocatalysis.
2. Carbon nanostructures: introduction and application in electrocatalysis

Carbon can form many allotropes, including such well-known forms as graphene, graphite, fullerene, nanotubes, and diamond. These allotropes have different properties and they are utilized in a variety of applications. The fundamental structure of these allotropes have been summarized in Figure 1. In this thesis, three allotropes of carbon, CNTs, fullerene-like structures and graphite, have been used to make novel active catalyst materials. CNTs have been used in publications I-IV as the catalyst support, fullerene-like structures have been used in publications I and II to encapsulate active iron NPs (Fe@C core-shell nanostructures), and graphite has been used in Publication III to compare the ability of the graphite to isolate the Pt individual atoms in comparison to the SWNTs.

![Allotropes of Carbon](image)

**Figure 1.** Schematic illustration of allotropes of carbon and their crystal structure (Reprinted with permission from ref. [28]).

2.1 Fullerene

Fullerene refers to any type of closed hollow carbon molecule that is either sphere-like (buckyball) or cylindrical (buckytube). Fullerene was discovered by Smalley and co-workers in the mid-1980s [29]. Based on the pentagon rule, the smallest stable member of the fullerene family is C\(_{60}\) which consists of 60 carbon atoms forming 20 hexagons and 12 pentagons [30,31]. The pentagon rule states that a stable fullerene is only formed when each pentagon is surrounded by a ring of hexagons, isolating each pentagon [30]. The incorporation of the pentagon in the structure creates positive curvature to the structure and forms the closed quasi-spherical shape of the buckyball structures [30].
2.2 Carbon nanotubes

A single-layer of hexagonal sp² hybridized carbon atoms is called graphene. Graphite is composed of layers of graphene interacting with each other through weak Van der Waals forces, making graphite soft and slippery.

After the discovery of fullerene, needle-like tube structures of carbon were systematically studied by Iijima in 1991 [32]. Those structures are known today as carbon nanotubes. CNTs are an allotrope of carbon with a cylindrical nanostructure with a very high aspect ratio. CNTs are classified as either single-walled carbon nanotubes (SWNTs) or multi-walled carbon nanotubes (MWNTs) which can be visualized as cylindrically rolled graphene or graphite sheets, respectively (Figure 2a). CNTs have attracted great interest due to their unique optical, electronic, thermal and mechanical properties that make them useful for various applications [30,31,33-35].

The properties of SWNTs depend on the way the graphene sheet is wrapped. The structure of SWNTs can be defined by using the (n, m)-notation, denoted as the number of unit vectors along two directions in the honeycomb crystal lattice of graphene (Figure 2b). The chirality of a SWNT describes how the graphene sheet is rolled up to make the SWNT and it can be defined by the chiral vector \( \mathbf{C}_h \). In a graphene sheet, \( \mathbf{C}_h \) can be defined by the unit vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) of graphene in real space (Figure 2b):

\[
\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 \quad (1)
\]

In a SWNT, the rolling angle, \( \theta \), and the radius of the SWNT, measured by the n and m numbers, describe the properties of the nanotube. The n and m chiral indices are integer numbers \( (n, m = 1, 2, ..., n \geq m) \) and if \( m = 0 \) \( (\theta = 0^\circ) \), the SWNT is called a zigzag nanotube; for \( n = m \) \( (\theta = 30^\circ) \), the tube is armchair; otherwise \( (0^\circ < \theta < 30^\circ) \) it is called chiral. In SWNTs, armchair tubes are metals; \( (n, m) \) tubes with \( n - m = 3j \) \( (j \text{ is a nonzero integer}) \) are low bandgap semiconductors (at room temperature, all these tubes can be also considered as metallic for most practical purposes); and the other tubes are wide bandgap semiconductors [34].
CNTs are quasi-1D nanomaterials with a high specific surface area which is typically ~ 400-900 m² g⁻¹ for SWNTs and ~ 200-400 m² g⁻¹ for MWNTs [37]. At cryogenic temperatures, SWNTs are quasi-ballistic conductors (where no significant scattering of the carriers occurs in the nanotube channel) and the conductance along the tube approaches the quantum conductance limit of $4e^2/h$ [38]. Because of strong chemical sp² carbon bonding in the CNTs, it has been found that short length SWNTs (~10-15 nm), can carry an ultra-high current density of ~ $4 \times 10^9$ A/cm². This value is one order of magnitude lower for longer tubes [39]. This large tolerable current is three orders of magnitude higher than that of the highest tolerable current in a typical metal such as Cu or Al before breakdown via electromigration [39]. For MWNTs, a multichannel quasi-ballistic conducting behavior has been observed [40], attributing to the participation of multiple walls in electrical transport.

2.3 Synthesis of carbon nanotubes

Carbon nanotubes have been successfully synthesized by various methods, but the three most widely used techniques are arc-discharge, laser evaporation/ablation and chemical vapour deposition (CVD) [41-43]. The synthesis principle in all of these methods is rather similar; but the properties, structure and purity of their products may differ. The arc-discharge is the first technique by which CNTs were synthesised and recognized by Iijima [32], however this method was earlier developed to allow mass production of fullerenes [44]. In this method, a high yield of highly crystalline CNTs can be synthesized, but the yield usually contains other carbon materials as well so that a further purification process may be required [45]. The laser evaporation method, was developed first for fullerene production [46] and afterwards for synthesis of CNTs [47,48]. The high energy density of lasers makes this technique suitable for vaporization of materials such as carbon, which have a high boiling temperature. By the laser evaporation method, CNTs with higher quality and purity compared to the arc-discharge technique can be synthesized [41,42]. The CVD synthesis method provides a more controllable route over diameter, length and morphology of the CNTs and it is a popular technique to yield high purity CNTs [43,49,50]. Furthermore, in comparison to the arc-discharge and the laser techniques, the CVD is a simple and economical method which can grow CNTs at ambient pressure and lower temperatures [41].

The CVD method is based on the catalytic decomposition of hydrocarbon or carbon monoxide feedstock (as the carbon-containing precursor) on the surface of transition metal NPs (which serve as catalysts for the growth of the CNTs). Catalytic CVD synthesis is usually performed in a flow furnace at atmospheric pressure [42]. In this technique the growth conditions can be modified to synthesize single-walled, double-walled or multi-walled tubes [49] and even to grow SWNTs with a narrow (n,m)-distribution [50].

The direction of the gas flowing through the CVD reactor can be either vertical or horizontal resulting in two types of the CVD reactor configuration. In the horizontal reactor, the carbon-containing precursor is passed over a catalyst bed (placed in the middle of the furnace) at temperatures ranging from 500 °C to 1100 °C. In the vertical reactor configuration, CNTs can be synthesized by an upward flow of the carbon feedstock gases through the supported catalysts in the middle of the reactor. Furthermore, in the vertical CVD reactor, the CNTs can be also synthesized by the aerosol (floating catalyst) CVD synthesis process, in which the catalyst and the carbon sources are injected at the top of the reactor and CNTs are collected.
downstream of the reactor. The aerosol CVD synthesis process can be used for continuous production of CNTs. In this technique, there is no need to stop the synthesis and open the reactor to collect the CNT product and introduce of fresh catalyst [51].

The aerosol synthesis method of the CNTs has shown a great capability to grow transparent conductive CNT films with excellent optoelectronic properties, when the tubes are grown using CO [52-54] and hydrocarbons [51] as the carbon precursors. The CO disproportionation reaction is slow and limited thermodynamically [55], unless at high pressure [56]. Therefore, at ambient pressure, the use of the hydrocarbons instead of CO is preferred for the synthesis of CNTs since hydrocarbons have shown a high reaction yield which is a key factor for industrial applications [51]. In Publications I and II, the CNTs and the Fe@C core-shell NPs have been synthesized simultaneously via the aerosol method using a hydrocarbon precursor.

2.4 Metal@C core-shell nanoparticles and carbon nanotubes in electrocatalysis

In metal@carbon (C) core-shell NPs, the active transition metal (TM) NPs are encapsulated in graphitic carbon shell(s), which protect the active TM core from oxidation in ambient air and agglomeration with neighboring TM NPs (Publication I) [57]. In the TM@C NPs, the metallic form of the TMs can be utilized in the different applications where the unprotected TMs are not stable under air [57-60]. Metal NPs encapsulated in multiple graphitic layers have been reported to catalyze the oxygen reduction reaction (ORR) [58-61] and HER [57,62,63]. However, the multiple layers of carbon in these structures prevent the desired access of the reactants to the vicinity of the metal NPs, decreasing the catalytic activity [64]. The electronic structure of the outermost carbon layer in the TM@C NPs can be only modulated, by electron transfer from the encapsulated metal, when less than three to four carbon layers surround the metal core [64-66]. In Publication I, we have reported that the encapsulation of iron NPs in a single-shell carbon layer results in a non-noble metal based catalyst with remarkable catalytic performance toward the HER in acidic electrolytes. The single-shell carbon-encapsulated iron NPs (SCEINs) were earlier reported in density-functional theory (DFT) calculations, as the nanostructures in which a considerable charge transfer from iron to carbon occurs, inducing catalytically active sites on the carbon cage [67]. Furthermore, the structure of the iron nanoparticle encapsulated in multiple graphitic layers has been electrochemically manipulated to activate them for other electrochemical reactions such as OER in alkaline media (Publication II).

CNTs are commercially available and have high-surface area, high-chemical stability, excellent electrical conductivity, and insolubility in most solvents. These properties introduce CNTs as extremely attractive supports for heterogeneous catalysts, energy storage and related applications [17,23-27,51]. Graphitic carbon nanostructures such as graphene and CNTs can be doped by heteroatoms such as nitrogen, sulfur, phosphorous, and boron, which have different electronegativity compared to plain carbon. The heteroatom doping of carbon nanomaterials can polarize adjacent carbon atoms, improving the catalytic activity of metal-free carbon-based electrocatalysts toward different electrochemical reactions such as ORR [68-70], HER [57,71-73] and OER [73,74]. Furthermore, CNTs can be utilized as the support for active TM NPs, to facilitate charge transfer and increase the number of active catalytic sites [23,26,75]. In CNTs, the curvature of the hexagonal sp² carbon structure causes the π-electron
density to shift from the concave interior surface to the convex exterior surface [76-78]. Consequently, the exterior and interior surfaces of the CNTs become electron-enriched and electron-deficient, respectively. This shift in the electron density, can affect the electronic properties of substances in contact with the outer or inner surface of the CNTs.

In catalysis, the local electronic structure of an active site or facets affects the catalytic properties of the site [13,79]. Catalyst-substrate interaction can alter the electronic properties of the catalyst and modify the binding energy of reaction intermediates [80]. Therefore, in CNT-supported metallic nanoparticle (MNP) catalysts, catalytic behaviour of the metallic active sites can be modified because of charge transfer between the CNT and the MNP [81,82]. A catalyst support can also directly participate in catalytic reaction and enable the existence of certain geometries of active sites [80]. Peljo et al. have shown recently [83] that when a MNP closely interacts with an electrode, the Fermi level of the MNP equilibrates with that of the electrode if the separation distance between the MNP and the electrode is less than the cut-off distance for electron tunnelling. This effect depends on the size of the MNP and is more pronounced for small particles (<10 nm). Furthermore, the change in the size and shape of the nanoparticle can solely affect the electronic structure and electrochemical properties of the particle [84,85]. Therefore, for an active MNP/CNT hybrid electrocatalyst, the final electrochemical activity depends at least on three main parameters: i) the strength of the interaction between the MNP and the CNT support, ii) the structure of the MNP, and iii) the structure of the CNT support. However, there are many other parameters which can control electrocatalytic activity of high surface-area nanoparticulate electrocatalysts [13]. Common effective factors and parameters on catalytic performance of a supported catalyst have been schematically illustrated in Figure 3 and summarized by Bandarenka and Koper in ref. [13].

![Figure 3](image)

**Figure 3.** Schematic illustration of common factors and parameters affecting catalytic performance of high surface area nanoparticulate electrocatalysts (Reprinted with permission from ref. [13]).

### 2.5 Stability of the carbon nanomaterials during electrochemical reactions

For the use of carbon-based materials in electrochemical reactions, the main concern is electrochemical oxidation of carbon, commonly referred to as carbon corrosion. The carbon
oxidation reactions are kinetically very slow so that carbon can be utilized without serious problems under conditions typically applied in fuel cells where the potential is less than 1.2 V vs. RHE [86]. However, some reactions, such as the OER, occur at higher potentials (the thermodynamic OER onset potential is 1.23 V vs. RHE) where the carbon oxidation rate is faster and only some carbon nanomaterials might provide stable performance. The oxidation rate of carbon strongly depends on the structure of the carbon-based materials as explained below.

In PEM fuel cells, both SWNTs [87] and MWNTs [88] have shown more corrosion-resistance compared to the current commercial carbon materials, such as carbon black. In 0.5 M sulfuric acid, a lower surface oxygen content has been measured for MWNTs than for carbon black, when the electrodes are held at 1.2 V for 120 h [89]. Moreover, the MWNTs have shown greater electrochemical stability than the SWNTs based on potentiostatic oxidation measurements at a fixed potential of 1.2 V in acidic media [90].

In alkaline media, CNTs (both SWNTs and MWNTs) have exhibited high stability even at the harsh oxidative condition of the OER measurements [91,92], introducing them as promising supports for OER electrocatalysts [75,93-95]. In acidic media, the degradation progress of MWNTs at a high potential of 1.8 V, has been considered [96]. Because of the higher oxidation susceptibility of amorphous carbon than graphitic carbon [97], it has been found that at high potentials initially residual amorphous carbon is removed from the surface of the MWNTs [96]. Afterwards, the outermost layers of the MWNTs (kept at a fixed potential of 1.8 V) are degraded while the inner graphitic walls beneath the defective carbon layers are protected from the degradation. Finally, the MWNT electrode, after prolonged oxidation exposure, can be kinetically stabilized under the OER conditions [96].

In MWNTs, when the outer graphitic layer is damaged the intact inner tubes still can serve as highly conductive pathways, which significantly promote the charge transfer process at the active sites on the surface of the outer layer [92]. This special feature of MWNTs allows their use as interesting supports even in conditions where their outer surfaces are damaged by electrochemical degradation or by covalent functionalization. It is also reported that few-walled CNTs (FWNTs) are electrochemically more active for OER than SWNTs in alkaline media [92]. Therefore, in Publications II and IV which have been reported for OER in alkaline media, we have used thin MWNTs, which can be also denoted as FWNTs, instead of SWNTs to ensure long-term stability and to improve catalytic activity.

We have shown in Publication II, that in Fe@C core-shell NPs the carbon shell is stripped off into the alkaline solution during the OER measurements while the graphitized carbon of the CNTs is preserved at that range of potentials. However, in a very recent work, it has been shown that a nitrogen–doped graphitized carbon (NC) shell with a spherical morphology encapsulating NiFe NPs has remarkable stability during the OER in alkaline media [98]. Comparison of these two studies suggests that doping of the carbon shell with nitrogen in metal@C core-shell NPs can make the shell more stable against corrosion, even during the OER measurements. This can also show that carbon corrosion not only depends on the carbon morphology, but also doping of the carbon structure.
3. General aspects of electrochemical reactions

3.1 Electron transfer at the electrode- electrolyte interface

We assume that the following reduction reaction takes place at the electrode- electrolyte interface, in which the reactant O in the solution is reduced to R by accepting an electron from the electrode.

\[ O + e^- \rightleftharpoons R \]  \hspace{1cm} (2)

A metallic electrode consists of atoms of metal closely packed and interacting with each other, constructing a continuum of energy levels of electrons as depicted in Figure 4a. The Fermi level is the maximum energy level occupied by an electron. The electrons are filled from the low energy levels up to the Fermi level. In contrast, a molecule or ion in electrolyte solution (O) has discrete orbital energies of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) [99,100].

The electron transfer process between the electrode (metal) and the O (aq) species in the electrolyte occurs through quantum mechanical tunnelling between the electrode and the reactant close to the electrode. If the Fermi level of the electrode is higher than the LUMO of the O, it is energetically favourable to transfer electrons from the electrode to the O species to reduce the O (Figure 4a) and form R in Equation 2 [99]. The energy difference between the Fermi level of the electrode and the LUMO of the O is the driving force for electron transfer [99,100]. After electron transfer, the Fermi level in the metal is lowered. This change in the energy levels continues until the Fermi level of the electrode lies in between the energy levels of the two species (O and R) in the solution [99]. In this situation, dynamic equilibrium is attained in which the rate of the electron transfer from the electrode to O (to form R) equals the rate of the electron transfer from R to the electrode (to form O).

If the Fermi level of the electrode is not energetically favourable to reduce the O, by applying a potential on the electrode the energy of the electrons within the metal electrode, and thus the Fermi level, can be altered until the reaction occurs. Applied positive potentials lower the Fermi level while negative potentials raise the Fermi level (Figure 4b) [100]. In addition to the change in the thermodynamic aspects of the reaction, the applied potential can also change the overall barrier height of the reaction (i.e. activation energy).
The electron-transfer kinetics is affected by mass transfer of the reactants from the solution toward the electrode surface. Mass transfer is the movement of the reactant species from one location in electrolyte solution to another one. There are three modes of the mass transfer: migration, diffusion, and convection [101]. Migration occurs for charged molecules or particles in the solution which can be attracted to or repelled from the electrode if the electrode is charged (a gradient of electrical potential). Diffusion occurs when the concentration of the reactants at the electrode surface is different from that in the bulk solution (a gradient of chemical potential). Convection occurs when the solution is mixed mechanically, for example, by stirring the solution or rotating the electrode. Convection changes the rate of the movement of the reactants toward the electrode and the rate of the removal of the reactants from the electrode.

3.2 Kinetics of electrochemical reactions and Tafel analysis

Electrochemistry is a branch of chemistry concerned with the study of chemical processes at the interface between an electronic conductor (the electrode such as metals or semiconductors) and an ionic conductor (the electrolyte) or at the interface between two electrolytes [102]. Electrochemistry focuses on chemical reactions in which electrons are transferred between the reactants. These particular chemical reactions are known as oxidation-reduction ("redox") reactions. In a redox reaction, the substance which is oxidized loses an electron (the oxidation state is increased) while the reduced substance gains an electron (the oxidation state is decreased). When electrons transfer between the electrode and the electrolyte, an electrical current is generated.

Electrocatalysis refers to the ability of an electrode material or surface to improve the rate of an electrochemical reaction [12]. In electrochemical reactions, the kinetics of the reactions at the electrode surface (electrocatalyst) is strongly affected by the electrode potential and mass transfer of the reactants. Theoretically, the current-potential dependence of a simple electrochemical redox reaction, can be described by the Butler-Volmer equation considering that both cathodic (reduction) and anodic (oxidation) reactions occur on the same electrode:[101,103]

$$ j = j_0 \cdot \left[ \exp (a_f \eta) - \exp (-a_c \eta) \right] \quad (3) $$
where \( j \) is the kinetic current density of the electrode; \( j_0 \) is the exchange current density; \( \alpha_a \) and \( \alpha_c \) are the dimensionless anodic and cathodic transfer coefficients, respectively; and \( f \) equals to \( nF/RT \) where \( n \) is the number of electrons involved in the electrode reaction; \( F = 96500 \text{ C mol}^{-1} \) is the Faraday’s constant; \( R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \) is the universal gas constant; and \( T \) is the absolute temperature. \( \eta \) is the overpotential which is defined as \( \eta = E - E_0 \), where \( E \) is the electrode potential and \( E_0 \) is the equilibrium (standard) potential.

If we assume that at the electrode, one of the anodic or cathodic reactions is the dominant reaction, then either the cathodic or anodic reaction rate becomes negligible in Equation 2 and thus the Butler-Volmer equation can be reformulated as the following equation:

\[
\eta = \frac{RT}{anF} \ln \left( j_0 \right) - \frac{RT}{anF} \ln \left( j \right)
\]

Where \( \alpha \) is the anodic or cathodic transfer coefficient. Equation 4 can be corresponds to the following Tafel equation:

\[
\eta = a + b \log (j)
\]

Where \( a \) is a constant and \( b \) is the Tafel slope given by:

\[
b = \frac{\partial \eta}{\partial \log j} = \frac{2.303RT}{anF}
\]

The Tafel equation is applied to a half-reaction of an electrochemical reaction. From Tafel analysis, two important parameters: exchange current density and Tafel slope can be measured for an electrochemical half-reaction [104]. When \( \eta \) is plotted vs log \( j \), \( j_0 \) can be calculated from the intercept and the Tafel slope can be obtained from the slope of the plot. The exchange current is the current at equilibrium (zero overpotential) which represents the intrinsic rates of an electrode reaction and a higher \( j_0 \) leads to a faster reaction [105]. The Tafel slope and \( j_0 \) cannot be well defined if the Tafel plot is not linear. There might be a variety of reasons for nonlinearity of Tafel plots, such as potential dependence of the transfer coefficients or activation energies as well as diffusion and concentration gradient effects [103]. The Tafel slope provides an insight into the reaction mechanism and the rate-determining step (RDS) in an electrochemical half-reaction. In chemical kinetics, the RDS is the slowest intermediate step of a chemical reaction, which approximately determines the overall speed (rate) of the reaction.

### 3.3 Electrochemical water-splitting for production of hydrogen

Among current technologies for \( \text{H}_2 \) production, water-splitting (i.e., \( \text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2\text{O}_2 \)) is one of the most attractive and simple methods to produce hydrogen. Electrochemical water-splitting can be divided into two half-reactions: the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) [10-12]. Water electrolysis can occur in acidic or alkaline media as depicted in Figure 5 with the associated HER and OER half-reactions (Table 1) [10]. However, base–acid hybrid electrolytic systems in which OER and HER occur in basic and acidic electrolytes respectively have also been developed with significantly lower onset voltage for the water electrolysis [106]. In base–acid hybrid electrolytic systems, \( \text{OH}^- \) and \( \text{H}^+ \) are consumed during water electrolysis, and thus these systems might employ waste acid and base
to produce hydrogen and oxygen, providing a new method for the management of waste acids and bases [106].

The electrolysis phenomenon (the decomposition of a substance by an electric current) was discovered by Troostwijk and Diemann in 1789 [107]. Since then, alkaline water electrolysis has been widely used to produce hydrogen up to the megawatt range and it is considered the most widely used electrolytic technology worldwide at a commercial level [9,108]. However, the current issues in the alkaline electrolyzers such as inefficient separators (diaphragms) to separate the product gases (H₂ and O₂), limited current density, and low operating pressure prevent the massive hydrogen production required for the hydrogen economy [5,10]. PEM electrolyzers, which are acidic water electrolysis cells, have shown the ability to overcome the drawbacks of the alkaline electrolyzers for higher production capacity. Furthermore, PEM electrolyzers have a more compact design than traditional alkaline cells. However, PEM electrolyzers suffer from high cost and technological issues for large-scale applications [5,9,10,108].

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>HER</th>
<th>OER</th>
<th>Overall reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic aqueous solution</td>
<td>2H⁺ + 2e⁻ → H₂</td>
<td>H₂O → 2H⁺ + 2e⁻ + ½ O₂</td>
<td>H₂O → H₂ + ½ O₂</td>
</tr>
<tr>
<td></td>
<td>E° = 0.00 V vs. NHE</td>
<td>E° = 1.23 V vs. NHE</td>
<td>E_{cell} = 1.23 V</td>
</tr>
<tr>
<td>Alkaline aqueous solution</td>
<td>2H₂O + 2 e⁻ → H₂ + 2OH⁻</td>
<td>2OH⁻ → ½ O₂ + H₂O + 2e⁻</td>
<td>H₂O → H₂ + ½O₂</td>
</tr>
<tr>
<td></td>
<td>E° = −0.83 V vs. NHE</td>
<td>E° = 0.40 V vs. NHE</td>
<td>E_{cell} = 1.23 V</td>
</tr>
</tbody>
</table>

3.4 Hydrogen evolution reaction

The hydrogen evolution reaction (HER) is one of the most intensely studied electrochemical reactions [109]. HER is an important reaction in a wide range of applications from energy storage by hydrogen production to electrodeposition and corrosion of metals.
The hydrogen evolution reaction is a simple reaction, which involves the transfer of two moles of electrons per mole of $H_2$:

In acidic solution: $2H^+ + 2e^- \rightarrow H_2$ \hspace{1cm} (7)

In alkaline solution: $2H_2O + 2 e^- \rightarrow H_2 + 2 OH^-$ \hspace{1cm} (8)

Different reaction pathways have been proposed for HER. The generally accepted mechanism for HER includes the following steps in which the cathodic evolution of $H_2$ occurs at the active site(s) denoted as S [109]:

Volmer step: $H^+ + e^- + S \rightarrow H^*$ \hspace{1cm} (9)

followed either by:

Tafel step: $2H^* \rightarrow H_2$ \hspace{1cm} (10)

or:

Heyrovsky step: $H^* + H^+ + e^- \rightarrow H_2$ \hspace{1cm} (11)

The initial discharge step is called the Volmer reaction where an adsorbed H intermediate, $H^*$, is formed. This $H^*$ is then either recombined with an adjacent $H^*$ (Tafel step) or electrochemically desorbed to react with a proton (Heyrovsky step) to generate $H_2$.

The exact HER mechanism on active sites of an electrocatalyst is not easily deduced. On different facets of the same material, HER can be catalyzed through different pathways [110]. However, it is widely accepted that the HER mechanism can be predicted from Tafel slope analysis [104]. The Tafel slope values of 120, 40, and 30 mV dec$^{-1}$ have been reported when Volmer, Heyrovsky, and Tafel are the RDSs, respectively [104]. When the Heyrovsky is the RDS, a Tafel slope of 120 mV dec$^{-1}$ can be also observed if the coverage of the electrode surface by intermediates, $\theta_H$, is high ($\theta_H > 0.6$) [104]. Therefore, a Tafel slope of 120 mV dec$^{-1}$ can be due to either the Volmer RDS or the Heyrovsky RDS with a high coverage of adsorbed hydrogen atoms on the electrode surface. Tafel slope and exchange current density for a specific material can change significantly based on the material structure. For example, for the HER on a platinum surface Tafel slope and exchange current density strongly depend on the structure and the crystallographic orientation of the platinum surface atoms [110].

### 3.4.1 Trends in catalytic activity for hydrogen evolution based on volcano plots

Volcano plots have been used for decades in heterogeneous catalysis to design active catalyst materials. Volcano curves are based on the Sabatier principle which states that the interactions between the catalyst and the reactant should be neither too strong nor too weak. In HER, if hydrogen atoms bond strongly to the catalyst surface releasing the product will be difficult and if they adsorb weakly to the surface initiating the HER is demanding [111]. Volcano plots for HER correlate HER exchange current densities with either the Gibbs free energy of hydrogen chemisorption on different materials [112,113] or the bond strength of the hydrogen atom to the surface [111,114]. Figure 6a shows one of the recent versions of the volcano-type relations observed for HER catalysts. In this HER volcano plot, the experimental exchange currents are
plotted as a function of the DFT calculated Gibbs free energy for the hydrogen adsorption ($\Delta G_{H^*}$) on the surface of the different materials [112,113]. If $\Delta G_{H^*}$ is positive, the rate of adsorption of hydrogen and formation of H* will dominate the activity. If $\Delta G_{H^*}$ is negative, the activity will be dominated by the rate of desorption of H₂. The maximum catalytic activity can be acquired when $\Delta G_{H^*}$ is close to zero. The volcano plots also reveal that Pt is the most efficient electrocatalyst for HER [112].

Figure 6 b, demonstrates $\Delta G_{H^*}$ as a function of different configurations of Pt atoms on the surface of a SWNT (Publication III). As shown in this figure the Pt configuration of the atoms on the SWNT support is a key parameter to achieve a $\Delta G_{H^*}$ which is close to zero.

![Volcano plot of the exchange current density as a function of the DFT-calculated Gibbs free energy for hydrogen adsorption on the surface of different pure metals and MoS₂ nanoparticle](image)

**Figure 6.** a) Volcano plot of the exchange current density as a function of the DFT-calculated Gibbs free energy for hydrogen adsorption on the surface of different pure metals and MoS₂ nanoparticle (reprinted with permission from ref. [113]). b) Hydrogen evolution free energy diagrams constructed from adsorption free energies, $\Delta G_{H^*}$, for a Pt atom immobilized on axial direction on a SWNT. This diagram also shows $\Delta G_{H^*}$ for the second Pt atom decorated on the 1st, 2nd, and 3rd adjacent sites onto axial, radial and diagonal directions from the first isolated axial Pt atom, as illustrated by the arrows in the schematic illustration of atomic structure (two of the free energy curves have been offset for clarity). (Reprinted from Supplementary Information Publication III).

### 3.5 Oxygen evolution reaction

The oxygen evolution reaction (OER) is a critical reaction in electrochemical water splitting (anodic reaction) and rechargeable metal–air batteries to generate and store clean energy. In comparison to HER which is a two electron-transfer reaction, OER is a four electron-proton coupled reaction. Therefore OER is more complicated than HER and requires a higher activation energy (higher overpotential), causing the OER to limit hydrogen production in a water electrolyzer [115].

The overall OER can be written as follows:

In acidic solution: $2H_2O \rightarrow 4H^+ + 4 e^- + O_2 \quad (12)$

In alkaline solution: $4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad (13)$

Different reaction pathways have been proposed for OER. However, it is generally accepted that the first step of OER is the discharge of water molecules (in acid) or OH⁻ (in alkali) on a surface active site (S) [116]:

Step I in alkali: $S + OH^- \rightarrow S-OH + e^- \quad (14)$
One of the proposed reaction pathways for oxygen evolution is the Krasil'shchikov path [116-118] where the following intermediate steps occur:

Step II: \( \text{S-OH + OH}^- \rightarrow \text{S-O}^- + \text{H}_2\text{O} \) (in acid: \( \text{S-OH} \rightarrow \text{S-O}^- + \text{H}^+ \))  \( (15) \)

Step III: \( \text{S-O}^- \rightarrow \text{S-O} + e^- \)  \( (16) \)

Step IV: \( 2\text{S-O} \rightarrow 2\text{S} + O_2 \)  \( (17) \)

Tafel slopes of \( \approx 120, 60, 40, \) and \( 30 \) mV dec\(^{-1}\) can be predicted if step I, II, III, or IV is RDS [118].

Under alkaline mechanism with the assumption of a single-site mechanism, the following oxygen evolution pathway can be also proposed based on the literature [104]:

Step I: \( \text{S + OH}^- \rightarrow \text{S-OH} + e^- \)  \( (18) \)

Step II: \( \text{S-OH + OH}^- \rightarrow \text{S-O} + \text{H}_2\text{O} + e^- \)  \( (19) \)

Step III: \( \text{S-O + OH}^- \rightarrow \text{S-OOH} + e^- \)  \( (20) \)

Step IV: \( \text{S-OOH + OH}^- \rightarrow \text{S-OO}^- + \text{H}_2\text{O} \)  \( (21) \)

Step V: \( \text{S-OO}^- \rightarrow \text{S} + O_2 + e^- \)  \( (22) \)

If the OER occurs through Equations 18-22, a Tafel slope of \( \approx 30 \) mV dec\(^{-1}\) has been observed when equation 19 is the RDS, while a Tafel slope of \( \approx 123 \) mV dec\(^{-1}\) can indicate that equation 18 is the RDS [104]. For metal oxides, depending on the electrode material and the electrolyte, a broad range of Tafel slopes have been observed in the literature as shown in section 6.2. Metal derived electrocatalysts of oxidized Ni, Co and Fe have exhibited a Tafel slope of \( \approx 40 \) mV dec\(^{-1}\) in NaOH or KOH solution, as reported in the literature [119,120].

Analyzing Tafel plots can predict the mechanism and the RDS of the catalytic process; however, for OER such analysis is complicated [104,121]. The OER Tafel slope can depend on the applied potential [104]. This dependence can be explained by different causes, such as changes in RDS, repulsion between adsorbed intermediates (which can be increased when the coverage of intermediates is increased at elevated overpotentials), and blockage of active sites by unreactive species and oxygen bubbles [121]. Furthermore, the Tafel plot is usually nonlinear where the Tafel slope changes, making Tafel analysis more complicated. Because of the complexity in the OER Tafel plot, usually the OER overpotential at a current density (per geometric surface area) of 10 mA cm\(^{-2}\) is used as the figure-of-merit for activity, instead of the exchange current density and the Tafel slope calculated from the Tafel plot [121].

### 3.5.1 Trends in catalytic activity for oxygen evolution based on volcano plots

Substantial efforts have been devoted to find the possible mechanisms for OER and develop OER volcano plots to design more efficient OER electrocatalysts [116,122,123]. As discussed in section 3.5, different OER mechanisms and RDSs have been proposed on different catalysts.
For many years the RDS, which is the elementary reaction with the highest kinetic activation barrier, has been considered as the central topic affecting the OER overpotential ($\eta^{\text{OER}}$) [122]. However, recent studies have highlighted the potential-determining step (PDS) which is defined as the elementary step with the maximum difference in the adsorption energy of the two subsequent adsorbed intermediates and PDS is attributed to the thermochemical aspects of the overpotential [116,122].

The following four-step OER reaction mechanism, known as the water nucleophilic attack (WNA) mechanism, has been mainly proposed for metal oxide surfaces and most molecular catalysts [20,124]. $\Delta G_{1-4}$ in Equations 23-26, represent the change in the standard Gibbs energy of formation of the respective species ($\Delta G_{\text{oxygenated species}}$) at each step [116,125-127].

\[
\Delta G_{1} = \Delta G_{\text{HO}^*} - \Delta G_{\text{H}_2\text{O}(l)} - eU + K_b T \ln a_{\text{H}^*} \\
\Delta G_{2} = \Delta G_{\text{O}^*} - \Delta G_{\text{HO}^*} - eU + K_b T \ln a_{\text{H}^*} \\
\Delta G_{3} = \Delta G_{\text{HOO}^*} - \Delta G_{\text{O}^*} - eU + K_b T \ln a_{\text{H}^*} \\
\Delta G_{4} = \Delta G_{\text{O}_2} - \Delta G_{\text{HOO}^*} - eU + K_b T \ln a_{\text{H}^*}
\]

Through these equations the effect of pH, which changes $a_{\text{H}^*}$, absolute temperature ($T$) and applied potential ($U$) on $\Delta G_{1-4}$ can be considered. The theoretical $\eta^{\text{OER}}$ can be defined under standard conditions at $U = 0$ V vs. standard hydrogen electrode (SHE) by the following equation [123]:

\[
\eta^{\text{OER}} = \left\{ \frac{\max(\Delta G_{1}, \Delta G_{2}, \Delta G_{3}, \Delta G_{4})}{e} \right\} - 1.23 \text{ V} \tag{27}
\]

Where 1.23 V (vs SHE) is the OER thermodynamic potential at pH = 0, and scales with pH (-0.059 eV per pH unit) according to the Nernst equation. For a thermodynamically ideal catalyst there is no overpotential due to thermodynamic hindrance (kinetic barriers are not considered here) and $\Delta G_{1} = \Delta G_{2} = \Delta G_{3} = \Delta G_{4}=1.23$ eV as shown in Figure 7a [123]. However, in a real catalyst $\Delta G_{1-4}$ differs from 1.23 eV as shown in Figure 7b for LaMnO$_3$ as an example.

For metals and oxide surfaces, a linear scaling relation between the chemisorption energies of the intermediates of $\text{O}^*$, $\text{HO}^*$, $\text{HOO}^*$ have been reported by Man et al [123] and Koper [128]. They have found that at $U = 0$ V, the scaling relationships basically fix the difference $\Delta G_{\text{HOO}^*} - \Delta G_{\text{HO}^*}$ at about 3.2 eV, while this difference is 2.64 eV for an ideal catalyst. The theoretical $\eta^{\text{OER}}$ can then be described by the following equation, under standard conditions and $U=0$:

\[
\eta^{\text{OER}} = \frac{\max(\Delta G_{\text{O}^*} - \Delta G_{\text{HO}^*}, 3.2 \text{ eV} - (\Delta G_{\text{O}^*} - \Delta G_{\text{HO}^*}))}{e} - 1.23 \text{ V} \tag{28}
\]
The OER catalysts that follow the WNA mechanism have a fundamental minimal overpotential of ca. 0.3 V because of the scaling relationship of ~3.2 eV between HO* and HOO* intermediates $\left(\frac{(3.2-0.2)-2.46}{2}\right) = -0.3 \text{ eV} [20]$. As shown in Figure 7c, volcano plots for the OER can be constructed for a wide variety of metal oxide surfaces using $\Delta G_{\text{HOO*}} - \Delta G_{\text{HO*}}$ as the descriptor [123, 125]. When experimental overpotentials at current density of 1 mA cm$^{-2}$ are plotted as a function of this descriptor, they overlay well on the theoretical overpotential [125].

**Figure 7.** Standard free energies at $U = 0 \text{ V}$ for a) an ideal catalyst and b) LaMnO$_3$. (Figures a and b have been reproduced with permission from ref. [123]). c) OER volcano plot for metal oxides. All the studied metal oxide surfaces in this figure obey a scaling relation of $\Delta G_{\text{HOO*}} - \Delta G_{\text{HO*}} = 3.2 \pm 0.2 \text{ eV}$ (reprinted with permission from ref. [125]).

Certain molecular catalysts have been shown to operate via the radical oxo coupling (ROC) mechanism, instead of the WNA [20, 124]. The first two steps of the ROC mechanism is similar to the WNA one (Equations 23 and 24) but the last two steps are as depicted in Figure 8; where two metal-oxoradical species (S-O*) form, and couple in a bimolecular reaction to release an oxygen molecule [20, 129].

**Figure 8.** Two proposed mechanisms for water oxidation: water nucleophilic attack (WNA) and radical oxo coupling (ROC). S is the surface active site on the electrocatalyst.

For catalysts with the ROC mechanism, a lower OER overpotential than 0.3 V is possible in principle [20]. Therefore, the development of such catalysts can provide very efficient OER electrocatalysts.
4. Methods

4.1 Electron microscopy characterization

In an electron microscope, a beam of accelerated electrons is used as a source of illumination to examine the topography (surface features), morphology (shape and size), composition and crystallographic information of objects with a very fine structure. The resolving power of a microscope is directly related to the wavelength of the irradiation beam utilized to take an image. In electron microscopes, the de Broglie wavelength of the electrons (resolving power) can be altered by changing the acceleration voltage of the electron beam. In general, faster electrons emit shorter wavelength radiation. When the electrons are accelerated up to a few hundreds kV, the wavelength of the electron beam can be up to around one million times shorter than that of a light beam, giving electron microscopes the capability to resolve nanoscale objects. In an electron microscope, scattered electrons from the specimen are detected to form an image.

Figure 9 summarizes different types of interactions between an incident electron beam and a specimen. For elastic and inelastic scattering no loss and some detectable loss of incident electron energy are resulted, respectively. Electrons, as one type of ionizing radiation, are capable of removing the tightly bound inner-shell electrons of the specimen to produce characteristic X-ray signals revealing chemical information about the specimen. These signals are used in energy-dispersive X-ray spectrometry (EDX) and electron energy-loss spectrometry (EELS) to identify the various elements present in different regions [130,131].

Figure 9. Types of interactions between incident electron beam and a specimen. The directions shown for each signal indicate where the signal is detected but do not show necessarily the physical direction of the signal.
4.1 Transmission electron microscopy

Transmission electron microscopy (TEM) is a technique to produce two-dimensional images of fine structures by detecting a beam of electrons which is transmitted through a thin specimen. The beam interacts with the specimen as it passes through it and the transmitted beam can be recorded by, for instance, a CCD (charge-coupled device) camera. In TEM, elastically scattered electrons are the major source of the contrast to form the image. In high-resolution TEM (HRTEM) the spherical aberration, as the primary limitation of TEM resolution, has been partially corrected to take the images with atomic-scale resolution.

The resultant TEM image, formed by the direct beam electrons, is called a bright-field (BF) image. BF imaging mode is the most common mode of operation for TEM. In this mode, the contrast of the image is formed directly by absorption of electrons in the specimen. In BF mode, the thicker part of the specimen or the regions with a higher atomic number block more electrons and appear darker in the image in comparison to the regions with no sample or a small atomic number [130,131]. In contrast, the image formed by the scattered electrons is called dark-field (DF) image. In DF images, diffracted beams are passed to the objective aperture while the directly transmitted beam is blocked. As a result, in DF images areas with larger atomic number, heavier density or greater thickness scatter electrons more strongly and thus appear brighter in the image [130,131].

Another type of TEM is scanning TEM (STEM) in which the images are formed by electrons focused to a fine spot which is then scanned over the sample in a raster. The scanning of the beam across the sample makes STEM suitable for analytical techniques such as high-angle annular dark-field (HAADF) imaging, EDX and EELS. These signals can be obtained simultaneously, allowing direct correlation of images and spectroscopic data. In HAADF imaging, the image is highly sensitive to variations in the atomic number of atoms in the sample (Z-contrast images). This Z-contrast of the HAADF-STEM images can be used to obtain atomic-level resolution images [130,131].

In this thesis a TEM/STEM equipped with an EDX spectrometer has been used to observe the structure of the materials to determine the diameter of the CNTs and size distribution of the metal NPs decorated on the CNTs, and to monitor the elemental composition of the material by EDX/TEM. In publication III, an aberration corrected STEM was used to observe the pseudo-atomic scale Pt on the sidewall of the SWNTs. Through STEM, formation of individual heavy atoms in the material could be discerned in the atomic resolution HAADF images [132-138]. By this method, the high-Z Pt atoms on the low-Z carbon support could be detected as spots with high contrast.

In this thesis, for TEM characterization, the materials were dispersed in ethanol (0.02 mg/ml) and then 2 µl of the solution was drop cast on a carbon coated TEM grid and then dried in ambient air. The samples were observed through a JEOL-2200FS, double Cs-corrected TEM at acceleration voltages of 80 or 200 kV.

4.1.2 Scanning electron microscopy

Scanning Electron Microscope (SEM) forms images by detecting secondary or backscattered electrons ejected from the surface of the specimen [131]. The Back-scattered electrons (BSEs)
are reflected from the specimen by elastic scattering. The BSE signal is strongly related to the atomic number of the specimen, providing a composition contrast in BSE images. In contrast, secondary electrons (SEs) are ejected electrons from the specimen surface and the number of detected SEs depends on the specimen topography. Thus, SE images display the topography of the sample surface. In the SE mode of SEM, the interaction between the incident electron beam is limited to a thin surface layer of the sample because SEs have low energies and thus only those SEs which are ejected from the surface of the material can escape from the specimen to the detector. The interaction depth from which SEs are detected depends on the beam energy. The SEM detector detects the ejected SEs in different directions in order to produce a 3D image. Generally, the SEM resolution is about an order of magnitude lower than the TEM resolution. However, SEM has a much greater depth of view than TEM, enabling it to image 3D structures of bulk samples. The chemical composition of the material can be also investigated simultaneously by EDX in SEM devices equipped with an X-ray detector.

The topography, morphology and composition of our materials were characterized using a field emission SEM and EDX (FESEM/EDX) at acceleration voltages of 5-10 kV. In publication III, FESEM/EDX was used to estimate the approximate amount of electroplated Pt on the surface of the SWNT electrode.

4.2 Raman spectroscopy characterization of carbon nanotubes

Raman scattering refers to the inelastic scattering of monochromatic light interacting with the material. When photons are scattered from an atom or molecule most photons are elastically scattered (Rayleigh scattering) such that the scattered photons have the same energy as the incident photons. The probability of scattering is significantly increased typically by a factor of $10^{-2}$ to $10^{-4}$ if there is a resonance situation in which the energy for either the absorbed or the emitted photon coincides with the electronic transition energy of the material under examination. There are two types of Raman scattering known as Stokes and anti-Stokes scattering (Figure 10). In Stokes scattering, an atom or molecule absorbs energy and thus, the scattered photon has lower energy than the incident photon but in anti-Stokes scattering the atom/molecule loses energy and thus the scattered photon has higher energy than the incident photon [139-142]. In both cases, the scattering happens in three steps: (i) an electronic excitation of the molecule through the absorption of the incident photon, (ii) the emission (in Stokes scattering) or absorption (in anti-Stokes scattering) of a phonon, and (iii) the emission of a photon. Stokes and anti-Stokes radiation occur when the molecule is in an excited state and a ground state, respectively, before absorbing the incoming photon. Based on the Boltzmann distribution, molecules in the ground state have a higher probability in comparison to molecules in excited states. Therefore, the intensity of Stokes radiation is generally higher in Raman spectrum and it is more common to study the Stokes Raman scattering during Raman spectroscopy. In a Raman spectrum, the intensity of the scattered light is plotted as a function of its frequency difference to the incident photons.

The most prominent Raman features in CNTs are radial breathing, D (disordered), G (graphite), and G' (second-order Raman scattering from D-band variation) modes. Although the D, G, and G' modes are found in graphite, the radial breathing mode (RBM) is specific to SWNTs.
Methods

SWNTs have sharp Van Hove singularities in their electronic density of states. This can induce strong resonant Raman effects for tubes whose bandgap matches the exciting wavelength of the incident or scattered light [143]. For SWNTs, the RBM frequencies are located in the range of 120 to 350 cm\(^{-1}\) with respect to the excitation line. The RBM is associated with symmetric movement of carbon atoms in the radial direction, as if the tubes are “breathing”. The presence of RBM features provides confirmation for the presence of single-walled (or double-walled) CNTs in a sample, and this mode is not present in graphite. The RBM frequency is proportional to the inverse tube diameter through the widely proposed relation \(\omega_{\text{RBM}} \text{ (cm}^{-1}) = A/d_t + B\) where the A and B parameters are determined experimentally [139,141,144]. The deduced RBM parameters of \(A = 223.5 \text{ cm}^{-1}\) nm and \(B = 12.5 \text{ cm}^{-1}\) have been reported for the usual diameter range of 1-2 nm [144].

The dominant peak in the Raman spectrum of CNTs is the G-band, which is located at \(\sim 1590 \text{ cm}^{-1}\). It corresponds to the in-plane tangential optical phonon involved in stretching of the bond between two carbon atoms in the graphene unit cell. The G-band of SWNTs includes two modes, a lower energy G\(^-\) peak at 1570 cm\(^{-1}\) and a higher energy G\(^+\) peak at 1590 cm\(^{-1}\). This splitting comes from symmetry-breaking effects associated with SWNT curvature, which makes an energy difference between the axial and transverse in-plane vibrational modes. The G\(^-\) and G\(^+\) features in SWNTs are associated with carbon atom vibrations along the axis and along the circumferential direction of the nanotube, respectively. It has been reported that the G\(^-\) feature is strongly sensitive to whether the nanotube is metallic (exhibiting Breit–Wigner–Fano lineshape) or semiconducting (exhibiting Lorentzian lineshape) [139,145]. Furthermore, although the G\(^-\) feature depends on the nanotube diameter, the frequency of the G\(^+\) peak is independent of both diameter and chiral angle of SWNTs [146]. Both main components of the G-band are shifted by charge transfer between dopant additions and SWNTs [139]. The G-peak full width half maximum (FWHM) broadening is an indicator of defect formation and/or CNT functionalization [147].

The scattering process associated with G band excitation is a first-order process which involves only one scattering event. Second-order Raman spectra, occurring from either two-phonon or defect-induced scattering, have a weaker intensity than the first-order Raman features. However, these features contain important information about the electronic and vibrational properties of CNTs that cannot be achieved by probing the first-order features. Two double resonance features commonly found in the Raman spectra of CNT bundles are the D band feature with a small peak at \(\omega_D \sim 1350 \text{ cm}^{-1}\) and its second harmonic (sometimes referred to as an overtone of the D band), G\(^'\) band, found at \(\sim 2 \omega_D\). The D band comes from one phonon
lattice vibrational process in which second-order Raman process involves one phonon and one defect. The ratio of the $I_G/I_D$ in Raman spectra conventionally shows the structural quality of CNTs. The so-called G’ band is observed in the Raman spectra of all kinds of sp² carbon materials, which is strongly sensitive to any perturbation to the $\pi$ electronic structure [148,149]. The G’ band comes from two phonon lattice vibrational process and, unlike the D-band, it does not need to be activated by proximity to a defect. Therefore, the G’ mode does not represent defects and is always a strong mode in SWNTs even if the D band is quite weak [139].

Raman spectroscopy is a powerful method to investigate changes in the structure and properties of CNTs. Doping of CNTs mostly affect the Raman D and G’ bands. The D band originates from the presence of sp³ defects, and thus the covalent functionalization of CNTs, which induces re-hybridization of sidewall C atoms, increases the ratio of the D to G band ($I_D/I_G$) [148,150]. The G’ mode is the most sensitive band to charge transfer between dopants and nanotubes [151,152], and it is used to assign p- and n-type doping in CNTs [149].

In this thesis, the Raman spectroscopy measurements were carried out with a JY LabRam 300 using 1.96 eV (633nm) laser excitation. The spectrum resolution was 1 cm⁻¹. Raman spectroscopy was used to determine the diameter of SWNTs, the quality of the CNTs, the doping effect of the functional groups on the CNTs, the type of iron oxide crystals (Publication II), and generally the structural changes in the CNTs after functionalization or modification.

### 4.3 X-ray photoelectron spectroscopy characterization

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique providing important information about the material under study such as elemental composition, empirical formula, chemical state and electronic state of the elements that exist in the top 1 to 10 nm of the material surface [153]. In XPS, the material is illuminated with a beam of X-rays (with energies in the keV range) and simultaneously the kinetic energy (KE) and the number of core (inner shell) electrons that escape from the material are analysed. The electron binding energy can then be calculated by measuring the KE of the emitted electrons. This binding energy is the elemental “fingerprint” and depends on the type of the element and its associated orbital from which the electron is emitted. Therefore, the XPS spectrum provides a quantitative surface elemental composition analysis of the examined material. The measured binding energy by XPS depends also on the chemical environment to which the atom is bound. This dependence on the surrounding chemical environment enables XPS to determine the chemical structure around the atom as well as the charge states of the atoms and ions in the structure.

In this thesis, XPS measurements were performed using a Kratos Axis Ultra or a Surface Science Instruments SSX-100 ESCA spectrometer with monochromated Al Kα radiation, using a pass energy of 40 eV and an X-ray power of 150 W. The samples were measured with an analysis area of roughly 700 μm × 300 μm. The binding energy scale for the CNT samples was referenced to the graphitic C 1s peak at 284.4 eV. The peak fitting of the nitrogen 1s region (Publication IV) was done using Gaussian peaks with positions fixed to within ± 0.1 eV of given values and with the full width at half maximum (FWHM) restricted to below 3 eV. The XPS analysis was utilized to measure the atomic percentages and charge states of the elements at the surface of the materials, as well as to monitor the change in the chemical environment of
the atoms after functionalization or modification. The XPS measurements were also performed to estimate the chemical structure of materials.

### 4.4 Electrochemical characterization

#### 4.4.1 Electrochemical cell

To study the electrochemical half-reactions on an electrode, the current vs potential plot can provide the most important information about the electrochemical reactions occurring on the electrode, as discussed in section 3.2. The electric current at the electrode can be experimentally measured by applying a potential to the electrode. The applied potential is in a potential range close to the equilibrium potential of the reaction under study.

The most common electrochemical set-up to measure the potential-current plot is the standard three-electrode electrochemical configuration consisting of a working electrode (WE), a reference electrode (RE) and a counter electrode (CE) as schematically shown in Figure 11. The WE is the electrode of interest covered with the electrocatalyst. The WE substrate supporting the catalyst is made of an inert and conductive material such as glassy carbon (GC) or other carbonaceous materials, Au, Ag, and Pt. In this thesis we have mainly used GC substrate since it is almost inactive in the applied potential range for the studied reactions (HER and OER) and it possesses a high electrical conductivity required to study the electrochemical reactions. When a half-reaction is carried out on the WE, the counter redox reaction occurs on the CE. The CE operates as the anode whenever the WE functions as the cathode and vice versa. The surface area of the CE should be much larger than that of the WE to ensure that the half-reaction taking place on the WE is not limited by the CE. The CE is made of electrochemically inert materials and in this thesis, carbon, Pt or Ti were used as the CE. The potential at the WE is applied with respect to that of the RE. The RE should have a stable and well-known electrode potential. Examples of common reference electrodes are standard hydrogen electrode (SHE), normal hydrogen electrode (NHE), silver-silver chloride electrode (Ag/AgCl) with a potential of 0.197 V vs NHE, saturated calomel electrode (SCE) with a potential of 0.242 V vs NHE, and reversible hydrogen electrode (RHE). For RHE, the electrode is in the actual electrolyte solution instead of a separated salt bridge and the potential depends on the pH of the solution. The potential of the RHE can be converted to other standard REs through the following equation:

\[
V_{\text{RHE}} = V_x \text{ vs NHE} + 0.0591 \cdot \text{pH} \tag{29}
\]

Where \(V_x\) is the potential measured relative to the RE in use. In this thesis, we have used SCE and RHE as the REs but in the electrochemical plots we have converted all the potentials to RHE since for HER and OER the results are often reported in RHE in the literature.

For electrolyte solution, common electrolyte choices are sulfuric (H\(_2\)SO\(_4\)) and perchloric (HClO\(_4\)) acids for acidic conditions, and NaOH or KOH for alkaline measurements. In the present thesis, 0.5 M H\(_2\)SO\(_4\), 0.1 or 1 M NaOH were utilized as the electrolyte solutions for acidic and alkaline electrochemical measurements, respectively.
In voltammetric measurements, a time-dependent potential is applied to the WE, which changes the WE potential relative to the fixed potential of the RE. The current during the applied potential is measured from the current that flows between the WE and CE. Through this three-electrode set up, the electrochemical behaviour of the electrode materials can be then analysed by various voltammetric techniques such as linear sweep voltammetry (LSV) and cyclic voltammetry (CV), as explained in the following sections.

4.4.2 Cyclic voltammetry

Cyclic voltammetry (CV) is a voltammetric technique in which the applied potential to the WE varies periodically [99,101,154]. The current at the WE is plotted versus the WE potential to give the cyclic voltammogram trace. When the potential is swept to more positive values the oxidation reaction of the species \( R \) takes place on the WE to form the oxidized species \( O \) (Equation 2). Reversing the direction of the potential sweep causes the reduction of \( O \) into \( R \). These redox reactions appear as waves in the voltammogram. The position of the peak current of the wave depends on the reduction potential of the reaction in interest [154]. For reversible reactions, the peak height depends on the square root of the potential scan rate [154]. In reversible reactions, the rate of the reaction is so fast, within the time scale of the CV, that the concentrations of the oxidized and reduced species at the electrode are in equilibrium with each other. The reduction potential of an electrochemical half-cell reaction (\( E_{\text{red}} \)) at non-standard conditions can be related to its standard half-cell reduction potential (\( E_{\text{red}}^0 \)) by the Nernst equation [154]:

\[
E_{\text{red}} = E_{\text{red}}^0 - \frac{RT}{nF} \ln \left( \frac{[R]}{[O]} \right) \tag{30}
\]

Where \( \frac{[R]}{[O]} \) is the equilibrium ratio between the reduced \( R \) and oxidized \( O \) species, \( R \) is the universal gas constant, \( F \) is the Faraday’s constant, \( T \) is the absolute temperature, and \( n \) is the number of electrons transferred per molecule.

From the shape, position and time-behavior of the experimental voltammograms, we can explore the electrochemical behavior of the electrode. CV is a powerful tool for analysis of the electroactive species generated at the electrode, determination of the electron transfer kinetics, and evaluation of the double-layer capacitance [99].
4.4.3 Linear sweep voltammetry

Linear sweep voltammetry (LSV) is similar to the CV but in LSV the applied potential on the WE is swept in one direction so that the potential is scanned from a lower limit to an upper limit (anodic sweep) or vice versa (cathodic sweep). The shape of the voltammogram depends on a number of factors such as the rate of the electron transfer at the electrode-electrolyte interface, the chemical reactivity of the electroactive species, and the potential scan rate.

The CV and LSV voltammograms can be affected by changing the potential scan rate. When the electron transfer processes is slow relative to the potential scan rate, the reactions are called quasi-reversible or irreversible in which case the equilibria are not established. In this condition the Nernst equation cannot be applied and, unlike the reversible reactions, the position of the maximum current in the voltammogram is shifted by changing the scan rate [154]. For the Tafel analysis and the calculation of the exchange current density, as discussed in section 3.2, low potential scan rates (usually 2-10 mV/s) are used; however, for the fast electrocatalytic reactions such as HER [16] applying a higher scan rate (such as 50 mV/s as used in Publication I) can still result in the same electrochemical results (polarization curves and Tafel plots). For normal CV measurements higher scan rates (usually around 50 mV/s) might be applied.

4.4.4 Rotating Disc and Rotating Ring Disc electrodes

The rotating disc electrode (RDE) technique is an electrochemical technique in which the WE (Figure 11) rotates in the solution during voltammetric measurements. This kind of electrochemical technique, which introduces controlled convective mass transport of reactants and products, is one example of a hydrodynamic method. In hydrodynamic methods, a steady state is obtained rather quickly and double-layer charging does not affect the electrochemical measurements, resulting in the measurement with a high precision [101]. Furthermore, in these methods the rates of mass transfer at the electrode surface are normally increased because of the increase in the convection mass transfer, leading to relatively smaller contribution of mass transfer to electron-transfer kinetics [101]. In this thesis, RDE measurements were performed to obtain HER and OER polarization curves. The rates of HER and OER are not affected significantly by mass transfer and thus the change in the rotation rate of the electrode does not change the polarization curves significantly. However, a suitable rotation rate is applied to remove the formed hydrogen and oxygen bubbles from the electrode surface and to get more precise measurements as discussed above.

Rotating ring disc electrode (RRDE) is similar to RDE but it also includes an independent ring electrode surrounding the disk. In RRDE technique, the product which is produced on the disk can be further analysed on the ring which is kept at a different potential from the disk. For example when we consider OER on an electrocatalyst, the origin of the measured anodic current on the electrode can be investigated with the RRDE technique [91,121,155,156]. In such RRDE measurements, the oxygen evolved at the disk is subsequently reduced at the surrounding Pt ring electrode that is held at, for example, 0.4 V which is the potential at which the oxygen is reduced to water (ORR) on the Pt ring. In such measurements, the current of the Pt ring electrode (attributed to the ORR) is detected when the disk electrode is swept to more positive potentials than the onset of the OER. Likewise, to monitor if H$_2$O$_2$ is also produced during the OER, the Pt ring is held at, for example, 1.4 V which is the potential at which any
produced $\text{H}_2\text{O}_2$ on the disk is subsequently oxidized on the ring and results in an oxidation current on the ring [91,121].

RRDE measurements can be also used to quickly screen the approximate Faradaic efficiency ($\varepsilon$). For example, in the case of $\text{O}_2$ evolution, $\varepsilon$ can be calculated by the following equation:

$$\varepsilon = \frac{100 \times j_{\text{ORR}}}{j_{\text{OER}} \times N}$$  \hspace{1cm} (31)

where $j_{\text{ORR}}$ and $j_{\text{OER}}$ are current densities measured on the Pt ring and the disc electrodes respectively, and $N$ is the collection efficiency of the RRDE [91,121,156]. It should be noted that small errors in the ring current and the collection efficiency can lead to relatively large errors in $\varepsilon$ [121]. There are also a number of other parameters that affect the faradaic efficiency measured by RRDE, such as the $\text{O}_2$ bubble formation on the disc (hindering $\text{O}_2$ dissolution into the electrolyte) and the error in the measured geometric surface area of the disc (resulting from inhomogeneous catalyst dispersion on the disk). However, RRDE measurements are still useful for rapidly screening the approximate Faradaic efficiency [121].

4.4.5 Electrochemical Impedance Spectroscopy

In electrochemical impedance Spectroscopy (EIS), a small amplitude AC signal is applied to the system and then the AC voltage–current response is measured to determine the impedance. EIS is a powerful tool to identify the sources of losses in the system. In this thesis (Publications II and IV) EIS was utilized to measure the ohmic electrolyte resistance ($R_u$) which affects the shape of polarization curves, especially in electrolyte solutions with a high resistance. For the Tafel analysis in high resistance solutions, the $iR$ compensation of the voltammogram is required, otherwise the analysis might result in the incorrect data interpretation. The uncompensated $R_u$ was determined by equating $R_u$ to the minimum total impedance in a non-Faradaic region measured between 10 Hz and 100 kHz, where the capacitive and inductive impedances are negligible and the phase angle was near zero.
5. Synthesis and characterization of the metal/CNT hybrid nanomaterials: results and discussion

5.1 Single-shell carbon-encapsulated iron nanoparticles (SCEINs) decorated on SWNTs

5.1.1 Synthesis of SCEIN/SWNT

As shown in Publication I, the SCEINs as the electrocatalysts and SWNTs as the catalyst support have been synthesized simultaneously using a one-step so-called floating catalyst (aerosol) CVD synthesis process. The same synthesis method has been utilized to fabricate highly conductive and transparent thin films of CNTs [51]. The synthesis reactor consists of a 5 cm diameter quartz tube inserted inside a furnace with a 60 cm long hot zone [51]. In this technique, all the reactions in the reactor happen in the gas phase. A feedstock solution of 1% wt. of ferrocene in toluene (C\textsubscript{7}H\textsubscript{8}), and 0.7% wt. of thiophene (C\textsubscript{4}H\textsubscript{4}S) was atomized by a nitrogen jet flow. The aerosolized feedstock solution was introduced into a high temperature reactor to produce Fe catalyst NPs. The feedstock introduction rate was 5.3 g/h. Then, this aerosol was carried into the reactor with hydrogen (H\textsubscript{2}) at a flow rate of 8 lpm through a quartz tube. Iron catalyst particles are produced by thermal decomposition of ferrocene at the synthesis temperature of 1100 °C. The SCEIN/SWNT material has been synthesized by catalytic decomposition of a mixture of ethylene (C\textsubscript{2}H\textsubscript{4}) and carbon dioxide (CO\textsubscript{2}) which were introduced into the reactor at the flow rates of 17 and 50 cm\textsuperscript{3}/min respectively. The mass flow controllers measure and control the gas flows. The growth was performed at atmospheric pressure and in laminar flow conditions inside the reactor. The SCEIN/SWNT sample was collected at the outlet of the reactor through a nitrocellulose membrane filter (Millipore, 0.45 µm diameter pores). A scheme of the synthesis reactor with the different incoming species is shown in Figure 12.

Thiophene is used as a sulfur containing promoter for the growth of CNTs and without the use of thiophene in the feedstock, CNTs are not synthesized [51]. Sulfur can modify the surface activity of Fe catalyst NPs [157,158] and decreases carbon solubility into iron in order to avoid carburization (a process in which carbon is transferred into iron) and the formation of dust of metal particles and carbon (coke) [159]. High amount of sulfur containing species can completely poison and deactivate the iron catalyst NPs [160]. Therefore, an optimal amount of sulfur is required to grow the desired structures of CNTs [51]. It is noteworthy that the use of thiophene is to modify the Fe catalyst particles and it seems unlikely that sulphur is doped into the sidewalls of the CNTs.
Ethylene is utilized as a carbon source for the synthesis of CNTs since hydrocarbons have shown a high reaction yield [51], which is a key factor for industrial applications. Carbon dioxide is used as an etching agent which can remove amorphous carbon coated on the surfaces of iron catalyst NPs. It can also prevent the formation of cementite (Fe₃C) which is believed to be an inactive phase for the growth of nanotubes [49,161,162].

Figure 12. A scheme of the synthesis reactor used for the growth of SCEIN/SWNT (MFC is referred to mass flow controller).

5.1.2 Characterization of SCEIN/SWNT

TEM observations of the SCEIN/SWNT material (Figure 13) indicate SCEINs with a size distribution of 2-3 nm on the sidewalls of the SWNTs. Single-layer carbon shells surrounding Fe NPs are clearly observed in HRTEM images. An average size of 2.6 nm for the iron NPs in SCEINs and an average diameter of 1.7 nm for SWNTs in the SWNT/SCEIN material were measured by measuring 200 individual NPs and 100 CNTs from the HRTEM images, respectively (Publication I).

Figure 13. a) HRTEM image of SCEINs supported on SWNTs showing distribution of the particles on the SWNTs, the inset indicates the (110) lattice plane of the Fe particles in SCEINs. b) HRTEM image of SCEINs decorated on the sidewalls of the SWNTs, indicating the larger Fe particles catalyze the growth of SWNTs while the smaller ones form SCEINs (arrows demonstrate the SWNT). (Publication I)
XPS analysis of the SCEIN/SWNT material (Publication I) confirmed that almost all the Fe NPs were completely covered by the carbon cage, since only binding energies attributed to metallic Fe were observed.

Based on the HRTEM images, the mechanism of the growth of SCEIN/SWNT can be proposed as follows. In the presence of an etching agent such as CO$_2$, the smaller particles have less probability to serve as a catalyst for the growth of CNTs [161]. For small particles (here 2-3 nm in diameter), the graphitic cap for the nucleation of CNTs is small and can be etched in the harsh oxidizing conditions. On the contrary, the larger particles have larger nucleation embryos which can survive to grow SWNTs. Therefore, the larger particles might serve as the active catalysts for the growth of CNTs while small particles are just encapsulated in a carbon shell. The latter might form in the cooling zone of the reactor, where carbon solubility and etching reaction rate decrease.

As discussed in section 5.1.1, sulfur (from thiophene) was used as an element for modifying the surface of the Fe catalyst particles to grow the CNTs. It was detected by EDX/SEM and XPS that sulfur (1.2 wt%) existed in the SCEIN/SWNT samples. However, EDX/TEM from the Fe NPs did not detect sulfur (Publication I), probably due to the very low amount of sulfur. Furthermore, HRTEM images exhibited crystalline Fe NPs with a small amount of defects incorporated in the bulk crystalline structure.

In the literature, two types of iron impurities during the growth of CNTs have been reported: iron oxide NPs and Fe NPs covered by multi-layer graphene or amorphous carbon [163-165]. In contrast, we presented here a synthesis method for CNTs by which the inactive Fe catalyst NPs for the growth of the nanotubes are encapsulated in a single-shell carbon and form SCEINs.

### 5.2 Maghemite ($\gamma$-Fe$_2$O$_3$) nanoparticles decorated on carbon nanotubes

#### 5.2.1 Synthesis of CEIN/CNT and its electrochemical modification to $\gamma$-Fe$_2$O$_3$/CNT

As discussed in section 2.5, MWNTs are preferred to SWNTs for OER. Therefore, to make active materials for OER, the synthesis process of SCEIN/SWNT described in section 5.1.1 was slightly changed to synthesize few-walled CNTs instead of SWNTs. To reach this goal, the CO$_2$ was no longer introduced into the reactor and the ferrocene concentration was increased to produce more Fe particles. The growth of CEINs is highly dependent on the amount of iron source so that the amount of CEINs can be decreased significantly by decreasing the ferrocene concentration [51]. Here, the liquid feedstock solution was prepared with 4% wt. of ferrocene in toluene, and thiophene was added to the solution so that the molar concentration of ferrocene and thiophene are both equal to 0.186 mol/L. The other growth parameters were similar to those explained in section 5.1.1. Following this growth process, we could produce few-shell carbon-encapsulated iron nanoparticles (CEINs) decorated on few-walled CNTs (CEIN/CNT).

As shown in publication II, when a cyclic voltammetry measurement in a potential range close to that of OER (1-1.65 V vs. RHE) is applied to the CEIN/CNT electrode in NaOH solution, carbon cages in CEINs and the caps of the CNTs are selectively oxidized and removed while the
hexagonal structure of the CNTs is preserved. Subsequently, hydroxide ions react with the metallic Fe core of CEINs to form highly crystalline maghemite ($\gamma$-$\text{Fe}_2\text{O}_3$) NPs. Likewise, Nieuwoudt et al. have shown by in-situ Raman microspectroscopy that the main passive film formed on iron in 0.05 M NaOH is $\gamma$-$\text{Fe}_2\text{O}_3$ if the applied potential to the iron is close to the OER potential range [166].

The presence of pentagonal rings and the great strain on the carbon atoms at the hemispherical tips of the CNTs and graphene layers surrounding the Fe particles in CEINs make them more reactive compared to the hexagonal structure of the sidewalls of the CNTs [167] so that they are selectively removed by reacting with hydroxide (OH$^-$) ions in the alkaline solution.

5.2.2 Characterization of the CEIN/CNT and the $\gamma$-$\text{Fe}_2\text{O}_3$/CNT samples

TEM observations of the CEIN/CNT material (Publication II and Figure 14) indicate the full encapsulation of Fe in CEINs on the sidewalls of the few-walled CNTs. In HRTEM images (Figure 14) we observe the CEINs with an average size of 5.4 nm. From the HRTEM images of the CEIN/CNT sample, we can see the Fe particles with different structures. Those Fe structures might represent the Fe catalyst at different growth steps of CNTs, as reported in the literature on the basis of in-situ observations during the growth of CNTs [168-170]. These steps in order are: the formation of graphene layers around the metal clusters; formation of a conical shape and the characteristic protrusion on the metal cluster which expels a CNT; and then, elongated iron particle formed by the large forces exerted by the surrounding carbon tube. Therefore, the CEINs might be synthesized at the end of the hot zone of the reactor where they do not have enough time to form CNTs.

![Figure 14. a) HRTEM image of CEIN/CNT, the inset shows a zoom in of the selected area. b-f) HRTEM representation of iron nanoparticles at different stages of the growth of CNTs such as: b) Carbon encapsulated iron nanoparticles; c and d) Iron nanoparticles with a conical shape and the formation of the carbon cap; e) Elongated iron particle surrounded by a CNT; f) The presence of all types of the shown iron particles with different structures in images a-d, in the CEIN/CNT sample.](image)

After potential cycling the structure of CEINs is changed to $\gamma$-$\text{Fe}_2\text{O}_3$ NPs with an average size of 6.3 nm (Figure 15a and b). Figure 15c shows the selective opening of a double-walled CNT after the OER potential cycling, indicating that the tube cap has been removed while the tube sidewall has been preserved without damage. The maghemite structure of the NPs has been characterized by the TEM crystallographic investigations and XPS (Publication II), as well as
Raman spectroscopy at low-frequency region (Figure 15d) where the Raman active modes of maghemite, \( E_g \) and \( A_{1g} \), are observed at around 350 and 700 cm\(^{-1} \), respectively [171,172].

Cyclic voltammetry (CV) indicates a significant change when the CEINs are transformed to \( \gamma\)-Fe\(_2\)O\(_3\) NPs (Figure 15e). For the CEINs, the two main anodic and cathodic peaks of iron at \(~0.25\) (peak I) and \(~-0.11\) V (Peak II) in active region of iron (between -0.45 and 0.45 V) are significantly less intense compared to those of the \( \gamma\)-Fe\(_2\)O\(_3\) NPs. These peaks come from reversible redox reactions of the iron particles: [166,173]

\[
\begin{align*}
\text{Peak I: } & \text{Fe(OH)}_2 \rightarrow \text{FeOOH} \\
\text{Peak II: } & \text{FeOOH} \rightarrow \text{Fe(OH)}_2
\end{align*}
\]

The intensities of these peaks in the initial CEIN/CNT sample are weak since most of the iron particles are covered by graphitic layers. After potential cycling the faradaic currents increase dramatically in the active region as a consequence of the removal of the carbon layers surrounding Fe NPs. This CV characterization is a powerful technique by which we can monitor the gradual change of the CEINs to \( \gamma\)-Fe\(_2\)O\(_3\) during OER cycling.

Figure 15. a) low- and b) high-magnification TEM images of the \( \gamma\)-Fe\(_2\)O\(_3\) nanoparticles supported on the CNTs; c) HRTEM image from an open-ended CNT, (arrows demonstrate the CNT); d) Raman spectra and e) CV curves of CEIN/CNT (black curves) and \( \gamma\)-Fe\(_2\)O\(_3\)/CNT (red curves). The CVs were measured at a scan rate of 20 mV s\(^{-1}\) in N\(_2\)-saturated 1 M NaOH alkaline solution. (Publication II)

5.3 Pseudo-atomic-scale platinum immobilized on SWNTs

5.3.1 Electrochemical modification of SWNTs with Pt

The electrodeposition of subnano Pt on the SWNT electrode was performed in 0.5 M H\(_2\)SO\(_4\) through an electroplating technique either by a three-electrode cell setup where Pt and SWNT were counter and working electrodes (CE and WE) respectively, or by a two-electrode setup where Pt and SWNT were positive and negative electrodes respectively. In the three-electrode setup, Pt electrodeposition was carried out through cycling the potential of SWNT-coated GC electrode between -0.55 V and 0.25 V vs. RHE. The cathodic sweep of the SWNT WE induces an anodic sweep on the Pt CE. When the WE potential is decreased to -0.55 V, the CE potential is increased to \(~2.2\) V. The dissolution onset potential for Pt in sulfuric acid is ca. 1.1 V vs. RHE [174-181] and thus above this potential the Pt CE starts dissolving as Pt ions (Pt\(^{2+}\) or Pt\(^{4+}\)) into the solution. Subsequently, the Pt ions are reduced on the SWNT WE. Likewise, in two-
electrode setup the subnano Pt is deposited on the SWNTs by an external power source applying a voltage of 2.5 V between the SWNT and the Pt electrodes.

The SWNT electrodes activated by the three-electrode setup and with 200 and 400 potential cycles are denoted as 200-SWNT/Pt and 400-SWNT/Pt samples, respectively. The SWNT electrode activated with Pt by the two-electrode setup for 4 h is denoted as 4 h-SWNT/Pt sample. In all of these samples pseudo-atomic scale Pt has been immobilized on the surface of the SWNTs and thus these samples, in general, can be also referred to as “SWNT/at-Pt” samples.

5.3.2 Characterization of the SWNT/at-Pt hybrid nanomaterials

Based on XPS analysis, only metallic Pt was observed in the SWNT/at-Pt samples (Publication III). XPS revealed the presence of 0.19, 0.75, and 0.41 at% Pt or 2.94, 10.22, and 5.95 wt% for the 200 and 400-SWNT/Pt and the 4 h-SWNT/Pt samples, respectively. This surface loading is significantly higher than earlier works [182-193] in which atomically dispersed Pt could be synthesized mostly on non-conductive metal oxide supports and only at very low loadings (the bulk loading has been < 1 wt%) because the utilized supports had small surface area and insufficient interaction with the Pt atoms. The maximum bulk Pt atomic loading (5 wt%) has been recently reported [194], but for immobilization of Pt ions (instead of metallic Pt) on a sulfur-doped zeolite-templated carbon.

No degradation of the SWNTs was observed during the activation with Pt based on Raman spectroscopy analysis (Publication III). The approximate Pt loading amount of 114-570 ng cm$^{-2}$ Pt in the SWNT/at-Pt catalysts deposited on GC electrodes was estimated based on the FESEM/EDX analysis as described in Publication III.

HAADF/STEM images were obtained to observe the formation of subnano Pt on the SWNT support. For such images, the SWNTs were first purified to remove iron impurities, as otherwise distinguishing between Fe and Pt atoms is difficult. The SWNTs were purified by 5 potential cycles between 1 and 1.7 V at a scan rate of 5 mV s$^{-1}$ in 0.5 M H$_2$SO$_4$ as a purification technique explained in publication II. Figure 16a and b show the STEM images of the purified SWNTs after 400 activation cycles. On an ultrathin layer of the activated SWNTs coated on a TEM grid, it is observed that Pt in atomic scales (mainly single atoms, two-dimensional Pt rafts, and small clusters) is uniformly and densely dispersed on the sidewalls of the SWNTs (Figure 16a and b). Only a few Pt NPs with a size of > 1 nm were detected on the tubes but the amount of those particles was almost negligible compared to that of subnanometer sized Pt. Therefore, this material is mainly composed of individual Pt atoms or small clusters of a few to tens of Pt atoms dispersed on the sidewalls of the SWNTs, referred to as a pseudo-atomic-scale Pt (at-Pt) system. The Pt atoms were quite stable at their positions on the SWNTs within the time scale of our TEM observation (~5 min) with highly energetic electron beam (200 kV). This can reveal that Pt atoms have been strongly stabilized on the SWNTs.

It is noteworthy that for the SWNT/at-Pt samples we observed an almost similar CV to that of the pristine SWNT electrode (Figure 16c). Characteristic CV features of Pt have been observed in the hydrogen region (0.05-0.4 V vs. RHE), because of the adsorption/desorption of hydrogen on Pt, and in the oxygen region (0.7-1.1 V vs. RHE), due to surface Pt oxide formation and reduction [195-199]. The CV features in the hydrogen region have been observed
even for an ultrathin (~ 0.2 nm) Pt film [198]. Therefore, we found that CV could not detect ultra-low amounts of at-Pt in the SWNT/at-Pt catalysts, although the CV of Pt is considered a sensitive analytical technique for trace Pt metal analysis. To determine such a low amount of Pt, we used a high resolution XPS.

![Figure 16. a) Bright field and b) corresponding HAADF STEM images obtained from an ultrathin film of the purified SWNTs activated by 400 activation cycles, deposited on a TEM grid. c) Cyclic voltammograms for pristine SWNT and SWNT activated with 200 and 400 activation cycles compared to 20 wt% Pt/C, in N₂ purged 0.5 M H₂SO₄ solution with a scan rate of 50 mV s⁻¹ (Publication III).]

### 5.4 Ni-bipyridine complexes immobilized on MWNTs

#### 5.4.1 Synthesis of Ni-bipy-MWNT

As discussed in section 2.5, among the carbon nanomaterials, MWNTs are excellent supports which can be also utilized as the conductive support even after covalent functionalization. This special property of the MWNTs motivated us in Publication IV to improve the electrocatalytic activity of organometallic Ni complexes by covalent immobilization onto the sidewalls of MWNTs. To make such catalysts, we functionalized MWNTs covalently via an aryl diazonium salt because of the high efficiency and versatility of this method which has been used for chemical modification of sp² hybridized carbon materials such as SWNTs [200-202], graphene [203-205], and glassy carbon [206], as well as sp³ carbon atoms of diamond [207,208]. The following reaction mechanism has been proposed previously [203,204,209] for the covalent functionalization of a graphene sheet with aryl diazonium salts, and the same mechanism can be also proposed for the other sp² carbon structures. First, the aryl diazonium cation is reduced by a delocalized electron spontaneously transferred from the carbon support, resulting in an aryl radical by evolution of a molecule of N₂. Afterwards, the extremely reactive aryl radical covalently bonds to a sp² carbon atom in the support and changes the hybridization to sp³ and displaces the modified carbon out of the graphene surface by ~0.7 Å [209]. The surface coverage of the functional groups on the graphene surface seems to be mainly dominated by the kinetics of the reaction of aryl radicals with the carbon supports, rather than thermodynamics, because these radicals are so reactive and thus the activation energy barrier of the reaction is quite low [203,204].

Figure 17 summarizes the synthetic process which is used in this thesis in order to covalently functionalize MWNTs with bipyridine (bipy) ligands, and subsequently graft Ni(II) as catalytically active sites on the Bipy-MWNT material. By this synthesis method, Ni- bipy
complexes can be stabilized on the MWNTs. The synthesis steps of the Ni-bipy-MWNT catalyst have been explained below in detail.

**Figure 17.** The schematic representation of the synthesis process of the Ni-bipy-MWNT hybrid material. The two possible Ni coordination complexes, Ni-bipy-(OAc)$_2$-MWNT and Ni-(bipy)$_2$-(OAc)$_2$-MWNT, are represented. In the schematic structure of the MWNTs only the outer layer, which is used for the functionalization, is depicted (Publication IV).

**Step I: Functionalization of the MWNTs with bipyridine (Bipy-MWNT):**

MWNTs (purchased from Nanocyl) were used as received and weighed (38.9 mg) into an oven-dried two-necked 100 mL flask and dispersed in 15.5 mL of acetic acid under argon atmosphere. The suspension was sonicated for 1 hour and stirred for another hour at ambient temperature. Afterwards, 4-amino-2,2'-bipyridine (1.11 g, 6.48 mmol) and subsequently sodium nitrite (626 mg, 9.08 mmol) were added to the dispersion of MWNTs and mixed. The reaction was exothermic and was performed in an open flask for the rapid evolution of N$_2$. After a few minutes, gas bubbling ceased. The mixture was stirred for 1 hour at room temperature under an argon atmosphere. The mixture was diluted by adding of 40 ml of dimethylformamide (DMF) and mixed. The functionalized MWNTs were filtered through PTFE filter and washed several times with DMF, ethyl acetate (EtOAc), and ethanol.

**Step II: Procedure for decoration of Ni(II) on Bipy-MWNT (Ni-bipy-MWNT):**

Bipy-MWNTs (10 mg) were weighed into an oven-dried 100 ml flask and dispersed in 13.5 ml of dry DMF by 3 min sonication. Afterwards, Ni(OAc)$_2$*4H$_2$O (104 mg, 0.42 mmol) was dissolved in 11 ml of dry DMF and added to the solution of Bipy-MWNT in DMF over a 20 minute period and the suspension was further sonicated for 11 hours. Afterward, the dispersion was filtered through a PTFE filter and washed several times with DMF, EtOAc and ethanol.

**5.4.2 Characterization of Ni-bipy-MWNT**

The most stable structure of Ni-bipy complexes in neutral and basic environments, were found by DFT calculations. The calculations show that the most stable coordination in neutral environment is Ni-bipy-(OAc)$_2$ but this structure is changed to Ni-bipy-(OH)$_2$ in basic environment. For the case of close enough bipy ligands, Ni-(bipy)$_2$-(OAc)$_2$ complex is the most stable one in neutral condition but it breaks to an isolated bipy ligand and one Ni-bipy-(OH)$_2$ in alkaline media (Publication IV).

The experimental characterizations are in agreement with the DFT calculations. The Ni-bipy-MWNT has been characterized in detail by XPS (publication IV). The shape of the XPS Ni 2p spectrum is consistent with that of Ni(II) compounds. The most informative XPS data was obtained from the XPS N 1s spectra of the materials (Figure 18). Table 2 shows the atomic
concentrations of the different nitrogen functionalities derived from the peak deconvolution of the nitrogen region of XPS. From the N1s spectra and Table 2, the formation of bipy ligands on the MWNTs, Ni(II) coordination to bipy ligands, and the change in the structure of Ni-bipy complexes during the OER in alkaline media can be characterized. For the bipy-MWNT the presence of the pyridinic-N is observed by the presence of N₁ peak at 398.9 eV. After grafting Ni (II) the pyridinic peak mainly shifts to the N₅ peak at ~ 400.1 eV, suggesting that most of the nitrogen on the surface is bound to Ni to form the Ni-bipy complex. Likewise, Lattimer et al. have observed that the nitrogen signal of bipy is shifted to a higher binding energy after metalation of bipy with Rhodium [210]. After OER cycles on the Ni-bipy-MWNT sample in alkaline media, the total amount of nitrogen in free bipy (N₁) and in complexes (N₅) remains rather constant but N₁/N₅ ratio is slightly increased. This change can be attributed to the change of the Ni-(bipy)₂-(OH)₂ complexes to an isolated bipy ligand and a Ni-bipy-(OH)₂ complex during the OER, as shown also by DFT calculations in alkaline media. The relative amount of nickel remains almost the same for Ni-bipy-MWNT before (Ni/C ratio ≡ 0.015) and after OER (Ni/C ratio ≈ 0.016), indicating that nickel ions are strongly grafted on the surface of the bipy–functionalized MWNTs.

![Figure 18. Characterization of MWNTs when they are functionalized by bipy ligands and then Ni-bipy complexes by Nitrogen 1s XPS spectra. The dashed lines show the deconvoluted components, N₁, N₂, N₃, N₄, and N₅ peaks (Publication IV).](image)

Table 2. The atomic percentages of the different nitrogen functionalities of Bipy-MWNT and Ni-bipy-MWNT before and after OER cycles derived from the peak fitting (BE = binding energy).

<table>
<thead>
<tr>
<th>N type</th>
<th>BE [eV]</th>
<th>Bipy-MWNT Conc. [%]</th>
<th>Ni-bipy-MWNT Conc. [%]</th>
<th>Ni-bipy-MWNT Conc. [%] after OER</th>
<th>Chemical group</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₁</td>
<td>398.9 ± 0.1</td>
<td>0.83</td>
<td>0.18</td>
<td>0.27</td>
<td>Pyridine [200, 202, 211]</td>
</tr>
<tr>
<td>N₂</td>
<td>400.0 ± 0.1</td>
<td>0.30</td>
<td>-</td>
<td>-</td>
<td>Azo/azoxy/amin [212-214]</td>
</tr>
<tr>
<td>N₃</td>
<td>401.2 ± 0.1</td>
<td>0.32</td>
<td>0.32</td>
<td>0.23</td>
<td>pyridinium salt [211]</td>
</tr>
<tr>
<td>N₄</td>
<td>405.4 ± 0.1</td>
<td>0.15</td>
<td>0.10</td>
<td>0.07</td>
<td>NO₃ [215]</td>
</tr>
<tr>
<td>N₅</td>
<td>400.1 ± 0.1</td>
<td>-</td>
<td>0.66</td>
<td>0.47</td>
<td>Ni bipyridine complex</td>
</tr>
</tbody>
</table>
Raman spectra (Figure 19a) show that the $I_D/I_G$ ratio is increased from ~ 1.4 for the pristine MWNT to ~ 1.9 for the Bipy-MWNT. This increase can be attributed to the covalent attachment of bipy ligands to the tubes. This ratio is further increased to 2.3 for Ni-bipy-MWNT, probably due to the decoration of Ni(II) on the defect sites of the MWNTs. Furthermore, the functionalization of MWNTs with bipy ligands induces an upshift of 6 cm$^{-1}$ in the G’ band which can be attributed to charge transfer from the tubes to the attached bipy species [216,217]. After adding Ni(II) to bipy-MWNT, the G’ peak shifts slightly down (2 cm$^{-1}$), probably due to charge transfer between Ni and functionalized MWNTs.

As shown in Figure 19b, MWNTs do not show any voltammetric response; however, functionalization with the bipy ligands induces a unique electrochemical CV response consisting of mainly an anodic and a cathodic peak current at potentials of 0.473 and 0.456 V vs RHE, respectively. It has been shown that non-covalent functionalized MWNTs with bipy do not show an electrochemical CV response [218]. However, for MWNTs which strongly interact with phenanthroline ligands, as the ligands with similar coordination properties to that of bipy, a similar CV response has been reported [218]. Likewise, the presence of the CV features for the Bipy-MWNT here can reveal a strong interaction between the MWNTs and bipy ligands as these features are also absent for the unsupported bipy ligands deposited on the GC (Figure 19b). Interestingly, these features are diminished when the ligands are coordinated to Ni(II) ions in the Ni-bipy-MWNT sample. Therefore, these CV measurements which are introduced for the first time here, can present a powerful technique to monitor the attachment of bipy ligands to CNTs and subsequently the formation of organometallic complexes on the sidewalls of the CNTs.

Figure 19. Characterization of the MWNTs before and after functionalization by a) Raman spectra and c) Cyclic voltammograms in N$_2$ purged 0.1 M NaOH solution with a scan rate of 50 mV s$^{-1}$. 
6. Development of novel hybrid carbon nanomaterials for hydrogen and oxygen evolution reactions: results and discussion

Reducing the price of the electrocatalysts, while improving catalyst activity is the key approach to design low-cost and efficient catalysts. One valuable approach for the design of such catalysts is to use highly active non-precious materials. Non-precious electrocatalysts for electrochemical reactions are mainly divided to two types of materials: i) non-metal (such as carbon nanomaterials) and ii) transition metal (TM)-based catalysts as earth-abundant and low-cost electrocatalysts. Another approach for reducing the price of electrocatalysts while using precious and scarce materials such as Pt, is to reduce the loading of the noble metal by designing catalysts with an enhanced number of active surface atoms (single-atom catalysis) [219-223]. In this thesis, we have focused on designing low-cost and efficient hybrid carbon nanomaterials for electrochemical hydrogen production by water electrolysis (HER and OER electrocatalysts). Hybrid carbon nanomaterials have shown extremely interesting electrochemical properties [224], introducing them as potentially promising electrocatalysts.

For OER in acidic electrolytes, Ir and Ru-based catalysts have been the only OER catalysts that have reasonable activity [225]. For HER in acidic electrolyte, Pt-based catalysts have shown the best performance. For non-Pt catalysts for HER in acidic media, molybdenum sulfide materials have been the most studied catalysts, which have been shown to possess high activity [125]. However, in recent years a number of other active non-Pt catalysts for HER have been also proposed, some of which are listed in Table 3. The HER performance of such non-Pt catalysts has been improved significantly in the last decade, so that considerable research has been devoted to design non-precious catalysts with activity approaching that observed for platinum [57,125].

For HER in alkaline media, TMs [226], and especially Ni metal and binary and ternary systems of Ni with other metals such as Mo, Fe, and Co [227] have been shown to exhibit activity comparable to the noble metals such as Pt and Pd. For OER in alkaline electrolyte, TMs and especially Ni based catalysts (some of the most active OER catalysts have been listed in Table 4) have exhibited the best performance. However, the main challenge in designing OER catalysts has been to introduce more efficient materials, showing smaller OER overpotential and greater stability.

In this thesis, we have addressed the two challenging questions for HER electrocatalysts in acidic environment i.e. the use of non-precious electrocatalysts with high activity and stability and designing ultra-low loading noble catalysts including mostly the active surface atoms.
Furthermore, we have introduced two types of TM/CNT nanohybrid electrocatalysts with improved stability and activity toward OER in alkaline media. Table 3 and Table 4 at the end of this chapter show the detail comparison of the activity of our electrocatalysts in Publications I-IV to that observed for some of the most active electrocatalysts recently reported for HER in acidic media and OER in alkaline media, respectively.

6.1 Development of catalyst materials for hydrogen evolution in acidic media

6.1.1 Development of non-noble metal electrocatalysts for HER

TM oxides are the materials widely used as non-noble metal electrocatalysts. However, the utilization of TMs in acidic conditions is restricted by their instability and dissolution in acidic electrolytes [228]. Furthermore, transition metals are not found in metallic form in ambient air since they are immediately oxidized. To address the aforementioned issues, we have shown in Publication I that encapsulation of Fe NPs in a single graphene layer (SCEIN nanomaterial) protects the metallic TM core from oxidation and dissolution into acidic electrolytes. For SCEINs a considerable charge transfer from iron to the carbon shell has been reported by density-functional theory (DFT) calculations [67] which can provide catalytically active sites on the carbon.

Because of the strongly acidic conditions met in PEM electrolyzers, originating from the mobility of protons, development of low-cost, efficient and stable non-noble-metal catalysts for HER for acidic media has attracted increasing attention. The SCEIN/SWNT material which was synthesized as described in section 5.1.1, revealed a high activity for HER in 0.5 H₂SO₄ as presented in Figure 20. As shown in Figure 20b, the SCEIN/SWNT material exhibits an onset potential of about 0 V vs. RHE which is similar to the thermodynamic HER onset (i.e. 0 V) and that of Pt. A Tafel slope of 40 mV/decade (η = 0-48 mV) for SCEIN/SWNT (Figure 20c) suggests that this material catalyzes HER via Volmer-Heyrovsky mechanism and the desorption of hydrogen is the RDS [109,229-232] as discussed in section 3.4. The HER exchange current density (j₀) of 0.19 mA cm⁻² was calculated from the Tafel plot by the extrapolation method (as explained in section 3.2). This j₀ value is higher than most of the active non-noble metal catalysts as compared in Table 3. The catalytic activity of SCEIN/SWNT toward HER is comparable to that of Pt and superior to the most active non-precious electrocatalysts reported so far (detailed comparison is in Table 3). Furthermore, the stability of the SCEIN/SWNT catalyst was measured according to the previously reported accelerated HER stability measurements [24,229,232-235]. The stability test of the SCEIN/SWNT catalyst was performed by 1,000 potential cycles between -0.15 (where j was ~50 mA cm⁻²) and 0.15 V at a scan rate of 100 mV s⁻¹, and time dependence (chronoamperometric) measurements of the current density at a static potential of -135 mV for 18 hours. These measurements revealed no significant decrease in the activity of the catalyst. The loss in the activity of SCEIN/SWNT was smaller than that for Pt/C [236] and similar to that for MoO₃@N-doped MoS₂ catalyst [236] for which approximately similar stability measurements were performed.

The SCEIN/SWNT catalyst has several unique properties: it is very stable; SCEINs are supported on the CNT network as a very stable and conductive support; and the material can
be synthesized in large quantities as the growth mechanism is very similar to that of the SWNTs which has been scaled-up.

In Publication I, no Pt was detected by FESEM/EDX on the SCEIN/SWNT electrode after the HER stability measurements, although Pt was used as the CE (unlike Publication III). Furthermore, the SCEIN/SWNT showed clearly a different electrochemical response; for instance, to the chronoperametric measurements than the pseudo-atomic-scale Pt (compare those measurements in Publications I and III). The absence of Pt on the SCEIN/SWNT after the HER stability tests can be due to the much smaller negative potential (lower limit of -0.15 V in stability cycles) used in publication I in comparison to what used for the activation of the SWNTs in Publication III (-0.55 V). Therefore, it can be concluded that the activity of the SCEIN/SWNT after the stability measurement does not stem from the adsorbed Pt from the CE on the WE.

6.1.2 Replacing bulk Pt with subnano Pt catalysts for HER

Noble metals, such as Pt, Pd, Ru, Rh, and Ir have been widely used as heterogeneous catalysts. However, the increasing demand for such precious metals has been limited by their high price and scarcity. One solution to address these issues is to significantly reduce the loading of the noble metals by decreasing the size or the thickness of the noble metal catalysts [219]. The reduction in the size of the noble metal catalysts can dramatically reduce the catalyst price, as depicted in Figure 21a for Pt [219]. Furthermore, decreasing the size increases the number of unsaturated coordinated surface atoms, as catalytically active sites, relative to the inactive atoms in the bulk with full coordination. Consequently, the catalytic activity of the metal particles can be improved [220]. The size reduction of the metal particles to the atomic-scale
can also change the catalytic properties of the catalyst [95,194,237], providing a method for selective tuning of catalyst activity.

As described above, decreasing the size of the noble metals without compromising catalytic activity, might overcome the barriers to commercial application of such catalysts. However, the smaller particles are less stable because of the higher surface free energy which enhances the rate of aggregation in small clusters [220]. In this condition, as show in Figure 21b, a suitable support that strongly interacts with ultra-small structures of the metal catalyst should be employed to immobilize the metal atoms sufficiently and prevent the aggregation of small clusters or individual atoms (pseudo-atomic-scale catalysts) [220]. Finding such a catalyst support and developing the methods to maximize the atom utilization efficiency of the supported noble metals have attracted increasing attention in recent years [182-194,220,238].

DFT calculations (Publication III) have revealed that a Pt atom is strongly immobilized on the axial C-C sites (parallel to the tube axis as illustrated in Figure 6 b) of the SWNTs. The calculations have shown that a Pt atom adsorbed on a radial site will spontaneously diffuse to an axial site where it is stabilized and the probability of Pt agglomeration is reduced (Publication III). Furthermore, the diffusion rate of Pt atoms has been calculated to be an order of magnitude faster on graphene than on SWNT (Publication III). Therefore, the probability of Pt agglomeration is higher for graphene than the SWNT. The difference in diffusion rates on graphene and SWNT is attributed to the curved graphitic structure and chirality of SWNTs, so that smaller diameter tubes stabilize the Pt atoms more efficiently [239].

The previously reported atomic scale Pt catalysts [182-193] suffer from the lack of Pt active sites on the surface and the poor electron conductivity of commonly used metal oxide supports (see discussions in section 5.3.2). These issues hinder the application of such atomic Pt catalysts in electrochemical reactions. In contrast, pseudo-atomic-scale Pt (at-Pt), with a high surface loading stabilized on the SWNTs (the synthesized SWNT/at-Pt materials as discussed in section 5.3) have shown a high electrocatalytic activity toward HER both experimentally and theoretically (Publication III). The HER activity of the SWNT/at-Pt catalysts are shown in Figure 22. As shown in Figure 22b, the HER mass activity of the SWNT/at-Pt electrocatalysts is significantly higher than that of commercial 20 wt% Pt/C. These SWNT/at-Pt materials with
a loading of 114-570 ng cm$^{-2}$ Pt on GC exhibited a similar activity to that of commercial Pt/C with two orders of magnitude higher Pt loading (20 wt%, 38,000 ng Pt cm$^{-2}$) for catalyzing HER (Publication III). The HER activities of the SWNT/at-Pt catalysts were significantly higher than those of the most active metal-free or non-precious metal catalysts for HER (detailed comparison is in Table 3).

Figure 22c indicates that the activation rate of the graphite (GR) electrode with Pt is significantly slower than that of the SWNT. This difference between the GR and the SWNT electrodes, can be attributed to the fast diffusion rate of Pt on the GR which prevents the atomic dispersion of Pt on the GR. These results are in agreement with the previous reports in the literature for activated GR and carbon nanohorns using a similar cathodic growth of platinum particles on the support [178,240]. In those studies, a similar HER activation to that of the Pt/C was only obtained when the activation process continued for a very long time until relatively large Pt particles (20-100 nm) were formed on the graphitic support.

A calculated Tafel slope of ~ 40 mV/dec for the SWNT/at-Pt materials (Table 3 and Publication III), can reveal that HER is catalyzed via the Volmer- Heyrovský mechanism as also concluded by the DFT calculations. In contrast, the Pt/C electrode resulted in a Tafel slope of 30 mV/dec which can be attributed to the Volmer-Tafel mechanism as discussed in section 3.4. Furthermore, the measured $j_0$ for the SWNT/at-Pt electrodes were similar to that of the Pt/C (see Table 3).

Dasgupta et al. [241] reported an ultra-low Pt loading (~100 ng cm$^{-2}$) deposited on Si nanowire arrays by atomic layer deposition. For such a material they observed a very low electrochemical HER activity in 0.5 M H$_2$SO$_4$, although that catalyst had much higher activity.
under exposure to light (photoelectrochemical HER). On the contrary, here the 200-SWNT/Pt catalyst with a similar Pt loading (~ 114 ng cm\(^{-2}\)) and in the same electrolyte solution revealed an extraordinary HER activity. This high activity can be attributed to the pseudo-atomic-scale Pt dispersion on the sidewall of the SWNTs with a large surface area and a high electrical conductivity. Very recently a similar potential-cycling activation method has been applied to activate CoP-based nanotube arrays by single Pt atoms to make a very active and stable HER catalyst in neutral media [222].

After 5,000 potential cycles (between -0.2 and 1.1 V vs. RHE at a scan rate of 50 mV s\(^{-1}\)) and after long time (6 months) storing in the ambient air, the HER activity of the SWNT/at-Pt catalysts is almost preserved (Publication III). These results revealed the high durability and stability of the SWNT/at-Pt catalyst for HER. We observed that the HER activity of the SWNT/at-Pt electrodes could be passivated by the adsorption of the possible impurities from the electrolyte solution (for example, alkali metal cations [242-244]) during the HER measurements. However, sweeping the WE potential to more than 1 V vs. RHE could completely strip off the possible adsorbed impurities and restore the high catalytic activity as shown by the chronoamperometric measurements in Publication III. A similar technique has been utilized in the literature [243,245], in order to sufficiently clean the surface of Pt and restore its activity.

6.2 Development of catalyst materials for oxygen evolution in alkaline media

6.2.1 γ-Fe\(_2\)O\(_3\)/CNT hybrid nanomaterials as active electrocatalysts for OER

As discussed in section 5.2.2, the CEIN/CNT material is transformed to γ-Fe\(_2\)O\(_3\)/CNT by applying potential sweeps or cycles in a potential range close to that of required for OER (schematically represented in Figure 23a). Figure 23b indicates that the first OER sweeps (specially the 1\(^{st}\) one) of the CEIN/CNT electrode have slightly higher oxidation currents that can be attributed to the oxidation of the hemispherical caps of the CNTs and the near-spherical carbon shells in the CEINs. We have monitored the structural transformation of the CEIN/CNT by the OER curves. When the OER currents are stabilized and the structural changes are completed, the CV curves (Figure 15e) are also stabilized as discussed in section 5.2.2. After a few OER sweeps the OER polarization curves are stabilized and a high OER activity is obtained (Figure 23c), but this activity is attributed to γ-Fe\(_2\)O\(_3\)/CNT instead of CEIN/CNT.

The RRDE measurements (Publication II) revealed that the measured anodic current in the OER polarization curve of γ-Fe\(_2\)O\(_3\)/CNT stems from the oxygen evolution with the approximate Faradaic efficiency (\(\varepsilon\)) > 90%, rather than the H\(_2\)O\(_2\) production on the γ-Fe\(_2\)O\(_3\)/CNT disk (see the method of RRDE measurements for OER in section 4.4.4). Furthermore, purified CNTs, in which γ-Fe\(_2\)O\(_3\) NPs have been removed from the surface of the CNTs, resulted in almost no anodic current in the potential range of 1.2-1.75 V (Publication II). This indicates that the anodic current of the OER polarization curve of the γ-Fe\(_2\)O\(_3\)/CNT catalyst does not arise from the oxidative corrosion of the CNT support. Therefore, the anodic current of the γ-Fe\(_2\)O\(_3\)/CNT catalyst in Figure 23c can be merely attributed to the oxygen evolution.
The $\gamma$-Fe$_2$O$_3$/CNT catalyst also revealed highly durable OER performance, tested by 100 cycles between 1 and 1.75 V (where $j$ is $\sim$ 30 mA cm$^{-2}$) at a scan rate of 50 mV s$^{-1}$ and the chronoamperometric measurements at a constant potential of 1.64 V (where $j$ is $\sim$ 10 mA cm$^{-2}$) for 25 h in 0.1 M NaOH (Publication II). The OER activity of this catalyst is comparable to the most active OER electrocatalysts reported so far (detailed comparison is in Table 4). Therefore, the $\gamma$-Fe$_2$O$_3$ NPs decorated on the CNTs can function as non-precious, active and durable electrocatalysts for catalyzing OER.

Figure 23. a) Schematic representation of transformation of CEIN/CNT to $\gamma$-Fe$_2$O$_3$/CNT during the OER measurements. b) The first five OER anodic potential sweeps for the CEIN/CNT sample in 1 M NaOH solution. c) The RDE voltammograms of Fe$_2$O$_3$/CNT, IrO$_2$, Pt/C (20 wt%), and SWNT in 0.1 M NaOH solution. The polarization curves were measured without $iR$ compensation (see Publication II for the $iR$ corrected curves) at a scan rate of 5 mV s$^{-1}$ and a rotation of 1600 rpm. (Publication II)

For $\gamma$-Fe$_2$O$_3$/CNT, Tafel slopes of 50 and 45 mV/decade were measured in 0.1 and 1 M NaOH, respectively. These values are smaller than those recently reported for carbon and/or metal hybrids [74,156,246,247]. Furthermore, the electrochemically active surface area (ECSA) and the roughness factor (RF) of the $\gamma$-Fe$_2$O$_3$/CNT catalyst were calculated to be 35 cm$^2$ and 280 respectively (Publication II), which are remarkably higher than corresponding values for previously reported highly active OER catalysts [91,121]. These values were estimated from the electrochemical double-layer capacitance of the catalytic surface [91,121] which had been calculated from the CVs at different scan rates [91,121,248] (see calculation details in Supporting Information of Publication II). The large ECSA of this catalyst can be one the reasons for the high OER catalytic activity.

A low OER catalytic activity has been reported for hematite ($\alpha$-Fe$_2$O$_3$) [249], Fe films [250] and modified CNTs with Fe$_2$O$_3$ (probably $\alpha$-Fe$_2$O$_3$) NPs [91]. Among iron oxide materials, maghemite ($\gamma$-Fe$_2$O$_3$) has been reported [251,252] as a promising photoanode material for photoelectrochemical water oxidation. Maghemite had not been considered for electrocatalytic water oxidation until recently when maghemite nanorods anchored on nitrogen doped CNTs exhibited a higher OER activity than other iron oxide materials [253]. However, the activity of
those maghemite nanorods was still significantly lower than that of observed for the state-of-the-art OER electrocatalysts [253]. In contrast, we have shown in Publication II that \( \gamma-\text{Fe}_2\text{O}_3 \) NPs decorated on CNTs demonstrate a high OER activity which is comparable to that of the most active OER electrocatalysts (see Table 4).

### 6.2.2 Organometallic Ni complexes immobilized on MWNTs as active electrocatalysts for OER

The immobilization of organometallic Ni complexes on the sidewalls of the MWNTs has been proposed in Publication IV as a promising technique to enhance the electrocatalytic activity of organometallic compounds. Here, we show that Ni bipyridine (Ni-bipy) complexes immobilized on the MWNTs are highly active and stable electrocatalysts for OER.

Figure 24a represents the schematic structure of the Ni-bipy-MWNT catalyst described in sections 5.4. Figure 24b exhibits the OER polarization curves of Ni-bipy-MWNT, bipy-MWNT and pristine MWNT in comparison to RuO\(_2\) as a highly active OER electrocatalyst. The pristine MWNTs and the functionalized MWNTs with the bipy ligands show almost no anodic current at potentials less than 1.7 V vs. RHE. This indicates that the anodic current of the OER polarization curve of the Ni-bipy-MWNT catalyst is not the result of oxidation/corrosion of the MWNT or bipy-MWNT support. Moreover, the RRDE measurements (Figure 24c) confirmed the formation of oxygen (instead of \( \text{H}_2\text{O}_2 \) as a possible side product) on the Ni-bipy-MWNT disk with the approximate \( \varepsilon > 90\% \) (see the RRDE measurements for OER in section 4.4.4). Since the oxidation peak current of Ni overlaps with the OER current at the potentials range of 1.4-1.5 V, the RRDE measurements could identify almost precisely the OER onset potential of the catalyst (the potential at which oxygen starts evolving on the catalyst), by defining the potential at which the oxygen produced on the disk starts reducing on the Pt ring. The measured OER onset potential for the Ni-bipy-MWNT catalyst is \( \sim 1.48 \) V (onset overpotential of 0.25 V). The activity of the Ni-bipy-MWNT catalyst has been compared with some of the most active OER electrocatalysts reported recently in Table 4. This activity comparison indicates that the Ni-bipy-MWNT catalyst can be ranked among the most active OER electrocatalysts reported so far.

Tafel slopes of 35, 60, 95, and 123 mV dec\(^{-1}\) were calculated for Ni-bipy-MWNT, RuO\(_2\), MWNT, and Bipy-MWNT, respectively (Publication IV). The difference between the Tafel slopes of these materials can be attributed to the change in the RDS of OER, as described in section 3.5. For the aged nickel electrodes a Tafel slope of \( \sim 40 \) mV dec\(^{-1}\) has been reported in the literature [250,254] which is similar to that of the Ni-bipy-MWNT.

In comparison to the recently reported [126] organometallic compound of \( \text{Ni}_6\text{(PET)}_{12} \) (PET = phenylethyl thiol) as an active OER electrocatalyst, the Ni-bipy-MWNT indicates a significant progress in the OER catalytic activity of organometallic Ni complexes (see Table 4 for a detailed comparison). This improvement in the activity can be ascribed to the great performance of CNTs for electrocatalysis when they are functionalized with organometallic Ni compounds.

Furthermore, the Ni-bipy-MWNT catalyst revealed a high durable OER performance (Publication IV) tested by 1,000 cycles between 1 and 1.65 V at a scan rate of 50 mV s\(^{-1}\) in 0.1 M NaOH, and chronoamperometric measurements at a constant potential of 1.54 V for 10 h in
0.1 M NaOH. It has been shown that Ni-bipy-MWNT is almost completely stable during 1,000 OER stability cycles, while RuO₂ is notably degraded during those cycles (Publication IV).

**Figure 24.** a) Schematic representation of OER on the Ni-bipy-MWNT catalyst material. b) The OER polarization curves obtained with Ni-bipy-MWNT, Bipy-MWNT, MWNT, and RuO₂ in 0.1 M NaOH solution. c) The RRDE measurements on the Ni-bipy-MWNT electrode to detect the generation of O₂ or H₂O₂ on the GC disk by the subsequent ORR or H₂O₂ oxidation on the ring at the ring constant potentials of 0.4 and 1.4 V, respectively. The polarization curves were measured at a scan rate of 5 mV s⁻¹ and a rotation of 1600 rpm. (Publication IV)
Table 3. Comparison of electrocatalytic HER activity in acidic conditions for SCEIN/SWNT and Pt/C in Publication I and SWNT/at-Pt samples and Pt/C in Publication III with some of the most active non-precious HER catalysts reported recently. The activity of the Pt/C strongly depends on the catalyst structure (as described in section 2.4 and Figure 3) and the crystallographic orientation of the platinum surface atoms [110] and this might be the reason of slightly different HER activities of the commercial Pt/C materials utilized in Publications I and III.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>η (mV)</th>
<th>j₀ (mA cm⁻²)</th>
<th>Tafel slope (mV dec⁻¹)</th>
<th>j (mA cm⁻²)</th>
<th>η (mV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCEIN/SWNT</td>
<td>~0</td>
<td>0.19</td>
<td>40</td>
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<td>42</td>
<td>I</td>
</tr>
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<td></td>
<td></td>
<td>10</td>
<td>77</td>
<td>Our work</td>
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<td></td>
<td></td>
<td></td>
<td>50</td>
<td>135</td>
<td></td>
</tr>
<tr>
<td>20 wt% Pt/C (loading 0.18 mg cm⁻² on the GC)</td>
<td>~0</td>
<td>0.17</td>
<td>37</td>
<td>10</td>
<td>66</td>
<td>I</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>50</td>
<td>106</td>
<td>Our work</td>
</tr>
<tr>
<td>200-SWNT/Pt</td>
<td>~0</td>
<td>1.15</td>
<td>40</td>
<td>10</td>
<td>40</td>
<td>III</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>100</td>
<td>170</td>
<td>Our work</td>
</tr>
<tr>
<td>400-SWNT/Pt</td>
<td>~0</td>
<td>1.94</td>
<td>38</td>
<td>10</td>
<td>27</td>
<td>III</td>
</tr>
<tr>
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<td></td>
<td>100</td>
<td>130</td>
<td>Our work</td>
</tr>
<tr>
<td>4h-SWNT/Pt</td>
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<td>1.73</td>
<td>41</td>
<td>10</td>
<td>32</td>
<td>III</td>
</tr>
<tr>
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<td></td>
<td>100</td>
<td>147</td>
<td>Our work</td>
</tr>
<tr>
<td>20 wt% Pt/C (loading 0.2 mg cm⁻² on the GC)</td>
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<td>1.22</td>
<td>30</td>
<td>10</td>
<td>28</td>
<td>III</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>123</td>
<td>Our work</td>
</tr>
<tr>
<td>[MoS₃]⁻ clusters on graphic paper</td>
<td>100</td>
<td>-2 x 10⁻⁴</td>
<td>40</td>
<td>10</td>
<td>-180</td>
<td>[232]</td>
</tr>
<tr>
<td>Exfoliated WS₂ nanosheets</td>
<td>80</td>
<td>-0.02</td>
<td>60</td>
<td>10</td>
<td>230</td>
<td>[255]</td>
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<tr>
<td>Double-gyroid MoS₂</td>
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<td>6.9 x 10⁻⁴</td>
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<td>2</td>
<td>190</td>
<td>[256]</td>
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<td></td>
<td></td>
<td></td>
<td>10</td>
<td>270</td>
<td></td>
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<tr>
<td>Mo₃C/CNT</td>
<td>-</td>
<td>0.014</td>
<td>55</td>
<td>10</td>
<td>152</td>
<td>[230]</td>
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<tr>
<td>Mo₃C/CNT - graphene</td>
<td>62</td>
<td>0.062</td>
<td>58</td>
<td>10</td>
<td>130</td>
<td>[25]</td>
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<tr>
<td>Nanoporous Mo₃C nanowires</td>
<td>70</td>
<td>-</td>
<td>53</td>
<td>10</td>
<td>-156</td>
<td>[257]</td>
</tr>
<tr>
<td>Core-shell MoO₃-MoS₂ Nanowires</td>
<td>150-200</td>
<td>-5.6 x 10⁻⁵</td>
<td>50-60</td>
<td>10</td>
<td>-250</td>
<td>[231]</td>
</tr>
<tr>
<td>Exfoliated metallic MoS₂ nanosheets</td>
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<td>-</td>
<td>43</td>
<td>10</td>
<td>187</td>
<td>[258]</td>
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<td>MoS₂/ amorphous carbon</td>
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<td>0.474</td>
<td>40</td>
<td>50</td>
<td>-138</td>
<td>[259]</td>
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<td>-</td>
<td>47.5</td>
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<td>[236]</td>
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<td>MoP</td>
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<td>[266]</td>
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<td>Network of MoP nanoparticles</td>
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<td>0.086</td>
<td>54</td>
<td>2</td>
<td>84</td>
<td>[261]</td>
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<td></td>
<td></td>
<td></td>
<td>10</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>Ni₃P nanoparticles</td>
<td>~50</td>
<td>0.033</td>
<td>46</td>
<td>10</td>
<td>-109</td>
<td>[235]</td>
</tr>
<tr>
<td>FeCo@NCNTs</td>
<td>~70</td>
<td>-</td>
<td>74</td>
<td>10</td>
<td>-275</td>
<td>[63]</td>
</tr>
<tr>
<td>FeP-graphene sheets</td>
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<td>0.12</td>
<td>50</td>
<td>10</td>
<td>123</td>
<td>[262]</td>
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<tr>
<td>C₃N₄@NG</td>
<td>~110</td>
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<td>51.5</td>
<td>10</td>
<td>-240</td>
<td>[263]</td>
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<td>Nitrogen and phosphorus dual-doped graphene</td>
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<td>2.4 x 10⁻⁴</td>
<td>91</td>
<td>10</td>
<td>-420</td>
<td>[71]</td>
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</table>
Development of novel hybrid carbon nanomaterials for hydrogen and oxygen evolution reactions: results and discussion

### Nanoporous CoP nanowire arrays on carbon cloth
- **Nanoporous CoP:** 38, 0.288, 51, 10, 67
- **Co-NR-CNT:** 5, 0.01, 80, 1, 140
- **CoP/CNT:** 40, 0.13, 54, 2, 70

### Table 4. Comparison of the OER activity in alkaline conditions for Ni-bipy-MWNT and $\gamma$-Fe$_2$O$_3$/CNT with several recently reported highly active transition-/noble-metal and non-metal electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>$\eta_{\text{onset}}$ (mV)</th>
<th>$\eta_{10}$ @10 mA cm$^{-2}$ (mV)</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>Mass loading (mg cm$^{-2}$)</th>
<th>Substrate</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>$\gamma$-Fe$_2$O$_3$/CNT</td>
<td>0.1 M NaOH</td>
<td>300</td>
<td>380</td>
<td>45-50</td>
<td>0.2</td>
<td>GC</td>
<td>II</td>
</tr>
<tr>
<td></td>
<td>1 M NaOH</td>
<td>340</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-bipy-MWNT</td>
<td>0.1 M NaOH</td>
<td>250</td>
<td>310</td>
<td>35</td>
<td>0.2</td>
<td>GC</td>
<td>III-V</td>
</tr>
<tr>
<td></td>
<td>1 M NaOH</td>
<td>290</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiFeO$_x$</td>
<td>1 M NaOH</td>
<td>N.A.</td>
<td>360</td>
<td>N.A.</td>
<td>N.A.</td>
<td>GC</td>
<td>[121]</td>
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<td>CoFeO$_x$</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>NiCoO$_x$</td>
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<td>NiCuO$_x$</td>
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<tr>
<td>CoO$_x$/CoPi</td>
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<td>NiO$_x$</td>
<td></td>
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<tr>
<td>NiCeO$_x$</td>
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<td>Electrochemically activated hydrothermally treated oxidized MWNTs</td>
<td>0.1 M KOH</td>
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<td>450</td>
<td>72</td>
<td>0.2</td>
<td>GC</td>
<td>[91]</td>
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<td></td>
<td>1 M KOH</td>
<td>360</td>
<td>41</td>
<td></td>
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<tr>
<td>Graphitic carbon nitride–CNT composite</td>
<td>0.1 M KOH</td>
<td>300</td>
<td>370</td>
<td>83</td>
<td>0.2</td>
<td>GC</td>
<td>[74]</td>
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<tr>
<td>IrO$_2$/CNT</td>
<td>0.1 M KOH</td>
<td>280</td>
<td>360</td>
<td>90</td>
<td>0.2</td>
<td>GC</td>
<td>[74]</td>
</tr>
<tr>
<td>System</td>
<td>KOH Conc.</td>
<td>Potential (V)</td>
<td>C (mA g(^{-1}))</td>
<td>EE (%)</td>
<td>AE (mA)</td>
<td>Support Material</td>
<td></td>
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<tr>
<td>--------------------------------</td>
<td>-----------</td>
<td>---------------</td>
<td>--------------------</td>
<td>--------</td>
<td>---------</td>
<td>-----------------</td>
<td></td>
</tr>
<tr>
<td>N-doped Co(_3)O(_4)/reduced mildly oxidized graphene oxide</td>
<td>0.1 M KOH</td>
<td>-300</td>
<td>-370</td>
<td>N.A.</td>
<td>0.24</td>
<td>carbon fibre paper</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 M KOH</td>
<td>-270</td>
<td>310</td>
<td>67</td>
<td>1</td>
<td>Ni foam</td>
<td></td>
</tr>
<tr>
<td>Nickel-intercalated birnessite</td>
<td>1 M KOH</td>
<td>-290</td>
<td>400</td>
<td>60</td>
<td>0.28</td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>NiD-PCC</td>
<td>1 M KOH</td>
<td>250</td>
<td>360</td>
<td>98</td>
<td>N.A.</td>
<td>Carbon cloth</td>
<td></td>
</tr>
<tr>
<td>Ni(<em>6)(PET)(</em>{12})</td>
<td>0.1 M KOH</td>
<td>314</td>
<td>-430</td>
<td>69</td>
<td>N.A.</td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>Hierarchical Ni–Co oxide</td>
<td>1 M NaOH</td>
<td>290</td>
<td>340</td>
<td>51</td>
<td>N.A.</td>
<td>FTO</td>
<td></td>
</tr>
<tr>
<td>N doped Co(_9)S(_8)/graphene</td>
<td>0.1 M KOH</td>
<td>280</td>
<td>409</td>
<td>82.7</td>
<td>0.2</td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>Ni–P nanoplate</td>
<td>1 M KOH</td>
<td>250</td>
<td>300</td>
<td>64</td>
<td>0.2</td>
<td>3D electrode</td>
<td></td>
</tr>
<tr>
<td>N and P co-doped porous carbon</td>
<td>0.1 M KOH</td>
<td>-440</td>
<td>-770</td>
<td>N.A.</td>
<td>0.15</td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>Cobalt-based borate ultrathin nanosheets/graphene hybrid</td>
<td>1 M KOH</td>
<td>-270</td>
<td>290</td>
<td>53</td>
<td>0.285</td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>Core-shell NiCo(_2)O(_4) nanowire</td>
<td>1 M NaOH</td>
<td>290</td>
<td>320</td>
<td>63.4</td>
<td>N.A.</td>
<td>Carbon cloth</td>
<td></td>
</tr>
<tr>
<td>LiCo(<em>{0.8})Fe(</em>{0.2})O(_2)</td>
<td>0.1 M KOH</td>
<td>260</td>
<td>340</td>
<td>50</td>
<td>0.232</td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>α-Ni (OH)(_2)</td>
<td>0.1 M KOH</td>
<td>310</td>
<td>330</td>
<td>42</td>
<td>0.2</td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>Electrodeposited Ni–Co oxide (10 at% Co)</td>
<td>1 M NaOH</td>
<td>-280</td>
<td>325</td>
<td>39</td>
<td>N.A.</td>
<td>Au/Cr</td>
<td></td>
</tr>
<tr>
<td>Ultrathin nickel–iron layered double hydroxide nanoplates on mildly oxidized MWNTs</td>
<td>0.1 M KOH</td>
<td>-270</td>
<td>-310</td>
<td>31-35</td>
<td>0.2</td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 M KOH</td>
<td>-220</td>
<td>-240</td>
<td></td>
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</table>


7. Conclusion

In this thesis, we have modified the synthesis process of the CNTs to grow Fe@C core-shell NPs (as active catalysts) and CNTs (as the support) simultaneously. In this novel, fast and low-cost one-step CVD synthesis method, we could grow single-shell carbon-encapsulated iron NPs decorated on SWNTs (SCEIN/SWNT). It has been observed that in the presence of Fe NPs with different particle sizes (mainly 2-5 nm) in the synthesis reactor, the small particles (~ 2-3 nm) form SCEINs while the larger particles catalyze the growth of the SWNTs. It is found that the SCEIN/SWNT is a highly active and stable electrocatalyst for HER in acidic media. The HER activity of the SCEIN/SWNT as a non-precious catalyst has been comparable to that of commercial Pt/C and superior to the best non-precious catalysts reported so far. The encapsulation of iron NPs in a single graphene layer provides a promising technique, by which the reactive metallic iron is protected from oxidation while the desired access of the reactants to the vicinity of the metal core is not prevented. Furthermore, the carbon encapsulation shell protects the Fe core from dissolution into acidic electrolytes and the shell prevents the agglomeration of neighboring NPs during electrochemical reactions, introducing highly stable materials. The same technique can be applied for the encapsulation of other TMs. This work opens new avenues for the growth of metal@C core-shell NPs to make efficient materials in various applications.

We have also found an electrochemical modification method to tune the structure of the carbon-encapsulated iron nanoparticles (CEINs) and CNTs to make active OER electrocatalysts. In this method, a potential above the thermodynamic potential of OER (1.23 V vs. RHE) is applied to the CEIN/few-walled CNT electrode, and consequently the CEINs are quickly changed to high quality crystalline maghemite ($\gamma$-Fe$_2$O$_3$) NPs with an average size of 6.3 nm. This electrochemical modification technique can also be used as a novel method for the selective opening of the CNTs, through which the caps of the CNTs are removed while the sidewalls of the CNTs are preserved. The $\gamma$-Fe$_2$O$_3$/CNT provides a high activity and durability for OER in alkaline media. This work opens new avenues for the electrochemical tuning of the structure of TM@C core-shell NPs and CNTs for different applications.

We have shown that SWNTs are able to atomically disperse Pt on their sidewalls through a simple electroplating method (the SWNT/at-Pt samples). The pseudo-atomic-scale Pt decorated on the SWNTs reveals almost similar HER activity to that of bulk Pt. The SWNT/at-Pt electrodes with the Pt loading of ~ 114-570 ng cm$^{-2}$ exhibit a comparable HER activity to that of the commercial Pt/C electrode with a Pt loading of 38,000 ng cm$^{-2}$. In the SWNT/at-Pt catalysts, the consumption of the expensive and scarce Pt can be minimized, by maximizing the number of active surface Pt atoms, without compromising the high HER catalytic activity. The flat surface of the graphite has shown a significantly lower activation rate with Pt than that...
of observed for SWNTs. This arises from the essential role of the curved structure of the SWNTs which can immobilize the Pt atoms and prevent Pt agglomeration on the surface. Therefore, this work marks a new method to produce highly active catalysts with ultra-low Pt loading and introduces SWNTs as a suitable support to stabilize pseudo-atomic-scale Pt for electrocatalysis.

We have also shown that immobilization of organometallic Ni complexes on MWNTs is a promising strategy to introduce active electrocatalysts. A facile synthesis method has been developed for the covalent immobilization of the Ni-bipyridine (bipy) complexes on the MWNT support. This work reveals that such complexes attached to the MWNTs serve as highly active and durable electrocatalysts for OER in alkaline media. The activity of Ni-bipy-MWNT for OER is superior to many of the active OER electrocatalysts, so that this catalyst can be categorized among the best OER electrocatalysts in alkaline media reported so far. This catalyst exhibited significantly higher activity and durability in comparison to the well-known RuO$_2$ electrocatalyst, which is rare and expensive in comparison to Ni and carbon-based materials. We have developed different characterization techniques such as XPS, Raman and cyclic voltammetry analysis for the organometallic Ni complexes stabilized on the CNTs. These techniques can make characterization of such complex systems easier as suitable analytical methods for these materials have not been widely reported in the literature. Organometallic compounds include a very wide range of materials. Therefore, the idea of using MWNTs to improve the catalytic activity of organometallic complexes can create a valuable technique for the synthesis of a wide range of efficient non-precious catalysts for different applications.
8. References

References

References


Water splitting (WS) is one of the most important non-polluting methods to produce highly pure hydrogen as a clean energy carrier. WS is also a promising technique to store intermittent electrical energy from renewable resources such as solar and wind energy in the form of hydrogen fuel. To expand the use of WS, efficient, stable and low-cost electrocatalysts should be designed to increase efficiency and reduce the cost of the current WS cells. In this thesis, a few synthesis methods have been developed to synthesize novel and low-cost electrocatalysts for WS with improved performance to that of current catalysts. Carbon nanotubes (CNTs) are known for their exceptional properties in various applications. Here, we have shown that CNTs can be also utilized to design highly active and durable electrocatalysts.