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Microwave-assisted Processing of Solid Materials for Sustainable Energy Related Electronic and Optoelectronic Applications

By

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A Doctoral Thesis Submitted in Partial Fulfilment of the Requirements for the Award of Doctor of Philosophy of Loughborough University

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List of Abbreviations

$E_t$ - Electromagnetic radiation energy

$\nu$ - Frequency

$\lambda$ - Wavelength

$\omega$ - Angular frequency

$h$ - Planck's constant

$c$ - Speed of light in vacuum

$P$ - Net polarization

$P_e$ - Electronic polarization

$P_t$ - Ionic polarization

$P_m$ - Molecular (dipole) polarization

$P_s$ - Interfacial (space-charge) polarization

$E$ - Electric field

$\varepsilon'$ - Dielectric constant

$\varepsilon$ - Permittivity

$\mu$ - Permeability

$\varepsilon^*$ - Complex permittivity

$\mu^*$ - Complex permeability

$\varepsilon''$ - Dielectric loss
\( \varepsilon_0 \)- Permittivity of free space

\( \varepsilon_r' \)- Relative permittivity

\( \varepsilon_{eff}'' \)- Effective relative loss factor

\( \mu' \)- Permeability

\( \mu'' \)- Magnetic loss factor

\( \mu_0 \)- Permeability of free space

\( \mu_r' \)- Relative permeability

\( \mu_{eff}'' \)- Effective relative magnetic loss factor

\( \tan \delta \)- Loss tangent

\( P \)- Microwave power absorbed

\( \sigma \)- Total effective conductivity

\( f \)- Frequency of microwaves

D- Penetration depth

\( \lambda_0 \)- Free space wavelength of microwaves

\( E_{vb} \)- Valence band energy level

\( E_{cb} \)- Conduction band energy level

Eg- Band gap

\( E_D \)- Lower edge of the conduction band energy level

\( E_A \)- Upper edge of the valence band energy level
$E_F$- Fermi energy level

$C_{id}$- Interfacial double layer capacitance

$C_{sc}$- Space charge double layer capacitance

$E_{fb}$- Flatband potential

$V_{oc}$- Open circuit potential

$J$- Photocurrent density

$Cp$- Specific heat capacity

$\Delta T$- Rise in temperature

$t$- Time

$P_w$- Power density

$m$- Mass

$n$ - An integer

$d$- Lattice spacing of a (h,k,l) plane

$\theta$- The angle between the incident ray and the scattering planes

$\eta_c$- Electron collecting efficiency

$\varphi_{inf}$ - Electron injection efficiency

$R$- Resistance

$d$- Thickness
Microwave-assisted processing of solid materials for sustainable energy related electronic and optoelectronic applications

Abstract

Materials processing using microwave radiation is emerging as a novel and innovative technology that has proven useful in a number of applications. It has various advantages over conventional processing, such as; time and energy saving, very rapid heating rates, considerably reduced processing time and temperature, fine microstructures and improved mechanical properties, better product performance, etc. Microwave irradiation has shown great potential for the processing of different semiconductor materials and inorganic solids for various advanced electronic and optoelectronic devices such as solar cells, batteries, supercapacitors, fuel cells etc. This work intends to investigate the effect of microwave radiation on various semiconductor materials and inorganic solids, in particular the changes in their chemical, physical and photoelectrochemical properties after microwave treatment. Microwaves have been used as an alternative method to conventional thermal annealing for post annealing of widely used semiconductors (TiO$_2$, ZnO nanorods), battery materials (lithium aluminium titanium phosphates), and synthesis of materials (ZnO, Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$). It is found that, in contrast to conventional thermal annealing, microwave treatment of such materials improves the crystallinity without any structural changes by preserving their nanostructure due to the difference in the heating mechanism (volumetric heating). The results demonstrate that microwave processing is a promising alternative method to the traditional conventional sintering for materials processing for advanced electronic and optoelectronic devices. Also the microwave annealing method offers energy savings of up to ~75%, which would make it highly desirable for industrial scale up.
Chapter 1

Introduction

Before and during World War II, microwave radiation was widely used for telecommunication purposes such as radar, navigation, and sensing.[1] The heating ability of microwaves was accidently discovered in 1947 by Dr. Percy Spencer, an engineer at the Raytheon Company, as he found a candy bar in his pocket had melted during his experiments on a microwave generation tube.[2] Since then, microwave heating has been applied to various fields.[3,4] Microwave ovens for the home were introduced in the early 1950s and by the mid-1970s they became more popular in domestic kitchens for cooking.[4,5] However, the oil shock or natural gas crisis in the 1970s promoted research on microwaves in western countries, due to political pressures to make use of electrical heating methods such as microwaves rather than oil or gas.[5] Since then many researchers have used microwave radiation as an alternative energy source in the synthesis and processing of polymers, ceramics, glass and other organic and inorganic materials. However, the lack of awareness of the fundamental properties of the microwave heating mechanism and its interaction with materials limited the potential use of microwave radiation for these purposes at that time.[3]

Microwave heat generation is fundamentally different from conventional heating methods as the microwave energy absorbed by the material is converted into heat instead of originating from the external heating elements.[6] Conventionally heated ovens and furnaces use resistance heating elements which generate heat by resisting the flow of electricity through them. The heat generated by the elements is then transmitted onto the material being heated through convection, conduction, and radiation, thus heating the materials from outside. Since all materials have a characteristic thermal conductivity, there will always be a thermal
gradient from the surface to the core of the sample. The temperature of the sample may also be lower than that of the furnace due to thermal inertia, with larger samples tending to lag more than smaller ones. In contrast, microwave energy is provided directly to the material through molecular interaction with the electromagnetic field.[7] Microwave heating is the transfer of electromagnetic energy to thermal energy and is energy conversion rather than heat transfer.[8] Due to the ability of microwave radiation to penetrate into the material and supply energy, heat can be generated throughout the volume of the material, resulting in volumetric heating which allows rapid and uniform heating. Therefore, the thermal gradient in a microwave processed material is the reverse of that in a material processed by conventional heating.[9] The temperature profiles of microwave and conventional annealing for a reaction are shown in figure 1-1.

![Figure 1-1. The temperature profiles of microwave and conventional annealing methods of the reaction mixture in the vessel.][10]

In conventional heating, slow heating rates are selected in order to reduce steep thermal gradients which lead to process-induced stresses. As a result, processing time and product quality has to be controlled closely.[8] However, due to the fact that microwaves transfer energy throughout the whole volume of the material there is a potential to reduce processing
time and enhance product quality by preserving the nanostructure. Furthermore, microwave characteristics such as penetrating radiation; controllable electric field distribution; rapid heating; selective heating of materials and self-limiting reactions lead to benefits and opportunities that are not available to conventional heating methods.[11] All in all, microwave heating is believed to be an advantageous alternative to conventional methods for the processing of materials.

The microwave absorbing characteristics of materials are related to the dielectric and magnetic properties such as, electric permittivity (ε) and magnetic permeability (μ) and the extent of heat generation by absorbed energy is determined by the loss tangent (tan δ) of the material. Therefore, when microwaves are in contact with materials of different dielectric properties, they will selectively couple with the higher loss tangent material and generate heat. The application of microwave energy to the processing of various materials such as ceramics, metals and composites offers several advantages over conventional heating methods.[12] These advantages include unique microstructure and properties, improved product yield, energy savings, reduction in manufacturing cost and synthesis of new materials. Due to the fact that materials are heated volumetrically, materials with a uniform microstructure can be produced using microwave heating, if energy losses from the surface are minimized. The nature of microwave heating is also much more efficient compared to resistance heating.[13] Due to these characteristics of microwave heating, microwave irradiation has great potential for the processing of different inorganic solids and semiconductor metal oxides (such as TiO₂, ZnO, NiO and iron oxides) which are used heavily in making many electronic and optoelectronic devices.[14-17] Also due to the lower processing temperature requirements, the microwave process can open up the possibility of fabricating thin films of photoactive semiconductors on conducting plastic substrates which are highly important in making flexible devices.[18]
Main objectives of the project

The main objectives of this project include, monitoring the structural and functional changes of metal oxides on post-treatment under microwave radiation, identify the morphological and structural changes of semiconductor materials against microwave and conventional radiant post-treatment methods and find out the physical properties of mixed metal oxides against microwave irradiation and microwave processing of widely used semiconductor materials and glass ceramics to make a significant contribution to the improved power performance of optoelectronic and energy storage devices.

The studies were conducted under the following themes in order to achieve the project objectives,

(a) Monitor the changes of the physical, chemical and photoelectrochemical properties of metal oxide thin films with different doses of microwave radiation.

(b) Identify the structural and morphological changes of the materials during the post treatment step under microwave radiation and conventional heating methods.

(c) Compare the different effects of microwave and conventional annealing techniques on a range of properties (i.e. structural, morphological, and functional) of different materials.

(d) Microwave processing of semiconductor materials and glass ceramics to make a significant contribution to the improved power performance of electronic and optoelectronic devices such as lithium-ion batteries and solar energy devices.

The thesis contains ten chapters including four results and discussion chapters. The first chapter is the introduction and is followed by the second chapter which consists of a literature review explaining the fundamentals of microwave radiation, physical aspects of sintering, microwave processing of materials, including the interaction of microwave and materials, and
the mechanism of microwave heating, the microwave effect and recent developments in the field of microwave processing and organic/inorganic material synthesis. Chapter three contains a description of the experimental methods used for thin film preparation and material characterisation of thin films and inorganic materials. Chapter 4 is the first result and discussion chapter which compares the effect of microwave annealing on the photoelectrochemical (PEC) properties of TiO$_2$ photoelectrodes. Chapter 5 focuses on the effect of post annealing on the structure and PEC properties of ZnO nanorods by conventional thermal and microwave heat treatments. Chapter 6 compares the efficiency of oxidation of electrodeposited metallic Zn to ZnO using conventional thermal and microwave annealing methods in terms of their PEC performance. The work conducted for Johnson Matthey Plc is reported in chapter 7 which contains two sub sections. The first section reports the structural and morphological changes of Pd$^{2+}$ incorporated TiO$_2$ (Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$) synthesised using microwave-assisted and conventional synthesis methods and the second section reports the effect on the electrical conductivity and structural properties of microwave and conventionally treated lithium aluminium titanium phosphate pellets. Each results and discussion chapter contains an overview, introduction, experimental, results and discussion and conclusion. Chapter 8 discuss the conclusions of the thesis along with the future work. Chapter nine and ten comprise the references and appendix respectively.
Chapter 2

Literature review

2.1 Theory and Background

2.1.1 Microwave fundamentals and microwave heating

Electromagnetic radiation is a form of energy that exhibits wave-like behaviour as it travels through space. It has both electric and magnetic field components, which oscillate in phase perpendicular to each other and perpendicular to the direction of energy propagation as in figure 2-1.[19] The electromagnetic theory was first presented by James Clerk Maxwell in 1864.[20]

![Figure 2-1. Electric and magnetic field components of electromagnetic radiation.[19]](image)

Electromagnetic radiation is classified by the wavelength into radio waves, microwaves, infrared radiation, visible light, ultraviolet radiation, X-rays and gamma rays as shown in Figure 2-2.
In the electromagnetic spectrum, microwaves are found in a transitional region between infrared and radio frequency radiation. The wavelengths are between 1 cm and 1 m and frequencies between 300 GHz and 300 MHz.[22] Microwaves can be further classified into three bands: the ultra-high frequency (UHF) band with frequencies ranging from 300 MHz to 3 GHz, the super-high frequency (SHF) band with frequencies ranging from 3 to 30 GHz and the extremely-high frequency (EHF) band with frequencies ranging from 30 to 300 GHz.[23] Although microwave frequencies range from 300 MHz to 300 GHz, most of the frequencies are restricted to government usage, leaving only a limited range of frequencies available for commercial and domestic usage.[24] The international telecommunication union (ITU) operating within the United Nations system provides the basic framework that is relevant for the international radio-regulatory arrangement. Regulatory authorities for different countries utilize the international table of frequency allocations of the ITU as a guideline to release certain bands termed as industrial, scientific and medical (ISM) bands for unregulated usage.[25] To avoid interference with telecommunications and cellular phone frequencies, heating applications must use unregulated ISM bands of 915 MHz, 2.45 GHz and 5.8 GHz.[26] Domestic ovens and laboratory microwave furnaces usually work at 2.45 GHz (i.e. wavelengths of 12.24 cm).[27]
Microwaves travel in the same way as light waves; they also change direction when travelling from one dielectric material into another; they are reflected by metallic objects, absorbed by some dielectric materials, and transmitted without significant absorption through other dielectric materials as shown in figure 2-3.[28]
microwave photon energy is not sufficiently energetic to break hydrogen bonds; it is also much smaller than that of Brownian motion. Therefore, there is no possibility to break chemical bonds of materials by absorbing microwave energy.

Table 1. Brownian motion and bond energies.[31]

<table>
<thead>
<tr>
<th></th>
<th>Brownian motion</th>
<th>Hydrogen bonds</th>
<th>Covalent bonds</th>
<th>Ionic bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (eV)</td>
<td>~0.017 (200 K)</td>
<td>~ 0.04 to 0.44</td>
<td>~ 4.51 (C-H); ~ 3.82 (C-C)</td>
<td>~ 7.6</td>
</tr>
<tr>
<td>Energy (kJ mol⁻¹)</td>
<td>1.64</td>
<td>~ 3.8 to 42</td>
<td>~ 435 (C-H); ~ 368 (C-C)</td>
<td>~ 730</td>
</tr>
</tbody>
</table>

2.1.2 Polarization mechanisms of materials

It has long been known that dielectric materials may be heated with the interaction of high frequency electromagnetic radiation. The heating effect arises from the interaction of the electric field component of the electromagnetic radiation with the dipoles in the material. When the dipoles of materials are subjected to an external electric field, it undergoes internal charge separation by aligning the positive end with the lower potential and the negative end with the higher potential.[32] This conversion of electromagnetic energy into molecular motion and through that into heat can be described by different mechanisms. The two main heating mechanisms, polarization and conduction are responsible for the heating of materials.[22] The interaction of electromagnetic radiation with dielectric materials can cause net polarization in materials. There are several mechanisms which are responsible for the polarization, including: electronic, ionic, molecular (dipolar) and interfacial (space-charge) polarization. Therefore, for a dielectric material the net polarization, \( P \), is determined by the sum of the contributions from each mechanism, this can be seen in equation 2.
where, \( P_e \) is electronic polarization, \( P_1 \) is ionic polarization, \( P_m \) is molecular (dipole) polarization and \( P_s \) is interfacial (space-charge) polarization.

2.1.2.1 Electronic polarization

This is caused by the displacement of the electron cloud of the material relative to its nucleus. Heating by electronic polarization originates by shifting of electrons from equilibrium, with respect to the positive nuclei, in the direction of the electric field \( (E) \) (Figure 2-4).

![Figure 2-4. The electronic polarization in dielectric materials.](image)

2.1.2.2 Ionic (atomic) polarization

Ionic polarization takes place due to the displacement of positive and negative ions toward the negative and positive electrodes, under an applied field \( (E) \), the resulting separation of charge yields a displacement of the cations and anions relative to their equilibrium positions (figure 2-5).
2.1.2.3 Molecular (dipolar) polarization

In their normal state, molecules are randomly oriented in the material in a way that there is no net charge present. In molecular or dipolar polarization permanent dipoles align parallel to the external field \( E \) (figure 2-6). Dipolar polarization is the phenomenon responsible for the majority of microwave heating effects specially observed in solvent systems.

2.1.2.4 Interfacial (Space-charge) polarization

In interfacial or space-charge polarization mobile charge carriers in a heterogeneous material migrate an appreciable distance through the dielectric until they are trapped or impeded by
physical barriers. This build-up of charge dictates the polarization of the material. Grain/phase boundaries and free surface are common barriers (figure 2-7).

![Figure 2-7. The interfacial (Space-charge) polarization in dielectric materials.](image)

2.1.3 Microwave heat generation

Under low frequency irradiation ($10^3$-$10^6$ Hz), dipoles of the material align themselves in phase with the electric field of the radiation. However, the overall heating effect is trivial. Conversely under very higher frequency radiation ($10^{15}$-$10^{18}$ Hz) the dipoles do not have sufficient time to respond to the changing electric field so generally no motion is induced in the dipoles. This means no energy transfer takes place and so no heating takes place either. In between these two extremes, at frequencies ranging from $10^9$-$10^{12}$ Hz (i.e. microwave region), is the ideal frequency to induce molecular rotations. The microwave frequency is low enough that the dipoles have time to respond to the alternating field, and therefore to rotate, but high enough that the rotations does not precisely follow the direction of the electric field. Due to this the dipoles of the material, lagging behind the changing electric fields, causes molecular friction, which in turn is converted into heat. Dipolar and ionic polarization mechanisms are the dominant mechanisms that cause heating of dielectric materials at microwaves frequencies.\cite{33} In dipolar polarization, dipoles of the material tend to align in
the direction of an external electric field and hence are polarized. The degree of polarization \( P \) is related to the dielectric properties of the material through the relation in equation 3,

\[
P = \varepsilon_0 (\varepsilon'_r - 1)E
\]

where \( \varepsilon_0 \) is the permittivity of free space (\( \varepsilon_0 = 8.86 \times 10^{-12} \text{ F m}^{-1} \)), \( \varepsilon'_r \) is the relative permittivity of the material and \( E \) the applied electric field strength.

When an oscillating electric field is applied to a material by microwave radiation, the dipoles are constantly trying to align with the changing electric field (Figure 2-8a). The frequency of the field determines the way in which the orientation of the dipole affects the material. The mechanism of ionic polarization is similar to that of dipolar polarization (Figure 2-8b). When charge carriers in a material are subjected to an electric field, they are subjected to a force. The alternation of the electric field causes the direction of the force to alternate equally. This alternation leads to molecular motion, and collision, and thus generates heat.

![Figure 2-8. Two main heating mechanisms under microwave irradiation: (a) dipolar polarization; (b) ionic polarization.][34]
2.1.4 Microwave-material interactions

The electric field component of the electromagnetic wave may be reflected, transmitted or absorbed by materials. Also certain materials such as magnetic materials interact with the magnetic field component of the electromagnetic wave. Generally materials can be categorized in to four types with respect to their interaction with the microwave field.

1. Transparent or low dielectric loss materials: low loss tangent materials or insulating materials, which reflect and absorb electromagnetic waves to a negligible extent and allow microwaves to pass through them easily with little attenuation (i.e. glass, ceramic, and air).

2. Opaque or conducting materials: typically conducting materials with free electrons, such as metals, that reflect and do not allow electromagnetic waves to pass through (i.e. most of metals including steel, Al, and Cu).

3. Absorbing or high dielectric loss materials: materials whose properties range from conductors to insulators. They are usually referred to as lossy dielectrics or high dielectric loss materials and absorb electromagnetic energy and convert it to heat (i.e. SiC, CuO, TiO$_2$, ZnO, and iron oxide).

4. Magnetic materials: materials such as ferrites which interact with the magnetic component of the electromagnetic wave and get heated (i.e. Fe$_2$O$_3$, Fe, Ni, and Co).

Microwaves pass through transparent or low dielectric loss materials with little attenuation, opaque or conducting materials reflect the radiation without penetration and absorbing or high dielectric loss materials absorb microwave radiation in different levels based on their dielectric properties. The exact nature of microwave-material interaction and hence heat generation depends upon the mobility of charges in dielectric materials. When the charges are bound as dipoles in the material, the changing electric field of the microwaves induces
motion until it is balanced by the electrostatic interaction which leads to polarization.[35]

Similarly, in ionic conduction, ions in the material are forced to move with the changing electric field until the net charge is balanced. If the charge carriers are mobile, the altering microwave field gives rise to a current flow which could cause resistive heating in the material. However, heat generation of composites or multi-phase materials upon microwave irradiation may involve both heating mechanisms and resistive heating.[36]

The interaction of microwaves with matter is quantified by the two complex physical quantities; dielectric permittivity, \( \varepsilon \), and permeability (magnetic susceptibility), \( \mu \).[31] In reality, the permittivity and permeability are complex quantities which are defined as \( \varepsilon^* \) and \( \mu^* \) respectively as below equations 4 and 5,[37]

\[
\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_0 \left( \varepsilon'_r - i\varepsilon''_r \right) \tag{4}
\]
\[
\mu^* = \mu' - i\mu'' = \mu_0 \left( \mu'_r - i\mu''_r \right) \tag{5}
\]

where \( \varepsilon' \) is the dielectric constant which represents the time-independent polarizability of a material in the presence of an external electric field, that is to say it measures the resistance encountered when forming an electric field in a medium. \( \varepsilon'' \) is the dielectric loss or loss factor of the material, this indicates the time-dependent component of the permittivity which quantifies the ability of the material to convert absorbed energy into heat. \( \varepsilon_0 \) is the permittivity of free space (\( \varepsilon_0 = 8.86 \times 10^{-12} \text{ F m}^{-1} \)) and \( \varepsilon'_r \) is the relative permittivity of the material which is the ratio of the permittivity of a substance to that of free space or vacuum. \( \varepsilon''_r \) is the effective relative loss factor. \( \mu' \) is the magnetic permeability, \( \mu'' \) magnetic loss factor, \( \mu_0 \) the permeability of free space (\( \mu_0 = 4\pi \times 10^{-7} \text{ H m}^{-1} \)), \( \mu'_r \) is the relative permeability of the material and \( \mu''_r \) is the effective relative magnetic loss factor.

The dielectric properties of materials vary with the frequency due to the effect of the changing electric field on the movement of the charged species. The figure 2-9 shows the
frequency response of dielectric constant and dielectric loss for a typical dielectric material showing various phenomena caused by different polarization mechanisms across the electromagnetic spectrum.[38] The decrease of the complex permittivity, $\varepsilon^*$ shows itself as a decrease in dielectric constant and rise of dielectric loss.

![Diagram of Frequency response of dielectric constant](image)

Figure 2-9. Frequency response of the complex permittivity for a typical dielectric material due to different polarization mechanisms.[39]

As discussed, the heating effect usually arises from the interaction of the electric field component of the microwaves with charged species in the materials. The dielectric constant signifies the ability of the material to absorb microwaves and store energy. Dielectric loss represents the ability of the material to convert absorbed energy into heat. The ratio of the dielectric loss to the dielectric constant is known as the loss tangent ($\tan \delta$) which is given in equation 6,[40]

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$  \hspace{1cm} (6)

The angle $\delta$ represents the phase lag between the polarization of the material and the applied electric field. In order for microwaves to interact with the material, a balanced combination of
moderate dielectric constant (to permit adequate penetration) and high loss tangent (for higher energy to heat conversion) are required.[41]

The microwave power absorbed per unit volume of a material, \( P \) (W m\(^{-3}\)) is expressed as,[37]

\[
P = \sigma |E|^2 = 2\pi f \varepsilon_0 \varepsilon'_r \tan \delta |E|^2
\]  

where, \( E \) (V m\(^{-1}\)) is the magnitude of the internal field, \( \sigma \) the total effective conductivity (Sm\(^{-1}\)) and \( f \) the frequency (GHz). The above equation demonstrates that the power absorbed by the material varies linearly with the frequency, the relative dielectric constant, loss tangent and the square of the electric field.[23]

The penetration depth (\( D \)) of microwaves is a measure of how deep microwave radiation can penetrate into a material. The penetration depth of a material can be calculated using equation (8), which shows how it depends on the dielectric properties of the material. The penetration depth of microwaves at which the incident power is reduced by one half is expressed in equation 8,[26]

\[
D = \frac{3\lambda_0}{8.686 \pi \tan \delta \sqrt{\varepsilon'_r}}
\]  

At a frequency of 2.45 GHz, the free space wavelength \( \lambda_0 \) is 122.4 mm. The calculated penetration depths for TiO\(_2\) and ZnO are 0.5 \( \mu \)m and 0.4 \( \mu \)m respectively.

In general, if the penetration depth exceeds sample thickness, the material behaves as transparent to microwaves. The volumetric heating only results when the penetration depth is comparable with the sample thickness. If the sample is too thick, absorption is limited to the surface.[42]

The relative dielectric constant and the loss tangent are the parameters that describe the behaviour of a dielectric material under the influence of a microwave field. During heating,
the relative dielectric constant and the loss tangent change with temperature. It is clear that
the power density will decrease exponentially from the surface to the core region. In order for
microwaves to interact with the material and heat generation, a balanced combination of
moderate dielectric constant (to permit adequate penetration) and high loss tangent (for
higher energy to heat conversion) are required. Therefore it is clear that microwave heat
generation in materials depends on many factors. These include power level, electric field
distribution and material properties including dielectric constant, penetration depth, loss
tangent, thermal and electrical conductivity, microstructure, size, shape of the grains, the
amount of porosity, pore size, the distribution of the pores in the structure etc. The post heat
treatment of semiconductor materials using microwaves or conventional methods helps to
improve particle inter-connections and produces structural and morphological changes. These
changes are very important in determining the electronic and photoelectrochemical
performance of a material.

2.1.5 Semiconductor photonic materials

The generation of current through exposure to light is of foremost importance in
semiconductor electrodes due to the photochemical properties of the
semiconductor/electrolyte interface which is vital in solar energy conversion. The electronic
structure of materials determines the properties of semiconductor and metallic electrodes. The
electronic structure of these materials is typically discussed in terms of energy bands, which
are made up of the atomic orbitals of the individual atoms.[43] Due to the large number of
atomic orbitals of such materials, the difference in the energy between adjacent orbitals
within a given energy band is quite small such that the band can effectively be considered a
continuum of energy levels. The highest and lowest energy levels of a band are referred to as
the band edges. The highest occupied energy band is called the valence band (E_{vb}) whereas
the lowest unoccupied energy band is called the conduction band ($E_{cb}$). The difference in energy between the upper edge of the valence band and the lower edge of the conduction band is the band gap ($E_g$), this determines the properties of the material. Conductivity of a solid state material requires that the electrons occupy partially filled orbitals which can be achieved by occupancy of the conduction band. For metals, the conduction and valence bands overlap, so the conduction band can be readily occupied.[44] For insulators, the band gap is sufficiently large that electrons cannot be promoted from the valence band to the conduction band. Forsemiconductors the band gap is not as large and electrons can be moved into the conduction band with relative ease. Figure 2-10 illustrates the electronic energies of metals, semiconductors and insulators.

Electrons can be excited either thermally or photochemically into a material’s conduction band, leaving behind positively charged vacancies in the valence band. Doping is another method for generating charge carriers (i.e., electrons or holes) within a semiconductor. Doping involves the addition of another element, which has different levels of charge, into the semiconductor. The introduction of a group V element (e.g., P, As, Sb) or a group III
element (e.g., Al, Ga, In) into a group IV element (e.g., Si, Ge) is a simple example of doping. Doped semiconductors can be categorized into two types depending on their dominant charge carriers. The addition of group V element into group IV elements introduces occupied energy levels into the band gap close to the lower edge of the conduction band ($E_D$), thus allowing facile promotion of electrons into the conduction band, as shown in figure 2-11. In this case the majority charge carriers are electrons and these semiconductors are referred to as n-type semiconductors.

![Diagram of an n-type semiconductor]

**Figure 2-11.** Schematic energy diagram of an n-type semiconductor.

The addition of group III elements introduces vacant energy levels into the band gap close to the upper edge of the valence band ($E_A$), this allows facile promotion of electrons from the valence band. This leads to the formation of holes in the valence band. The figure 2-12 illustrates the schematic energy diagram of a p-type semiconductor.
Undoped semiconductors are referred to as intrinsic semiconductors and the schematic energy diagram is shown in figure 2-13.
The Fermi level is another important concept in solid state materials. The energy of the least tightly held electrons within a solid is specified by the Fermi level ($E_F$), which was first proposed by Enrico Fermi. The Fermi energy is the value of the Fermi level at absolute zero ($−273.15 °C$) and each solid has a unique Fermi energy value. However, the position of the Fermi level changes with the electron density of the energy levels of the solid. To define it the Fermi level is any energy level having the probability that it is exactly half filled with electrons. Levels with lower energy than the Fermi level tend to be entirely filled with electrons, whereas energy levels higher than the Fermi tend to be empty. For an intrinsic semiconductor the Fermi level lies at the mid-point of the band gap (Figure 2-13) whereas Fermi levels of n-type and p-type semiconductors reside just below the conduction band (Figure 2-11) and just above the valence band (Figure 2-12) respectively. The position of the Fermi level changes with addition or removal of electrons from a solid. When solids with different individual Fermi levels are placed in contact, electrons flow from the solid with the higher Fermi level into the solid with the lower Fermi level. This transfer of electrons raises the lower Fermi level and lowers the higher Fermi level until the Fermi levels of the two solids are equal. The photoelectrochemical performance of semiconductor electrodes is usually determined in three electrode systems using an aqueous electrolyte. The band theory of solid/liquid interfaces is discussed in the next paragraph in order to understand the band energetic of such systems.

The Fermi level of a semiconductor or metallic electrode varies with the applied potential, i.e. moving to more negative potentials will raise the Fermi level and vice versa. In order for the semiconductor and electrolyte phases to be in equilibrium in the idealized semiconductor interface, their electrochemical potential must be equal. The electrochemical potential of the solution is determined by the redox potential of the electrolyte solution and the potential of the semiconductor is determined by the Fermi level. The redox potential of the solution and
the Fermi level of the semiconductor should lie at the same energy in order to equilibrate the two phases which can be achieved by a movement of charge between the semiconductor and the electrolyte. Unlike metallic electrodes, the excess charge located on the semiconductor at equilibrium does not lie at the electrode surface, but extends into the electrode for a significant distance ranging 100-10,000Å. Generally, this region is referred to as the space charge region, and has an associated electrical field generated by the associated charge separation. Therefore due to this, there are two double layers to be considered in the electrode/electrolyte system namely the interfacial (electrode/electrolyte) double layer and the space charge double layer. These layers act much like a capacitor. The capacitance associated with the space charge double layer is much smaller than the electrode/electrolyte double layer. Typical values for interfacial double layer capacitance ($C_{id}$) range from 10-100 µF cm$^{-2}$ whereas, space charge double layer capacitance ($C_{sc}$) range from 0.001 – 1 µF cm$^{-2}$. Since these capacitors are in series, the smallest capacitor will govern the response of the system as confirmed from equations 9 and 10.[45]

$$\frac{1}{C_T} = \frac{1}{C_{id}} + \frac{1}{C_{sc}}$$  \hspace{1cm} (9)

Therefore,

$$C_T = \frac{C_{id} C_{sc}}{C_{id} + C_{sc}} = C_{sc} \text{ if } C_{id} \gg C_{sc}$$  \hspace{1cm} (10)

The bands in the bulk of the semiconductor will move with changes in applied potential and the potential drop will appear in a region near the surface of the semiconductor (i.e. space charge region). Thus, for an ideal semiconductor/electrolyte interface, the major portion of the potential drop occurs in the semiconductor with very little in the solution side.
2.1.6 Energetics at semiconductor-electrolyte interface

For an n-type semiconductor electrode at open circuit, the Fermi level is typically higher than the redox potential of the electrolyte, and hence electrons will be transferred from the electrode into the solution. Therefore there is a positive charge associated with the space charge region and this is reflected in an upward bending of the band edges (figure 2-14). Since the majority charge carrier of the semiconductor has been removed from this region, this region is also referred to as a depletion layer.

![Depletion Region Diagram](image)

**Figure 2-14.** Band bending of an n-type semiconductor.

For a p-type semiconductor, the Fermi layer is generally lower than the redox potential, hence electrons must transfer from the solution to the electrode to attain equilibrium. This generates a negative charge in the space charge region which causes a downward bending in the band edges (Figure 2-15). Since the holes in the space charge region are removed by this process, this region is again a depletion layer.
The Fermi level of a metallic electrode varies with the applied potential as the electron population of the electrode changes. The band edges in the interior of the semiconductor also vary with the applied potential in the same way as the Fermi level. However, the energies of the band edges at the interface are not affected by changes in the applied potential. Therefore there is a change in the energy of the band edges between the interior of the semiconductor and the interface, hence the magnitude and direction of band bending varies with the applied potential. At a certain potential the Fermi energy lies at the same energy as the solution redox potential. There is no net transfer of charge and hence there is no band bending. This potential is therefore referred to as the flatband potential ($E_{fb}$). The energy band diagrams of n-type and p-type semiconductors at flat band conditions are shown in figures 2-16 and 2-17 respectively.
Depletion regions arise at potentials positive of the $E_{fb}$ for an n-type semiconductor and at potentials negative of $E_{fb}$ for a p-type semiconductor. Figures 2-18 and 2-19 show the energy band diagrams of n-type and p-type semiconductors under depletion conditions at various applied potentials respectively.
Figure 2-18. The energy band diagrams of an n-type semiconductor when applied potential is higher than the $E_{fb}$.

Figure 2-19. The energy band diagrams of a p-type semiconductor when applied potential is lower than the $E_{fb}$.

At potentials negative of the $E_{fb}$ for an n-type semiconductor there is now an excess of the majority charge carrier (electrons) in this space charge region, this is referred to as an accumulation region. An accumulation region arises in a p-type semiconductor at potentials more positive than the $E_{fb}$. Figures 2-20 and 2-21 show the energy band diagrams of n-type
and p-type semiconductors under accumulation conditions at various applied potentials respectively.

Figure 2-20. The energy band diagrams of an n-type semiconductor when applied potential is lower than the $E_{fb}$.

Figure 2-21. The energy band diagrams of a p-type semiconductor when applied potential is higher than the $E_{fb}$.

The charge transfer abilities of a semiconductor electrode depend on whether there is an accumulation layer or a depletion layer. If there is an accumulation layer, the behaviour of a
semiconductor electrode is similar to that of a metallic electrode, since there is an excess of the majority of charge carrier available for charge transfer.

In contrast, if there is a depletion layer, then there are few charge carriers available for charge transfer and electron transfer reactions occur slowly. If the electrode is exposed to radiation of sufficient energy electrons will be promoted to the conduction band. If this process occurs in the interior of the semiconductor, recombination of the promoted electron and the resulting hole typically occurs together with the production of heat. However if it occurs in the space charge region, the electric field in this region will cause the separation of the charge. Metallic contacts are used to collect the separated electrons and holes in solid-state devices whereas redox species are used as carriers to collect electrons and holes in photoelectrochemical devices. In photoelectrochemical devices, band edges of n-type semiconductors at positive potentials \( (E > E_{fb}) \) curve upwards and hence the hole moves towards the semiconductor/electrolyte interface whilst the electron moves to the interior of the semiconductor. The hole is a high energy species that can extract an electron from a redox species in the electrolyte. The suitability of the redox species is determined by the type of semiconductor and its energetic positions. The energy levels for redox species arise by virtue of the donors \((Red)\) and acceptors \((Ox)\) in electrolyte.[46]

\[
Ox + e^- \leftrightarrow Red
\]

Redox species in the electrolyte are oxidized at the surface of illuminated n-type semiconductors whereas reduction occurs at illuminated p-type semiconductors. A simplified picture of the charge separation at the semiconductor/electrolyte interface of n-type and p-type semiconductors under illumination conditions is given in figures 2-22 and 2-23 respectively.
Figure 2-22. A simplified picture of the charge separation at the semiconductor/electrolyte interface for an n-type semiconductor under illumination conditions.

Figure 2-23. A simplified picture of the charge separation at the semiconductor/electrolyte interface for a p-type semiconductor under illumination conditions.
2.1.7 Ideal behaviour of an n-type semiconductor under dark and light

The Ideal behaviour for an n-type semiconductor electrode in the dark and under light is shown in figure 2-24.

Figure 2-24. Ideal behaviour for an n-type semiconductor in (a) dark and (b) under light in an electrolyte.

As there is no electric field to separate any generated charge carriers at the $E_{fb}$, no current is generated either in the dark or under the light (R2). An accumulation layer exists when the potential is negative to the $E_{fb}$. Under these conditions the electrode can act as a cathode under both light and dark (R1). Under these conditions the electrode is referred to as a dark cathode. At potentials positive to the $E_{fb}$ a depletion layer exists, so there is no oxidative current in the dark (R3). Under the light conditions however, a photocurrent can be observed at potentials negative of the redox potential of the electrolyte (which lies at $E_o$). Some of the energy required for the oxidation reaction is provided by the radiation (via the high energy hole). Using similar reasoning, it can be shown that p-type semiconductor electrodes are dark anodes and photocathodes.
2.2 Microwave synthesis and processing of materials

In organic and inorganic material synthesis, some or all the reactants involved in the reaction should have a high coupling efficiency with microwaves. This provides adequate energy to overcome the activation energy barrier, allowing the reaction to proceed. The microwave absorbing properties of the reactants facilitate the rapid heating and lead to successful synthesis of the target material within a very short period of time. In the microwave-assisted synthesis, one often selects alternative reactants with favourable dielectric properties in order to achieve maximum product yield. If there are no alternative microwave absorbing reactants available for material synthesis, it is usually possible to find a secondary material that can act as a heat source; this is commonly referred to as a microwave susceptor. Microwave susceptors are substances that have the ability to absorb microwave energy and convert it to heat. In other words, a susceptor is a material that has a high dielectric loss tangent. Graphitic or amorphous carbon,[47-49] silicon carbide[49-51] and copper (II) oxide[52,53] are some of the examples of commonly used susceptors. These susceptor materials can be kept either in direct contact with the sample (by mixing with the other regents) or placed outside (surrounding the sample). In some cases adding a susceptor into a reaction mixture can cause problems with the final product purity, yield and reaction rate.[35] Microwave susceptors can also be used in material post heat treatments to ramp up the temperature of poorly microwave absorbing materials. In such cases, the penetration depth plays a vital role in the heat generation. If the penetration depth exceeds susceptor thickness, the susceptor behaves as if it is transparent to microwaves.[54] The volumetric heating only occurs when the penetration depth is comparable to the sample thickness. If the sample is too thick, absorption is limited to the surface. The physical nature of materials, such as particle size, density and the medium
the material is present in, also determines the microwave penetration depth.[55] The variation of the penetration depth of SiC with the above physical properties is shown in figure 2-25.

![Figure 2-25. The variation in the penetration depth of microwaves with the density and the dispersion medium of SiC.](image)

As indicated in the figure 2-25 the penetration depth of SiC varies with the density and the nature of the particle dispersion in the medium. This affects the microwave coupling and heat generation. Generally SiC is an abrasive material with a high density. The microwaves couple with SiC as a whole and penetrate well into the material to generate heat effectively because of its high density (figure 2-25a). When the SiC particles are dispersed in a dielectric medium, (such as water, ethanol etc.) microwaves interact with SiC particles as well as the dielectric medium to generate heat. Since both media couple well with microwaves, the penetration depth of such system (which determines by the sum of the contributions from each material’s dielectric properties) are reasonably high, this leads to heat generation (figure 2-25b). In the case of SiC powders the voids between the particles are filled with air which is transparent to microwaves. Thus heat generation is only influenced by the particle size of SiC (figure 2-25c). In order to generate volumetric heating in SiC powders the penetration depth of microwaves needs to be comparable with the particle size of SiC (diameter of the particles). Therefore, it is not possible to heat SiC nanoparticles (< 100 nm) by microwaves unless they are mixed with another dielectric matrix.
2.2.1 Semiconductor metal oxides

Over the past decade many oxide compounds have been synthesised using microwave radiation. In most of the literature it is claimed that use of microwaves in microwave-assisted synthesis shortens the reaction times and reaction temperatures significantly compared to conventional synthetic techniques.[56] It is also noted that lattice distortions, electronic structure variations, nanostructure size and shape for metal oxides are affected when synthesised using microwave radiation.[56,57] Table 2 shows some of the metal oxides that have been synthesised using microwave radiation. They are listed by main experimental conditions, size and morphological features of the resulting nanostructures, mechanistic pathways involved, and growth-governing factors.

Table 2. The list of microwave-assisted synthesised metal oxides.[58]

<table>
<thead>
<tr>
<th>Metal oxide</th>
<th>Precursors</th>
<th>Formation mechanism</th>
<th>Crystalline features</th>
<th>Reaction condition</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>Mg(OAc)$_2$</td>
<td>polymer-assisted growth</td>
<td>amorphous powders; 3.2 nm particles after annealing</td>
<td>30 min</td>
<td>[58]</td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td>Bi(NO$_3$)$_3$</td>
<td>polymer-assisted growth</td>
<td>rods (2×30 μm)</td>
<td>6 min reflux</td>
<td>[59]</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>Ce(NO$_3$)$_2$</td>
<td>ligand-assisted growth self-aggregation</td>
<td>14 nm spheres assembled in hollow spheres (range 260 nm)</td>
<td>&gt;30 min 170 °C</td>
<td>[60]</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>(NH$_4$)$_2$Ce(NO$_3$)$_6$ CeCl$_3$</td>
<td>ion-assisted growth</td>
<td>spheres, 1.5–20 nm rods 7.5×30 nm</td>
<td>&gt;60 min 160 °C</td>
<td>[61]</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>(NH$_4$)$_2$Ce(NO$_3$)$_6$</td>
<td>polyl-assisted growth</td>
<td>spheres average 2 nm</td>
<td>10 min 30 s MW cycles (9 s on/21 s off)</td>
<td>[62]</td>
</tr>
<tr>
<td>Compound</td>
<td>Formula</td>
<td>Precipitation Method</td>
<td>Product Description</td>
<td>Conditions</td>
<td></td>
</tr>
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<td>---------------</td>
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<td>-----------------------------------------------------------</td>
<td>---------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>(NH$_4$)$_2$Ce(NO$_3$)$_6$</td>
<td>Polyol-assisted growth</td>
<td>Spheres 2–3 nm</td>
<td>10 min 30 s MW cycles (9 s on/21 s off) 100 °C 1 atm</td>
<td></td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>(NH$_4$)$_2$Ce(NO$_3$)$_6$</td>
<td>Co-precipitation</td>
<td>Spheres 5.1±0.1 nm</td>
<td>5–240 min 194 °C 3–14 atm</td>
<td></td>
</tr>
<tr>
<td>Cd(OH)$_2$</td>
<td>Cd(NO$_3$)$_2$</td>
<td>Oriented aggregation</td>
<td>Nanowires 5–30 nm×0.3 μm</td>
<td>5 min</td>
<td></td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>Co(NO$_3$)$_2$</td>
<td>Ligand-assisted growth</td>
<td>Nanocrystals no singular shapes</td>
<td>15 min</td>
<td></td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>CoCl$_2$</td>
<td>Ligand-assisted growth (crystallization requires annealing at 300 °C required)</td>
<td>Nanowires 80 nm×2 μm</td>
<td>6 h 110 °C</td>
<td></td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>Co(NO$_3$)$_2$</td>
<td>Ligand-assisted growth</td>
<td>Flakes arranged in Flower-like shapes 2–3 μm</td>
<td>15–90 min 85 °C</td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>Cu(OAc)$_2$</td>
<td>Ligand-assisted growth</td>
<td>Spheres average 4 nm</td>
<td>10 min 30 s MW cycles (6 s on/24 s off) reflux</td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>CuCl$_2$</td>
<td>Ion-assisted growth</td>
<td>Flower-like or leaf-like nanocrystals</td>
<td>10 min 80 °C</td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>CuCl$_2$</td>
<td>Oriented attachment</td>
<td>Urchin-like structures</td>
<td>15 min 100 °C</td>
<td></td>
</tr>
<tr>
<td>CuO.Cu$_2$O$_3$.Cu</td>
<td>Cu(OAc)$_2$</td>
<td>Ligand-assisted growth</td>
<td>Wiskers: 80 nm×10 nm Cubes: 50 nm; Spheres: 100–120 nm ellipsoids ca. 300 nm</td>
<td>15 min 100–197 °C</td>
<td></td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>Cu(OAc)$_2$</td>
<td>Ostwald ripening</td>
<td>Nanorings outer diameter 100 nm Cubes, spindles</td>
<td>30 min 70 °C</td>
<td></td>
</tr>
<tr>
<td>α-Fe$_2$O$_3$</td>
<td>FeCl$_3$</td>
<td>Ion-assisted oriented attachment</td>
<td>Nanoparticles 14.7–40 nm polydispersed and agglomerated</td>
<td>1–150 min 150 °C &gt;1 atm</td>
<td></td>
</tr>
<tr>
<td>α-Fe$_2$O$_3$</td>
<td>FeCl$_3$</td>
<td>Solvent-assisted growth</td>
<td>Nanoparticles 14.7–40 nm polydispersed and agglomerated</td>
<td>1–150 min 150 °C &gt;1 atm</td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Conditions</td>
<td>Shape/Details</td>
<td>Notes</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>α-Fe₃O₄</td>
<td>Fe(OAc)₂, Fe(acac)₃</td>
<td>solvent-assisted growth</td>
<td>spherical 4–9 nm polydisperse and agglomerated</td>
<td>30 s–3 min 200 °C &gt;1 atm [76][77]</td>
<td></td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>FeCl₃</td>
<td>solvent-assisted growth</td>
<td>spheres 31–66 nm</td>
<td>2–8 h 100–160 °C [78]</td>
<td></td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>FeCl₃</td>
<td>ligand-assisted growth</td>
<td>spheres 400–800 nm</td>
<td>20 min reflux [79]</td>
<td></td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>FeCl₃</td>
<td>polymer-assisted oriented attachment</td>
<td>ellipsoids 100×200 nm</td>
<td>10 min 100 °C [80]</td>
<td></td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>FeCl₃</td>
<td>polyol-assisted growth</td>
<td>amorphous 3–5 nm particles</td>
<td>10 min 30 s MW cycles (15 s on/15 s off) [81]</td>
<td></td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>Fe(NO₃)₃</td>
<td>polymer-assisted growth</td>
<td>octahedral 300 nm</td>
<td>24 h 200 °C [82]</td>
<td></td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>FeCl₃</td>
<td>solvent-assisted growth</td>
<td>&lt;20 nm</td>
<td>15 min 150 °C [83]</td>
<td></td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>Fe(NO₃)₃</td>
<td>solvent-assisted growth</td>
<td>rhombic-shaped 18–38 nm</td>
<td>0.5–48 h 100–120 °C [84]</td>
<td></td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>K₄[Fe(CN)₆]</td>
<td>solvent-assisted growth</td>
<td>snowflake-like, pinetree-like assemblies 2–4.5 μm polydisperse</td>
<td>0.5–3 h 120–220 °C &gt;1 atm [85,86]</td>
<td></td>
</tr>
<tr>
<td>Cr₂O₃MoO₂</td>
<td>K₃[Cr(CN)₆] K₃[Mo(CN)₆]</td>
<td>solvent-assisted growth</td>
<td>snowflake-like assemblies 1–5 μm polydisperse</td>
<td>3 h 180 °C &gt;1 atm [87]</td>
<td></td>
</tr>
<tr>
<td>MeFe₃O₄</td>
<td>Fe(NO₃)₃, Ni(NO₃)₂, Co(NO₃)₂, Mn(NO₃)₂</td>
<td>solvent-/surfactant-assisted growth</td>
<td>spherical 4–9 nm σ=10–30 %</td>
<td>1 h 160 °C &gt;1 atm [88]</td>
<td></td>
</tr>
<tr>
<td>Fe₁ₓO₄</td>
<td>FeSO₄</td>
<td>Solvent-assisted growth</td>
<td>aggregates of ca. 35 nm particles</td>
<td>8 min 80 °C [89]</td>
<td></td>
</tr>
<tr>
<td>Fe₁ₓO₄</td>
<td>FeSO₄</td>
<td>polyol-assisted anisotropic growth</td>
<td>wires 30–50 nm×&gt; 1μm</td>
<td>15 min 180 °C &gt;1 atm [90,91]</td>
<td></td>
</tr>
<tr>
<td>Fe₁ₓO₄</td>
<td>FeCl₃</td>
<td>polyol-assisted or surfactant-assisted growth by oriented attachment</td>
<td>clusters made of &lt;20 nm NCs 100 nm–5 μmσ=20–30 %</td>
<td>15–60 min 160–210 °C &gt;1 atm [92,93]</td>
<td></td>
</tr>
<tr>
<td>Fe₁ₓO₄</td>
<td>Fe(acac)₃</td>
<td>surfactant-assisted growth</td>
<td>spheres 6 nmσ=30 %</td>
<td>5–10 min 250 °C [94]</td>
<td></td>
</tr>
<tr>
<td>Name</td>
<td>Formula</td>
<td>Preparation Method</td>
<td>Additional Information</td>
<td>References</td>
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<tr>
<td>In$_2$O$_3$</td>
<td>InCl$_3$</td>
<td>NH$_2$OH-assisted (In(OH)$_3$ converted into In$_2$O$_3$ after calcination at 700 °C)</td>
<td>hexagons 22 nm σ=10 %</td>
<td>[95]</td>
<td></td>
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<tr>
<td>Mn$_3$O$_4$</td>
<td>Mn(OAc)$_2$</td>
<td>Ostwald ripening</td>
<td>cubes rhombohedra 15–40 nm</td>
<td>[96]</td>
<td></td>
</tr>
<tr>
<td>MnO$_2$</td>
<td>KMnO$_4$</td>
<td>growth confined in oil-in-water microemulsions Ostwald ripening</td>
<td>nanowires/belts polydisperse</td>
<td>[97]</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>Mn(OAc)$_2$, Mn(acac)$_2$</td>
<td>solvent-assisted ester elimination</td>
<td>cube-like 30–50 nm</td>
<td>[98]</td>
<td></td>
</tr>
<tr>
<td>PdO</td>
<td>H$_2$[PdCl$_6$]</td>
<td>polymer-assisted growth</td>
<td>spheres 1.8–3.2 nm σ=25 %</td>
<td>[99]</td>
<td></td>
</tr>
<tr>
<td>PtO$_2$</td>
<td>H$_2$[PtCl$_6$]</td>
<td>polymer-assisted growth</td>
<td>spheres average 1.68 nm</td>
<td>[100]</td>
<td></td>
</tr>
<tr>
<td>SnO</td>
<td>SnCl$_2$</td>
<td>solvent-assisted growth</td>
<td>crystalline powders</td>
<td>[101]</td>
<td></td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>SnCl$_4$</td>
<td>solvent-assisted growth</td>
<td>spheres 3 nm polydisperse</td>
<td>[102]</td>
<td></td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>SnCl$_4$</td>
<td>solvent-assisted growth</td>
<td>average 5 nm</td>
<td>[103]</td>
<td></td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>SnCl$_4$</td>
<td>solvent-assisted growth</td>
<td>average 3 nm</td>
<td>[104]</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Ti(OBu)$_4$, TiCl$_4$</td>
<td>growth confined in polymer micelles</td>
<td>spheres 5 nm σ=5 % rods 30–50 nm×0.5–1 μm</td>
<td>[105,106]</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Ti(OBu)$_4$, Ti(OiPr)$_4$</td>
<td>solvent-assisted growth</td>
<td>spherical aggregates ca. 200 nm</td>
<td>[107,108]</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Ti(OiPr)$_4$</td>
<td>MW-induced recrystallization of TiO$_2$ colloidal solutions</td>
<td>3–5 nm</td>
<td>[109]</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>TiCl$_4$</td>
<td>solvent-assisted growth</td>
<td>aggregates 150 nm polydisperse</td>
<td>[110]</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>TiCl$_4$</td>
<td>solvent-assisted growth</td>
<td>aggregates 70 nm polydisperse</td>
<td>[111]</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>Source</td>
<td>Growth Method</td>
<td>Morphology/Size</td>
<td>Temperature/Times</td>
<td>References</td>
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<tr>
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<tr>
<td>TiO₂</td>
<td>TiCl₄</td>
<td>solvent-assisted growth</td>
<td>&lt;100 nm</td>
<td>5–120 min 100–160 °C</td>
<td>[112]</td>
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<tr>
<td>TiO₂</td>
<td>TiCl₄</td>
<td>solvent-assisted growth</td>
<td>aggregates 800 nm polydisperse</td>
<td>30–120 min 120–180 °C</td>
<td>[113]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>TiCl₃</td>
<td>ion-assisted growth</td>
<td>cubes: 25 nm rods: 4×17 nm spheres: 8 nm spheres (10 nm), rods (10×100 nm)</td>
<td>20–60 min</td>
<td>[114]</td>
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<tr>
<td>TiO₂</td>
<td>TiOCl₂</td>
<td>solvent-assisted growth</td>
<td>spheres 20–200 nm</td>
<td>5–60 min 195 °C</td>
<td>[115]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>(NH₄)₂TiF₆</td>
<td>solvent-assisted growth</td>
<td>aggregates 800 nm polydisperse</td>
<td>10–60 min 70 °C</td>
<td>[116]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Ti(OiPr)₄</td>
<td>solvent-assisted growth</td>
<td>truncated cubes 8–10 nm</td>
<td>40 min 1 atm</td>
<td>[117]</td>
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<tr>
<td>TiO₂</td>
<td>TiF₄</td>
<td>solvent-assisted growth</td>
<td>sheets 2 μm×2 μm</td>
<td>90 min 210 °C &gt;1 atm</td>
<td>[118]</td>
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<tr>
<td>WO₃</td>
<td>WCl₆</td>
<td>solvent-assisted growth</td>
<td>aggregates of 5–30 nm particles</td>
<td>5–15 min 210 °C</td>
<td>[119]</td>
</tr>
<tr>
<td>WO₃</td>
<td>Na₂WO₄</td>
<td>ion-assisted anisotropic growth</td>
<td>nanowires 20–30 nm×&gt;1 μm</td>
<td>20 min–3 h 150 °C &gt;1 atm</td>
<td>[120]</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zn(OAc)₂</td>
<td>polymer-assisted oriented attachment sequential seeding</td>
<td>clusters of 8 nm NCs 50–275 nm</td>
<td>1–5 min steps 120–180 °C 1 atm</td>
<td>[121]</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zn(acac)₂</td>
<td>solvent-assisted oriented attachment</td>
<td>clusters of 10–30 nm NCs 50–180 nm</td>
<td>4 min &gt;1 atm</td>
<td>[122]</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zn(OAc)₂Zn(acac)₂</td>
<td>solvent-assisted growth</td>
<td>aggregates of 20–30 nm particles rods:100 nm×1 μm bipods, tripods, multipods</td>
<td>0.5–3 min 200 °C</td>
<td>[123]</td>
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<tr>
<td>ZnO</td>
<td>Zn(NO₃)₂</td>
<td>oriented attachment</td>
<td>rods or needles or stars or disks or balls range 0.4–5 μm</td>
<td>2–30 min 90 °C</td>
<td>[124]</td>
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<tr>
<td>ZnO</td>
<td>Zn(NO₃)₂Zn(OAc)₂</td>
<td>ligand-assisted growth</td>
<td>needles 11 μmσ=20–30 %</td>
<td>15 min 90 °C</td>
<td>[125]</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zn(NO₃)₂</td>
<td>solvent-assisted growth</td>
<td>rods range 1 μm</td>
<td>120 min 192 °C</td>
<td>[126]</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zn(NO₃)₂, Zn(OAc)₂ ZnSO₄ZnCl₂</td>
<td>ion-assisted growth</td>
<td>needles 11 μmσ=20–30 %</td>
<td>&gt;15 min</td>
<td>[127,128]</td>
</tr>
<tr>
<td>Material</td>
<td>Formula</td>
<td>Method</td>
<td>Characteristics</td>
<td>Conditions</td>
<td></td>
</tr>
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<tr>
<td>ZnO</td>
<td>Zn(OAc)$_2$</td>
<td>solvent-assisted growth</td>
<td>rods diam. 25–7 nm, len. 0.5–1.5 μm</td>
<td>10 min [129]</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>Zn(OAc)$_2$</td>
<td>solvent-assisted growth</td>
<td>dumbbells 2×5 μm</td>
<td>5–10 min [130]</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>Zn(OAc)$_2$</td>
<td>polymer-assisted seeded growth</td>
<td>rods packed in micrometer-sized bundles, spheres or flowers</td>
<td>different MW cycling modes 60–90 min [131]</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>Zn(OAc)$_2$</td>
<td>polymer-assisted growth</td>
<td>rods 50–250 nm diameter×70–300 nm length</td>
<td>30 min 140 °C [132]</td>
<td></td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>Zr(NO$_3$)$_4$</td>
<td>polymer-assisted growth</td>
<td>aggregates of 2 nm particles</td>
<td>6 min (MW cycles: 10 s on/20 s off) 320 °C [133]</td>
<td></td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>ZrOCl</td>
<td>Solvent-assisted growth</td>
<td>spheres 10–20 nm</td>
<td>120 min 194 °C 14 atm [134]</td>
<td></td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>Zr(OiPr)$_4$</td>
<td>ligand-assisted growth</td>
<td>spheres 100 nm</td>
<td>50–100 mL min$^{-1}$ 6 0 °C 15 atm [135]</td>
<td></td>
</tr>
</tbody>
</table>

2.2.2 Non-oxide semiconductors

Materials other than metal oxides have been produced using microwave-assisted synthesis. The reported literature on this illustrates the remarkable synthetic flexibility given by microwave assisted synthetic routes over the traditional methods. Table 3 summarizes reaction conditions, product characteristics, and main formation mechanisms of metal chalcogenides synthesised under microwave radiation which has been reported in a latest review article.[136]
Table 3. A summary of some metal chalcogenides synthesised by microwave irradiation.

<table>
<thead>
<tr>
<th>Material</th>
<th>Precursors</th>
<th>Formation mechanism</th>
<th>Crystalline features</th>
<th>Reaction condition</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>CdS</td>
<td>CdCl₂</td>
<td>solvent-assisted growth</td>
<td>aggregated spheres 9 nm polydisperse</td>
<td>20 min reflux</td>
<td>[137]</td>
</tr>
<tr>
<td>CdS</td>
<td>Cd(OAc)₂</td>
<td>solvent-assisted growth</td>
<td>spheres &lt;5 nm polydisperse</td>
<td>18 s 1 atm 80 °C</td>
<td>[138]</td>
</tr>
<tr>
<td>CdSe</td>
<td>CdSO₄, Na₂SeSO₃</td>
<td>surfactant-assisted growth</td>
<td>agglomerated spheres ca. 5 nm polydisperse</td>
<td>0.5 min 1 atm reflux</td>
<td>[139]</td>
</tr>
<tr>
<td>CdSe</td>
<td>Cd(OAc)₂, Se</td>
<td>polyol-assisted growth</td>
<td>spherical aggregates of tiny clusters 6–7 nm</td>
<td>60 min reflux</td>
<td>[140]</td>
</tr>
<tr>
<td>CdTe</td>
<td>CdCl₂, Na₂TeO₃, NaBH₄</td>
<td>ligand-assisted growth</td>
<td>irregular spheres ≈3 nm</td>
<td>10–40 min &gt;1 atm 80–140 °C</td>
<td>[141]</td>
</tr>
<tr>
<td>CdTe</td>
<td>CdO TeTBP</td>
<td>surfactant-assisted growth</td>
<td>Spheres ca. 4.4 nm σ=5–10 %</td>
<td>1–90 min 1 atm 180–280 °C</td>
<td>[142]</td>
</tr>
<tr>
<td>CdZnSe</td>
<td>Cd(OAc)₂, Zn(OAc)₂, Se</td>
<td>polyol-assisted growth</td>
<td>aggregated spheres ca. 6 nm polydisperse</td>
<td>60 min MW cycles (21 s on/9 s off) reflux</td>
<td>[143]</td>
</tr>
<tr>
<td>CuS</td>
<td>Cu(OAc)₂, thioacetamide</td>
<td>ligand-assisted growth</td>
<td>irregular spheres 5–10 nm</td>
<td>20 min reflux</td>
<td>[144]</td>
</tr>
<tr>
<td>CuInS₂</td>
<td>CuCl₂, InCl₃, Na₂S</td>
<td>ligand-assisted growth</td>
<td>spheres 3 nm</td>
<td>30 min 90 °C</td>
<td>[145]</td>
</tr>
<tr>
<td>CuInS₂</td>
<td>CuI, InCl₃, S</td>
<td>surfactant-assisted growth</td>
<td>irregular spheres 3–10 nm polydisperse</td>
<td>20–30 min &gt;1 atm 120–220 °C</td>
<td>[146]</td>
</tr>
<tr>
<td>CuInTe₂</td>
<td>CuCl, In, Te</td>
<td>ligand-assisted growth</td>
<td>irregular spheres ca. 94 nm</td>
<td>60 min 1 atm reflux</td>
<td>[147]</td>
</tr>
<tr>
<td>PbS</td>
<td>Pb(OAc)₂, S</td>
<td>ligand-assisted growth</td>
<td>irregular spheres 20–30 nm polydisperse</td>
<td>20 min 1 atm reflux</td>
<td>[148]</td>
</tr>
<tr>
<td>PbSe</td>
<td>Pb(OAc)₂, selenourea</td>
<td>surfactant-assisted growth</td>
<td>polyhedrons, cubes 5–15 nm σ=5–10 %</td>
<td>1 min 3 bar 160 °C</td>
<td>[149]</td>
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</table>

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<table>
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<tr>
<th>Material</th>
<th>Precursor</th>
<th>Growth Assisted</th>
<th>Growth Properties</th>
<th>Reaction Conditions</th>
<th>Reference</th>
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<td>clustered spheres</td>
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<td>spheres ca. 7 nm</td>
<td>1–12 min MW</td>
<td>[151]</td>
</tr>
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<td>thiourea</td>
<td>growth</td>
<td>polydisperse</td>
<td>30 s cycles (9 s on/21 s off) 1 atm</td>
<td></td>
</tr>
<tr>
<td>ZnSe</td>
<td>Zn(OAc)$_2$, Se</td>
<td>surfactant-assisted</td>
<td>aggregated spheres/ellipsoids</td>
<td>20 min &gt;1 atm</td>
<td>[152]</td>
</tr>
<tr>
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<td></td>
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<td>20–500 nm polydisperse</td>
<td>180 °C</td>
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<td></td>
<td>growth</td>
<td>140 °C</td>
<td>1 atm</td>
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<tr>
<td>ZnSe</td>
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<td>nano-rods/wires</td>
<td>0.5–3 min (400 W)</td>
<td>[154]</td>
</tr>
<tr>
<td></td>
<td>selenourea</td>
<td></td>
<td>1–1.5 nm×5–450 nm</td>
<td>&gt;1 atm</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>σ=6–12 %</td>
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</tbody>
</table>

2.2.3 Metal oxide thin films

It is clear that microwave assisted material synthesis is widely acceptable for inorganic/organic material production as it gives more advantages than the conventional synthesis methods. However use of microwave radiation for materials post annealing treatment is a novel technological advancement alternative to conventional sintering. Recently a particularly interest has been made to improve the chemical, physical and hence photoelectrochemical performance of semiconductors by post-synthesis microwave treatment. The improved performance is attributed to improvements in the crystallinity and the particle-necking properties and the densification by microwave irradiation of thin film electrodes. Recent examples demonstrate that microwave processing is a promising alternative to conventional sintering for thin film post treatments for better photoelectrochemical performance. It is reported that the photoelectrochemical performance of microwave annealed α-Fe$_2$O$_3$ and TiO$_2$ thin films can be improved compared to those heated conventionally.[155][156] Also our recent study concluded that the microwave irradiation
caused sintering of individual ZnO nanorods resulting in the growth of rod diameter whilst the conventional thermal annealing deformed the hierarchical ZnO structure of thin films. However, to the best of my knowledge, there is very little literature available on the microwave post treatment of metal oxide semiconductor thin films which can be used in advanced electronic and optoelectronic devices.

2.3 Industrial use of microwaves for material processing

Microwave heating of materials offers many significant advantages over conventional heating methods. This technique has a huge number of applications for technology in industry. Microwave treated materials can be used as a high performance, nanostructured host for the preparation of advanced materials that exhibit specific optic, optoelectronic, and electrochemical properties suitable for supercapacitors, display devices, molecular wires, quantum electronics and non-linear optical devices.[157,158] As summarized in the previous section, a number of preparations of nano-scale materials on nanostructured template have been demonstrated using microwave technology. Iron oxide based magnetic materials have been extensively used as recording materials because of their good magnetic properties. The emergence of nano-magnetic technology has imposed new demands upon magnetic materials to fabricate ultrahigh density and ultrahigh speed data storage devices.[159]

Microwaves represent an alternative way of adding energy to chemical reactions and material processes. Although microwave radiation has been used in many industries as a heating method to improve the quality of final products, this method is yet to apply for the materials involving in energy storage devices such as supercapacitors and fuel cells. Supercapacitors are an energy storage device based on simple charge-separation at an electrochemical surface between an electrode and electrolyte. They have attracted more attention recently due to their
higher power density and longer life cycle compared to batteries.[160] Inter-particle connections and surface area of such supercapacitor materials can be improved by post synthesis treatment of the electrodes with microwave radiation. This is useful in getting better charge-separation properties. Fuel cells are also promising power sources for various applications, because of their low operating temperatures, relatively quick start-up, and high power density. Iron, iron oxides and ferrous alloys are used in an extensive range of applications in these kinds of energy storage devices. Microwave treatment of such metal oxides can improve the better inter-particle connections and surface area which is vital in better fuel cell operation characteristics. Walkiewicz et al[161] reported successful microwave heating of metallic powders for the first time. In the 1990s microwaves were used in the synthesis of intermetallic alloys, carbides and nitrides.[162,163] Later, Cheng et al[164] carried out a comprehensive study on microwave sintering of metals including ferrous alloys and concluded that microwave sintering not only provided a faster process at lower processing temperatures but the properties of final products were also improved significantly. Therefore, the microwave annealing method offers improved materials properties with energy savings, which would make it highly desirable for industrial scale up.

2.4 Unique performance characteristics to microwaves

Microwaves possess several characteristics that provide unique features that are not available in the conventional processing of materials. Some of the key characteristics of microwaves’ interactions with materials are,

1. Penetrating radiation

The depth of penetration depends on several factors, including the wavelength of the radiation and the dielectric (and magnetic) properties of the material.
2. Controllable electric field distributions

In microwave applicators such as microwave furnaces, the electric field distributions can be focused and controlled to provide very high field strengths which provide a proper tuning to heat low-loss materials at low temperatures and heat selected regions between two materials to promote welding, brazing, or bonding or to generate plasmas for microwave-assisted sintering or chemical vapour deposition.

3. Rapid heating

For many materials, dielectric losses above a critical temperature accelerate with increasing temperature, allowing very rapid (bulk) heating that can result in very significant reductions in processing time. This rapid increase in dielectric loss can lead to uneven heating and thermal runaway. However this can be controlled by using hybrid heating or insulation.

4. Selective heating of materials

The range of dielectric responses of different materials and their ability to couple with microwaves is one of the most widely used features of microwave processing.

5. Self-limiting absorbance

Self-limiting absorbance can be occurred within the material when irradiated with microwaves when it contains two or more materials with different dielectric properties. These characteristics, either singly or in combination, represent opportunities and benefits not available from conventional heating or processing methods.
2.5. Microwave generators

Microwave generators include the magnetron, power grid tubes, traveling wave tubes (TWTs), Crossed field amplifiers (CFAs), klystron and gyrotron.[165] The selection of the types of microwave generators for use depends on various factors including power, frequency, efficiency, gain, bandwidth, phase, size, weight and cost. The magnetron is the most commonly used microwave generator because of its high efficiency, compact size and low cost.[166] Figure 2-26 shows a 2kW power magnetron which is used in domestic and industrial microwave ovens. A cross-section of a typical magnetron is shown in figure 2-27. It is used widely in microwave ovens and radar systems. A magnetron converts electrical energy to microwave radiation and typically operates at a frequency of 2.45 GHz.

Figure 2-26. Magnetron of 2kW power.[167]
The magnetron is essentially a thermionic diode that converts electrical energy to microwave radiation. In the magnetron, heated cathodes act as a source of electrons. The cathode is surrounded by a circular anode having an array of radial slots acting as resonators tuned to the desired operating frequency. The electric field created by the applied DC voltage draws the electron from the cathode to anode region. In the presence of a magnetic field, the electrons cannot travel radially outward to the anode but they are forced to rotate circularly in the coaxial space between the cathode and the anode. Consequently, the bunching of the electron cloud occurs. The electron cloud would appear as a rotating spoke wheel. In the presence of an electromagnetic field, the electrons entering the positive microwave electric field gradient will accelerate and those entering the negative gradient will decelerate. The changes in the kinetic energy of the electrons leaving the cathode and arriving at the anode will result in the generation of the microwaves. The transfer of power from the DC power input to the microwave power is extremely efficient. The microwaves are then directed towards a target with the use of microwave guides which are usually made of sheet metals. The output microwave power can be generated in two ways; pulsed or continuous. Pulsed magnetrons produce output power of kilowatts to several megawatts for short durations while continuous magnetrons produce output power of a few watts to kilowatts continuously.
Chapter 3

Experimental Methods and Materials Characterization

3.1 Experimental Methods

3.1.1 Aerosol-assisted chemical vapour deposition

The aerosol-assisted chemical vapour deposition (AACVD) technique has been used to fabricate TiO$_2$ and ZnO thin films on fluorine-doped SnO$_2$ (FTO) glass substrates.[169] In the AACVD deposition method, an aerosol precursor solution is used which is transported into the reaction chamber by use of a carrier gas, whereby the solvent is evaporated and precursor molecules decompose onto the substrate.[170] The figure 3-1 shows a schematic diagram of the aerosol-assisted chemical vapour deposition apparatus.

![Figure 3-1. Schematic of the aerosol-assisted chemical vapor deposition apparatus.][171]

The precursor solution can be a pure liquid, single source precursor or a mixture of several liquid chemicals, or can be prepared by dissolving solid or liquid starting materials in an solvent. Usually, a criterion for the selection of solvents for AACVD is high solubility of the precursor, low vapour pressure, and low viscosity. Depending on the nature of the decomposition, the deposition can be take place by homogenous and heterogeneous
mechanisms. At higher substrate temperatures, the major decomposition may occur much earlier in the vapour phase, leading to homogenous nucleation and the formation of fine particles on substrate. In the heterogeneous mechanism, preliminary decomposition of vaporized precursor may occur in the gas phase.[172] Either one or both these mechanisms can involve in growing TiO$_2$ and ZnO thin films on FTO glass substrates.

3.1.2 Chemical bath deposition

The chemical bath deposition (CBD) method for the preparation of thin films has recently been shown to be an attractive technique because of its simplicity, convenience, low cost and low temperature, and it has been successfully used for depositing metal oxide nanorods. This is a solution phase technique which allows fabricating semiconductor thin films from aqueous solutions. The CBD technique is widely used for the deposition of various metal oxides and chalcogenide thin films. This allows the control of growth factors such as film thickness, deposition rate and quality of crystallites by varying the solution pH, temperature and bath concentration.[173] The deposition of a film can be due to two types of nucleation in solution: homogeneous nucleation and heterogeneous nucleation. Homogeneous nucleation leads to rapid formation of large particles throughout the solution, as a precipitate. Conversely, heterogeneous nucleation occurs at the substrate surface and particles grow slowly to form a film.[174] The pre-treatment of the substrate with a seed layer avoids the disruption to heterogeneous nucleation which is the key to obtain hierarchical structures of materials. Growing of ZnO nanorods on FTO/ITO glass substrates from an alkaline solution requires a seed layer. A schematic of the CBD set-up is shown in figure 3-2.
3.1.3 Annealing procedures

3.1.3.1 Conventional annealing

Conventional thermal annealing was carried out in a tube furnace (MTF-10-25-130, Carbolite, Hope Valley, UK) with a ramp rate of 15 °C/min to the desired temperature. Both ends of the tube were kept open to allow for the flow of air. After annealing the furnace was turned off and the samples were left in the furnace to cool down. The temperature of the samples was measured using a K-type thermocouple. An image of MTF-10-25-130 tube furnace is shown in figure 3-3.
3.1.3.2 Microwave-assisted annealing

Microwave-assisted annealing was performed using an industrial microwave furnace (MRF 16/22, Carbolite Ltd, UK) capable of producing a tuneable continuous power output up to a maximum of 2 kW operating at 2.45 GHz frequency (figure 3-4) and a modern microwave oven (Microwave research Applications Inc. BP-211/50, USA) operating at 2.45 GHz frequency with a maximum power of 3000 W (figure 3-5). The samples were placed inside a high purity insulator blocks to minimise the heat loss during the microwave processing. The thermal imaging cameras (Micro-Epsilon/ TIM 400 and M67/M67S IR temperature transmitter) are placed on top of the furnaces and temperature was recorded during the microwave treatment of samples (Figure 3-6) using itools software.
Figure 3-4. The images of (a) industrial MRF 16/22 microwave furnace with Micro-Epsilon/TIM 400 thermal imaging camera. (b) Microwave furnace chamber and the insulator blocks.

Figure 3-5. The images of (a) custom processing BP-211/50 microwave furnace with M67S IR temperature transmitter. (b) Microwave furnace chamber and the insulation.
Figure 3-6. A screen shot of a thermal image of the itools software analysing the reading taken from the thermal imaging camera.

Power measurements in a microwave system are derived from elementary thermal concepts based on the heat capacity of a mass at constant pressure. Specific heat capacity, $C_p \text{ (JK}^{-1}\text{kg}^{-1})$ is that quantity of heating experienced by a given mass per degree of temperature from energy absorbed to provide a rise in temperature, $\Delta T$. If a quantity of energy is delivered for a unit of time, then $P_w$, the power absorbed by a substance (power density) in the microwave cavity may be expressed in the following relationship,

$$P_w = \frac{KC_p m\Delta T}{t}$$  \hspace{1cm} (12)

where, $K$ is the conversion factor, $m$ is the mass of the sample and $t$ is the time. The power calibration of the microwave furnaces was performed by using water test method as described elsewhere.[176]
3.1.3.3 Microwave-assisted synthesis

Microwave-assisted synthesis was performed in a Biotage Initiator EXP 8 reactor in 10-20 mL crimped vials. Figure 3-7 demonstrates a Biotage Initiator EXP 8 reactor which was used to the synthesis the materials.

Figure 3-7. Biotage Initiator EXP 8 reactor.

3.2 Materials Characterization

3.2.1 X-ray diffraction

X-ray diffraction (XRD) is one of the primary techniques that can be used to determine the crystalline structure of solid materials. When the X-rays interact with atoms in the crystal lattices of a solid, a diffraction pattern is generated. Since, each crystalline solid has a unique atomic architecture, the generated XRD pattern is characteristic of the material from which is obtained and can be used as a fingerprint to identify the crystalline phases and its structure (i.e. packing density of the atoms, crystalline state, shape, stresses in the crystal lattice and size of the unit cell etc.).
English physicists Sir W.H. Bragg and his son Sir W.L. Bragg developed a relationship in 1913 to explain why the incident X-ray beams reflects at certain angles when they are interact with atoms of the crystalline phases of solids. When X-rays interact with atoms in two lattice planes, and the path length difference between rays equals a whole multiple of the wavelength of the radiation, constructive interference occurs (Figure 3-8). Bragg’s law describes the conditions for constructive interference in certain directions and the production of diffracted scattered X-rays:

\[ n\lambda = 2dsin\theta \]  

where \( n = \) an integer, \( \lambda = \) the wavelength of the X-rays, \( d = \) the lattice spacing of a (h,k,l) plane, \( \theta = \) the angle between the incoming X-ray and the atomic layer.

X-rays are scattered by atoms in the different crystalline planes (hkl) and are picked up by the detector, which then converts them into intensity against 2θ spectrum. The XRD analysis enables to identify the material without destroying the sample.

![Figure 3-8. An X-ray diffraction beam schematic [177], showing the incident and scattered X-rays, from a pair of atoms in different lattice planes.](image-url)
Figure 3-9 shows a photograph of the Bruker D8 X-ray diffractometer (XRD) operating with monochromatic high-intensity Cu Kα (λ= 0.154 nm) radiation and a PSD detector which was used to characterise the thin films and the powder samples.

![Figure 3-9](image.jpg)

Figure 3-9. Photograph of the Bruker D8 X-ray diffractometer used in this study, the X-ray source is on the left, the sample is in the middle and the detector is on the right.

3.2.2 Raman spectroscopy

Raman spectroscopy is a technique used to collect a unique chemical fingerprint of molecules by observing inelastic (Raman) scattering from the sample. Here, the incident laser photons interact with the molecules and the scattered photons are shifted in frequency. Since each molecule has a unique set of vibrational energy levels, the emitted scattered photons show characteristic wavelength shifts. In Raman spectroscopy, the intensity of the emitted photons is recorded against the wavenumber to identify the corresponding molecules in a sample. The different peaks in the spectrum correspond to different Raman excitations which are important in materials characterization.
Raman spectroscopy was performed using a HORIBA Jobin Yvon LabRAM HR (with 632.8 nm He-Ne laser) Raman spectrophotometer (Figure 3-10) (HORIBA Jobin Yvon Ltd., Middlesex, UK). The spectra were obtained in the range of 100 to 1200 cm\(^{-1}\).

3.2.3 Field emission gun scanning electron microscopy

A field emission gun scanning electron microscopy (FEG-SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of high-energy electrons (figure 3-11). The high-energy electrons interact with atoms in the sample, producing various signals which contain information about the sample's surface topography, orientation and composition.
The incident electron beam is scattered in the sample, both elastically and inelastically and gives rise to various signals such as secondary electrons, backscattered electrons, auger electrons, X-rays and cathode luminescence (figure 3-12).
FEG-SEM equipment mainly detects secondary electrons that result from interactions of the electron beam with atoms at or near the surface of the sample. In the standard secondary electron imaging mode, the FEG-SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. Due to the very narrow electron beam, FEG-SEM surface topographic images have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample.

Figure 3-13. Leo 1530 VP FEG-SEM set-up.

The surface topographical images of samples and cross-sectional images of thin films were taken by a Leo 1530 VP FEG-SEM, Jeol Hertfordshire, UK (figure 3-13), with an accelerating voltage of 5 kV, and a working distance of 5 mm (this is the distance between the operating lens and the sample). The sample is required to be clean, vacuum compatible and electrically conductive. A thin layer of Pd-Au is sputter coated on to the surface of the
electrode to enhance the electrical conductivity of the samples. The system works by scanning the surface of the sample with a focused beam of electrons, which frees electrons from the atoms at the surface (from a depth of a few nm), as well as being reflected back from the sample. The secondary electrons are considered to be electrons with energies less than 50 eV. Secondary electrons are collected by an Everhard-Thornley detector and are converted in to a signal which is processed in to an image of the surface. Reflected electrons have energies greater than 50 eV and can be collected by a second detector. These electrons are commonly referred to as backscattered electrons and provide elemental analysis as elements with large atomic numbers generate a higher number of back scattered electrons than those with lower atomic numbers. When secondary electrons are knocked out of an inner energy orbital, the atom is left in an excited state, however as the atom relaxes an electron from a higher energy level may drop in to this orbital. In doing so, the electron releases energy which can be in the form of X-rays. As these X-rays are unique for each element, elemental analysis of the sample can be conducted.

3.2.4 UV-Vis optical absorbance

Optical absorbance measurements were conducted using a dual beam Perkin-Elmer Lambda 35 UV-Vis spectrometer (figure 3-14). Use of a dual beam allowed the absorbance to be automatically corrected, as a reference (in this case a plain FTO glass slide) was measured alongside the sample. The light source was provided by a tungsten and deuterium lamp with wavelengths ranging from 900 nm to 300 nm, so that infrared, visible and ultra violet regions of light were transmitted. The light passes through a series of slits and gratings before it is split in two equal beams (i.e. the dual beams). Consequently the light that passes to the samples travels in one direction and little scattering occurs. As the light travels through the sample, some of the light is absorbed by the various layers in the electrode. Light that is
transmitted is detected by the photodiode, which generates an electrical current proportional to the amount of light absorbed at different wavelengths, resulting in absorbance vs. wavelength spectrum.

Figure 3-14. Lambda 35 Perkin-Elmer UV-Vis spectrophotometer.

3.2.5 Incident photon to electron conversion efficiency

The incident photon to current conversion efficiency (IPCE) is determined by the light-harvesting efficiency, the quantum yield for electron injection to the conduction band of the semiconductor, and the collection efficiency of the electron at the back-contact.[179] IPCE is represented by the following equation,

\[ IPCE = LHE \times \varphi_{inj} \times \eta_c \]  

(14)

where, LHE is the light harvesting efficiency, \( \varphi_{inj} \) is the electron injection efficiency and \( \eta_c \) is the electron collecting efficiency at back contact.
The IPCE was obtained by measuring the incident photon flux using a 75 W Xenon lamp connected to a monochromator (TMc300, Bentham Instruments Ltd., Berkshire, UK). The light was calibrated using a silicon photodiode. Photocurrent spectra were measured at a constant potential vs. Ag/AgCl using a combination of a lock-in amplifier (Bentham 485, Bentham Instruments Ltd., Berkshire, UK) and an in-house built potentiostat. Readings were collected at 5 nm intervals. The figure 3-15 shows the Xenon lamp, monochromator and lock-in amplifier used for the IPCE measurements.

3.2.6 Surface area measurements – dye adsorption-desorption studies

In order to find out the internal surface area of the deposited films, dye adsorption-desorption studies were performed. The surface area of thin films plays a significant role in determining the photoelectrochemical performance. Therefore, it is vital to estimate the internal surface area of electrodes after film fabrication and post treatment. Dye adsorption-desorption studies of TiO_2 and ZnO films were carried out by soaking the films in an ethanol solution of 1mM N719 dye for overnight.[180,181] Then the adsorbed acidic dye on the films was desorbed using NaOH solution. The concentration of the desorbed dye in a 0.1 M NaOH solution was recorded by measuring the absorbance (Lambda 35 Perkin-Elmer UV-Vis spectrometer).
Prior to recording the absorbance spectra, the solution was acidified by adding an appropriate amount of 0.1 M aqueous HCl solution. On the basis of the optical absorbance data of desorbed dye solution, the desorbed dye concentration was evaluated with the aid of the Beer-Lambert law (the extinction coefficient of the N719 dye at 525 nm, \( \varepsilon_{525} = 11,400 \text{ M}^{-1} \text{ cm}^{-1} \)).[182] Then, the total number of adsorbed dye molecules was calculated by taking into account the optical absorbance of desorbed dye solution at 525 nm. The surface area occupied by dye on a given film was determined by considering the area occupied by each dye molecule, 1.46 nm\(^2\).[182] The internal surface area of the film was then estimated by taking into account the projected surface area of the electrode.
Chapter 4

Enhancement of Photoelectrochemical Performance of AACVD-produced TiO\textsubscript{2} Electrodes by Microwave Irradiation while Preserving the Nanostructure

4.1 Overview

TiO\textsubscript{2} electrodes are deposited on FTO-glass substrates at 350 and 400 °C by aerosol-assisted chemical vapour deposition (AACVD) and the deposited TiO\textsubscript{2} electrodes are irradiated with different microwave (2.45 GHz) power levels of 80, 200, 400, 800 W. These different power levels are equivalent to 10, 25, 50 and 100% microwave irradiation percentages of the furnace. The X-ray diffraction (XRD) reflections show that the deposited electrodes have the anatase phase TiO\textsubscript{2} oriented in the (101) direction, and the crystallinity of these electrodes increases after microwave treatment. Field emission gun scanning electron microscopy (FEG-SEM) surface topography analysis proves the preservation of the nanostructure after exposure to various percentages of microwave radiation. The photoelectrochemical (PEC) studies prove a threefold enhancement of photocurrent density of AACVD-produced TiO\textsubscript{2} electrodes after 100% microwave irradiation. This improved performance of PEC properties is attributed to improvements in the crystallinity and the particle-necking properties. The results presented demonstrate that microwave processing is a promising alternative method to conventional sintering for TiO\textsubscript{2} photoanodes.
4.2 Introduction

Titanium dioxide (TiO$_2$) is one of the most interesting semiconductor materials because of its excellent optical,[183] electrical,[184] photocatalytic,[185] and thermal properties.[186] Interest in TiO$_2$ is mainly due to its non-toxicity and good stability in various environments.[187,188] TiO$_2$ is a wide band gap semiconductor that is transparent to visible light and has excellent optical transmittance which makes it a promising candidate for optoelectronic devices.[189,190] Conversion efficiencies of TiO$_2$ photoelectrodes have remained relatively low, mainly due to the slow charge transfer kinetics and low light absorption properties resulting from poor adherence between individual particles and particle-substrate.[191] Sintering may be considered to be the main process which improves the particle connections. TiO$_2$ can be deposited at high temperatures using methods such as atmospheric pressure chemical vapour deposition (APCVD)[192,193], aerosol assisted chemical vapour deposition (AACVD)[194], and spray pyrolysis[195]. However the major drawback of these deposition techniques is the particle growth and consequent collapse of the nanostructure as a result of the conventional annealing treatment.[196] This decreases the porosity and effective surface area which in turn affect the photoelectrochemical (PEC) performance.

It is very important to obtain particle-to-particle connections on the nanometer scale in order to fabricate efficient optoelectronic devices.[197] Particle interconnection (or necking) improves the electrical contact and conductivity of nanoparticle-based thin films which enhance the charge transfer properties and performance of the resulting electrodes.[198] The use of conventional sintering for materials processing, however, causes changes to the nanostructure and physical nature, which may lead to poor PEC performance.
Microwave processing is a relatively novel technique that offers new approaches to improving the physical properties of materials, as well as having economic advantages such as energy savings and accelerated product development. [199] There has been considerable interest in microwave processing on advanced semiconducting materials. [200,201] Meek and Blake [202] showed a significant difference between conventional and microwave processing of oxide ceramics. The microwave heat treatment of TiO$_2$ has been studied by Xie et al. [203] and they found that the microwave-sintered samples were densified more rapidly and at a much shorter time and lower temperature than that of the conventionally sintered samples. Similarly, Yarahmadi et al. [196] claimed that the improved PEC performance is attributable to the lower processing temperatures and rapidity of the microwave method that help to retain the nanostructure of the thin films whilst improving the degree of crystallinity of microwave-treated iron oxide films. However, to the best of our knowledge, there is very little literature available on the microwave processing of nanocrystalline TiO$_2$ thin films for the improvement of PEC performance. This chapter shows that microwave treatment of AACVD-produced TiO$_2$ electrodes appears to be an effective method of improving the electrode crystallinity without affecting its nanostructure, resulting in a significant improvement in the TiO$_2$ PEC characteristics.

The objective of this study is to compare the effect of microwave annealing on the PEC properties of TiO$_2$ photoelectrodes prepared at 350 and 400 °C by AACVD. The results obtained in this study show an enhanced PEC performance of TiO$_2$ electrodes on exposure to various percentages of microwave radiation (2.45 GHz). This improved performance in photocurrent density is attributed to improvements in the crystallinity and the particle-necking properties. The results demonstrate that microwave processing is a promising alternative to conventional sintering for TiO$_2$ photoanodes, providing the electrodes with increased photocurrent densities for various electronic and optoelectronic applications.
4.3 Experimental

Nanocrystalline TiO$_2$ films were prepared on FTO-glass substrates (1 cm $\times$ 2 cm) (TEC 8 Pilkington, 8 $\Omega$/sq.) at temperatures of 350 and 400 °C by the AACVD technique.[204] Titanium(IV) isopropoxide (Sigma-Aldrich) (2.85 g) precursor was added to a mixture of toluene (80 mL) and ethanol (20 mL) in order to obtain a 0.1 M solution of the precursor in 100 mL volumetric flask. The AACVD-produced films were treated with various microwave power levels (80, 200, 400, 800 W) [which is equivalent to 10, 25, 50, 100% of microwave radiation percentages] for 20 min, using a microwave furnace (MRF 16/22, Carbolite Ltd, UK) operating at a frequency of 2.45 GHz. The photoelectrochemical properties of the TiO$_2$ electrodes were measured using a standard, three-electrode electrochemical cell fitted with a quartz window. The reference and counter electrodes were Ag/AgCl and Pt, respectively. All the measurements were carried out in 0.1 M Na$_2$SO$_4$ aqueous electrolyte at 298 K. Current-voltage measurements of the cells were carried out using a potentiostat (Eco Chemie micro-Autolab type III) under illumination from a halogen lamp at 100 mW cm$^{-2}$ light intensity, calibrated by a solar pyranometer (Solar Light Co., PMA2144 Class II). Surface morphology of the TiO$_2$ films was studied using a Leo 1530 VP FEG-SEM at an accelerating voltage of 5 kV and a working distance of 5 mm. Phase and crystallinity of the electrodes were characterized using a Bruker D8 XRD operating with monochromatic intensity Cu K$_\alpha$ ($\lambda = 1.54$ Å) radiation using a PSD detector. All the measurements were repeated at least three times to check the consistency and repeatability of the results.

4.4 Results and Discussion

TiO$_2$ electrodes with two different morphologies were deposited by AACVD at 350 and 400 °C to study the effect of microwave annealing on the structure, texture, morphology and
PEC performance. The electrodes deposited at 350 °C showed a morphology with rod-like features randomly oriented throughout the film, while the electrodes deposited at 400 °C demonstrated a granular morphology with nanoparticles sintered together to form clear, cauliflower-like features. It is well established that changing the temperature in AACVD experiments is very effective at changing the morphology and structure of the deposited thin films.[205,206] Unlike conventional sintering, microwave sintering preserves the nanostructure while improving the electrode performance.

4.4.1 XRD characteristics

The phase and crystallinity of the deposited films before and after microwave treatment has been studied by XRD. Figures 4-1 and 4-2 show XRD diffractograms of the TiO₂ thin films deposited at 350 and 400°C before (0%) and after microwave annealing at 10%, 25%, 50%, and 100% irradiations.

Figure 4-1. XRD diffractograms of TiO₂ electrodes deposited by AACVD at 350 °C and treated with different % of microwave radiation.
The XRD diffractograms show reflections from the dense SnO$_2$ coating of the FTO substrate along with strong reflections of TiO$_2$. The reflections indexed by (*) correspond to the SnO$_2$ layer of the FTO substrate. XRD analysis shows that the deposited films have crystalline structure of the anatase phase oriented in the (101) direction. The diffraction reflections at 2θ values of 37.75° correspond to both TiO$_2$ (anatase) and SnO$_2$. The XRD diffractograms also show that the films are oriented in the (101) direction. The higher intensity of reflections at 2θ values of 37.75° is due to the overlapping of SnO$_2$ reflections.

The overall XRD reflection of anatase remains unchanged after microwave treatment, but a slight increase in the reflection intensities has been observed, which we believe is due to the partial conversion of the amorphous TiO$_2$ phase to anatase crystallites. Anatase to rutile phase conversion is very common in TiO$_2$. Many researchers have found that anatase to rutile phase transition begins above 400 °C. In the current study, it was found that the anatase phase remains unchanged after annealing under microwave radiation, however it improves
the PEC performance of the deposited films. The XRD results proved that the microwave treatment is a promising alternative to traditional sintering for TiO$_2$ photoanodes in order to enhance the optoelectronic properties by increasing the crystallinity and particle connections while keeping the phase and orientation unaltered.

4.4.2 Morphological properties

The FEG-SEM images show the surface morphology of two sets of AACVD-produced TiO$_2$ electrodes treated with different microwave percentages. Figures 4-3 to 4-6 show the randomly oriented, rod-like structure and Figures 4-7-4.10 indicate the granular morphology of TiO$_2$ crystallites deposited at 350 °C and 400 °C, respectively, and treated with 25%-100% microwave radiation (i.e. 200 to 800 W). At higher microwave percentages, these TiO$_2$ crystallites grow and sinter to form well interconnected crystalline structures. In Figures 4-6 and 4-10 images show the change of rod-like orientation to ordered TiO$_2$ crystallite orientation, and granular morphology to sintered cauliflower-like structures, respectively. The cross-sectional image of AACVD-produced TiO$_2$ electrodes deposited at 400 °C is shown in figure 4-11. The image shows that the deposited TiO$_2$ film thickness is around 1 µm which is higher that the penetration depth of TiO$_2$ (i.e. 0.5 µm). It is clear that microwave radiation improves the crystal growth and crystallite necking properties to form highly porous crystallites which contribute to increase electrode-electrolyte interfaces throughout the electrode surface. Therefore, the resulting structural orientations with the microwave irradiation will favour electrolyte to be in contact with the electrode, which may be directly involved in improving the charge transfer kinetics of the electrode. SEM images clearly show that microwave irradiation enhanced the particle connections and porosity with a sligth chang in the nanostructure, which cannot be achieved with conventional sintering techniques. Therefore, microwave treatment of TiO$_2$ electrodes shows a good degree of crystallinity and
porosity while retaining the nanostructure, which promotes the photocurrent density of the electrodes.

Figure 4-3. SEM image of AACVD-produced TiO$_2$ electrodes deposited at 350 °C and treated under 0 % microwave radiation.

Figure 4-4. SEM image of AACVD-produced TiO$_2$ electrodes deposited at 350 °C and treated under 25 % microwave radiation.
Figure 4-5. SEM image of AACVD-produced TiO$_2$ electrodes deposited at 350 °C and treated under 50 % microwave radiation.

Figure 4-6. SEM image of AACVD-produced TiO$_2$ electrodes deposited at 350 °C and treated under 100 % microwave radiation.
Figure 4-7. SEM image of AACVD-produced TiO$_2$ electrodes deposited at 400 °C and treated under 0 % microwave radiation.

Figure 4-8. SEM image of AACVD-produced TiO$_2$ electrodes deposited at 400 °C and treated under 25 % microwave radiation.
Figure 4-9. SEM image of AACVD-produced TiO$_2$ electrodes deposited at 400 °C and treated under 50 % microwave radiation.

Figure 4-10. SEM image of AACVD-produced TiO$_2$ electrodes deposited at 400 °C and treated under 100 % microwave radiation.
4.4.3 Photoelectrochemical properties of electrodes

It is well known that Photoelectrochemical (PEC) performance of many semiconductor electrodes suffers from poor minority carrier collection and slow interfacial charge transfer reactions under illumination (often referred to as ‘the kinetic bottleneck’). The hole collection can generally be improved by having electrodes, fabricated with nanostructured fine texture, in which the feature size is comparable to the hole-diffusion length.[209] Modifying the electrode texture in such a way to improve the inter-particle connections is essential for better PEC performance of the electrode. The better inter-particle connections in the electrode may lead to a reduction in the recombination (in grain boundaries) and improve the charge collection efficiency. It has been proven in the literature that semiconducting electrodes deposited by AACVD have a better performance than those deposited using other techniques as this method allows one to control the nanostructure of electrodes.[210,211] In this study, we found that the PEC performance of TiO$_2$ electrodes can be enhanced by microwave irradiation. Electrodes deposited by AACVD showed two different morphologies; a compact film (deposited at 350 °C), and a relatively porous film with cauliflower-like features deposited at 400 °C. These were then exposed to different percentages of microwave irradiation. Figures 4-12 and 4-13 show the current-voltage (J-V) characteristics in 0.1 M Na$_2$SO$_4$ electrolyte for the TiO$_2$ electrodes deposited by AACVD at 350 and 400 °C before
and after microwave irradiation at 10, 25, 50% and 100% power levels respectively. The illumination was chopped manually to reveal the light and dark current. The photocurrent shows anodic behaviour, and the dark current is negligible up to 0.7 V vs. Ag/AgCl, beyond which it is dominated by the oxygen evolution. No photocurrent saturation is observed indicating strong recombination under depletion. The sharp anodic and subsequent cathodic spikes in the photocurrent transients indicate that the recombination is relatively high in the region where the space charge layer width is narrow. It is believed that, during AACVD in the low substrate temperature regime, the decomposition was incomplete and, as a result, the nanocrystals became rich in defects, leaving dislocations and kink sites. These dislocations and kink sites may act as the recombination centres for the photogenerated electron-hole pairs and consequently show poor photocurrent density. The exposure of electrodes to microwaves reduced these defects and improved the inter-particle connections while preserving the nanostructure. The improved PEC performance after microwave treatment can also be attributed to the increased orientation of crystallites in the (101) direction. Batzill [212] has proved that, on anatase (101) the water-oxygen bonds to a five-fold Ti surface atom, and the surface geometry allows both hydrogen atoms of the water molecule to form hydrogen bonds with two-fold surface oxygen atoms at the same time, and this orientation is quite active for water splitting. The XRD analysis also shows an improvement in the (101) direction after microwave treatment, which also contributes to the enhanced PEC performance of the deposited electrodes.
Figure 4-12. J-V Characteristics of TiO$_2$ photoelectrodes fabricated at 350 °C and irradiated under various % microwaves.

Figure 4-13. J-V Characteristics of TiO$_2$ photoelectrodes fabricated at 400 °C and irradiated under various % microwaves.
Figures 4-14 and 4-15 show the current-voltage characteristics in 0.1 M Na₂SO₄ electrolyte for the TiO₂ electrodes before (0%) and after microwave irradiation at 100% (800 W) for the electrodes deposited by AACVD at 350 and 400 °C respectively. It is clear that the photocurrent density trebled when the electrodes were irradiated with 100% microwave radiation. The corresponding incident photon to current conversion efficiency (IPCE) plots are shown in figure 4-16 and agree well with the observed photocurrent densities. The enhancement in the photocurrent density with the different microwave power levels is summarized in figure 4-17.

Figure 4-14. J-V characteristics of TiO₂ photoelectrodes fabricated at 350 °C under various percentages of microwave irradiation (2.45 GHz) [The data has been taken from figure 4.11].
Figure 4-15. J-V characteristics of TiO₂ photoelectrodes fabricated at 400 °C under various percentages of microwave irradiation (2.45 GHz) [The data has been taken from figure 4.12].

Figure 4-16. IPCE plots for as deposited film at 400 °C and after 100 % microwave treatment.
Figure 4-17. The variation of the photocurrent density of AACVD deposited TiO$_2$ electrodes at 350 °C and 400 °C against microwave power level.

The effect on the photocurrent density under conventional thermal annealing and microwave annealing is compared based on the corresponding J-V plots at same power level (Figure 4-18). The temperature-time profiles for each of the heat treatment methods are also constructed in order to find out the energy efficiencies of each process. The temperature-time profile of each electrode for the same power conditions is shown in figure 4-19. Under the same power levels, the area under the temperature-time plot gives an idea about the energy consumption by the furnace. The temperature-time profile clearly indicates reduction of post annealing temperature when using microwave radiations compared to conventional heating method. Microwave irradiation is a faster processing method which can be applied on an industrial scale. Furthermore, eco-friendly microwave annealing saves more than 70% of the total energy (figure 4-19).
Figure 4-18. Variation of the photocurrent density against microwave and conventional annealing.

Figure 4-19. Temperature- time profile of microwave and conventionally deposited samples at 400 °C at the same power conditions.
4.5 Conclusions

AACVD was used to deposit TiO$_2$ electrodes on FTO-glass substrates at 350 and 400 °C. The deposited electrodes were irradiated with various percentages of microwave radiation (10, 25, 50, and 100%) and the electrodes showed improved PEC performance when subjected to increased microwave radiation. XRD analysis confirmed that the deposited films show the anatase phase of TiO$_2$ oriented in the (101) direction. XRD analysis also shows an improvement in the crystallinity of the electrodes after microwave treatment. The surface topographical analysis shows that the nanostructure and texture of the films are less affected after microwave treatment. The $J$-$V$ characteristics showed a three-fold increase in the photocurrent density after microwave treatment. The results demonstrate that microwave treatment is a promising alternative to conventional sintering for TiO$_2$ electrodes to enhance the optoelectronic performance while keeping the texture and nanostructure unaltered, and we believe that this method can open up a new research strategy for the engineering of the properties of semiconductor materials.
Chapter 5

Hierarchical ZnO nanorod electrodes: Effect of post annealing on structural and photoelectrochemical performance

5.1 Overview

Zinc oxide (ZnO) nanorods were deposited on ZnO seeded fluorine doped tin oxide (FTO) glass substrates by chemical bath deposition and the deposited films were treated under microwave irradiation and conventional thermal annealing. XRD diffractograms revealed that there is no significant difference in the film crystallinity. FEG-SEM images of microwave irradiated ZnO nanorods indicate that microwave radiation caused sintering between individual rods and bundling them up thereby creating new rods with large diameter, without significantly affecting the hierarchical rod structures. It shows that the internal surface area of treated films decreased compared to that of as-deposited film. The photoelectrochemical characteristics showed a decrease in the current density of the treated films compared to that of as-deposited film. The reduction of the photocurrent corresponding to conventional thermal annealed ZnO electrodes is more pronounced presumably due to deformation of rod structure and poor charge transport.
5.2 Introduction

Synthesis of numerous ZnO nanostructures has recently attracted a significant interest due to their promising applications in solar cells,[181] transparent conducting film,[213] ultraviolet-protection films,[214] catalysis,[215] and gas sensors.[216] In particular, ZnO nanorods have received extensive attention in photonic, electronic, optoelectronic and electrochemical devices due to ease of fabrication at ambient conditions.[217]

Post-deposition heat treatment is one of the well-known processes that can be used to enhance electronic communication between substrate and electrode material by improving the adherence.[218] Conventional annealing using a furnace or hot plate is a common technique for the post-annealing of nano-materials containing electrodes.[219] A great deal of interest has been received in recent years for irradiation with microwaves as an alternative advanced material processing technique.[220,221] This technique is capable of improving particle necking and crystallinity with a minimum effect on the electrode texture which is due to the fact that microwave irradiation generates a completely different heating profile compared to that of conventional thermal heating. Microwave radiation interacts with lossy materials that result in rapid and uniform heating throughout the material which cannot be achieved by conventional thermal heating methods.[222] This in turns minimizes the thermal gradient, particle diffusion and the processing time.[223] It has also been reported that the materials fabricated using low temperature techniques contain certain amorphous regions that can be converted to crystalline phases by microwave irradiation without affecting the film texture (i.e. micro and nanostructure).[155] Processing materials under microwave irradiation is a relatively novel area of research and hence there is a scarcity of information in the literature. Therefore, further research is essential to understand the effect of microwave irradiation on processing of various materials.
This chapter focuses on the post annealing effect of ZnO nanorods by conventional thermal and microwave heat treatments on the structural and photoelectrochemical (PEC) properties. The results demonstrate that although the hierarchical texture of ZnO is retained to some extent during the microwave treatment, it reduces the internal surface area. Further, it appears that there is no significant advantage of the microwave treatment (i.e. improvements in contacts between rods and substrate by selective heating). As anticipated the conventional thermal heat treatment completely deforms the electrode texture thereby deteriorating the PEC performance.

5.3 Experimental

Fluorine doped tin oxide (FTO) glass substrates (TEC 8 Pilkington, 8 Ω/sq.) were cleaned and sonicated sequentially in acetone, ethanol and deionised water and stored in absolute ethanol. The effective area of the film was maintained at 1 cm². Aerosol assisted chemical vapour deposition (AACVD) was used to deposit a thin ZnO seed layer on FTO glass substrates at 400 ºC using a precursor solution of 0.1 M zinc acetate (BDH Chemicals Ltd) in methanol. The deposition was carried out for 4 min and the thickness of the seed layer was in the order of 50-100 nm.[224] After deposition of the seed layer, electrodes were placed in a tube furnace and further annealed at 400 ºC for 1 hour. The ZnO nanorods were grown on ZnO seeded FTO by chemical bath deposition (CBD) method using a mixture of 0.8 M sodium hydroxide (Fisher Scientific) and 0.02 M zinc nitrate (Sigma Aldrich) solution maintained at 80ºC for 50 minutes. Reactions occurring during chemical bath deposition in the formation of ZnO nanorods on the surface of FTO-glass substrate at 80ºC are as follows,[225]
Dried ZnO nanorod films were subjected to 100% microwave irradiation or conventional thermal annealing for 30 min using a microwave furnace (MRF 16/22, Carbolite Ltd, UK) operating at a frequency of 2.45 GHz and 2 kW power (during the heat treatments the temperature was maintained at 300 °C). The phase and crystallinity of as deposited and annealed ZnO nanorod films were studied using Bruker D8 XRD, operating with monochromatic Cu Kα (λ = 1.54 Å) radiation and PSD detector. Topographic images for the as-deposited, microwave treated and conventionally annealed ZnO nanorods were taken using Leo 1530 VP field emission gun scanning electron microscopy at an accelerating voltage of 5 kV and a working distance of 6 mm. Surface areas of the films were investigated by conducting dye adsorption/desorption measurements.[226] The current-voltage characteristics of heat treated and untreated electrodes were studied by potentiostat (Eco Chemi micro-Autolab type III) by chopping the illumination from halogen lamp at 100 Mw cm\(^2\) light intensity. All the measurements were reapertered at least three times to check the consistency and repeatability of the results.

5.4 Results and Discussion

5.4.1 XRD characterization

X-ray diffraction (XRD) diffractograms of ZnO nanorods grown on FTO glass substrates show the wurtzite crystallites of ZnO of (100), (002), (101), (102), (103), (200) and (110) orientations. [224] The figures 5-1, 5-2 and 5-3 show the diffractograms of as deposited, microwave treated and conventional thermal annealed ZnO nanorod electrodes respectively.
Figure 5-1. XRD diffractogram of as-deposited ZnO electrode.

Figure 5-2. XRD diffractogram of microwave treated ZnO electrode.
The diffractograms reveal that there is no significant difference in the thin film crystallinity of as deposited, microwave irradiated and conventional thermal annealed ZnO nanorods. The XRD reflections indexed by asterisk (*) represent the SnO$_2$ coating on FTO glass substrate. The results indicate that the ZnO nanorods are in highly crystalline form; therefore microwave and conventional annealing do not have any further effect on its crystallinity (Figure 5-4). As discussed in chapter 4, microwave treatment of AACVD-TiO$_2$ films slightly improved the crystallinity due to the partial conversion of amorphous to crystalline TiO$_2$.\cite{221}

The grain size along the (103) peak can be evaluated by using the Debye Scherrer equation

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]  

(17)
where, $D$ is the grain size of the crystallite, $\lambda$ (0.154 nm) is the wavelength of the X-ray used, $\beta$ is the broadening of diffraction line measured at half of its maximum intensity in radians and $\theta$ is the angle of diffraction.

The results indicate that as-deposited ZnO nanorods are highly crystalline in nature; therefore microwave and conventional annealing do not enhance the crystallinity any further. The grain size (along the (103) reflection) is evaluated by using the Debye-Scherer equation. The calculated values for the grain size of as-deposited and microwave irradiated ZnO nanorods are 34.4 and 67.9 nm respectively which closely agreed with the estimated grain size using FEG-SEM images (Figures 5-7 and 5-8).

Figure 5-4. XRD diffractograms of (a) as-deposited, (b) microwave irradiated and (c) conventional thermal annealed ZnO electrodes. [The data has been taken from figures 5-1, 5-2 and 5.3]
5.4.2 Optical characterization

ZnO films were also characterized based on their optical properties. The absorbance spectrum of ZnO film was recorded in the wavelength range between 320-600 nm and contour indicates the significant absorption in the UV region as shown in Figure 5-5. The corresponding optical band gap ($E_g$) value was obtained from equation 18.[229]

$$ (a h \nu) = A(h \nu - E_g)^n $$

where $A$ is a constant, $h \nu$ the photon energy and $n$ an exponent which is equal to 2 or 1/2 for direct or indirect transition respectively. The band gap values of the film were determined from $(ah\nu)^2$ versus $h\nu$ plot (Figure 5-6) by extrapolating the linear part of the absorption spectrum and found to be 3.2 eV which agrees well with literature value reported for ZnO nanorods.[230]

![UV-Vis spectrum of ZnO nanorods on the FTO glass substrate.](image)

Figure 5-5. UV-Vis spectrum of ZnO nanorods on the FTO glass substrate.
Figure 5-6. The plot for direct band gap determination of ZnO films.

5.4.3 Morphological properties

FEG-SEM has been used for the topographic study of as-deposited, microwave and conventional thermal annealed ZnO nanorod electrodes and the respective images are given in figures 5-7, 5-9 and 5-10. Figure 5-7 illustrates that as deposited ZnO nanorods are oriented almost perpendicular to the substrate. The figure 5-8 shows the cross-sectional image of as-deposited ZnO nanorod film. The thickness of the nanorods is estimated to be 0.6 µm which is higher than the calculated microwave penetration depth for ZnO (0.4 µm).
Figure 5-7. The FEG-SEM images of as deposited ZnO nanorods (a) low magnification (b) higher magnification.
Figure 5-8. Cross-sectional image of ZnO nanorods grown on ZnO seed layer.

The topographical image of microwave irradiated ZnO nanorods indicates that microwave treatment of the films has caused sintering especially at the locations where the individual rods are close to each other, without significantly affecting the hierarchical structures (Figure 5-9). This is due to the fact that microwave heat generation takes place within the material by energy conversion rather than heat transfer, and hence there is less room for coagulation of individual rods.
Figure 5-9. The FEG-SEM images of microwave treated ZnO nanorods (a) low magnification (b) higher magnification.

The effect of conventional thermal annealing (at 300 °C) on the surface morphology of ZnO nanorods were clearly identifiable in figure 5-10. It appears that ZnO nanorods have sintered together and deformed the hierarchical structure. There is also evidence to show that necking has occurred and boundaries (between remaining rod-like features) have formed during the thermal annealing step.
5.4.4 Internal surface area determination

The internal surface area of each electrode was determined by dye adsorption/desorption studies.[231] The projected surface area of ZnO electrodes of as deposited, microwave irradiated and conventionally thermal annealed are $1.47 \times 10^2 \pm 10$, $1.3 \times 10^2 \pm 10$ and $0.96 \times 10^2 \pm 20$ cm$^2$ (over 1 cm$^2$ of projected area) respectively. This indicates that the internal
surface area of microwave irradiated and conventional thermal annealed ZnO nanorods electrodes have decreased compared to that of the as-deposited counterpart. This is due to the secondary growth and agglomeration of individual rods as evident from the SEM images. This effect is more pronounced in conventional thermal annealing than microwave treatment causing the destruction of the hierarchical structure. It has been reported elsewhere [232] that the average grain size of the film increased with annealing. Grain boundaries are developed between different crystallographic phases which are responsible for specific properties of the materials.

5.4.5 Photoelectrochemical characterization

The photoelectrochemical (PEC) performance of ZnO electrodes was studied by evaluating the current density-voltage (J-V) characteristics for as-deposited, microwave irradiated and conventional thermal annealed samples. The chopped J-V plots uncorrected for internal surface area differences of as deposited, microwave treated and conventional thermal annealed electrodes are shown in figure 5-11.
Figure 5-11. Current density versus voltage ($J-V$) characteristics of (a) as-deposited, (b) microwave irradiated and (c) conventional thermal annealed ZnO electrodes. The current density of each electrode is uncorrected for the internal surface area.

The plots illustrate that all the electrodes are resistive in nature. The current density of microwave irradiated electrodes decreases compared to that of the as-deposited electrodes. The reduction of the photocurrent corresponding to conventional thermal annealed ZnO electrodes is more pronounced, presumably due to deformation of the rod structure. This appeared to be due to the poor charge transport within the electrode containing deformed features in nanoscale. It is well known that the charge transport within ZnO nanorods is more efficient compared to randomly oriented nanostructured electrodes.[233] The $J-V$ plots indicate the same trend with the calculated projected surface areas of the electrodes. The variation of the estimated surface area against the corrected photocurrent density for internal surface area of as-deposited and treated ZnO electrodes is plotted in figure 5-12.
Figure 5-12. The comparison of estimated internal surface area versus corrected photocurrent density for internal surface area of as-deposited and treated ZnO electrodes.

It is evident in the present work that the microwave treatment preserves the structure of nanorods better than in the case of conventional thermal annealing. TiO$_2$ electrodes showed that microwave processing facilitates the growth of crystallites and inter-particles connections while preserving the electrode texture and improving the PEC properties appeared to be due to the enhanced charge collection.[221] It is clear from the present work that post annealing of ZnO nanorod has less effect on improving PEC performance as it leads to reduced internal surface area of the electrodes. Furthermore, the conventional thermal heat treatment completely deforms the electrode texture thereby deteriorating the PEC performance. The reduction of surface areas of the films mainly affects the PEC performance of the films which is confirmed by normalized $J$-$V$ plot (Figure 5-13). The normalized $J$-$V$ plots show the light current is almost same for as deposited, microwave and conventionally annealed electrodes.
which proves the PEC behaviour corresponds to the changes occurred in the electrode surface areas due to the microwave irradiation and conventional annealing.

Figure 5-13. The normalised J-V plots of as-deposited, microwave irradiated and conventionally annealed ZnO electrodes.

5.5 Conclusions

Zinc oxide nanorods were grown on FTO-glass substrate by CBD method after depositing a seed layer by AACVD. The structural properties of as-deposited, microwave irradiated and conventional thermal annealed ZnO nanorods were studied by XRD. X-ray diffraction measurements show that ZnO nanorods grown in wurtzite crystal phase. There is no apparent change of the crystallinity of as-deposited, microwave irradiated and the conventionally annealed electrodes. The SEM images show that the microwave irradiation caused sintering of individual rods resulting in the growth of rod diameter whilst the conventional thermal
annealing deformed the hierarchical ZnO structure. The PEC studies indicate that all electrodes are resistive in nature. The current density of microwave irradiated electrode decreases compared to that of as-deposited electrode. The reduction of the photocurrent corresponding to conventional thermal annealed ZnO electrodes is more intense presumably due to deformation of rod structure. This appeared to be due to the poor charge transport in deformed electrodes.
Chapter 6

Microwave-assisted low temperature fabrication of nanostructured ZnO thin film electrodes for solar energy conversion

6.1 Overview

Metallic zinc (Zn) thin films were electrodeposited on to fluorine-doped tin oxide (FTO) substrates by electrodeposition and the deposited Zn was oxidised to zinc oxide (ZnO) using conventional radiant and microwave annealing methods. The oxidation temperatures of both methods were varied and the respective photoelectrochemical (PEC) performance was evaluated for each electrode. The best PEC performance of a photocurrent of 93 µA cm\(^{-2}\) at 1.23 V vs. NHE (0.74 V vs. Ag/AgCl) and an incident photon-to-electron conversion efficiency (IPCE) of 4.5% was achieved after oxidation of Zn at 425 °C for 15 min under conventional radiant annealing. X-ray diffractograms showed that the oxidation of Zn to ZnO was not 100% efficient during the annealing period as evidence for metallic Zn was still seen. Further increases in temperature resulted in lower photocurrents. For the microwave oxidation of Zn to ZnO, the best photocurrent of 130 µA cm\(^{-2}\) at 1.23 V vs. NHE and an IPCE of 6% were observed after annealing for 3 min, during which time the temperature reached 250 °C. The photocurrent was 40% higher for the microwave annealed sample compared to conventional radiant annealing at the same applied potential; this increase was attributed to higher surface area, confirmed by SEM surface topographical analysis, and better yields of conversion to crystalline ZnO. SEM analysis confirmed that the higher temperature used in the thermal annealing process leads to sintering of the nanostructure.
which reduces the effective surface area. The oxidation of Zn to ZnO using microwave annealing was achieved at much lower temperatures and therefore the high surface area of the films was maintained while preserving the nanostructure. Overall, it was demonstrated that oxidation of Zn to ZnO can be accomplished by microwave annealing five times faster than conventional annealing and with much lower temperature, and this resulted in a ~75% power saving. This highly efficient microwave processing offers significant economic advantages for industrial scale up.
6.2 Introduction

The global increase in the demand for energy and the rapid depletion of non-renewable energy sources, such as natural gas coal and oil, has led researchers to search for new means of generating and storing energy. Hydrogen gas, as a mean of storing chemical energy has long been thought of as a possible alternative to fossil fuels, providing that it could be generated in a cheap and environmentally friendly way. Hydrogen gas can be generated in-situ using photoelectrochemical (PEC) water splitting at a semiconductor/electrolyte interface, or alternatively photovoltaic thin film technology can be used to supply the potential required to drive the water splitting reaction.[234] For all such solar harvesting devices, metal oxide semiconductors, for example Fe₂O₃,[235] TiO₂,[236,237] ZnO[238] and WO₃,[239] have been extensively studied because they are inexpensive, inert and scalable for industrial production purposes, and are thus of great interest. ZnO in particular, has found applications in wide variety of devices ranging from photovoltaic devices (PEC cells,[240] dye-sensitized solar cells,[241] solid state solar cells[242]) to electronic devices (sensors,[243] field effect transistors,[244] Schottky diodes,[245] light emitting device arrays[246]) due to its unique and diverse properties; thus it is appropriate to develop low-cost and industrially scalable methods for its fabrication.

In the case of metal oxide thin films, photovoltaic device fabrication at an industrial scale usually involves a post deposition thermal annealing process.[247] This annealing process is essential as it controls the bulk properties of the material. For example annealing can improve the thin film’s adhesion to the substrate, change the materials phase and crystallinity and hence conductivity, and change the surface morphology and therefore surface area of the material.[156] Such properties greatly influence the semiconductor performance in its respective device. As the typical annealing process makes use of extreme temperatures, it is
vastly energy intensive and time consuming, which has negative economic consequences.[247] Other drawbacks for thermal annealing are that the high temperatures can cause collapse of the nanostructure which greatly reduces the porosity and consequently the surface area, which in turn affects the PEC performance.[248] A promising alternative to conventional thermal annealing is microwave processing.[249-251] Microwave processing has been shown to offer significant cost savings though reduced processing times, reduced floor space and selective heating.[252,253]

The heating mechanism of thermal and microwave annealing is fundamentally different. In the conventional thermal annealing process, heat is transferred from the surroundings (i.e. from the furnace or hotplate) to the sample, whereas in microwave annealing, heat is generated within the sample itself (volumetric heating), which is a distinct advantage as it can minimize energy losses associated with energy transfer.[252] In thermal annealing, there is huge potential for energy losses in the process of heat transfer from the heating element to the sample. In general, there are two possible mechanisms in which energy conversion from microwave radiation to heat can occur – polarization or conduction. Polarization involves displacement of charge through the formation and rotation of electric dipoles, whereas conduction involves long range transport of charge.[252] The rotation of the electric dipole causes molecular friction which generates heat, and ionic conduction causes molecular motion and collision, which also results in heat generation. The ability to absorb microwave radiation and hence heat generation is determined by the dielectric loss (ε") and loss tangent (tan δ) of the materials. In order for microwaves to interact with the material, a balanced combination of moderate dielectric constant (to permit adequate penetration) and high loss tangent (for higher energy to heat conversion) are required. However, use of microwave radiation to process post deposited semiconductor materials and material synthesis has shown promising results over conventional heating methods.
Microwave annealing has already shown great potential for low-cost processing of TiO$_2$[156], ZnO[248] and $\alpha$-Fe$_2$O$_3$[247] thin films. Not only has microwave annealing proven to be a match for conventional thermal annealing, the thin films processed by microwave annealing have shown enhanced properties in terms of their PEC performance.[156] This has been attributed to an increase in the crystallinity of the material without significantly affecting its nanostructure. It has also been shown that processing times are greatly reduced compared with thermal annealing.[247] This chapter compares the efficiency of oxidation of electrodeposited metallic Zn to ZnO using conventional radiant and microwave annealing methods in terms of their PEC performance. A 40% increase in the photocurrent is seen when ZnO is produced using microwave annealing rather than conventional. Also better conversion yields and faster processing times at lower temperatures were achieved with microwave annealing; features that are highly desirable for large-scale industrial production of ZnO based electronic and optoelectronic devices.

### 6.3 Experimental

Fluorine-doped tin oxide (FTO) glass substrates (FTO, TEC8, Pilkington Glass, Ltd, St Helens UK) were cut to 1 x 2 cm$^2$ slides and were cleansed via a series of 15 min sonication treatments in 2-propanol, acetone, ethanol and deionized water (resistivity = 18.2 M$\Omega$) and finally stored in absolute ethanol. The electrochemical solution of aqueous Zn(NO$_3$)$_2$ was prepared by dissolving 1 mM Zn(NO$_3$)$_2$.6H$_2$O (reagent grade, Sigma Aldrich, Dorset, UK) in 100 mL deionized water. The electrochemical deposition of Zn films was performed in a three-electrode configuration where the FTO was used as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode. When Zn was electrochemically deposited on FTO coated glass substrates, the area of the film was maintained at 1 cm$^2$. A potential of -1.25 V for 1800 s (total number of charges- 1 x 10$^3$ C)
was applied which resulted in a grey metallic Zn on the FTO conducting surface. The films were then washed with deionized water and left in air to dry. The calculated film thickness was ~600 nm. The oxidation of Zn to ZnO was studied using both conventional thermal and microwave annealing. Conventional thermal annealing was carried out in a tube furnace (MTF-10-25-130, Carbolite, Hope Valley, UK) with a ramp rate of 15 ºC/min to its desired temperature which were within the range of 400 to 600 ºC. Both ends of the tube were left open to allow air to flow in. After annealing, the furnace was turned off and the samples were allowed to cool in the tube furnace until the temperature reached to room temperature. Microwave assisted annealing was performed using a modern microwave oven (Microwave research Applications Inc. BP-211/50, USA) operating at 2.45 GHz frequency with a maximum power of 3000 W. A microwave monitor (CELTEK, S/N: 771459) was used to observe any radiation leakage and as the monitor read 0 mW cm\(^{-2}\) thus no leakage was observed. The Zn films were oxidised using the microwave furnace from 3 min to 10 min durations and they were covered with an insulator, in order to minimise the heat loss. The temperature of the annealed substrates was monitored using an infrared temperature probe (Mikron infrared Inc. M67/M67S series, USA) with an error of ± 5 ºC. The PEC performance of the annealed ZnO films was measured using a three-electrode configuration in 1 M Na\(_2\)SO\(_4\) aqueous electrolyte, Ag/AgCl as the reference electrode and Pt wire as the counter electrode. The potential of the photodeode was controlled using computer-controlled software and a potentiostat (microAutoLab, type III, Windsor Scientific Limited, Berkshire, UK). The electrodes were illuminated through the electrolyte side and the illumination area was 1 cm\(^2\). The illumination source was AM 1.5 class A solar simulator (16S – 300 solar simulator, Solar Light Co., Inc., PA, USA) equipped with a 300 W xenon lamp. The intensity of the light was calibrated at 100 mW cm\(^{-2}\) using a class II pyranometer (PMA2144, Solar
Light Co., Inc., PA, USA) equipped with a digital photometer (PMA2100, Solar Light Co., Inc., PA, USA).

The microstructure and surface morphology of the thin films were investigated using field emission gun scanning electron microscopy (FEG-SEM, Leo 1530 VP) at an accelerating voltage of 5 keV and a working distance of 5 mm. The phase and crystallinity of the as deposited and annealed ZnO nanorod films were studied using Bruker D8 XRD, operating with monochromatic Cu Kα (λ = 1.54 Å) radiation and PSD detector. The incident photon to electron conversion efficiency (IPCE) was obtained by measuring the incident photon flux using a 75 W xenon lamp connected to a monochromator (TMc300, Bentham Instruments Ltd. Berkshire, UK). The light was calibrated using a silicon diode. Photocurrent spectra were measured at 0.65 V vs. Ag/AgCl (1.23 V vs. NHE) using a combination of a lock-in amplifier (Bentham 485, Bentham Instruments Ltd., Berkshire, UK) and a custom built potentiostat.

6.4 Results and Discussion

6.4.1 Electrodeposition of Zn

Electrodeposition of Zn films on conductive substrates by cathodic reduction of Zn$^{2+}$ ions is a well known process which is reported elsewhere.[254]

6.4.2 XRD characterisation

Metallic Zn thin films were deposited by electrodeposition and its oxidation to ZnO was conducted using conventional radiant annealing or microwave annealing. The phase and crystallinity of the films as a function of annealing temperature were studied using XRD.
Figure 6-1 shows the XRD reflections of as-deposited, conventionally annealed and microwave annealed samples. The XRD reflections of electrodeposited Zn (Figure 6-1a) confirmed that the sample consists only of Zn with an hcc crystal structure and a preferred orientation in the (101) direction. When the electrodes are conventionally annealed at 425 °C for 15 min in air, the deposited Zn is oxidised to ZnO with a wurtzite crystallites of (100), (002), (101), (102), (103), (200) and (110) orientations. However, during the 15 min annealing process not all of the Zn is oxidised as confirmed by the corresponding (101) reflection of Zn in the XRD diffractogram (Figure 6-1b). As shown in figure 6-1c, the XRD diffractogram of the microwave annealed sample at 250 °C for 3 min shows only ZnO reflections which indicate complete oxidation to ZnO. The corresponding ZnO wurtzite crystallites of (100), (002), (101), (102), (103), (200) and (110) reflections are more intense and well-defined compared to the films that are annealed under conventional heating, which indicates a higher degree of crystallinity of microwave annealing. This clearly indicates microwave treatment is an efficient way of oxidising Zn to ZnO compared with conventional heating. Another advantage is that microwave annealing resulted in the oxidation of Zn at a much lower temperature (i.e. 250 °C) with less processing time (i.e. 3 min) in contrast to conventional heating.
Figure 6-1. XRD diffractograms of (a) as electrodeposited Zn, (b) conventionally annealed at 425 °C for 15 min and (c) microwave annealed at 250 °C for 3 min. The (101) peak of Zn is shown with an arrow. The standard XRD reflections of SnO₂, Zn and ZnO are also shown.

6.4.3 Morphological properties and particle size

The impact of the annealing method on the morphology of the nanostructure was studied using FEG-SEM. Figures 6-2 shows the surface morphology of as deposited and annealed samples at different temperatures using thermal annealing. The respective magnified images are shown in figures 6-3. The surface of as-deposited Zn is shown in figure 6-3a which comprises nanostructures in the nanometre range having a broad size distribution. The particle shape is more or less spherical with some cluster/agglomeration between the particles. The large particles are spatially distributed on the surface which is surrounded by a blanket of clustered/agglomerated small Zn particles. The post annealing of Zn films resulted
in oxidation and sintering which lead to various morphological changes of the film depending on the annealing temperature, as shown in figures 6-3b-d. At 425 °C (figure 6-3c) the ZnO nanostructure adopts a cauliflower-like structure with high apparent surface area. Heating at a higher temperature of 600 °C resulted in agglomeration and sintering of the nanostructure (figure 6-3d), resulting in a lower apparent surface area.

Figure 6-2. Surface topographical images of (a) as electrodeposited Zn, conventionally annealed Zn electrodes at (b) 400 °C (c) 425 °C and (d) 600 °C.
As found by XRD reflections, the microwave oxidation of electrodeposited Zn films to ZnO was shown to occur at lower temperatures and the rate of oxidation was higher compared to conventional thermal annealing. The surface morphology of the as-deposited and microwave oxidised films is shown in figure 6-4 for annealing temperatures of 180, 250 and 300 °C and the respective magnified images are shown in figures 6-5. For microwave annealing temperatures of 180 and 250 °C (figure 6-5b and 6-5c), there appears to be no significant change in the surface morphology compared with the as-deposited metallic Zn film. Evidence of particle agglomeration and sintering/melting begins to be observed at a higher microwave annealing temperature of 300 °C (figure 6-5d). However, it was shown from the XRD data that complete oxidation of Zn to ZnO occurs at 250 °C, hence the use of higher temperatures
is not required. As evident from the SEM images it is clear that microwave annealing preserves the nanostructure of the film compared to conventionally annealed samples due to its rapid and volumetric heating capabilities. This phenomenon agrees well with our previously reported articles and the literature.[156,247,253]

Figure 6-4. Surface topographical images of (a) as electrodeposited Zn, Microwave annealed Zn electrodes at (b) 180 °C (c) 250 °C and (d) 300 °C.
Figure 6-5. The magnified SEM images of (a) as electrodeposited Zn, microwave annealed Zn electrodes at (b) 180 °C (c) 250 °C and (d) 300 °C. [Respective magnified images of figure 6-4].

7.4.4 Photoelectrochemical properties of electrodes

Photoelelctrochemical (PEC) studies were carried out for the annealed electrodes in order to find the effect on the performance for different annealing methods. The electrodes were scanned from -0.3 V to 1 V with reference to Ag/AgCl. The obtained current density-potential plots for electrodeposited Zn electrodes oxidised using both conventional and microwave heating are shown in figures 6-6 and 6-7 at various temperatures, respectively. The inset in the respective figures show the photocurrent densities obtained for microwave and conventionally annealed electrodes at at 1.23 V vs. NHE (0.74 V vs. Ag/AgCl) as a function of annealing temperature. As shown in figure 6-6, the photocurrent density reached its maximum value, 93 μA cm$^{-2}$ at 1.23 V vs. NHE, for the electrodeposited Zn films
conventionally annealed at 425 °C for 15 min. Further annealing at higher temperatures resulted in the reduction of the photocurrent density to 38 μA cm\(^{-2}\) at 600 °C. This was most likely due to a reduction in the surface area caused by sintering of the nanostructure; this is confirmed by the differences seen in the surface morphology (figure 6-3d). The samples annealed at temperatures lower than 400 °C showed negligible photocurrent with a reasonable dark current due to the unconverted Zn in the film. Figure 6-7 shows the chopped photocurrent densities obtained for electrodeposited Zn electrodes oxidised by microwave radiation at various temperatures. The PEC performance of the microwave annealed electrodes showed an improvement until the sample temperature rose to 250 °C. Microwave annealing at temperatures higher than 250 °C resulted in lower photocurrents, most likely due to reduction in surface area caused by sintering and agglomeration of the nanostructure, as evidenced by the SEM images (figure 6-5d). The electrode annealed at 180 °C under microwave radiation showed a photocurrent density, about 73 μA cm\(^{-2}\) at 1.23 V vs. NHE, whereas the electrode annealed at 250 °C showed a much higher photocurrent density of 130 μA cm\(^{-2}\) at 1.23 V vs. NHE.
Figure 6. The chopped photocurrent density-applied potential plot of conventionally annealed electrodeposited Zn electrodes at various temperatures. Inset shows photocurrent densities obtained for the electrodes at 1.23 V vs. NHE annealed at corresponding temperatures using conventional heating.

Figure 7. The chopped photocurrent density-applied potential plot of microwave annealed electrodeposited Zn electrodes at various temperatures. Inset shows photocurrent densities
obtained for the electrodes at 1.23 V vs. NHE annealed at corresponding temperatures using microwave heating.

Figure 6-8 compares the highest PEC performance obtained for conventional and microwave treated samples and the inset represents the highest photocurrent density obtained at 1.23 V vs. NHE. The maximum photocurrent (at 1.23 V vs. NHE) achieved by conventional thermal annealing was 93 μA cm$^{-2}$, whereas the maximum photocurrent achieved for the microwave annealed sample was 130 μA cm$^{-2}$, which was 40% higher.

![Figure 6-8](image)

Figure 6-8. The plot of photocurrent density vs. applied potential for the electrodeposited Zn electrodes annealed at 425 °C for 15 min and 250 °C for 3 min using conventional and microwave heating respectively. Inset shows the photocurrent density obtained at 1.23 V vs NHE as a function of annealing temperature for the samples.

The 40% increase in the photocurrent achieved by microwave annealing compared with conventional thermal annealing could be attributed to three possible factors – an increase in crystallinity, more efficient oxidation of Zn to ZnO and higher surface area. Evidence for
these factors has already been seen in the XRD patterns and SEM images. For the best performing conventionally annealed sample (at 425 °C) the XRD pattern showed the presence of unconverted Zn. No such peak was seen for the microwave annealed sample, which therefore shows a complete oxidation to ZnO at low temperatures. Also, it can clearly be seen from the intensity of the ZnO reflections in the XRD patterns that the crystallinity of the microwave annealed sample is higher. The increase in the photocurrent also was confirmed by IPCE measurements conducted at 1.23 V vs. NHE, shown in figure 6-9. An IPCE of 4.5% and 6% was observed for the conventionally and microwave oxidised samples, respectively. This confirms the increase in charge generation most likely due to the increased surface area.

Figure 6-9. IPCE spectra as a function of wavelength at 1.23 V vs. NHE for electrodeposited Zn electrodes annealed under conventional and microwave radiation at 425 °C for 15 min and 250 °C for 3 min respectively.
6.4.5 Temperature-time profile

The benefit of using microwave radiation as an alternative to the conventional thermal annealing method is demonstrated by the temperature-time profiles. Figure 6-10 depicts the temperature-time profiles of both the annealing processes in a conventional furnace and in a microwave furnace for the samples with best PEC performance under each method. The area under the graph (not including the cooling process), roughly estimates the energy consumed during each annealing process, and shows that microwave annealing requires only 25% of the energy needed for conventional thermal annealing while operating at nearly one tenth of the maximum power level. Moreover, the microwave method also produced ZnO electrodes with 40% higher photocurrent than that of the conventionally annealed electrodes.

Figure 6-10. Temperature-time profile of the samples annealed at 425 and 250 °C for 15 and 3 min using conventional and microwave-assisted annealing respectively. The maximum power used at the soaking temperature corresponding to each annealing technique is also mentioned.
6.5 Conclusions

The oxidation of electrodeposited Zn films to ZnO was conducted using microwave and conventional thermal annealing methods at various temperatures and comparisons were drawn. A 40% higher photocurrent (at 1.23 V vs. NHE) was achieved for the microwave annealed films compared to their conventionally annealed counterparts. XRD patterns showed that the oxidation of Zn to ZnO was not 100% efficient as evidence for metallic Zn was seen. For the conventionally annealed film the highest performing film showed unconverted Zn whereas a microwave annealed film did not show any sign of Zn. The improvement in the PEC properties was attributed to higher surface area, confirmed by SEM surface topographical analysis, and better yields of Zn oxidation to ZnO, and higher crystallinity. It was found that the higher temperatures used in the thermal annealing result in sintering of the nanostructure which reduces the overall surface area. However, in contrast to conventional thermal annealing, microwave annealing preserves the nanostructure of the electrodes due to the difference in the heating mechanism (volumetric heating). Microwave annealing allowed complete oxidation to ZnO with excellent crystallinity. Also oxidation using microwave annealing was achieved five times faster. The techno-economic impact was considered by assessing the overall energy usage. This evaluation shows that the microwave annealing method offers energy savings of up to ~75%, which would make it highly desirable for industrial scale up. Also the lower oxidation temperatures could open up possibilities for ZnO processing for low temperature flexible substrates.
Chapter 7

Microwave-assisted synthesis and processing of inorganic materials for electronic and optoelectronic applications

7.1 Microwave assisted in-situ activation of lattice oxygen of TiO$_2$ by Pd$^{2+}$ ion; Microwave-assisted synthesis of Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ powders

7.1.1 Overview

Microwave-assisted chemistry is becoming very attractive in organic and inorganic synthesis due to its advantages over conventional heating methods. Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ powder samples have been synthesised by conventional and microwave-assisted methods. The X-ray diffraction (XRD) shows that the observed reflections correspond to the anatase phase of TiO$_2$ for both conventional and microwave assisted methods. However, the absence of Pd metal or PdO diffraction lines in XRD diffractigrams confirmed that the Pd ions are substituted in TiO$_2$. The corresponding anatase reflections are more intense and notable for the Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ sample synthesised using microwave-assisted method compared to the conventional synthesised method. The Raman spectra do not show any significant difference of the Raman peaks for the powders made by these two methods. The field emission gun scanning electron microscope (FEG-SEM) surface topography images showed a significant difference in the shape and the size of the Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ powder synthesised by microwave-assisted and conventional methods. The average crystallite size of Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ synthesised using microwave radiation is found to be in the range of 1-2 nm which is much smaller than the reported value for Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ made by conventional method. The Brunauer–Emmett–
Teller (BET) measurements further confirm that the microwave synthesised Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ powder has a slightly higher surface area (244 m$^2$/g) than the conventionally synthesised powder which is 210 m$^2$/g.

7.1.2 Introduction

In recent years, microwaves are being explored as an efficient alternative energy source to traditional forms of heating (i.e. isomantles, oil baths, hot plates etc.) in material synthesis.[255] It has been shown that the use of microwave radiation for material synthesis has shown promising results over conventional heating methods in terms of the product yield and the reaction rate.[256] Over the past few decades, most of the microwave heating in chemistry has been limited to organic synthesis. More recently the use of microwave radiation for heating reactions in the laboratory has expanded to inorganic and materials chemistry.[257]

Titanium dioxide (TiO$_2$) has attracted extensive interest because of its wide applications in photocatalysis,[258] chemical sensors,[259] solar cells,[260] and hydrogen storage materials.[261] Due to the wide band gap of TiO$_2$ (Eg – 3.2 eV) it has limitations for practical applications as it absorbs only from the UV region of the solar spectrum. Due to the poor charge generation and high recombination rates of photogenerated electron-hole pairs in TiO$_2$ electrodes results undesirable impact on such applications.[209] To overcome these difficulties, much effort has been made to modify TiO$_2$ nanoparticles by incorporating platinum group metals (i.e. Pd, Ru, Rh, Pt) into the structure.[262] The incorporation of these metal ions into the anatase phase of TiO$_2$ activates the lattice oxygen, which is of great interest due its ability to act as an active site for catalytic oxidation–reduction reactions.[263]
Among the other platinum group metals, palladium is the cheapest and most commonly used metal for such applications.

Microwave-assisted incorporation of Pt group metal ions into the structure of anatase TiO$_2$ is very attractive because it gives competitive advantages over other conventional synthesis methods. This section of the chapter reports the structural and morphological changes of Pd incorporated TiO$_2$ ($\text{Ti}_{0.97}\text{Pd}_{0.03}\text{O}_{1.97}$) synthesised using microwave-assisted and conventional synthesis methods.

7.1.3 Experimental

7.1.3.1 Synthesis of Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ by traditional method

Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ was prepared by solution combustion method.[264] In the synthesis 9.7 mmol of TiO(NO$_3$)$_2$ solution is taken, which is prepared by Ti(OC$_3$H$_7$)$_4$ (sigma Aldrich), 0.3 mmol of Pd(NO$_3$)$_2$ (Alfa Aesar), and 1.11 mmol of glycine (sigma Aldrich) as fuel in a 300 mL crystallizing dish. The components were fully dissolved in 15 mL of water. The solution was kept in a preheated conventional furnace at 350 °C for 2 hrs. The combustion takes place after the dehydration and the solid product is left behind.

7.1.3.2 Synthesis of Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ by microwave assisted method

A solution mixture of 9.7 mmol of Ti(OC$_3$H$_7$)$_4$ (sigma Aldrich), 0.3 mmol of Pd(NO$_3$)$_2$ (Alfa Aesar), and 1.11 mmol of glycine (sigma Aldrich) as fuel (the self-sustained combustion process of glycine produces a high exothermic heat during the reaction which facilitates the facile intercalation of Pd$^{2+}$ in to the TiO$_2$ structure) was added to the 20 mL microwave reaction vessel with a magnetic stirrer. The components were fully dissolved in 15 mL of
water. The components were fully dissolved and heated to 150 °C for 3 min. Microwave assisted synthesis was performed in a Biotage Initiator EXP 8 reactor in 10-20 mL crimped vials. After 3 min of microwave treatment, a black coloured fine solid dispersion was obtained. The solid was separated by centrifuge and kept in a desiccator overnight. The incorporation of Pd into the TiO₂ structure is qualitatively understood by the colour change of the reaction mixture after irradiated to microwaves (figure 7.1-1). The microwave reactor conditions during the microwave treatment are shown from the figure 7.1-2.

![Before Microwave | After Microwave | Ti₀.97Pd₀.03O₁.97 Powder](image)

Figure 7.1-1. The images of reaction mixtures and the product at various preparation stages.
Figure 7.1-2. The microwave reactor conditions during the microwave treatment (a) power curve (b) Pressure curve (c) temperature curve.

7.1.3.3 Characterization

X-ray diffraction (XRD) analysis was employed to determine the crystalline structure of Ti_{0.97}Pd_{0.03}O_{1.97} powder samples using Bruker D8 XRD, operating with monochromatic Cu Kα (λ = 1.54 Å) radiation and PSD detector. The Jobin -Yyon LabRam HR 800 (He-Ne laser (632.8 nm) / CCD detector) Raman spectroscope was used to obtain the Raman spectra. The surface morphology of the powders was obtained using a field emission gun scanning electron microscopy (FEG-SEM, Leo 1530 VP) at an accelerating voltage of 5 keV and
working distance of 5 mm. The Brunauer–Emmett–Teller (BET) measurements were conducted at Johnson Matthey Technology Centre, Sonning Common UK.

### 7.1.4 Results and Discussion

#### 7.1.4.1 Structural characterization

The reported XRD diffractograms of Pd$^{2+}$ ion substituted TiO$_2$ (i.e. Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$) is shown in Figure 7.1-3. The patterns are indexed to anatase TiO$_2$ polymorph of TiO$_2$ (Tetragonal, I$4_1$/amd, JCPDS no. 21−1272).[264]

![Figure 7.1-3. The rietveld refined XRD profile of Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$][264]

Figure 7.1-4 indicates that the XRD reflections obtained for Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ which was synthesised using the reported method and microwave-assisted method. The reflections
correspond to anatase TiO$_2$ is observed in both conventional and microwave heating methods. The absence of Pd metal or PdO diffraction lines in Figure 7.1-3 and 7.1-4 indeed confirm that the Pd ions are substituted in TiO$_2$ structure. However, the corresponding anatase reflections are more intense and distinguished for the Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ sample synthesised using microwave irradiation which indicates that microwave-assisted synthesis enhances the anatase crystalline phase of TiO$_2$.

![XRD Reflections](image)

Figure 7.1-4. XRD reflections obtained for Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ powder samples made using conventional and microwave assisted methods.

Figure 7.1-5 illustrates the Raman peaks corresponding to Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ powder samples. The Raman spectra do not show any significant difference of the Raman peaks of corresponding anatase phase of TiO$_2$ at 153, 400, 503, 635 cm$^{-1}$ for the powders made by
these two methods. However, the peak height of the microwave-assisted $\text{Ti}_{0.97}\text{Pd}_{0.03}\text{O}_{1.97}$ sample is comparatively high compared to the conventionally made sample.

Figure 7.1-5. The Raman spectra obtained for $\text{Ti}_{0.97}\text{Pd}_{0.03}\text{O}_{1.97}$ under conventional and microwave assisted methods.

7.1.4.2 Surface morphology

The FEG-SEM surface topography images showed a significant difference in the shape and the size of $\text{Ti}_{0.97}\text{Pd}_{0.03}\text{O}_{1.97}$ synthesised by microwave-assisted and conventional methods. Figure 7.1-6 shows the SEM images of $\text{Ti}_{0.97}\text{Pd}_{0.03}\text{O}_{1.97}$ powder from the microwave-assisted synthesis and figure 7.1-7 indicates the morphology of the conventionally made powder. In microwave assisted synthesis the powder consisted of spherical nanoparticle clusters, whereas in the conventional method the particles look like disks (layer structure) with much larger particle size. It is clear that microwave radiation improves the crystal growth to form
highly porous spherical nanocrystallites which leads to a higher internal surface in the powder.

Figure 7.1-6. The SEM images of $\text{Ti}_{0.97}\text{Pd}_{0.03}\text{O}_{1.97}$ powder synthesised using microwave radiation.
The surface topographical images confirmed that the average crystallite size of Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ synthesised using microwave radiation is found to be in the range of 1-2 nm. However, the size is much smaller than the reported value for Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ made by conventional method which in the range of 13 ± 2 nm. The particle size of the composite made by conventional method is higher than the reported value; it is in the range of 1-3 μm. The Brunauer–Emmett–Teller (BET) measurements indicated that the microwave synthesised Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ powder has a slightly higher surface area (244 m$^2$/g) than the conventionally synthesised powder which is 210 m$^2$/g.
7.1.5 Conclusions

Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ was prepared by solution combustion method crystallizing in anatase TiO$_2$ structure. The compound was synthesised by using conventional sintering and microwave sintering methods and compared structural and morphological differences. The XRD patterns confirmed that the corresponding reflections of anatase phase has increased by microwave assisted synthesis than the conventional method. Raman spectroscopy indicated that the phases and the structure of the compound prepared by microwave and conventional methods were in good agreement. The SEM images confirmed a significant difference in the shape and the size of Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ crystallites made under conventional and microwave methods. The average crystallite size of Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ synthesised under microwave radiation is found to be in the range of 1-2 nm which is much smaller than the reported value for Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ under conventional heating method. The BET measurements further confirmed that the microwave synthesised Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ powder has slightly higher surface area than the conventionally synthesised powder which is well agreed with the surface topographical images.
7.2 The effect of post annealing on the electrical conductivity of lithium aluminium titanium phosphate pellets

7.2.1 Overview

Nowadays, lithium ion batteries are widely used in our daily life as they are the main power source for the most mobile devices. Electrolytes with high conductivity, good mechanical properties and good chemical stability are essential to be used in lithium ion batteries. Lithium aluminum titanium phosphate (LATP) is a potential inorganic solid electrolyte for lithium ion batteries with NASICON (Na-Super-Ionic-Conductor) type structure. Post-deposition heat treatment is one of the ways to improve ionic conductivity by enhancing the electronic communication between particles and crystallinity. In this section of the chapter, the effect of post heat treatment on the electrical conductivity of the LATP pellets by electrochemical impedance spectroscopy (EIS) is discussed. The differences in structural and morphological properties of the LATP pellets were studied using XRD, Raman spectroscopy and FEG-SEM. The XRD and Raman analysis showed that the post heat treatment increase the crystallinity of the pellets without any structural changes. The SEM images confirmed that crystallized grains of microwave treated LATP is more uniform and the crystallites are fairly small in size compared to the conventionally annealed pellets. The EIS results confirmed that the comparable conductivities to conventional annealing at 800°C for 1 hr can be obtained when the LATP pellets are irradiated with microwave for 3 min. This is attributed to formation of improved crystallinity, grain homogeneity and contacts by microwave post treatment of LATP pellets.


7.2.2 Introduction

Lithium aluminum titanium phosphate (LATP) has shown a great research interest as it is a very good candidate electrolyte material which has a comparable ionic conductivity in bulk form with the ionic conductivities currently found in the liquid-type electrolytes of Li-ion batteries.[265] Better electrochemical properties of these electrolyte materials can be obtained by varying the crystal sizes with different morphologies, homogeneity of the chemical composition with a higher phase purity and crystallinity. Post-deposition heat treatment is one of the well-known processes that can be used to enhance electronic communication between particles of these materials by improving the crystallinity and the nanostructure. In recent years, a great deal of interest has been focused on irradiation with microwaves as an alternative advanced material processing technique. This technique is capable of improving particle necking and crystallinity with a minimal effect on the material’s nanostructure. In order for microwaves to interact with the material and generate heat, a balanced combination of moderate dielectric constant (to permit adequate penetration) and high loss tangent (for higher energy to heat conversion) are required. Since the dielectric properties of the materials are temperature dependent, the microwave absorption properties can be enhanced by elevating the temperature of materials using hybrid heating or microwave susceptors. This section of the chapter discusses the effect on the electrical conductivity and structural properties of microwave and conventionally treated LATP pellets.
7.2.3 Experimental

The Lithium Aluminium Titanium Phosphate (LATP) pellets (Johnson Matthey Technology Centre, Sonning Common UK) were sintered using microwaves and conventional sintering methods. The conductivity of the post treated pellets with microwave and conventional thermal methods were compared with the as prepared LATP sample. During the microwave treatment, temperature of the LATP samples was increased using a SiC tile as it generates heat rapidly when irradiated with microwaves. The monitored temperature of the microwave sample placed on SiC tile after 180 S is ~ 600 °C. Microwave treatment was performed using a furnace operating at a frequency of 2.45 GHz and 2 kW radiation power (MRF 16/22, Carbolite Ltd, UK). For comparison, temperatures of 600 °C and 800 °C were used to fire the pellets for 1 hr under conventional sintering method using a tube furnace (MTF-10-25-130, Carbolite, Hope Valley, UK) with a ramp rate of 15 °C/min to its desired temperature. Both ends of the tube were left open to allow air to flow in. After annealing, the furnace was turned off and the pellets were allowed to cool in the tube furnace to room temperature. X-ray diffraction (XRD) analysis was employed to determine the crystalline structure of LATP pellets using Bruker D8 XRD, operating with monochromatic Cu Kα (λ = 1.54 Å) radiation and PSD detector. The Jobin -Yvon LabRam HR 800 (He-Ne laser (632.8 nm) / CCD detector) Raman spectroscope was used to obtain the Raman spectra. The surface morphology of the pellets was obtained using a field emission gun scanning electron microscopy (FEG-SEM, Leo 1530 VP) at an accelerating voltage of 5 keV and working distance of 5 mm. Electrochemical impedance spectroscopy measurements were carried out to determine ionic conductivity of the pellets using a potentiostat (Eco Chemie Autolab PGSTAT302N) and the measurements were performed in the frequency range from 0.01 Hz to 1 MHz. The results were analyzed using Zview Software (v3.2d, Scribner Associate, Inc.,
USA). Aluminium plates were places either sides of the pellet for the better electrical contacts for the electrical impedance measurements.

### 7.2.4 Results and Discussion

#### 7.2.4.1 X-ray diffraction analysis

X-ray diffraction (XRD) analysis was employed to determine the crystalline structure of LATP pellets. Figure 7.2-1 shows the X-ray diffraction (XRD) pattern of LATP powder pellet obtained from Johnson Matthey (JM) Technology Centre UK. From the XRD reflections, it can be seen that the LATP pellets consist with two phases of LiAl(PO₄)₃ and LiTi₂(PO₄)₃ and the sharp reflections indicated that the phases are crystallized. The XRD suggested the LATP is obtained by doping Al into the major phase of LiTi₂(PO₄)₃ which can be indexed to a rhombohedral (R3-c) NASICON structure.[266]

![X-ray diffraction pattern of LATP powder pellet obtained from JM.](image)

Figure 7.2-1. X-ray diffraction pattern of LATP powder pellet obtained from JM.
The figure 7.2-2 shows the XRD reflections of as prepared and post treated powder pellets. The peak intensity of post treated pellets confirmed that the crystallinity of LATP is improving with the conventional and microwave heating without any structural changes. The major 2 reflections correspond to mixed phases of LATP at 21° and 25° significantly increased with microwave treatment and conventional heating at 800 °C. The crystallinity of conventionally annealed samples at 800 °C for 1 hr is slightly higher than microwave treated and conventionally annealed samples 600 °C. However, microwave treated pellet at 600 °C for 3 min showed a better crystallinity than the conventionally annealed sample at 600 °C for 1 hr.

![XRD reflections of LATP pellets](image)

Figure 7.2-2. The XRD reflections of (a) as-prepared, (b) conventionally annealed at 600 °C (c) conventionally annealed at 800 °C and (d) microwave treated LATP pellets.
7.2.4.2 Raman analysis

The figure 7.2-3 shows the Raman spectra of as prepared, conventionally annealed and microwave treated LATP pellets. In the Raman spectra several strong broad Raman bands are appeared mainly in the ranges of 300–500 and 900–1300 cm\(^{-1}\). The observed Raman peaks agree well with the published results for Li\(_{1.3}\)Al\(_{0.3}\)Ti\(_{1.7}\)(PO\(_4\))\(_3\).[267] The bands in the range of 300–500 cm\(^{-1}\) are assigned to symmetrical bending vibrations of PO\(_4\) group, while those in 900–1100 and 1100–1300 cm\(^{-1}\) are ascribed to the stretching vibrations of PO\(_3\) and PO\(_2\) in LATP sample respectively. The intensity of the Raman bands increased after conventional and microwave post annealing. Microwave treated LATP showed very sharp peaks compared to the conventionally annealed samples. The Raman analysis confirmed that there is no structural change in the LATP pellets after microwave or conventional annealing as there are no peak shifts observed in the spectra.

![Raman spectra of as-prepared, conventionally annealed at 600 °C and 800 °C and microwave treated LATP pellets.](image)

Figure 7.2-3. Raman spectra of as-prepared, conventionally annealed at 600 °C and 800 °C and microwave treated LATP pellets.

7.2.4.3 Morphology and microstructure
The scanning electron microscopy (SEM) images of as-prepared, microwave irradiated and conventionally annealed LATP pellets are shown in figure 7.2.4. It is interesting that the edges of the crystallites of microwave treated LATP pellets are smoother compared to conventionally annealed samples. The average crystallite size of as-prepared, microwave treated and conventionally annealed LATP pellets is about 1-1.5 µm, 0.5 µm and 1 µm respectively. The crystallized grains of microwave treated LATP are more uniform than conventionally annealed pellets. Due to the difference in the heating profile of microwave and conventional annealing, it is highly likely that comparatively large crystallites will be obtained by melting the agglomerated small crystallites during the conventional sintering process. The difference in particle size and uniformity may be the factors affecting the electrochemical performance of the LATP crystallites.
Figure 7.2-4. The SEM images of LATP pellets; (a-c) as-prepared, (d-f) microwave irradiated and (g-i) conventionally annealed at 800 °C.

7.2.4.3 Impedance analysis

The conductivity properties of LATP pellets are critical to its practical application in Li ion batteries. The ionic conductivity was studied by electrochemical impedance spectroscopy (EIS). In EIS measurements are presented in Nyquist plots as shown in figure 7.2.5.
Figure 7.2-5. Nyquist plots of (a) as-prepared and post treated LATP pellets (b) the respective equivalent circuit model.

The total resistance of the LATP pellet can be determined from the Nyquist plots. The total ionic resistance of a LATP pellet is a combination of bulk ($R_b$) and grain boundary ($R_{gb}$) resistance of the pellet. The $R_b$ can be obtained from the left intercept of the semicircle with the real axis ($Z'$) whereas $R_{gb}$ can be acquired from the right intercept of the semicircle with the $Z'$. The semi-circles in the complex plain indicate that the post treatment greatly reduces the total resistance of LATP pellets. With the conventional and microwave treatment the semicircles move to higher frequencies (to the left). It is clear that with the conventional and microwave treatment, the equivalent resistance decrease which means the conventional and microwave annealing decrease especially the $R_b$ of LATP. However, the effect on $R_b$ by
microwave annealing is much more pronounced than the conventionally annealed sample at
600 °C. The resistance of microwave treated sample for 3 min is almost same with the
conventionally annealed sample at 800 °C for 1 hr. The values of $R_b$ and $R_{gb}$ are used to
calculate the total conductivity by the following equation 19.

$$\sigma = \frac{d}{AR}$$

where $d$ is the thickness of pellet, $A$ is the area of the electrode and $R$ is the total resistance
($R_b + R_{gb}$) obtained from the Nyquist plot. The calculated total conductivities of as-prepared
and post treated LATP pellets are summarised in table 4. The table shows that the almost the
same conductivity of sample conventionally annealed at 800 °C for 1hr can be obtained under
microwave treatment for 3 min on SiC tile.

Table 4. The summary of the total conductivities of as-prepared and post treated LATP pellets.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Resistance (M Ω)</th>
<th>Conductivity x $10^{-8}$ (Sm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared</td>
<td>312</td>
<td>2.83</td>
</tr>
<tr>
<td>Microwave treated</td>
<td>80</td>
<td>11.10</td>
</tr>
<tr>
<td>Conventional (600 °C)</td>
<td>131</td>
<td>6.77</td>
</tr>
<tr>
<td>Conventional (800 °C)</td>
<td>72</td>
<td>12.31</td>
</tr>
</tbody>
</table>
7.2.5 Conclusions

Lithium aluminium titanium phosphates (LATP) pellets were obtained from Johnson Matthey (JM) Technology Centre UK. The pellets were post annealed using microwave radiation and conventional thermal heating. As-prepared and treated pellets were compared in order to find the differences in the structural, morphological and electrical properties using XRD, Raman, SEM and EIS. The XRD and Raman analysis showed that the post heat treatment increased the crystallinity of the pellets without causing any structural changes. The SEM images confirmed that crystallized grains of microwave treated LATP were more uniform and the crystallites were fairly small compared to the conventionally annealed pellets. The EIS results confirmed that the comparable conductivities to conventional annealing at 800 °C for 1 hr could be obtained when the LATP pellets were irradiated with microwave for 3 min. The enhancement in the ionic conductivity in microwave treatment is due to the uniformity and the lower resistance of the LATP crystallites acquired from better sintering characteristic from the microwave post treatment. Therefore, microwave post treatment of LATP is more advantageous than conventional annealing in terms of energy saving and the production cost.
Chapter 8

8.1 Conclusions

Microwave processing of materials is a relatively novel technology advancement alternative to conventional sintering that offers new approaches to improve the physical properties of materials as well as economic advantages through energy savings and accelerated product development. Microwave irradiation has shown a great potential for processing of different inorganic solids and semiconductor materials. The main aim of this thesis was to understand the microwave effect on various materials and then investigate the viability of using them in various advance optoelectronic devices.

TiO$_2$ is one of the most widely used semiconductor materials for various optoelectronic devices; therefore the microwave effect on such materials has been studied. The AACVD method was used to deposit TiO$_2$ electrodes on FTO-glass substrates at 350 and 400 °C. The deposited electrodes were irradiated with different percentages of microwave radiation (10, 25, 50 and 100%) and the electrodes showed improved photoelectrochemical performance when irradiated with more power level percentages of microwave radiation. The XRD analysis confirmed that the deposited films has anatase phase of TiO$_2$ oriented in (101) direction. The XRD analysis also shows an improvement in the crystallinity of the electrodes after microwave treatment. The surface topographical analysis shows that the nanostructure and texture of the films remains unchanged after microwave treatment. The current-voltage characteristics showed a 3 fold increase in the photocurrent density after microwave treatment. Further work such as quantum efficiency calculations and charge transport...
measurements are under progress to find out the reason for the enhancement of the photocurrent density after microwave treatment.

ZnO is a unique material that exhibits semiconducting and piezoelectric dual properties which use as optoelectronic material in fabrication of advance devices. In particular, ZnO nanorods have received extensive attention in photonic, electronic, optoelectronic and electrochemical devices due to ease of fabrication at ambient conditions. The effect of different post annealing methods on ZnO nanorods was studied. ZnO nanorods were grown on FTO-glass substrate by chemical bath deposition method after depositing a seed layer by AACVD technique. The structural properties of as-deposited, microwave irradiated and conventional radiant annealed ZnO nanorods were studied by XRD. X-ray diffraction measurements show that ZnO nanorods grow in a wurtzite crystal phase and no apparently change is observed in the crystallinity after microwave and conventional post annealing. The SEM images show that the microwave irradiation caused sintering of individual rods resulting in the growth of rod diameter whilst the conventional radiant annealing deformed the hierarchical ZnO structure. The current density of microwave irradiated electrode decreases compared to that of as-deposited electrode. The reduction of the photocurrent corresponding to conventional radiant annealed ZnO electrodes is more intense presumably due to deformation of rod structure. This appeared to be due to the poor charge transport in deformed electrodes.

The oxidation of electrodeposited Zn films to ZnO was conducted using microwave and conventional thermal annealing methods at various temperatures and comparisons were drawn. A 40% higher photocurrent was achieved for the microwave annealed films compared to their conventionally annealed electrodes. XRD patterns showed that the oxidation of Zn to
ZnO was not 100% efficient as evidence for metallic Zn was seen. For the conventionally annealed film the highest performing film showed unconverted Zn whereas a microwave annealed film did not show any sign of Zn. The improvement in the PEC properties was attributed to higher surface area, confirmed by SEM surface topographical analysis, and better yields of Zn oxidation to ZnO, and higher crystallinity. Microwave annealing preserves the nanostructure of films compared to conventional annealing due to the difference in the heating mechanism (volumetric heating). Microwave annealing allowed complete oxidation to ZnO with excellent crystallinity. Also oxidation using microwave annealing was achieved five times faster and offers energy savings of up to ~75%, which would make it highly desirable for industrial scale up.

The incorporation of Pd ions into the anatase phase of TiO$_2$ offers active site for catalytic oxidation–reduction reactions for energy devices. Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ was synthesised by using conventional sintering and microwave sintering methods and compared structural and morphological differences. The XRD patterns confirmed that the corresponding reflections of anatase phase has increased by microwave assisted synthesis than the conventional method. Raman spectroscopy indicated that the phases and the structure of the compound prepared by microwave and conventional methods were in good agreement. The SEM images confirmed a significant difference in the shape and the size of the crystallites by two different synthesis methods. The average crystallite size of Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ synthesised under microwave radiation is found to be in the range of 1-2 nm which is much smaller than the reported value under conventional method. The BET measurements further confirmed that the microwave synthesised Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ powder has slightly higher surface area than the conventionally synthesised powder.
Lithium aluminum titanium phosphate (LATP) is a potential inorganic solid electrolyte for lithium ion batteries. The LATP pellets were post treated using microwaves and conventional annealing methods and the differences in the structural, morphological and electrical properties of the post treated pellets were studied using XRD, Raman, SEM and EIS. The XRD and Raman analysis showed that the post heat treatment increased the crystallinity of the pellets without causing any structural changes. The SEM images confirmed that crystallized grains of microwave treated LATP were more uniform and the crystallites were fairly small compared to the conventionally annealed pellets. The electrochemical impedance results confirmed that the conductivities of the LATP pellets can be improved by microwave treatment at relatively low temperature and time. This improvement in the ionic conductivity is due to the uniformity and the lower resistance of the LATP crystallites acquired from better sintering characteristic from the microwave post treatment. Therefore, microwave post treatment of LATP is more advantageous than conventional annealing in terms of energy saving and the production cost.

Overall, the results of the thesis demonstrate that microwave treatment is a promising alternative method to the conventional sintering and it opens up a new research strategy for the engineering of semiconductor materials properties while keeping the texture and nanostructure unaltered for use in advanced electronic and optoelectronic devices.
8.2 Further Work

Microwaves have been explored as an efficient alternative energy source in thin film processing and materials synthesis for advance electronic and optoelectronic devices. Although the use of microwaves has shown promising results over conventional heating methods, further work is essential to develop a comprehensive understanding of how microwaves interact with mixed oxide materials and non-oxides materials under different processing environments and conditions. One approach that could be used in the future is to change the gas environment whilst microwave processing semiconductor electrodes. This allows one to understand the impact on structural, morphological and photoelectrochemical properties when using an alternative environment to atmospheric microwave processing conditions. Further work on the effect of microwave heating on thin films with the ferrite structure such as ZnFe$_2$O$_4$, CuFe$_2$O$_4$ and CoFe$_2$O$_4$; pervoskite structure such as CaTiO$_3$ and MnZnO$_3$; metal chalcogenides and metal nitrides will be carried out using a hybrid microwave methodology. This is where both radiant and microwave heat is present. In this study the effects of microwave heating can be understood by varying the microwave power level whilst the conventional radiant heat is kept at a constant. This will lead to enhanced properties of functional nano-materials through unusual nanostructures and unique phases. These will be useful in the development of advanced energy harvesting and storage devices.

Also due to its lower processing temperature requirements, the microwave process can also open up the possibility of fabricating thin films of photoactive semiconductors on conducting, flexible, plastic substrates which are highly important in making flexible solar cells and other renewable energy applications.
Chapter 9

References


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Chapter 10

Appendix

10.1 Awards

1. Awarded the Loughborough University Graduate School Research Student Prize 2014.
5. Best Poster Award, Energy and Sustainability Expo 2013, Loughborough University.
7. Best Poster Award 2011, Great Western Electrochemistry Group Meeting, University of Bath, 6th June 2011.
8. Second Best Poster Award 2011, Midlands Electrochemistry Group Meeting, University of Warwick, 5th May 2011.
10.2 Peer-reviewed and submitted articles in scientific journals


11. Muhammad Mazhar, Muhammad Ali Ehsan, Huang Nay Ming, V McKee, **T. A. Nirmal Peiris**, Upul Wijayantha and Zainudin Arifin, Vysotskite structured photoactive
palladium sulphide thin films from dithiocarbamate derivatives, New J Chem. 2014, Accepted Manuscript, DOI: 10.1039/C4NJ00564C.


17. **T. A. Nirmal Peiris**, Jagdeep S Sagu and K. G. Upul Wijayantha, Microwave-assisted low temperature fabrication of nanostructured ZnO thin film electrodes for solar energy conversion, **2014**, submitted to *Journal of Materials Chemistry A*.


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10.3 Conference participations and presentations

1. The IET Seminar on Microwave Heating and Processing of Materials, Nottingham University, 2 February 2011.


33. **T. A. Nirmal Peiris** and Upul Wijayantha, Photoelectrochemical studies of microwave treated electrodes, *ISE Satellite Student Regional Symposium: Great Western Photoelectrochemistry Meeting 2013*, University of Bath, 10 June 2013.


36. Hussain Alessa, Jagdeep S Sagu, **T. A. Nirmal Peiris**, Ijaz Ahamad Bhatti, K. G. Upul Wijayantha, ZnO Nanorods on glass and plastic based substrates for various energy applications, *Electrochem 2013*, University of Southampton, 01-03 September 2013.


41. UK representative in *Researcher Links workshop between Egypt and the UK*, Nottingham University, 31 March- 3 April 2014.


49. T. A. Nirmal Peiris, Subhashi Jayathilake, Hussain Alessa, Jorge García-Cañadas and Upul Wijayantha, Electrochemical Analysis of the Effect of Electrodeposited Mg(OH)$_2$; Efficient Flexible Solar Cells, *Great Western Electrochemistry Meeting*, University of Bath, 2 June 2014.


56. T. A. Nirmal Peiris, Extracurricular skills development during the PhD, Research That Matters: Research Challenges in Focus, Loughborough University, 18 June 2014.