THREE–DIMENSIONAL ZINC OXIDE NANOSTRUCTURE SYNTHESIS
AND PHOTONIC APPLICATIONS

A Dissertation in
Electrical Engineering

by

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ABSTRACT

The objective of this study was to investigate zinc oxide (ZnO)-based photonic nanostructure fabrications and their applications to solar energy. In the first section, a three-dimensional (3-D) ZnO nanoforest with large surface areas and good electron transport properties has been synthesized successfully by a two-step hydrothermal process and applied to the photoelectrode for a dye-sensitized solar cell (DSSC). The experimental results show that the solar conversion efficiency of the 3-D ZnO nanoforest is much higher than that of one-dimensional (1-D) ZnO nanorod arrays owing to its much larger surface areas. In the second section, zinc oxide/titanium dioxide (ZnO/TiO₂) nanocomposite photoelectrodes for DSSC with density-controlled capability are presented. A high open-circuit voltage of up to 0.93 V was successfully achieved. To the best of the author's knowledge, this is the highest open–circuit voltage reported in the literature; this is beneficial for achieving a high-efficiency DSSC. The physical mechanism of high open-circuit voltage has been demonstrated and confirmed by electrochemical impedance spectroscopy; a reduced recombination loss was achieved with an improved charge carrier diffusion path. In addition, ZnO/TiO₂ nanocomposite photoelectrodes have proven to further improve solar conversion efficiency as compared to conventional TiO₂ nanoparticles photoelectrodes. In total, several future research topics that could benefit from the analysis in this dissertation have been examined.
Although the development of ZnO nanostructures has been studied extensively by various synthesis methods in the past decade, this dissertation is focused on the practical aspect of synthesizing ZnO nanostructures on transparent conductive oxide substrates directly for the application of dye-sensitized solar cells in a low-cost manner. The dissertation is divided into six chapters and the contents of every chapter is briefly introduced as follows.

Chapter 1 introduces the motivation of the dissertation. Chapter 2 presents the synthesis and characterization of ZnO nanostructures for one-dimensional (1-D) and three-dimensional (3-D) systems. 1-D ZnO nanostructures—ZnO nanowires—were delivered by a rapid growth microwave-assisted vapor–liquid–solid method. 3-D ZnO hierarchical nanostructures—ZnO nanoforest—were synthesized via a cost-effective hydrothermal method. The obtained ZnO nanoforest has the potential to break through the limitation of the surface areas of DSSC. Chapter 3 presents the synthesis and characterization of ZnO/TiO2 composite nanostructures. The discussions were focused on the density-controlled capability of ZnO nanorod arrays and the conformal shell coating of ZnO–TiO2 core–shell nanostructures which have the feasibility to provide a direct electron transport pathway for conventional TiO2 nanoparticles DSSC. Chapter 4 investigates the DSSC performances from ZnO nanoforest photoelectrodes and ZnO/TiO2 nanocomposite photoelectrodes. Moreover, a high open-circuit voltage is reported and the physical mechanism is discussed and verified with electrochemical impedance
spectroscopy. Furthermore, the overall solar conversion efficiency can be improved by this nanocomposite photoelectrode.

In addition, radiation detection has been investigated during my Ph.D. studies. Chapter 5 demonstrates the standoff alpha radiation detection technique based on the physical mechanism of excited state absorption of air molecules. Both theoretical analysis and experimental verifications were conducted. The experimental results confirmed that the radiation could be detected at a 10 m standoff distance.

Chapter 6 summarizes the dissertation with two developed photoelectrodes with the improvement of surface areas and electron transport property for a high solar conversion efficiency of DSSC and proposes potential future works regarding to further enhanced the efficiency.
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Chapter 1

Introduction

With the increasing demand for energy and the detrimental effect of fossil fuels on the environment, renewable energy sources are fast emerging as an important alternative to traditional energy sources. Among the alternatives, solar energy holds great potential because of the enormous amount of solar radiation the Earth receives.

Solar cells can be classified into three generations. Up to now, the majority of commercially available photovoltaic technologies with high efficiencies require high costs and highly energy consuming preparation methods. Therefore, finding a low-cost photovoltaic with a marketable efficiency is crucial. The primary products in the solar cell market are still dominated by first generation devices because of their high energy conversion efficiency (up to 24%); however, they require expensive solid-state materials. Even though second generation devices utilize thin-film technology, which greatly reduces the cost of source materials, their conversion efficiency is relatively low. The commercial efficiency ranges are quite modest (~5–11%) while they exhibited laboratory efficiencies around 15%. In addition, the byproducts are toxic and may pollute the environment. Consequently, third generation devices are discussed here as an efficient alternative, which have the potential to deliver sufficient efficiency at an economically
viable cost. Among various third generation solar cells, dye-sensitized solar cells (DSSC) are chosen for the following reasons:

- **Low fabrication cost**: DSSC can be fabricated simply and inexpensively by using common wet chemistry laboratory methods and ordinary low-cost equipment instead of requiring expensive cleanroom environments;
- **Emerging development of nanotechnology**: metal-oxide nanostructures with different morphologies (zero-dimensional, one-dimensional, and three-dimensional nanostructures) are rapidly developing in recent years;
- **Expanding the light absorption spectrum**: unlike other solar cells, the light absorption spectrum can be tuned through different synthesis methods and adopted to different applications.

Ever since the dye-sensitized solar cell was first invented by Gratzel in 1991, it has attracted great attention because of its low fabrication cost, environment friendliness, and ease of manufacture with earth-abundant materials [1]. However, there are still challenges to be overcome, mainly focused on the relatively low solar conversion efficiency that is due to the limitation of surface areas and recombination loss during the electron transport.

Inorganic semiconductor materials play an important role in the systems for energy conversion in DSSC. In particular, these materials are used either as the passive materials for light absorption or as charge transport media in solar cells. The most
suitable materials for these applications require that they have appropriate optical and electronic properties as well as large surface areas. Many metal-oxide materials have been studied extensively for the n-type photoelectrode in DSSC [2]–[5]. Although titanium dioxide (TiO_2)-based DSSC are most commonly used in DSSC solar cells, among different metal-oxide materials, zinc oxide (ZnO) has still attracted considerable attention as an alternative to TiO_2 photoelectrodes because of the following properties:

- Low cost of raw material: ZnO is an earth abundant material;
- Visible light transparency: ZnO is a wide band-gap material (3.37 eV) similar to TiO_2 (3.2 eV) which makes it also a good candidate for the photoelectrode in DSSC;
- Suitable energy levels: Effective electron injection from dye molecules to ZnO due to the position of the conduction band edge of ZnO being lower than the excited-state energy level, lowest unoccupied molecular orbital (LUMO), of photodyes;
- Fast electron transport: ZnO has higher electron mobility (2–3 orders of magnitude) than TiO_2 which is beneficial for reducing recombination loss [6], [7];
- Ease of crystallization and anisotropic growth: Numerous functional nanostructures have been studied, including nanoparticles, nanowires (or nanorods), nanotubes, nanobelts, and nanoflowers. ZnO shows more flexibility in synthesis and morphologies than TiO_2 [8]–[15].
To date, the highest energy conversion efficiency of DSSC is still based on nanoparticles (zero-dimensional) photoelectrode. The major advantage of nanoparticle-based films is that they provide large surface areas with relatively easy synthesis methods. In contrast, the disadvantage is that since nanoparticles are highly disordered nanostructures, electrons tend to hop over the nanoparticles network which slows down the transport dynamics and results in charge recombination during inter-particle percolation.

In order to achieve high charge collection efficiencies, the electron transport should be faster than the charge recombination with the electrolyte and photodyes. One-dimensional (1-D) nanostructures were developed to provide a direct pathway for an excellent electron transport ability in order to minimize the chances of charge recombination. For instance, nanowires have the potential to improve the transport characteristics since they have fewer defects and grain boundaries acting as electron traps at inter-particle contacts in which the lattice imperfections or grain boundaries will accelerate electron–hole recombination [16]. This means that they can be laid as thicker films on substrates, extending the absorption of light, thus improving the solar conversion efficiency. In addition, the morphology, dimension, and even the crystallization of nanostructures can be controlled in various aspects. Even though 1-D nanostructures have proven a significant improvement in the electron transport characteristics to 0-D nanostructures, the major drawback in this stage of the development is their insufficient
surface area, hence the solar conversion efficiency is still comparatively lower.

Our goal is to develop a new type of photoelectrode which breaks through the bottleneck for the advancement of the solar conversion efficiency of DSSC. The investigations were focused on two aspects:

(1) Improvement of surface areas;

(2) Improvement of the electron diffusion property during electron transport.
Chapter 2

Synthesis of 3-D ZnO Nanostructures

2.1 Introduction

Dye-sensitized solar cells (DSSCs) based on oxide semiconductors have emerged as the most promising candidate systems for achieving efficient solar energy conversion. These systems are flexible, inexpensive, and easy to manufacture. Even though TiO$_2$ has been the primary wide-bandgap oxide semiconductor for the photoelectrode, offering increased surface area for dye molecule adsorption, ZnO has been studied extensively as an alternative DSSC photoelectrode material. ZnO possesses physical properties and an energy band structure similar to TiO$_2$, but with a much higher electron mobility—about 2–3 orders of magnitude higher—which is beneficial for the charge transport process [6], [7]. As such, ZnO is expected to exhibit faster electron transport with reduced recombination loss. Although the solar conversion efficiencies of ZnO-based DSSCs are generally much lower than those of TiO$_2$-based DSSCs, ZnO is still the most promising alternative photoelectrode to TiO$_2$ due to its ease of crystallization and anisotropic growth [8].

Numerous nanostructured photoelectrodes, such as 1-dimensional (1-D) ZnO nanostructures, have been studied extensively; these studies have demonstrated
improvement of the electron diffusion length by proving a direct conduction pathway [5], [8], [11], [13], [17]. The direct pathway along 1-D nanostructures minimizes the chances of charge recombination during inter-particle percolation from the conventional TiO₂ nanoparticles network. However, the disadvantage is due to insufficient surface areas of 1-D nanostructures, which limit the dye loading and result in low solar conversion efficiency. Therefore, constructed hierarchical nanostructure configurations are particularly desirable for obtaining increased surface areas and conversion efficiencies.

Recently, many researchers have presented 3-dimensional (3-D) ZnO hierarchical architecture photoelectrodes for DSSC. For instance, dendrite-like structures of ZnO nanowires were fabricated by chemical vapor deposition (CVD) for DSSC [18], [19]. These experiments required expensive equipment, and they also facilitated relatively low efficiencies due to the lack of sufficient surface area. In addition, ZnO nanoflowers and branched ZnO nanowires have been introduced using a hydrothermal method for DSSC [13], [17]. Although these hierarchical structures were synthesized in a low-cost fashion, they still have shown low efficiency due to insufficient surface areas. Most importantly, the secondary branched growths lacked uniformity due to their non-uniform, randomly distributed seed layer. For this reason, developing a technique to deposit a uniform high-density seed layer is desirable for manufacturing densely packed branched nanostructures.

As a matter of fact, increasing the overall film thickness can further enlarge the
surface areas. Specifically, providing a large region for the length of the backbone of hierarchical nanostructures, while maintaining adequate spacing for the growth of branched nanostructures, is crucial. However, this is usually not the case for hierarchical nanostructures. This is because by extending the length of the backbone by multistep synthesis, the diameter is usually increased as well; this results in a smaller spacing. Therefore, our goal is to propose a convenient and lost-cost approach for constructing a 3-D ZnO hierarchical nanostructure photoelectrode for DSSC.

In the first section of this chapter, a novel microwave heating process is applied to accomplish rapid growth of 1-D ZnO nanostructures via the chemical vapor transport and condensation method. It was demonstrated that (001) oriented single crystal ZnO nanowire pillar arrays can be grown vertically and uniformly on a-plane sapphire wafers. However, due to its selectivity for the substrates, and the higher cost of high-temperature systems, we decided to synthesize the 3-D ZnO hierarchical nanostructures using a low-temperature solution-phase method.

In the second section, tree-like 3-D hierarchical nanostructures, ZnO nanoforest, were fabricated through a hydrothermal synthesis. The backbone of these hierarchical nanostructures was synthesized in long length with high aspect ratio while obtaining enough spaces for the secondary branched growth. In addition, a uniform high-density ZnO seed layer coating has been established for the growth of densely packed branched nanostructures via a modified sol-gel process.
2.2 Microwave-Assisted Vapor–Liquid–Solid Synthesized ZnO Nanostructures

The microwave heating process is a relatively new technique for heating the semiconductor material to grow nanostructures [20] that is fundamentally different from conventional heating processes. In a conventional process, the heat is generated by the external heating elements, and transferred to the materials through radiation. The temperature on the surface is always higher than the internal material. On the other hand, in a microwave process, the opposite occurs; the heat is first generated internally within the material, and is then transferred outward. This creates an inverted temperature distribution compared to the conventional process. One of the advantages of the microwave process is that the material can be heated up quickly, with less energy lost from the surface by radiation, conduction, and convection. The primary electromagnetic fields can significantly enhance the reaction, leading to an increase in the crystal growth rate through a reduction of the energy consumption (as microwave energy transforms into heat inside the material directly) [21]. In addition, both the material and the substrate have high thermal run-away properties while applying the microwave process. As such, this results in energy savings and time reduction [22]. For these reasons, the microwave-assisted heating process is a good candidate for the synthesis of ZnO nanostructures.

ZnO nanowires have drawn much attention due to their unique structural and
physical properties, which offer fascinating potential for future technological applications. The microwave-assisted fabrication process for producing ZnO nanowires is based on the vapor–liquid–solid (VLS) method. In the following subsections, the microwave-assisted heating technique is introduced for the growth of vertically-aligned single crystal ZnO nanowire pillar arrays.

2.2.1 Growth Mechanism – Vapor–Liquid–Solid Process

The ZnO nanowire pillar arrays were grown using the vapor–liquid–solid [23], [24] crystal growth method via catalyzed epitaxial crystal growth [32,37]. This is considered a bottom-up assembly mechanism, also known as the chemical vapor transport and condensation method. Figure 2-1 presents the schematic diagram of ZnO nanowire growth. The Au catalyst was first deposited on the sapphire wafer substrate. With temperature increasing above 500°C, the Au thin film was annealed to form nanoparticles/nanoclusters. Once the source was heated at the high temperature zone, ZnO interacted with graphite, it vaporized and produced Zn and CO/CO₂ vapors. Since the whole process occurred under low pressure (300 Torr) and at a high temperature (above 900 °C), carbon assisted ZnO in reducing into Zn by reacting directly with ZnO according to the following reactions [25], [26]:

\[
\text{ZnO(s) + C(s) } \rightarrow \text{Zn(g) + CO(g).} \tag{2.1}
\]

\[
\text{CO(g) + ZnO(s) } \rightarrow \text{CO_2(g) + Zn(g)} \tag{2.2}
\]
In this case, the melting temperature (about 419 °C) was relatively low, since the reaction was surrounded by Zn instead of ZnO. Zn vapor played a crucial role for the nucleation of ZnO nanostructures; it was generated by carbothermal reduction of ZnO. As the Zn vapor was transported to the substrate at the lower temperature zone (500–600 °C), it performed condensation and the re-oxidation process that formed the hemispherical liquid alloy droplets as nuclei for ZnO nanostructures. These alloy droplets controlled the diameter of the nanowires. Smaller droplets favored the growth of thinner nanowires. When the droplets became supersaturated, nanowires were formed by the reaction between Zn and CO. After an initial period of nucleation, ZnO nanowires grew continuously along the preferred c-axis (001) direction with more Zn vapor transported to the substrate and re-oxidized on the existing ZnO nanostructures. This was due to good epitaxial interface between the (0001) plane of growth orientation of ZnO nanowires and the a-plane (110) sapphire wafer [27].

Figure 2-1. Schematic diagram of the ZnO nanowire growth mechanism [28].
2.2.2 Experimental Methods and Procedures - ZnO Nanowires

A multimode microwave system used to synthesize the ZnO nanowires consists of a magnetron, a circulator, a directional coupler, an E–H tuner, a quartz reactor, and gas feeders. The microwave generator (CoberMuegge) could operate at 10–100% of maximum output power 3000 W with an operating frequency of 2.45 GHz. The purpose of the circulator is to prevent power from being reflected by the load. The E–H tuner is a mechanical device for optimizing the impedance matching for maximum output power. Adjusting the stubs will experimentally match the impedance of the source to the load, minimizing the reflected power. A quartz tube is placed in the reaction chamber, with cooling water running through the outside of the tube at both ends and passing through the cavity. The ambient gas runs from one end of the quartz tube and flows out at the other end. The flow rate can be controlled by a mass flow controller. The temperature at the source is primarily monitored by an optical fiber pyrometer system (Luxtron Accufiber Model 10) with blackbody radiation detection. Another optical pyrometer (Leeds & Northrup Co.) is used to calibrate the thermometer measurement through the transparent window on one end of the quartz tube.

Sapphire single-crystal wafers (Epistone) with a-plane surface orientation were prepared in sizes of 5 mm x 5 mm x 430 μm. Since the a-plane (110) sapphire wafer has a twofold symmetric, the anisotropy plane is vital for growing high quality c-oriented ZnO nanowires [29]. This type of heteroepitaxial growth of vertically-aligned arrays is easier
to achieve, as the lattice mismatch is relatively small between the substrate and the ZnO nanowires [30]. The sapphire wafers were first ultrasonically cleaned with acetone and rinsed in isopropanol, followed by a de-ionized (DI) water rinsed. Then, a thin layer of gold (Au) was deposited on the substrates by E-beam/thermal evaporator (Kurt J. Lesker Company). This thin film works as a catalyst in the synthesis to guide the growth of ZnO nanowires. The ZnO source material was prepared from a mixture of ZnO powder with a purity of 99.9% (Alfa Aesar) and graphite powders with a purity of 99.99% (Fisher Scientific) in a 1 to 1 weight ratio. Each mixed powder source was compressed to a quarter inch diameter cylinder with weight to the nearest 0.220 g. During the growth process, the substrates were placed in a quartz reactor with a length of 45 cm and an inner diameter of 5 cm.

Figure 2-2 presents the schematic diagram of the microwave growth of ZnO nanowires. The ZnO source was positioned in the center of the cavity for maximum exposure, leading to highly efficient microwave heating. ZnO has a high melting point of 1975 °C and a flash point of 1436 °C. These properties indicate that ZnO, typically decomposes and vaporizes when the temperature is above 1400 °C. However, with the graphite mixed with the ZnO powder, also known as the carbothermal route, the nanowires can be grown at around 900–1100 °C. Generally, this involves heating the metal oxide with a sufficient quantity of carbon in order to form an oxidic species in the vapor phase, which eventually transforms into the final crystalline products.
Another key issue is monitoring the temperature of the substrate. Since the heat is generated directly within the source in the cavity, it tends to absorb much more microwave energy than the substrate; this leads to a higher source temperature in comparison with the substrate. In order to obtain the nanowire pillar arrays, we need to verify the temperature gradient at each position beyond the source inside the tube. By experimentally adjusting the location of the substrate to 4 to 6 cm away from the source downstream, we achieve a nanowire type structure grown on a substrate at temperatures of approximately 500–600 °C in this microwave system; this is the suggested growing condition for ZnO nanowires [25].

For the actual experimental conditions, the sample was prepared with a 2-nm-thick Au catalyst. The ZnO source was irradiated by microwave energy, heating it up to 950 °C to 1050 °C at a rate of 40 °C /min under a pressure of 300 Torr with ambient
argon gas. The Ar gas was kept constantly flowing between 25 sccm to 75 sccm. The growth time discussed in this process lasts for five minutes. After five minutes, the microwave power was shut off and the sample cooled down to room temperature under flowing argon gas.

The morphologies, crystalline nature, and chemical composition are characterized in the following subsections. The nanostructures were imaged by a field-emission scanning electron microscope (FESEM, LEO 1530) operated at 3 kV for structural and morphological characterization. The phase compositions were analyzed by an X-ray diffractometer (XRD, PANalytical XPert Pro MPD), operating at 45 kV and 40 mA using Cu Kα radiation with wavelength 1.540Å in the 2θ angular range of 0–60°. A transmission electron microscope (TEM, Phillips 420) and selected-area electron diffraction (SAED) have been used to characterize the nanostructures in detail. The TEM system also equipped with energy-dispersive X-ray spectroscopy (EDX) for element analysis. The TEM samples were prepared by ultrasonicking the nanostructures off the substrates; these were then dispersed in isopropanol and dripped onto carbon-coated copper grids. The optical properties of the grown nanostructures are obtainable from photoluminescence (PL) measurements; these data were collected from a fluorescence spectrophotometer (Ocean Optics) at room temperature.
2.2.3 Results and Discussion - 1-D Controlled Growth of ZnO Nanowires

By adjusting the microwave growth experimental conditions, such as the orientation of substrates, growth temperature, gas flow rate, and Au catalyst layer thickness, the dimensions of ZnO nanowires can be controlled. Figure 2-3 shows the morphology and size of ZnO nanowire pillar arrays from field-emission scanning electron microscope images with operating voltage 3 kV, grown by microwave heating processing. Both the images were taken from the top view at a tilted angle. By utilizing the proper substrate and reaction conditions, the products grown consist almost completely of ZnO nanowires that were vertically aligned. These well-aligned nanostructures covered all of the area of the a-plane sapphire substrate uniformly. This sample was grown under conditions of 300 Torr, 50 sccm Ar flow rate, and 1000 °C for 5 minutes with 20 Å Au catalyst. The growth rate of the ZnO nanowires by microwave heating was about 200 nm/min and the aspect ratio was roughly 25. From the lower magnification in Figure 2-3(a), the image shows that the ZnO nanowires were grown homogeneously on a large area of the substrate. On the other hand, from the higher magnification in Figure 2-3(b), most of the nanowires were parallel to each other; they were aligned vertically and uniformly, with diameters ranging from 30 to 50 nm, and 1 μm in length. This shows that the nanowires were grown perpendicular to the substrate, along the c-axis (001) direction.
Figure 2-3. FESEM images of ZnO nanowire pillar arrays growth on a-plane (110) sapphire wafer coated with Au-catalyst 20 Å, Ar flow rate 50 sccm, and 1000C at (a) low magnification with 300 nm scale bar and (b) high magnification with 100 nm scale bar, tilted at 30° [28].

In addition, there were spherical tips on top of the nanowires, created by the 20 Å Au catalyst deposited. The Au catalyst was quiet important for this type of process. By varying the thickness of the Au catalyst film, the diameters of nanowires can be controlled [31], [32]. With a thicker Au catalyst of 80 Å, the diameter of the ZnO nanowires was about 100 nm. The results show that increasing the thickness of the Au layer will lead to the growth of thicker nanowires. Moreover, the ZnO nanowires were also grown under different gas flow rates. By decreasing the gas flow rate to 25 sccm, the nanowires tended to be denser; they also grew faster, reaching about 2 μm in length with about the same diameter. Furthermore, the ZnO nanowires were sensitive to the growth temperature. The products collected from the different temperature zones tended to have different dimensions in diameter and length. As such, the appropriate temperature was critical for the formation of different morphologies of nanowires. For example, the diameters of the nanowires were temperature-dependent; low growth temperature will
result in small diameters.

X-ray diffraction measurements were used to investigate the crystal structure and orientation of the microwave grown ZnO nanowire pillar arrays. In order to avoid intense signals from the substrate, the measurement was performed under grazing incidence X-ray diffraction (GIXRD). Figure 2-4 shows the rocking curves collected from the GIXRD 2θ scan data of ZnO nanowires with a fixed grazing incidence angle of 2˚. The predominant peak at 34˚ with the (002) plane obtained a relatively high intensity. From this pattern, the distinguished (002) peak corresponded to a wurtzite ZnO hexagonal structure with the lattice constants of \(a = 3.25 \text{ Å}\) and \(c = 5.2 \text{ Å}\). This represented that these ZnO nanowires were single crystalline, and grew along the preferential c-axis orientation that was normal to the substrate.

Figure 2-4. XRD pattern of ZnO nanowires on a-plane (110) sapphire substrate [28].

In addition, the ZnO nanowires were also characterized by a transmission
electron microscope (TEM) for the crystallography. Figure 2-5(a) presents the morphology of an individual ZnO nanowire. The image clearly illustrates the Au alloy droplet at the tip of the 1 μm long nanowires, indicative of a growth process by the VLS mechanism. The droplet was roughly hemispherical in shape with an average diameter similar to the nanowires. From the energy dispersive X-ray spectroscopy (EDX) spectrum of the tip of a nanowire in Figure 2-5(c), the Au element is clearly present. However, there was also a Zn element inside the alloy tip, consistent with the VLS mechanism's supersaturation nucleation process [33], [34]. However, the copper and carbon signatures were from the carbon-coated copper TEM grids. The single crystalline hexagonal structure can be determined from the spot pattern of the diffraction pattern by the selected-area electron diffraction (SAED) in Figure 2-5(b). Also, the specified growth orientation was along the (0001) direction, reflected to XRD peak (002) in Figure 2-4. It is worth pointing out that the analysis revealed structural uniformity without any crystalline defects of dislocations or stacking faults in the microwave grown nanowires. The ZnO nanowires have wurtzite structure with lattice constants of \( a = 3.25 \) Å and \( c = 5.21 \) Å.
Figure 2-5. (a) TEM image of an individual ZnO nanowire. (b) SAED pattern of a nanowire. (c) EDX spectrum obtained from the tip of a nanowire [28].

From the characterizations above—FESEM, XRD pattern, and TEM—it was found the single crystal ZnO nanowires tend to grow on the a-plane (110) sapphire wafer in c-axis (001) orientation. This shows that there was a good epitaxial interface between the (0001) plane of the ZnO nanowires and the (110) plane of the sapphire substrate. Thus,
the ZnO nanowires on the sapphire (110) wafer should be preferentially oriented in the c-axis direction.

The photon emission characteristics of ZnO nanowires can be examined by the photoluminescence (PL) spectrum. The requisite measurements were done at room temperature using a fluorescence spectrophotometer with a UV laser as the excitation light source. The operating wavelength was 355 nm with a repetition rate of 2 kHz and 4 to 7 ns pulse width for an average power of 15.5 mW. The laser beam was focused on the side wall of these ZnO nanowires at an incident angle of 45° to the symmetric axis of the ZnO nanowires, and the photon emissions were collected in the direction normal to the substrate by a spectrometer with a fiber optic cable used for light collection. As shown in Figure 2-6, for the well-aligned ZnO nanowire pillar arrays under optical excitation, the PL emission peak at 381 nm corresponded to the near band-edge emission; the green light emission at 520 nm corresponded to the lattice defects related to the singly ionized oxygen vacancy [35]. This spontaneous emission had a full width at half maximum (FWHM) of 15 nm. The strong UV emission in the PL spectrum was due to the wide band gap of ZnO, which confirmed these ZnO nanowires had a good crystal quality with a low concentration of oxygen vacancies [31].
2.3 Hydrothermal Synthesized ZnO Nanostructures

2.3.1 Growth Mechanism – Hydrothermal Process

This is also considered a bottom-up process which can synthesize crystalline materials from high-temperature solutions at high vapor pressure. Hydrothermal synthesis is proceeded in an aqueous solution, which can provide the control over the size, morphology and crystallinity of different nanostructures by modifying the growth conditions, such as, temperature, time, precursors, solvents, and substrates.

2.3.2 Experimental Methods and Procedures – ZnO Nanoforest

Before synthesizing ZnO nanostructures, we first gathered all necessary reagents and materials. Zinc acetate dihydrate (ZAD), zinc nitrate hydrate (ZNH),
hexamethylenetetramine (HMTA), polyethylenimine (PEI), titanium (IV) butoxide (TiBO), and polyethylene glycol (PEG) were acquired from Sigma-Aldrich. All the reagents used were of analytical grade, and were used as received. Fluorine-doped SnO$_2$ conductive glass (FTO) with sheet resistance 6–8 $\Omega$ sq$^{-1}$ was purchased from Cytodiagnosics.

The hydrothermal synthesis was carried out in either a Teflon reactor (PTFE cup with cover, 23 mL, A280AC, Parr Instrument Co.) or a Teflon-lined glass vial (20 or 40 mL). Generally, a Teflon reactor placed inside an autoclave metal bomb was used for the reaction due to the above-boiling operating temperature of the solvent. However, in the case of synthesized ZnO nanomaterials, since the operating temperature is below 100 °C with the solvent of DI water, it was more convenient to fabricate the nanostructures with a Teflon-lined glass vial for ease of handling and lower cost of supplies. The byproducts from both containers were shown to obtain the same morphologies and dimensions. The heating oven was utilized for the hydrothermal synthesis of the ZnO nanomaterials, and the thermal furnace was used to remove residual organic reactants and for the crystallization of the nanomaterials.

To ensure that there was no contamination, the FTO substrates were first ultrasonically cleaned in acetone, isopropanol, and ethanol, and then rinsed thoroughly in de-ionized water (DI water). After drying under a stream of nitrogen, the substrates were baked at 80 °C for three hours to evaporate any water molecules before synthesis was
initiated.

The ZnO nanoforest was grown by the hydrothermal synthesis with a two-step process. The first step was to synthesize trunked ZnO nanorod arrays on the FTO substrate, and the second step was to grow branched ZnO nanowires for the secondary growth on the trunked ZnO nanorods. A flow chart for the hydrothermal synthesis of the ZnO nanoforest is illustrated in Figure 2-7.

![Flow chart for the synthesis of the ZnO nanoforest by the hydrothermal process.](image)

Figure 2-7. A flow chart for the synthesis of the ZnO nanoforest by the hydrothermal process.

To synthesize trunked ZnO nanorod arrays, the FTO substrate was first coated with a catalyst thin film of either a ZnO seed layer or a TiO$_2$ nanocrystal template before the first hydrothermal synthesis. In the case of the ZnO seed layer, the ZnO sol was
prepared by dissolving zinc acetate dehydrate in a methanol solution at room temperature; the solution was stirred for 30 minutes to yield a clear and homogeneous sol. For the TiO₂ nanocrystal template, the TiO₂ sol was prepared by dissolving titanium (IV) butoxide in a concentrated ethanol solution at room temperature. It was also stirred for 30 minutes to yield a clear and homogeneous sol. A sol-gel dip-coating technique was then performed by immersing the FTO substrate into the solutions for 15 seconds before withdrawing at a speed of 3 cm min⁻¹. Subsequently, the FTO substrate with the ZnO seed layer or the TiO₂ nanocrystal template was annealed at 350 °C or 450 °C for one hour, respectively. At this point, the samples were ready for the first hydrothermal process.

The trunked ZnO nanorod arrays were grown on the ZnO seed layer or the TiO₂ nanocrystal template by immersing the substrate in an aqueous solution containing zinc nitrate hydrate, hexamethylenetetramine, and polyethylenimine in a Teflon-lined glass vial at 90 °C. After synthesis, the nanorod arrays were rinsed with DI water and baked at 350 °C in air for 30 minutes to remove any initial residual organic reactants before the secondary growth of branched ZnO nanowires was initiated.

The second step in the process was to synthesize branched ZnO nanowires on the previously synthesized ZnO nanorods, according to the following procedure. Similar to the first step, before the hydrothermal synthesis, a catalyst thin film formed via a dip-coating technique. This time, the ZnO sol for a ZnO seed layer was prepared by dissolving zinc acetate dehydrate with polyethylene glycol in a methanol solution under
three cycle depositions. Right after the secondary seeding process, the samples were heated to 350 °C in air for 30 minutes for crystallization and removal of the PEG. Then, in the second hydrothermal process, the branched ZnO nanowires were synthesized in an aqueous solution containing only the zinc nitrate hydrate and the hexamethylenetetramine in an equal molar ratio at 90 °C for three hours. Finally, the nanoforest samples were rinsed with DI water several times, and annealed at 400 °C for one hour for crystallization.

The morphology properties of the ZnO nanostructures were examined by field-emission scanning electron microscopy (FESEM, JEOL LEO1530) operated at 3 kV. In addition, the structural properties of the ZnO nanoforest were analyzed by a Bruker X-ray diffractometer (XRD, 40 kV, 30 mA) with Cu Kα (λ = 0.15406 nm) radiation at a scanning rate of 1° min⁻¹ from 10° to 70° (20). All measurements were performed at room temperature.

2.3.3 Results and Discussion – 3-D Controlled Growth of ZnO Nanoforest

In order to obtain a high solar conversion efficiency, one of the key issues is to maximize the surface-to-volume ratio. As such, it is critical to control the synthesized dimensions of trunked ZnO nanorods and branched ZnO nanowires. To examine these characteristics, we performed different sets of experiments to explore the correlation parameters.
Since for this type of nanostructures, the nanoforest, the majority of the surface areas comes from the branched nanowires, the main task is to create enough space between the trunked nanorods for the branched nanowires to grow, while maintaining a relatively small diameter with a high aspect ratio of the trunked nanorods.

In the initial stage, we started off by applying the general hydrothermal synthesis method of ZnO nanostructures, this gave dimensions of 1.5 μm in length and 50 nm in diameter with an aspect ratio of approximate 30 within three hours of growth. The FTO substrates were first coated with a ZnO seed layer via ZAD (0.1 M) and then placed in the hydrothermal solution of ZNH (0.05 M) and HMTA (0.05 M) at 90 °C for three hours [5]. Although the aspect ratio is high, the spacing between the trunked nanorods was low; this is not conducive for optimal growth of branched nanowires. In theory, the seed layer was correlated to the nucleation site: the higher the concentration level, the more nucleation sites available. However, even if the concentration of ZAD (0.003 M) is reduced for the ZnO seed layer, the spacing between the trunked nanorods is still below 500 nm. This also reduces the aspect ratio in half, to 15. Figure 2-8 shows the FESEM images of trunked ZnO nanorods with ZnO seed layers from (a) ZAD (0.1 M) and (b) ZAD (0.003 M), respectively.
Figure 2-8. FESEM images of trunked ZnO nanorods with ZnO seed layers from (a) ZAD (0.1 M) and (b) ZAD (0.003 M), respectively. Scale bar, 100 nm.

However, without the ZAD seeding, the trunked ZnO nanorods could grow directly on the FTO substrate. The growth rate is 1 μm/hr, twice as faster as with the ZAD seeding (500 nm/hr). Most importantly, a spacing of larger than 2 μm can be achieved between the trunked nanorods, even though the aspect ratio is relatively lower (<10).

Due to the low aspect ratio of the synthesized trunked ZnO nanorods without a seed layer, a replacement of the synthesis solution is required repeatedly for further extension of the length of ZnO nanorods, as the solution was exhausted every three hours. The expected aspect ratio of greater than 10, with length greater than 5 μm and diameter of around 500 nm, can be achieved with multiple synthesis with ZNH concentration of 0.05 M and HMTA concentration of 0.05 M. It seems that the aspect ratio of the ZnO nanorods gradually increased as the length increased, but the amount of the additional length for each synthesis was shorten under multiple synthesis. Therefore, it is difficult to obtain an ultra-long length of trunked ZnO nanorods with a sufficient aspect ratio in a
relatively short period of time [36].

In addition, as the trunked ZnO nanorods with multiple synthesis were characterized by problematically expanded diameters, we need to constrain the gradually increasing diameter of the trunked nanorods from elongation. To do so, the polymer-assisted and the solvent-assisted methods were attempted in the hydrothermal solution to restrain lateral growth and minimize the diameter of the trunked nanorods [37], [38]. For the solvent-assisted hydrothermal synthesis, it seems that not only the diameter cannot be decreased; the overall lengths also tend to decrease by mixing the solvent of DI water with a non-polar solvent (like ethanol and IPA), in a 1 to 1 ratio. When applying a 100% organic solvent, the byproducts had the spherical shape. On the other hand, polymer-assisted synthesis might be capable of constraining the incremental growth of the diameter of the trunked nanorods. This work is still in progress, and requires further confirmation.

Since our goal is to obtain an ultra-long length of trunked ZnO nanorods with a sufficient aspect ratio, investigations were carried out to provide a template on the substrate for synthesis to occur. Our experiments have shown that with the assistance of a TiO$_2$ nanocrystal template, the trunked ZnO nanorods can be synthesized with a relatively small diameter compared to trunked nanorods grown from the ZnO seed layer. This could be due to the fact that the TiO$_2$ sol tends to have smaller nucleation sites compared to ZnO sol, resulting in a higher aspect ratio. It has been demonstrated that the density of
ZnO nanorods can be controlled efficiently by the TiO$_2$ nanocrystal template; the details will be discussed in Chapter 3.

To synthesize the TiO$_2$ nanocrystal template, the TiO$_2$ sol was first prepared by dissolving titanium (IV) butoxide (TiBO) (0.3 mL) in a concentrated ethanol (10 mL) solution. Figure 2-9 shows the FESEM images of the trunked ZnO nanorods synthesized without seeding and with a TiO$_2$ nanocrystal template, respectively. The diagram shows that the diameter (300 nm) synthesized with a TiO$_2$ nanocrystal template is smaller than that synthesized without any seeding (500 nm) with an adequate spacing.

![Figure 2-9. FESEM images of trunked ZnO nanorods synthesized from (a) no seed layer and (b) TiO$_2$ nanocrystals, respectively. Scale bar, 1 µm.](image)

In addition, researchers have limited the growth in the lateral direction of the nanorods due to the constraint on the $<110>$ plane by implementing the PEI polymer into the hydrothermal synthesis solution, as reported in [5], [10]. Theoretically, a higher concentration of the PEI will generate a larger aspect ratio of the ZnO nanorods by greatly constraining the lateral diameter. Therefore, the concentration ratio between the
zinc precursor (ZNH) and the polymer (PEI), ZNH/PEI, is critical: the lower the value of this ratio, the higher the relative concentration of the PEI. At values below 5, the synthesis becomes difficult; no ZnO nanorods can be produced. In our system, it was found that the synthesis solution of ZNH (0.05 M), HMTA (0.05 M), and PEI (0.01 M) yielded the best results.

Under the synergies of the TiO$_2$ nanocrystal template and the PEI-assisted hydrothermal synthesis, we were able to both limit the lateral growth and further extend the length of the ZnO nanorods to over 15 $\mu$m while maintaining a high aspect ratio (~50), without replacing the synthesis solution. The direct growth vertically-aligned ZnO nanorods could then be used as the backbone of the hierarchical ZnO nanoforest. Figure 2-10 shows the FESEM images of the trunked ZnO nanorods synthesized with the PEI-assisted hydrothermal process from a TiO$_2$ nanocrystal template.

![FESEM images of trunked ZnO nanorods](image)

Figure 2-10. FESEM images of trunked ZnO nanorods synthesized with the PEI-assisted hydrothermal process from a TiO$_2$ nanocrystal template. Scale bar, 1 $\mu$m.
In order to synthesize the branched ZnO nanowires, a secondary seeding was required. In addition, before providing this secondary seeding, a heat treatment was applied to remove the polymer, HMTA and PEI, attached to the nanorod's surface from the first hydrothermal synthesis. The polymer was removed by heating the trunked ZnO nanorods at 350 °C for 30 minutes. This step is critical, since HMTA and PEI will hinder lateral growth but allow drastic axial growth of the ZnO nanostructures in the solution [6]. The secondary seeding on the trunked nanorods without polymer removal would result in sparse growth of branched nanowires due to the suppression by HMTA and PEI. Consequently, the polymer removal process induces the growth of densely packed branched nanowires. However, the diameter of first-generation trunked nanorods might increase due to lateral growth after the removal of the polymer layer.

After polymer removal, a secondary seeding on the trunked ZnO nanorods was applied in order to provide the nucleation site for the branched ZnO nanowires. A uniformly coated high-density ZnO seed layer is also a significant factor for growing densely packed branched nanowires. Previous work has carried out the coating of a seed layer with only ZnO nanoparticles or nanocrystallites [6]. This could still result in a growth of sparsely branched ZnO nanowires; however, with the assistance of a polymer, polyethylene glycol, high quality hierarchical branched ZnO nanowires can be achieved. In the experiment, ZAD (0.1 M) was dissolved in a methanol solution before mixing with the PEG solution. The volume ratio between the PEG and the methanol was 1:5, which is
adequate for the ZnO nanoparticles to conformally coat onto the trunked nanorods. In addition, the polymer-assisted seed layers were coated under two different techniques: spin-coating and dip-coating. Figure 2-11 shows the FESEM images of the polymer-assisted secondary seeding on the trunked ZnO nanorods by spin-coating and dip-coating techniques, respectively. Branched ZnO nanowire growth from the spin-coated PEG-assisted secondary seed layer may be less favorable than from the dip-coating process, as the dip-coated ZnO seed layer seems to generate a higher density film than the spin-coating technique.

Figure 2-11. FESEM images of the secondary seeding on the trunked ZnO nanorods by (a) dip-coating only, (b) PEG-assisted spin-coating, and (c) PEG-assisted dip-coating techniques, respectively. Scale bar, 100 nm.

Additional structural characterizations of the PEG-assisted secondary seeding by the dip-coating technique are shown in Figure 2-12. It illustrates that the ZnO nanoparticles were coated conformally on the trunked ZnO nanorods from top to bottom. This signifies that both polymer removal from first generation and polymer-assisted secondary seeding with the dip-coating technique are important for realizing high-density hierarchical branched ZnO nanowire growth.
Figure 2-12. FESEM images of (a) the PEG-assisted secondary seeding coated conformally on the trunked ZnO nanorods by the dip-coating technique. Scale bar, 2 μm. (b) The top and (c) the bottom of the coated trunked ZnO nanorods, respectively. Scale bar, 100 nm.

In addition to the procedures above, an investigation has taken place on the different concentration levels of the Zn precursor, ZNH, in the hydrothermal solution for the branched ZnO nanowires. Figure 2-13 shows the FESEM images of the ZnO nanoforest synthesized under different concentration levels of ZNH: 0.05 M, 0.15 M, and 0.2 M, respectively. The dimensions of branched nanowires vary with different concentration levels of ZNH. With a single growth step of branched nanowires synthesized from ZNH 0.05 M, ZNH 0.15 M, and ZNH 0.2 M, the lengths average 0.6 μm, 0.83 μm, and 1.08 μm, respectively; diameters are around 40 nm, 140 nm, and 160 nm, respectively. It is notable that the diameters of the branched nanowires are always much smaller than the diameters of the trunked nanorods, which is attributed to the fact that branched nanowires extend from the faces of the trunked nanorods. In addition, the ZnO nanoforest synthesized under the concentration level of ZNH (0.15 M) obtained the
greatest surface-to-volume ratio. The solar conversion efficiency of different synthesized ZnO nanoforest will be characterized in Chapter 4.

Figure 2-13. FESEM images of the ZnO nanoforest synthesized under different concentration levels of ZNH: (a) 0.05 M, (b) 0.15 M, and (c) 0.2 M, respectively. Scale bar, 3 μm.
It is worth noting that the hierarchically branched ZnO nanowires grew perpendicular to the vertically-oriented trunked ZnO nanorods' surface, as shown in the FESEM image in Figure 2-14(a). Also, Figure 2-14(b) shows that the branched nanowires have hexagonal cross sections, and grew along the c-axis of the wurtzite crystal. This suggests that there is an epitaxial growth of the branched ZnO nanowires.

Figure 2-14. FESEM image of the branched ZnO nanowires, which (a) grew perpendicular to the trunked ZnO nanorods and (b) obtained hexagonal cross sections. Scale bar, 200 nm.
3.1 Introduction

Dye-sensitized solar cells have demonstrated conversion efficiencies that exceed 11% with a combination of a TiO$_2$ semiconductor electrode, ruthenium (Ru) complex dye, and an iodine-based electrolyte [39]–[41]. Two major advantages of employing a DSSC as an organic-based photovoltaic cell are the low cost of the semiconductor materials, and the possibility of preparing the electrode using a rapid printing process. Inorganic semiconductors are currently receiving increased interest as light sensitizers for low-cost photovoltaic devices. Nanocrystalline TiO$_2$ has been used extensively as the semiconductor material for photoelectrodes in high-efficiency DSSCs [42].

A TiO$_2$ mesoporous semiconductor film for the photoelectrode—with ruthenium complexes as the sensitizer, and electrolytes containing iodide and triiodide ions, $I^-/I_3^-$—was employed as a common paradigm for DSSC. However, TiO$_2$ nanoparticles photoelectrodes tend to have poor electron scattering, increased trapping at the contacts between nanoparticles, and lower electron transport rates. Therefore, an efficient way to enhance the performance of DSSCs is to increase electron transport rate. Since TiO$_2$ nanoparticle-based DSSCs have a limitation on the thickness of the photoelectrode film
due to the diffusion length of electrons in TiO\textsubscript{2} nanoparticles, composite photoelectrodes with TiO\textsubscript{2} nanowires came into play. They tend to have a longer diffusion length, which could extend the thickness of the photoelectrode and result in a higher overall conversion efficiency [43].

There are several methods that can be used for preparing TiO\textsubscript{2} nanowires; however, these are not ideal, as both the synthesis and purification processes require longer timespans for the achievement of well-formed and highly crystalline TiO\textsubscript{2}. In order to minimize the costs of semiconductor materials for DSSCs, simple production methods are necessary for controlling the crystal structure, crystallization, and nanostructure size. There are some reports of other metal oxides—including SnO\textsubscript{2}, Nb\textsubscript{2}O\textsubscript{5}, and ZnO—being used as semiconductor materials for DSSC composite photoelectrodes [44], [45]. In particular, ZnO can be easily formed into different types of nanostructures using wet synthesis methods; the formation size and crystal shape can be modified by varying the temperature and duration of the process [46], [47]. Moreover, ZnO nanowire is expected to improve cell performance, with higher intrinsic electron mobility and a direct diffusion path for charge collection [48], [49].

Many research groups have discussed composite photoelectrodes; however, the outcomes of their efforts were not convincing. The major problem is the lack of filling TiO\textsubscript{2} nanoparticles between nanorods effectively. Therefore, constructing a suitable spacing between the ZnO nanorods for the efficient infiltration of TiO\textsubscript{2} nanoparticles to
achieve maximal surface areas is critical. Researchers have controlled the spacing through costly patterning methods, including attaching an anodic aluminum oxide (AAO) membrane on the substrate and photolithography in the cleanroom. Our goal is to propose an easy and low-cost method to achieve the density-controlling capability.

In addition, there is a drawback of the ZnO material: the chemical instability. As many previous research studies show, the use of ZnO in DSSCs results in a relatively low open-circuit voltage and fill factor. The main reason was the corrosion of ZnO upon reacting with an acid, and the low amount of dye adsorption [50], [51]. For example, the most commonly used dyes for TiO$_2$ sensitizers, ruthenium bipyridyl complex dyes, are not suitable for ZnO due to the acidic conditions of carboxylic acids as the anchoring group; this leads to the dissolution of the ZnO. In order to solve the problem, research groups used atomic layer deposition (ALD) to coat ZnO nanorod with thin layers of TiO$_2$ [52]. However, these techniques were not cost-effective. As such, the goal is to develop a simple and competitive method for covering ZnO nanorod arrays with a chemically stable metal oxide in order to prevent the ZnO aggregation caused by acid attack.

Here, we developed a facile and low-cost method for the synthesized direct growth of ZnO nanorod arrays with an ability to control density through the hydrothermal process. We form ZnO–TiO$_2$ core–shell nanostructures by covering ZnO nanorod arrays with a TiO$_2$ coating via a sol-gel process, which avoids using expensive systems and multiple deposition steps.
3.2 Synthesizing ZnO/TiO$_2$ Composite Nanostructures

Figure 3-1 illustrates the synthesis process of the ZnO/TiO$_2$ composite nanostructures, including (1) synthesizing ZnO nanorod arrays; (2) preparing ZnO–TiO$_2$ core–shell nanorod arrays; and (3) dispersing TiO$_2$ nanoparticles in ZnO–TiO$_2$ core–shell nanorod arrays.

![Figure 3-1. A schematic diagram of the formation of the ZnO/TiO$_2$ composite nanostructures.](image)
3.2.1 Reagents and Materials

To synthesize the ZnO/TiO₂ nanocomposite photoelectrode, we first acquired all necessary reagents and materials. Zinc acetate dihydrate (ZAD), zinc nitrate hydrate (ZNH), hexamethylenetetramine (HMTA), polyethylenimine (PEI), titanium (IV) butoxide (TiBO), polyethylene glycol (PEG), titanium (IV) chloride (TiCl₄), acetylacetone, 1-methyl-3-propylimidazolium iodide (PMII, 98%), Iodine (I₂, 99.999%), and acetonitrile were all acquired from Sigma-Aldrich. TiO₂ nanoparticles (Aeroxide, P25) were acquired from Evonik. The Triton X-100 was acquired from Promega. The Guanidine thiocyanate (GuNCS, 99%) was purchased from Alfa Aesar, and the Ru dye, Ruthenizer 535-bisTBA, cis-di(thiocyanato)-bis(2,2’-bipyridyl-4,4’-dicarboxylate) ruthenium (II) (N719), was purchased from Solaronix. All the reagents used were of analytical grade, and were used as received. Fluorine-doped SnO₂ conductive glass (FTO), with sheet resistance 6–8 Ω sq⁻¹, was purchased from Cytodiagnostics.

3.2.2 Synthesis of ZnO Nanorod Arrays

The direct growth of ZnO nanorod arrays was conducted in an aqueous solution with a two-step synthesis process. The first step was to synthesize a sol-gel TiO₂ nanocrystal template on the conductive glass substrates; the second was to grow the ZnO nanorod arrays on the nanocrystal template. We utilized a TiO₂ nanocrystal template rather than a conventional ZnO seed layer because our experiments have shown this
template to give better control of spacing for the growth of ZnO nanorod arrays.

To ensure that there was no contamination from the substrates, conductive glass substrates (FTO) were first ultrasonically cleaned in acetone, isopropanol, and ethanol, and then rinsed thoroughly in de-ionized water (DI water). After drying under a stream of nitrogen, the substrates were baked at 80 °C for three hours to evaporate any water molecules before the synthesis was initiated.

To synthesize the TiO$_2$ nanocrystal template, the TiO$_2$ sol was first prepared by dissolving titanium (IV) butoxide (TiBO) in a concentrated ethanol (10 mL) solution at room temperature. The resulting solution was stirred for 30 minutes to yield a clear and homogeneous sol. Given that the sol is easily dehydrated, the entire process was sealed in a parafilm to avoid water molecules in the air to interact with the sol. Then, the TiO$_2$ nanocrystal template was deposited on the FTO substrate by immersing the FTO glass into the TiO$_2$ sol solution for 15 seconds before withdrawing at a speed of 3 cm/min. In order to construct a sparse nucleation site, the process was done only for a single cycle. Subsequently, the nanocrystal template was annealed at 450 °C at a heating rate of 2 °C/min for one hour.

In the second step, the ZnO nanorod arrays were grown on the TiO$_2$ nanocrystal template by immersing the substrate in an aqueous solution containing zinc nitrate hydrate (50 mM), hexamethylenetetramine (50 mM), and polyethyleneimine (10 mM) (branched, low molecular weight) at 90 °C for 24 hours. The 35 mL growth solution was
sealed in a 40 mL Teflon-lined glass vial. After growth, the nanorod arrays were rinsed with DI water and baked at 350 °C in air for 30 minutes to remove any residual organic reactants and to improve the crystallinity. This procedure resulted in arrays of ZnO nanorods with a fast growth rate and a high aspect ratio in a single growth, without replacing the solution.

3.2.3 Preparation of ZnO–TiO₂ Core–Shell Nanorod Arrays

In order to shell the ZnO nanorod arrays, titanium (IV) butoxide was utilized as the precursor for conformally coating a TiO₂ layer via a dip-coating technique to form the ZnO–TiO₂ core–shell nanorod arrays. In the experiment, titanium (IV) butoxide (300 μL) and the polyethylene glycol (1 mL) was prepared in ethanol (10 mL). The addition of the polyethylene glycol was used to form a better conformal shell coating. Then, the TiO₂ shell layer was dip-coated three times, and calcined at 450 °C for crystallization.

3.2.4 Dispersion of TiO₂ Nanoparticles in ZnO–TiO₂ Core–Shell Nanorod Arrays

The TiO₂ nanoparticle film was dispersed into the ZnO–TiO₂ core–shell nanorod arrays using a screen-printing technique, also known as the doctor-blade method. To disperse TiO₂ nanoparticles uniformly into the ZnO–TiO₂ core–shell nanorod arrays, the TiO₂ paste was first prepared by stirring the P25 TiO₂ nanoparticle powder with acetylacetone (1 mL) and triton X-100 (1 mL) in DI water (25 mL) with a ceramic mortar at room temperature for an hour. The Triton X-100 was treated as a surfactant to increase
the conductivity of the film. Second, the TiO\textsubscript{2} paste was dispersed into the core–shell nanorod arrays and the sample was relaxed for three hours in order to reduce surface irregularities and mechanical stress. This was followed by sintering the photoelectrode at 500 °C for one hour. To achieve the desired TiO\textsubscript{2} nanoparticle film thickness, this screen-printing procedure was repeated several times. Subsequently, a post-treatment, TiCl\textsubscript{4} surface treatment, was conducted by immersing the composite nanostructure sample in a TiCl\textsubscript{4} (50 mM) aqueous solution at 70 °C for 30 minutes, followed by a rinse with DI water and calcining at 500 °C in air for one hour. The formation of the ZnO/TiO\textsubscript{2} composite nanostructures is again shown schematically in Figure 3-1.

3.2.5 Material Characterization of ZnO/TiO\textsubscript{2} Composite Nanostructures

The morphology properties of the ZnO/TiO\textsubscript{2} composite nanostructures were examined using field-emission scanning electron microscopy (FESEM, JEOL LEO1530) operated at 3 kV, and transmission electron microscopy (TEM, JEOL 2010F) operated at 200 kV. The ZnO nanorods were scratched off the FTO substrate, and sonicated vigorously in an ethanol solution. Then, a drop of the solution was placed on a carbon-coated copper grid. In addition, the thickness of the nanoparticles’ film was determined by using an Alpha-step 200 surface profilometer (Tencor Instruments). The elemental profiles were characterized by energy dispersive spectroscopy (EDS) in conjunction with TEM observation. The elemental mappings were characterized by
another EDS installed in a SEM (Nova NanoSEM 630, FEI). The structural properties of
the ZnO–TiO₂ core–shell nanorod arrays were analyzed by a Bruker X-ray
diffractometer (XRD, 40 kV, 30 mA) with Cu Kα (λ = 0.15406 nm) radiation at a
scanning rate of 1° min⁻¹ from 10° to 70° (2θ). All measurements were performed at room
temperature.

3.3 Results and Discussion

3.3.1 Characterization of ZnO Nanorod Arrays

In the experiment, we demonstrated an innovative method for controlling the
density of ZnO nanorod arrays. By applying the procedures as described in the previous
section, high aspect ratio ZnO nanorods with lengths exceeding 20 μm and diameters of
several hundred nanometers could be synthesized on the FTO substrate in one
single-round hydrothermal process. The spacing (or density) of the ZnO nanorod arrays
was controlled by the TiO₂ nanocrystal template. By varying the concentration of the
titania precursor-titanium (IV) butoxide for the preparation of the nanocrystal template,
the densities of the ZnO nanorod arrays could be controlled efficiently.

Figure 3-2 shows the FESEM images of vertically-aligned ZnO nanorod arrays
at different concentration levels of the titania precursor: 0.05 mL, 0.1 mL, 0.2 mL, and
0.3 mL, respectively. It can be seen that the higher the concentration level of the
precursor, the smaller the spacing of ZnO nanorod arrays will be. In other words, the
density of ZnO nanorod arrays increases with low concentration levels of the precursor, and decreases with high concentration levels of the precursor. However, the heights of differently-spaced ZnO nanorod array samples were similar (~20 μm) because the same hydrothermal synthesis time was used in the experiment. Furthermore, the diameter of ZnO nanorod arrays decreased as the precursor concentration level increased. Generally, an increase of the precursor concentration level leads to more synthesized nanorods, and then results in a decrease of the diameter of nanorod arrays owing to energy conservation. For instance, the average diameters of ZnO nanorod arrays are 1000 nm, 650 nm, 400 nm, and 250 nm for the precursor concentration levels of 0.05 mL, 0.1 mL, 0.2 mL, and 0.3 mL, respectively. It is worth noting that by applying this simple and low-cost synthesis method, the spacing of ZnO nanorod arrays can be controlled efficiently with a rapid growth rate in one single-round hydrothermal process. This cost-effective technique is non-trivial for density-controlled nanorod array fabrication without using sophisticated, costly equipment unlike in top-down techniques (including, for example, lithography).
Figure 3-2. FESEM images of ZnO nanorod arrays grown under different concentration levels of titania precursor (a) 0.05 mL, (b) 0.1 mL, (c) 0.2 mL, and (d) 0.3 mL, respectively. Scale bar, 10 μm.

In addition, Figure 3-3 depicts the systematic study that reveals the relationship between the diameters of synthesized ZnO nanorod arrays and the different concentration levels of the titania precursor. The diagram that as the concentration level decreases, the diameter of the nanorods gradually increases while the ZnO nanorod array population decreases markedly based on conservation of energy. In the case of high concentration levels, though, the nanorods were densely packed with a high population; this can cause difficulties for the infiltration of TiO$_2$ nanoparticles and, therefore, effectively limits the maximum surface areas. This result further confirms that the density (spacing) of ZnO
nanorod arrays can be controlled by using the TiO$_2$ nanocrystal template.

![Graph showing the diameters of ZnO nanorod arrays versus different concentration levels of the titania precursor.](image)

Figure 3-3. The diameters of ZnO nanorod arrays versus different concentration levels of the titania precursor [53].

In order to achieve the best performance for the DSSC, which will be discussed in Chapter 4, it is crucial to control the spacing of the ZnO nanorod arrays grown so that an optimized trade-off between light harvesting and charge recombination can be achieved. While differently-spaced ZnO nanorod arrays could be synthesized, the concentration level of 0.1 mL for the titania precursor was selected for expected optimum performance for the rest of the experiment. With an average length of around 20 μm and a diameter of around 650 nm, the ZnO nanorod arrays with high aspect ratio (up to 30) have been synthesized for the backbone of the composite nanostructures. Most
importantly, the designated spacing between nanorods is around 5 μm.

The main reason for the spacing chosen is to match the electron diffusion length of TiO₂ nanoparticles [54]–[56]. There was a linear relationship between the overall efficiency and the film thickness under 5 μm, which suggested that within this length, the minimum factor of electron diffusion length could influence overall efficiency [43]. Generally, larger spacing is preferred for the infiltration of TiO₂ nanoparticles. However, in this case, the maximum spacing of ZnO nanorod arrays is limited by the electron diffusion length of TiO₂ nanoparticles dispersed in the ZnO–TiO₂ core–shell nanostructures. In addition, the volume ratio between the nanorods and the composite nanostructures was less than 20%; the total internal surface area was expected to be similar to that of a TiO₂ nanoparticles-only photoelectrode [43].

Under these circumstances, the composite nanostructures can utilize advantages from both building blocks: (1) a high surface-to-volume ratio from the nanoparticles, and (2) long electron diffusion length, fast electron transport, and high light scattering effect from the nanorods. In this case, the electron transport is expected to be more efficient, as the recombination loss can be greatly reduced with the addition of direct growth ZnO nanorod arrays in this designated spacing.

The crystal quality of ZnO nanorod arrays grown was also characterized by XRD and TEM. Figure 3-4(a) shows the XRD pattern, which presents the crystalline nature of direct growth vertically-aligned ZnO nanorod arrays. It shows that these ZnO
nanorod arrays were grown in the prominent direction of (002) from the diffraction peak, confirming the hexagonal wurtzite phase; this observation is also consistent with the standard XRD pattern of ZnO (i.e., JCPDS card number 36-1451). As such, it has a single-crystalline structure, which is beneficial for the electron transport. Figure 3-4(b) presents the bright field TEM image of a single ZnO nanorod, and shows that the nanorod is uniform throughout its length. The diameter is around 550 nm—consistent with the FESEM result. The selective area electron diffraction (SAED) pattern also shows that the nanorod exhibits a single-crystalline nature, as it grew along the c-axis, the [0001] wurtzite direction, as presented in the inset of Figure 3-4(b). To the best of our knowledge, this is the first attainment of the capability to control the density of single-crystalline ZnO nanorod arrays synthesized on a TiO2 nanocrystal template.

Figure 3-4. Characterization of the ZnO nanorod arrays. (a) XRD pattern of the ZnO nanorod arrays. (b) TEM image of a single ZnO nanorod. Scale bar, 200 nm. The inset is the SAED pattern of the ZnO nanorod.
It should be noted that titanium (IV) butoxide was used as the precursor to create the TiO$_2$ nanocrystals. These sparsely-distributed tiny TiO$_2$ crystallites were generated on the FTO substrate and served as the template to grow density-controlled ZnO nanorod arrays. The farther the distance between the adjacent TiO$_2$ nanocrystals, the larger the separation between the adjacent ZnO nanorods.

The reason that the TiO$_2$ nanocrystal template was prepared for the hydrothermal process is that TiO$_2$ sol tends to have a smaller nucleation site compared to ZnO sol for the growth of better spacing-controlled ZnO nanorod arrays. In our system, the ZnO nanorod arrays synthesized from the ZnO seed layer cannot be controlled as efficiently as the TiO$_2$ nanocrystal template in both diameter and density simultaneously. Also, the ZnO seed layer seems to generate a larger diameter of the ZnO nanorods for the designated density compared to the TiO$_2$ nanocrystal template. Figure 3-5 illustrates the ZnO nanorod arrays synthesized from (a) a ZnO seed layer (ZAD 0.006 M) and (b) a TiO$_2$ nanocrystal template (TiBO 0.05 mL). It shows that the diameter of ZnO nanorod arrays synthesized on a ZnO seed layer (<2 μm) is larger compared to ZnO nanorod arrays synthesized on a TiO$_2$ nanocrystal template (1 μm).
In addition, the TiO$_2$ nanocrystal template can be treated as the nucleation site for the growth of ZnO nanorod arrays. This is because they had close structural similarities, close lattice match properties, and also shared a similar pH environment, sufficient to form an epitaxial relationship. Ever since the TiO$_2$ nanocrystal template was coating, the growth substrate came from FTO-only to a composite substrate that contained FTO and TiO$_2$ nanocrystals; the lattice condition changed from mismatch to partial-match. Hence, ZnO clusters started to grow on the traps between the TiO$_2$ nanocrystals and the FTO substrate. Once the active nucleus formed, 1-D growth was prompt—ZnO nanorods could grow from the TiO$_2$ nanocrystal template. As discussed above, the concentration level of the titania precursor controlled the density of the nucleation site, resulting in the density-controlled growth of ZnO nanorod arrays. This finding is reasonable but still does not give the whole picture. The exact mechanism is still under investigation, and will be established in the future.
3.3.2 Characterization of ZnO–TiO₂ Core–Shell Nanorod Arrays

Due to the easily aggregation interaction between the ZnO materials and the photodyes that led to recombination loss during electron transport, a conformal coating layer has been grown as a shell on the synthesized ZnO nanorod arrays for separation. In this case, a simple sol-gel process is used to deposit a conformal TiO₂ layer; the materials was chosen because TiO₂ has the advantages of excellent chemical and photochemical stability. Figure 3-6 presents the FESEM images of a ZnO nanorod before and after conformally dip-coating a TiO₂ layer. It can be seen that the TiO₂ shell layer was conformally coated on the ZnO nanorod core with the PEG-assisted sol-gel solution, and that the two have the same shape with no difference in morphology.

Figure 3-6. FESEM images of (a) the ZnO nanorod and (b) the ZnO–TiO₂ core–shell nanorod. Scale bar, 100 nm.

To further characterize the core–shell structure, Figure 3-7(a) shows the FESEM image of the ZnO nanorod arrays with a breakage spot of the TiO₂ shell layer. Moreover, Figure 3-7(b) shows the zoomed-in FESEM image of a selected single ZnO–TiO₂ core–shell nanorod. The thickness of the TiO₂ layer was around 90 nm after three cycles
It is also worth noting that other researchers have performed synthesis of ZnO–TiO$_2$ core–shell nanostructures using e-beam evaporator, magnetron sputtering, atomic layer deposition (ALD), chemical vapor deposition (CVD), liquid-phase deposition, and TiCl$_4$ treatment [52], [57]–[61]. Most of these procedures involved sophisticated equipment and costly for fabrication. Among many other methods for the formation of the TiO$_2$ shell coating, a TiCl$_4$ treatment is another possible option for low-cost applications.

During the TiCl$_4$ treatment, similar to the work carried out by other research groups, a TiO$_2$ shell layer is generated from the ion exchange between the Zn$^{2+}$ and the Ti$^{+1}$ [62]. The physical mechanism is given in the equilibrium reaction:

$$2\text{Zn}O + \text{TiCl}_4 \rightarrow \text{TiO}_2 + 2\text{ZnCl}_2$$

(3.1)

However, in our system, the ZnO nanorod arrays tend to be etched away while forming the TiO$_2$ shell layer at the same time. We suspect that what actually happened...
during the TiCl₄ treatment is that the mixed solution between the TiCl₄ and the DI water first generated an HCl solution, which reacted easily with ZnO to form ZnCl₂—soluble in water:

\[
\text{TiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{HCl} \tag{3.2}
\]

\[
\text{ZnO} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2\text{O} \tag{3.3}
\]

As such, we encountered deficient ZnO nanorod arrays; the rate of dissolution of ZnO is higher than that of TiO₂ deposition. Even though we have tried to anneal the ZnO nanorod array samples at a higher temperature (600 °C) for a longer period of time for better crystalline properties, and also to lower the synthesis temperature down to 25 °C (even further to 4 °C) to slow the reaction, the ZnO nanorod arrays were still etched off of the FTO substrate.

In order to extend the investigation of the structural characteristics of the core–shell structure, a dark field TEM experiment was carried out. Figure 3-8(a) shows the dark field TEM images of a single ZnO–TiO₂ core–shell nanorod. There is an outer layer conformally covering the inner nanorod, as expected. Moreover, the EDS spectrum of the red spot in Figure 3-8(a) is revealed in Figure 3-8(b). The atomic composition of the core–shell composite nanostructures confirmed that the elements present in the composite are composed of Ti, O, Zn, and Cu atoms. The diagram shows that the Ti element, which came from the TiO₂ shell layer, is dominant. The Cu peak came from the copper grids.
Figure 3-8. (a) Dark field TEM of a single ZnO–TiO$_2$ core–shell nanorod and (b) EDS spectrum of the TiO$_2$ shell layer on the red spot in part (a).

To further prove the presence of the TiO$_2$ shell layer on the ZnO nanorod arrays, elemental mapping analysis was utilized. Figure 3-9 presents the EDS spectrums with the corresponding atomic ratios of different elements, and the elemental mapping images of the synthesized ZnO nanorod arrays and the ZnO–TiO$_2$ core–shell nanorod arrays, respectively. Figure 3-9(a) shows only the elemental distribution of Zn, O, and Sn. On the other hand, Figure 3-9(b) shows that the Ti element also appeared. In addition, from the elemental mapping, there is a uniform distribution of Ti along the nanorod arrays. All of these characterizations demonstrate, that the TiO$_2$ shell layer can be homogeneously coated by the simple sol-gel process.
3.3.3 Characterization of ZnO/TiO₂ Composite Nanostructures

Previously, the designated spacing of the ZnO–TiO₂ core–shell nanorod arrays was discussed in considering the trade-off between light harvesting and charge recombination. The general idea is to avoid using too-low concentration levels of the
titania precursor; these lead to a low population of ZnO nanorod arrays, resulting in spacing exceeding the diffusion length of the electrons of TiO$_2$ nanoparticles. Figure 3-10(a) and Figure 3-10(b) present the FESEM images of the ZnO/TiO$_2$ composite nanostructures with the designated spacing. The images show that the TiO$_2$ nanoparticles were uniformly dispersed into the ZnO–TiO$_2$ core–shell nanorod arrays. However, it is difficult to apply efficient pore filling for the TiO$_2$ nanoparticles when the spacing chosen is too small. For instance, there is a difficulty with the infiltration of the TiO$_2$ nanoparticles in a densely packed (<5 μm) ZnO–TiO$_2$ core–shell nanorod arrays, as presented in Figure 3-10(c) and Figure 3-10(d). It seems that the TiO$_2$ nanoparticles could not disperse easily down to the floor of the ZnO–TiO$_2$ core–shell nanorod arrays. As a result, the core–shell nanorod arrays could be crushed by the bulky TiO$_2$ nanoparticles.
In addition, it is also critical to find an adequate recipe for TiO$_2$ nanoparticle dispersion in ZnO–TiO$_2$ core–shell nanorod arrays. Consequently, the infiltration of TiO$_2$ nanoparticles has been studied systematically. Figure 3-11 presents the relationship between the thickness of a single layer of TiO$_2$ nanoparticle film and the concentration levels of a solution dispersed TiO$_2$ nanoparticles for FTO-only and ZnO–TiO$_2$ core–shell nanorod array substrates. It shows that the TiO$_2$ nanoparticle dispersion in the ZnO–TiO$_2$ core–shell nanorod arrays attained a much more rapid single layer deposition rate compared to the TiO$_2$ nanoparticles on the FTO substrate, due to the complicated nanorod
array structure. This is essentially because it is more difficult to perform infiltration with a high concentration level of the solution of dispersed TiO$_2$ nanoparticles in the ZnO–TiO$_2$ core–shell nanorod arrays. In order to obtain a better measurement of solar cell efficiency from the complete infiltration of TiO$_2$ nanoparticles, further dilution of the concentration of the solution can be carried out; this will help to decrease the thickness of single layer TiO$_2$ nanoparticle deposition rate to 2 μm per layer.

Figure 3-11. The film thickness versus the concentration levels of TiO$_2$ nanoparticles for FTO-only and ZnO–TiO$_2$ core–shell nanorod array substrates.

After forming the ZnO/TiO$_2$ composite nanostructures, we then applied the post-treatment. The TiCl$_4$ surface treatment has two functions: (1) to help to generate a larger surface-to-volume ratio by creating the tiny TiO$_2$ nanocrystallites, and (2) to
provide a linkage between TiO₂ nanoparticles for electron transport [63], [64]. Generally, with the TiCl₄ (0.05 mM) surface treatment at 70 °C, the thickness of the thin film at 15 minutes, 30 minutes, and 60 minutes, is around 12.5 nm, 25 nm, and 50 nm, respectively [65].
Chapter 4

Applications of Three-Dimensional ZnO Nanostructures to Solar Cells

4.1 Dye-Sensitized Solar Cells

In the past two decades, the dye-sensitized solar cell (DSSC) has attracted considerable interest as a renewable energy source because of its low material and production cost [1], [66]. For instance, in comparison with conventional silicon p-n junction cells, the DSSC holds the promise of a lower fabrication cost, its efficiency is comparable to amorphous silicon solar cells, and there is still plenty of room for further improving its efficiency [39]–[41].

DSSC utilizes a photosensitive dye monolayer on a wide band gap semiconductor with a conductive back contact and space between the electrodes filled with an electrolyte. When the photons hit the dye–semiconductor interface, electron–hole pairs are generated. The electrons reach the electrode through the semiconductor, while the holes are recombined in the electrolyte. To further illustrate, when the dye molecule absorbs a photon, it generates an exciton that dissociates into an electron–hole pair. The electron gets injected into the conduction band of the semiconductor and the oxidized dye molecule is regenerated by the electrolyte which in turn gets reduced at the counter
electrode. This process constitutes a complete electrical loop as shown in Figure 4-1.

Figure 4-1. Schematic diagram of dye-sensitized solar cells.

The solar conversion efficiency ($\eta$) of the DSSC is calculated from the short-circuit current density ($J_{SC}$), the open-circuit voltage ($V_{OC}$), the fill factor ($ff$) of the cell, and the intensity of the incident light ($P$).

$$\eta = \frac{J_{SC} \times V_{OC} \times ff}{P}$$

Therefore, it required simultaneous enhancement of the three parameters, $J_{SC}$, $V_{OC}$, and $ff$ in order to improve the overall efficiency, $\eta$.

Generally, from a device structure point of view, two of the key factors corresponding to the efficiency of the DSSC are the charge generation and the charge transport which took place at the semiconductor–dye interface and at the semiconductor and the electrolyte, respectively. In addition, the optimization of the spectral properties
can be done by modifying the dye alone. Also, the carrier transport properties can be improved by optimizing the semiconductor and the electrolyte composition.

4.1.1 Cell Fabrication of Dye-Sensitized Solar Cells

The different photoelectrodes for DSSC were fabricated by the following process: First, the samples were packaged in a 25 μm-thick hot-melt spacer (SX-1170-25PF, Solaronix Inc.) and preheated at 120 °C for 30 minutes and then immediately immersed in a 0.3 mM solution of ruthenium (Ru) dyes, N719 (Solaronix Inc.) at room temperature to allow complete dye adsorption. The N719 is known as Ruthenizer 535-bisTBA, cis-di(thiocyanato)-bis(2,2’-bipyridyl-4,4’-dicarboxylate) ruthenium (II) bis(tetrabutylammonium). Second, the hot-melt spacer was sandwiched between the photoelectrode and the counter electrode of platinum (Pt)-coated FTO glass while the latter was prepared using an E-gun evaporator (Kurt Lesker Lab-18) with a thickness of 100 nm. The photoelectrode and the counter electrode were arranged according to a face-to-face cell layout. For better performance of the cell, sealing the spacer properly could prevent the electrolyte leakage which results in current shorting from the device. Finally, the internal space of each cell was filled with a liquid redox electrolyte (0.6 M PMII, 30 mM I₂, 0.1 M GuNCS in acetonitrile) by capillary action. The active area for the photoelectrode was typically 0.25 cm².

To test its performance, the I–V measurements were carried out under a standard
AM 1.5 G solar simulator (410 W xenon lamp, Newport Corp.) at 100 mW/cm². The current of the I–V characteristics was measured by using a digital source meter (Keithley model 2420). The light intensity was confirmed and calibrated with standard amorphous silicon photovoltaics to 1 sun.

In addition, the electrochemical impedance measurements (EIS) were performed with a computer-controlled Autolab potentiostat (EG&G 273A) equipped with a frequency response analyzer (EG&G 1025) operated with the Nova 1.10 software package. The EIS measurements of the cells were characterized under 1 sun illumination and carried out at the applied bias of $V_{OC}$. The operating frequency is in the range of 1–100 kHz and the magnitude of the alternative AC signal is 10 mV. All impedance measurements were carried out under the same condition as the I–V measurements of the same irradiation source. The obtained spectra were fitted with Z-View software in terms of an appropriate equivalent circuit.

4.1.2 DSSC Performance of the ZnO Nanoforest Photoelectrode

In order to obtain a good solar conversion efficiency for the dye-sensitized solar cell, construction of a large surface area of the photoelectrode was essential. In Chapter 2, a new type of synthesis method for the ZnO nanoforest was presented. Different sets of experiments were performed to synthesize different dimensional nanostructures. Here, we applied these constructed ZnO nanostructures to the photoelectrode of the dye-sensitized...
solar cell and the solar conversion efficiency is evaluated in this section. The ZnO nanoforest was synthesized with the combination of trunked ZnO nanorods and branched ZnO nanowires. The corresponding FESEM images of the ZnO nanoforest photoelectrode in different stages of the process are presented in Figure 4-2.

Figure 4-2. FESEM images of the ZnO nanoforest photoelectrode in different stages of the process: (a) trunked ZnO nanorods, (b) secondary seeding on ZnO nanorods, and (c) ZnO nanoforest, respectively. Scale bar, 3 μm.

In general, the majority of the surface areas comes from the branched ZnO nanowires for the nanoforest type of architecture. Therefore, it is important to construct a high aspect ratio trunked ZnO nanorods with suitable space for the growth of the high-density ZnO nanowire branches. Figure 4-3 shows the picture of a fabricated ZnO nanoforest photoelectrode-based DSSC. It shows that the trunked nanorods obtained a length of greater than 15 μm with a high aspect ratio (~50) and the branched nanowires were synthesized in a high-density hierarchical structure. The cells were immersed in N719 Ru dyes for 6 hours.
A set of ZnO nanoforest photoelectrode-based DSSCs synthesized by different concentration levels of Zn precursor, ZNH (0.05–0.2 M), were generated and used as the testing samples by using the procedures as described in Chapter 2. The major parameters of the solar cells, including the short-circuit current, the open-circuit voltage, and the fill factor, were measured and calculated into the overall conversion efficiency. For the purpose of comparison, the DSSC based on the trunked ZnO nanorods (NR)-only photoelectrode was also synthesized.

Figure 4-4 shows the experimentally measured I–V curves of the ZnO nanoforest photoelectrode-based DSSCs with different morphologies that were synthesized by different concentration levels of ZNH 0.05 M, 0.15 M and 0.2 M, of the hydrothermal solution for sample 1, 2, and 3, respectively, and compared with the trunked ZnO NR-based DSSC for sample 0. Table 4-1 summarizes the measured parameters based on the I–V curves, shown in Figure 4-4. First, one can see that all three
samples of ZnO NF photoelectrode-based DSSCs have higher short-circuit currents but lower open-circuit voltages when compared with the trunked ZnO NR photoelectrode-based DSSC. The high short-circuit current is due to the much larger surface area, which came from the synthesized branched ZnO nanowires, with more than tenfold improvements. The relatively low open-circuit voltage is owing to the longer electron pathway of the nanoforest structure. In this case, electrons have to travel from the branched nanowires through the trunked nanorods and then to the FTO substrate for which the recombination rate could be higher.

Second, the open-circuit voltages were almost the same for all three ZnO NF photoelectrode-based DSSCs which shows that they have similar recombination rates. However, the ZnO NF photoelectrode synthesized using ZNH 0.15 M obtained the best short-circuit current of all. It shows that there is a larger surface areas compared to other nanoforest photoelectrodes. Moreover, the fill factor seems to increase as the concentration levels of ZNH increase. This could be explained by the lower electron leakage from the electrolyte to the FTO substrate with smaller void spaces.

Last, it is noteworthy that the ZnO-based DSSC generally has a lower solar conversion efficiency compared to the TiO₂-based DSSC, mainly owing to the low open-circuit voltage (0.5–0.7 V) of ZnO-based photoelectrodes, including ZnO nanowires, ZnO hierarchical, and ZnO nanowire/nanoparticle composite structures [5], [6], [67]. In principle, there is a detrimental interaction between ZnO materials and acid dyes which
caused the formation of $\text{Zn}^{2+}$/dye complex aggregation which results in reduction of electron transport and leads to low open-circuit voltage. The detailed explanation of the physical mechanism of the open-circuit voltage will be discussed in following sections.

![Figure 4-4. I–V characteristics of DSSC samples based on ZnO nanoforest (NF) photoelectrodes and the trunked ZnO nanorods (NR) photoelectrode.](image)

**Table 4-1.** Photovoltaic properties of DSSCs based on trunked ZnO nanorods photoelectrodes and the ZnO nanoforest photoelectrodes synthesized by different concentration levels of ZNH.

<table>
<thead>
<tr>
<th>Photoelectrodes</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>$V_{OC}$ (V)</th>
<th>$FF$ (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0</td>
<td><strong>Trunked ZnO NR</strong></td>
<td>0.324</td>
<td>0.659</td>
<td>50.95</td>
</tr>
<tr>
<td>S1</td>
<td>ZnO NF (ZNH 0.05M)</td>
<td>3.182</td>
<td>0.565</td>
<td>37.58</td>
</tr>
<tr>
<td>S2</td>
<td>ZnO NF (ZNH 0.15M)</td>
<td>5.263</td>
<td>0.565</td>
<td>48.32</td>
</tr>
<tr>
<td>S3</td>
<td>ZnO NF (ZNH 0.2M)</td>
<td>3.619</td>
<td>0.566</td>
<td>58.81</td>
</tr>
</tbody>
</table>
4.1.3 DSSC Performance of the ZnO/TiO₂ Nanocomposite Photoelectrode

Ever since ZnO nanostructures have proven to be a great candidate for the improvement of the electron transport [68], various ZnO/TiO₂ composite nanostructures have been investigated for DSSCs [44], [69]. However, there are usually additional larger pores caused by the integration of ZnO nanostructures into the TiO₂ nanoparticles matrix with incompatible morphologies and length scales. For instance, some interspaces between ZnO nanostructures cannot fully filled with TiO₂ nanoparticles [70]. In addition, even though these composite nanostructured photoelectrodes have shown excellent electron transport properties, most of them were not grown directly on the substrates [44]. Thus, there is still ample room for improvement.

In order to improve the performance for the conventional TiO₂ nanoparticles photoelectrode DSSC, it is crucial to control the spacing of the direct growth of ZnO nanorod arrays so that an optimized trade-off between the light harvesting and charge recombination can be achieved. From Chapter 3, it has been demonstrated that the spacing of ZnO nanorod arrays can be controlled by changing the concentration levels of the titania precursor. In the case of high concentration levels, the nanorods were densely packed to a high population. This can cause difficulties for the infiltration of TiO₂ nanoparticles and therefore limits the maximum potential surface area from the amount of carrying photodyes. Therefore, we proposed the designated spacing of around 5 μm which is adequate for the efficient infiltration to fill the interstitial voids.
The corresponding FESEM images of the ZnO/TiO$_2$ nanocomposite photoelectrode in different stages of the process are presented in Figure 4-5. First, Figure 4-5(a) demonstrates the high aspect ratio of ZnO nanorod arrays synthesized by a hydrothermal process from the TiO$_2$ nanocrystal template. Second, the ZnO–TiO$_2$ core–shell nanorod arrays were demonstrated with a TiO$_2$ shell layer shown in Figure 4-5(b). The inset illustrates that the shell layer is about 90 nm. Last, the ZnO/TiO$_2$ nanocomposite structures were formed by TiO$_2$ nanoparticles dispersion in core–shell nanostructures as shown in Figure 4-5(c).

In Chapter 3, we described the development of a composite nanostructure based on a direct growth of ZnO nanorod arrays which can offer a better electron transport pathway. The ZnO/TiO$_2$ nanocomposite represented a versatile structure while the TiO$_2$ nanoparticles provided large surface areas for sufficient dye adsorption and the ZnO–TiO$_2$ core–shell nanorod arrays enhanced the electron transport rate and light harvesting owing to its higher diffusion coefficient and induced optical path length in the
film, respectively.

Figure 4-6 shows the picture of a fabricated ZnO/TiO$_2$ nanocomposite photoelectrode-based DSSC. Generally speaking, larger spacing is preferred for the infiltration of TiO$_2$ nanoparticles. However, the maximum spacing of ZnO nanorod arrays is limited by the electron diffusion length of TiO$_2$ nanoparticles (~5 μm) dispersed on the ZnO–TiO$_2$ core–shell composite nanostructure. Thus, 5 μm spacing was selected. The cells were immersed in N719 Ru dyes for 12 hours.

![Figure 4-6. A picture of fabricated ZnO/TiO$_2$ nanocomposite photoelectrode-based DSSC. Scale bar, 5 μm.](image)

A set of ZnO/TiO$_2$ nanocomposite (NC) photoelectrode-based DSSCs with different thicknesses of photoelectrodes, from 4 μm to 12 μm, were synthesized and used as the testing samples by using the procedures as described in Chapter 3. The major parameters of the solar cells, including the short-circuit current, the open-circuit voltage, and the fill factor, were measured and calculated into the overall conversion efficiency. For the purpose of comparison, the DSSC based on the TiO$_2$ nanoparticles (NP)-only
photoelectrode was also synthesized.

Figure 4-7 shows the experimentally measured I–V curves of the ZnO/TiO₂ NC photoelectrode-based DSSCs with the different thicknesses of 4 μm, 8 μm, and 12 μm for samples 1, 2, and 3, respectively, and compared with the TiO₂ NP-based DSSC for sample 0. First, one can see that the ZnO/TiO₂ NC photoelectrode-based DSSC (red curve) has a better performance than that of conventional TiO₂ NP-based DSSC (black curve) in terms of two major parameters—open-circuit voltage and short-circuit current—when they have the same 4 μm thickness. It is due to the fact that ZnO–TiO₂ core–shell nanorod arrays can enhance the light harvesting and electron transport rate. In a conventional DSSC, TiO₂ nanoparticles have the size of 15–20 nm which is much smaller than the wavelength of visible light; thus, the film is transparent with minor light scattering. Therefore, by implementing nanorod arrays, which can be treated as light scattering centers, the optical path length in the film can be increase. As a result, the light harvesting can be enhanced [70], [71]. Second, the short-circuit current increases as the thickness of the nanocomposite photoelectrode increases although there is a slight drop in the open-circuit voltage as expected. Generally, as the thickness of TiO₂ mesoporous film gradually increases, the short-circuit current density will increase with higher surface area and the open-circuit voltage will decrease with higher recombination owing to the longer electron pathway.
Figure 4-7. I–V characteristics of DSSC samples based on ZnO/TiO$_2$ nanocomposite (NC) photoelectrodes and the conventional TiO$_2$ nanoparticles (NP) photoelectrode.

Table 4-2 summarizes the measured parameters based on the I–V cures shown in Figure 4-7. It can be seen that the ZnO/TiO$_2$ NC photoelectrode-based DSSC has a high open-circuit voltage. The highest achieved $V_{OC}$ close to 0.93 V with the overall conversion efficiency close to 4.43%, which is noticeably higher than that of the TiO$_2$ NP-based DSSC, 0.78 V, with the same thickness. This indicates an approximate 18% improvement of the $V_{OC}$ with the nanocomposite architecture. Even with a 12 μm thick film, the $V_{OC}$ can still exceed 0.85 V, with the overall conversion efficiency reaching 6.59%.

Despite the fact that the enhancement of $V_{OC}$ was previously observed for the
DSSC based on the composite photoelectrodes [44], this was the first time a high $V_{oc}$ was realized, reaching the theoretical limit solely by modifying the photoelectrode and without changing the electrolytes and the photodyes. It is vital to understand the physical mechanism behind this major advancement of the obtained high open-circuit voltage which will be discussed in detail in the following sections.

Table 4-2. Photovoltaic properties of DSSCs based on the TiO$_2$ nanoparticles photoelectrode and the ZnO/TiO$_2$ nanocomposite photoelectrodes with different thicknesses of the film.

<table>
<thead>
<tr>
<th>Photoelectrodes</th>
<th>Thickness (μm)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$ (%)</th>
<th>$η$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0 TiO$_2$ NP</td>
<td>4</td>
<td>8.31</td>
<td>0.784</td>
<td>59.23</td>
<td>3.86</td>
</tr>
<tr>
<td>S1 ZnO/TiO$_2$ NC</td>
<td>4</td>
<td>8.97</td>
<td>0.928</td>
<td>53.16</td>
<td>4.43</td>
</tr>
<tr>
<td>S2 ZnO/TiO$_2$ NC</td>
<td>8</td>
<td>10.12</td>
<td>0.901</td>
<td>62.63</td>
<td>5.71</td>
</tr>
<tr>
<td>S3 ZnO/TiO$_2$ NC</td>
<td>12</td>
<td>11.68</td>
<td>0.856</td>
<td>65.88</td>
<td>6.59</td>
</tr>
</tbody>
</table>

During the I-V characterization, we sometimes ran into high $V_{oc}$ and $FF$, but with a low $J_{sc}$. This might be caused by the fact that TiO$_2$ nanoparticles did not fully contact with the FTO substrate, as some of them were floating between the ZnO nanorod arrays which has been confirmed with the FESEM. Also, there were times we could not obtain any short-circuit current from the I-V measurement which we believed they were owing to current shorting as the electrolyte leakage from the poor packaging. Therefore, better sealing of the spacer is critical.

For the ZnO/TiO$_2$ nanocomposite photoelectrode DSSC, we have tried different recipes for the preparation of ZnO–TiO$_2$ core–shell nanorod arrays. We started off by comparing the number of dip-coating cycles under the same concentration of TiBO (300
μL) in ethanol (10 mL). It seems that the overall conversion efficiency is improved (~20%) for three cycles deposition compared to two cycles deposition which might be due to an enhancement of the conformal shell coating. Then, the experiments were used to compare the sol-gel solution with and without the PEG-assist. It seems that the overall efficiency is further improved (~10%) with the PEG-assisted TiO2 shell coating.

In addition, we investigated the ZnO/TiO2 NC photoelectrode DSSC under different post-treatment processes. Instead of using the TiCl4 as a typical surface treatment [72], [73], we have tried to utilize the TiBO (300 μL, 600 μL, and 900 μL) for the post-treatment process. It seems that both the $V_{OC}$ and $FF$ tends to increase as the concentration level of TiBO goes up; however, the TiO2 nanoparticles’ film will gradually transform into a bulk TiO2 in a smaller surface-to-volume ratio which results in a low current density. Also, by comparing the post-treatment between TiCl4 (0.05 M) and TiBO (900 μL), we found that even though the samples with TiBO post-treatment will provide a marginally higher $V_{OC}$ and $FF$; the $J_{SC}$ is much lower than the ones with TiCl4 surface treatment. Therefore, in general, we went with the TiCl4 post-treatment since it results in a higher overall conversion efficiency with $V_{OC}$ greater than 0.8 V and $FF$ close to 60% and most importantly with a sufficient $J_{SC}$.

It is worth noting that with the assistance of ZnO nanorod arrays, this composite photoelectrode can form a better electron transport network. This has been explained by the continuous increment of the current density even when the film thickness is above 12
Therefore, the thickness of the film is expected to be further extended in order to overcome the limitation of the diffusion length of the electrons in TiO₂ nanoparticles by the enhanced electron transport from this architecture.

### 4.2 Physical Mechanism of High Open-Circuit Voltage

During the development of the ZnO/TiO₂ nanocomposite DSSC, an interesting phenomenon appeared as this nanocomposite photoelectrode provided extra high open-circuit voltage values than the conventional TiO₂ mesoporous DSSC while there was no modification neither on the photodyes nor the electrolyte. As the maximum $V_{OC}$ value for the DSSC using TiO₂ electrodes and $I^-/I_3^-$ electrolytes is known to be around 0.9 V, the $V_{OC}$ values higher than 0.9 V obtained in this study are noteworthy.

DSSC efficiency is primarily determined by the short-circuit current ($J_{SC}$) and open-circuit voltage ($V_{OC}$). The larger the $J_{SC}$ and $V_{OC}$, the higher the DSSC's efficiency will be. Through the years, there have been considerable efforts at—and achievements in—improving $J_{SC}$ [40], [41]. However, only limited improvements have been achieved in terms of $V_{OC}$ [66], [74], [75]. The highest reported $V_{OC}$ for TiO₂-based photoelectrodes with iodide-based electrolytes and ruthenium-based dyes does not exceed 0.9 V. The value of $V_{OC}$ is mainly limited by charge recombination during the charge transport process, particularly at the interfaces of the TiO₂ photoelectrode/electrolyte and the TiO₂ photoelectrode/dye [76]–[79].
One approach for improving the $V_{OC}$ is to add a pyridine derivative, 4-tert-butyl pyridine (tBP), into the electrolyte. In this case, an improvement in $V_{OC}$ levels was indeed observed, and believed to be due to the suppression of the dark current from the interface between the photoelectrode and electrolyte [80], [81]. However, the amount of improvement was still well below the maximum theoretical limitation. Another approach is to improve the photoelectrode itself. A number of efforts have been made to optimize photoelectrodes, such as considering the structure of TiO$_2$ mesoporous photoelectrodes [41], [66], [82]–[84]. However, the highest value of $V_{OC}$ was still around 0.7–0.8 V. Therefore, it is found to be very difficult to achieve a high $V_{OC}$ by just harnessing a single-element photoelectrode.

To overcome the limitation of a single-element photoelectrode, we found that the ZnO/TiO$_2$ nanocomposite photoelectrode enables both the improved charge carrier diffusion path and the reduced recombination rate. In this instance, a high $V_{OC}$ up to 0.93 V was successfully achieved, and, to the best of our knowledge, the first successful $V_{OC}$ close to the theoretical limit by solely modifying the photoelectrode. This, in turn, is very helpful for achieving a high-efficiency DSSC.

In brief, the origin of the obtained $V_{OC}$ will thus be explained according to the synergy parameters. Possible reasons explaining the achieved high $V_{OC}$ based on the ZnO/TiO$_2$ nanocomposite photoelectrode are summarized as follows: (i) direct growth ZnO nanorod arrays leads to a better electron pathway; (ii) the conduction band edge
position modified by the ZnO/TiO$_2$ nanocomposite photoelectrode; (iii) an energy barrier reduced the electron recombination with the surface blocking effect.

It is well known the open-circuit voltage is determined by the potential difference between the Fermi level of the photoelectrode ($E_{Fn}$) under illumination and the Nernst potential of the redox couple ($E_{red}$) in the electrolyte. In addition, the $E_{Fn}$ is determined by the potential of the conduction band edge ($E_{CB}$) and the electron density ($n$) in the photoelectrode. Therefore, $V_{OC}$ could be described as [85]–[88]

$$V_{OC} = E_{red} - E_{CB} - \frac{\gamma k_B T}{e} \ln \left( \frac{N_e}{n} \right)$$  \hspace{1cm} (4.2)

where $\gamma$ is a characteristic constant of the photoelectrode tailing states, also known as trap states, $k_B$ is the Boltzmann constant, $T$ is the temperature, $e$ is the elementary charge of the electrons, and $N_e$ is the effective density of states at the conduction band in the photoelectrode. Considering that $E_{red}$ is constant, and both $\gamma$ and $N_e$ do not change much under similar conditions, the $V_{OC}$ will be determined by the position of the conduction band edge, $E_{CB}$, and the concentration of electrons in the photoelectrode, $n$. The position of the conduction band edge is decided by the surface charge. Therefore, any change in the surface charge leads to the shifting of the conduction band edge position. In addition, the number of electrons in the photoelectrode is resolved by the balance between electron injection and electron recombination. To achieve a high open-circuit voltage, one has to maximize the electron transport pathway and minimize the recombination rate.

The open-circuit voltage of the ZnO/TiO$_2$ nanocomposite DSSC is illustrated
from the energy diagram as shown in Figure 4-8. The theoretical maximum value of $V_{OC}$ is 0.9 V while the Nernst potential of the triiodide/iodide-based redox electrolyte is close to $+0.4$ V and the energy of the conduction band edge of TiO$_2$ is located at $-0.5$ V. Yet, the experimentally observed $V_{OC}$ for various sensitizers is generally smaller than the difference between the conduction band edge and the redox couple because of the competition between electron transfer and charge recombination pathways.

![Energy Band Diagram](image)

**Figure 4-8.** Energy band diagram and of a conceptual illustration of charge recombination of the ZnO/TiO$_2$ nanocomposite DSSC. (1) Reduction of the oxidized dye and (2) reduction of the oxidized species in the electrolyte.

First, there is always a competition between the rapid electron transport in the photoelectrode and the recombination in diffusion process. In previous studies, one-dimensional nanostructures have proven to be an effective way to facilitate electron transport [5], [89], [90]. In addition, ZnO, instead of TiO$_2$, was selected as the core of the nanorod arrays because it was reported that the ZnO nanorods have demonstrated a
higher mobility and diffusion rate than that of TiO$_2$ nanoparticles which is more favorable for electron transport [5]. Generally, in a conventional TiO$_2$ mesoporous photoelectrode, electrons transport via an indirect pathway through the nanoparticles and are readily trapped by surface states which result in the increment of electron–hole recombination. Hence, implementing the ZnO nanorod arrays provided the competitive edge over plain TiO$_2$ mesoporous structure for a more efficient electron pathway by facilitating electron diffusion from TiO$_2$ nanoparticles to ZnO nanorods. For instance, as soon as the electrons were transported from the photodyes to TiO$_2$ nanoparticles, they were quickly transported to the transparent conductive oxide, FTO, substrate instead of hopping over the TiO$_2$ nanoparticles by creating a preferable direct line through the ZnO nanorods, as shown in Figure 4-9.

However, because of the drawbacks of the corrosion of ZnO on reacting with
acid dyes forming Zn$^{2+}$/dye complex aggregation occurred in the vicinity of the surface, ZnO-based DSSCs could not conduct better efficiency than TiO$_2$-based DSSCs. The reason of passivation for dye molecules is because of the unfriendly environment for the ZnO in the dye solution since the point of zero charge of ZnO is reported to be pH = 8–9 and the pH value for the dye sensitization process is approximately at 5 [8], [91]. On the other hand, for comparison, TiO$_2$ has the point of zero charge with pH = 5.5–6.5 which is similar to the pH of the dye solution; consequently, the formation of metal-ion/dye complex does not take place [92], [93]. Herein, with the addition of the TiO$_2$ conformal shell coating as a blocking layer, the aggregation interaction between ZnO and dye could be avoided by separating the dye and the ZnO nanorod to improve the stability of the ZnO nanorod arrays.

Second, the band-edge energetics is another factor that can be examined in order to account for the open-circuit voltage enhancement. As the conduction band edge position is moved, the band-edge movement is expected to be modified by the ZnO/TiO$_2$ nanocomposite photoelectrode, which led to the negative shifts of the conduction band, thus producing a higher quasi-Fermi level and resulting in an increase in the $V_{OC}$. In other words, the higher $V_{OC}$ of the nanocomposite cells can be explained as a consequence of reduced recombination by excellent electron transport properties of the inner nanorod network, which results in an increase of electron density in TiO$_2$; thus, the shift of Fermi level. In our device, the superior transport properties of the nanocomposite structure may
allow for large electron lifetimes and a suppression of back electron transfer from the electrode to the electrolyte.

Last, an energy barrier has been created to improve the open-circuit voltage by reducing the interfacial charge recombination at the ZnO/dye and ZnO/electrolyte interfaces. Generally, there will be appearance of electron recombination with I$_2$ and/or I$_3^-$ acceptor species from the electrolyte at the surface of ZnO nanorods. The TiO$_2$ energy blocking layer prevented back electron transfer from ZnO nanorod to electrolyte and increased the electron lifetime of the ZnO nanorod. Hence, this energy barrier reduced the electron recombination rate from the electrolyte which enhanced the dye adsorption and the electron injection efficiency. In addition, this TiO$_2$ conformal coating layer not only covered the ZnO nanorod arrays, it also covered the open areas on the FTO conductive substrate which separates from the dye and the electrolyte in order to further reduce the recombination.

It is worth noting that even though there were titania precursor (TiBO) coated on the FTO substrate before the hydrothermal synthesis, only sparsely distributed tiny TiO$_2$ crystallites were formed and used as the template of synthesized ZnO nanorod arrays. Since the dimension of TiO$_2$ nanocrystals were so small (<=5 nm), it had negligible influence on electron transport. Hence, there is no blocking layer between the ZnO nanorod arrays and the FTO substrate.

It was noticed that ZnO–TiO$_2$ core–shell nanorod arrays and/or TiO$_2$
nanoparticles employing in DSSC were also reported recently. However, these previous works had a lower open-circuit voltage, which was due to following reasons:

- **Previous work based on dense directly grown ZnO–TiO$_2$ core–shell nanorod arrays + dispersed TiO$_2$ nanoparticles** [94], [95]. In these previous works, ZnO nanorods grown on the transparent conductive substrate were too dense. The spacing between the adjacent gaps was only tens of nanometers, which made it very hard to achieve a good TiO$_2$ nanoparticles filling. Even with the assistance of ultrasonic irradiation, it is still quite difficult to infiltrate TiO$_2$ nanoparticles efficiently. Therefore, the $V_{OC}$ of this previous work was mainly based on the voltage difference between conduction band edge of ZnO and the redox potential of the electrolyte, which resulted in a low open-circuit voltage.

- **Previous work based on non-directly grown ZnO–TiO$_2$ core–shell nanorod arrays + dispersed TiO$_2$ nanoparticles** [44]. Since ZnO–TiO$_2$ core–shell nanorods were not directly grown on the transparent conductive substrate, there was large contact resistance between the nanocomposite (including ZnO–TiO$_2$ core–shell nanorod arrays and TiO$_2$ nanoparticles) and the transparent conductive substrate.

- **Previous work based on ZnO–TiO$_2$ core–shell nanorod arrays only** [52]. Since the open-circuit voltage of ZnO–TiO$_2$ core–shell nanorod arrays was mainly determined by the voltage difference between the conduction band edge of ZnO...
and the redox potential of the electrolyte, it had a low open-circuit voltage. For instance, we made a DSSC sample with a ZnO–TiO₂ core–shell nanorod array only photoelectrode with otherwise the same parameters. The experimental measured $V_{oc}$ was only 0.7 V.

- Furthermore, the thickness of TiO₂ shell layer of our nanocomposite structure was thicker (~90 nm) than the previously reported ZnO–TiO₂ core–shell nanorod arrays. Such a thicker layer ensured that the ZnO core was fully protected from the reaction with the acid dyes. We conducted experiments for two different TiO₂ shell layer thicknesses (60 nm and 90 nm) of ZnO/TiO₂ nanocomposite photoelectrodes. The experimental results confirmed that higher open-circuit voltage was achieved for the cell having a 90 nm shell thickness as demonstrated in Table 4-3. It was also speculated that once the ZnO core was fully protected, further increase of the thickness of the TiO₂ shell would not result in the further increase of $V_{oc}$. It is worth to note that in the amorphous phase, the $V_{oc}$ drops when the thickness of the TiO₂ shell layer increases. However, in the crystalline phase, the $V_{oc}$ increases when the thickness of the TiO₂ shell layer increases, as long as the quality of crystalline phase is sufficient [52].
Table 4-3. Open-circuit voltages of different TiO₂ shell layer thickness of ZnO/TiO₂ nanocomposite photoelectrodes for DSSC.

<table>
<thead>
<tr>
<th>Photoelectrodes</th>
<th>Open-circuit voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO/TiO₂ nanocomposite w/ 60 nm (TiO₂ shell layer)</td>
<td>0.82</td>
</tr>
<tr>
<td>ZnO/TiO₂ nanocomposite w/ 90 nm (TiO₂ shell layer)</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Most importantly, the $V_{OC}$ of the ZnO/TiO₂ nanocomposite photoelectrode is mainly based on the TiO₂ nanoparticles as it dominated the electron transport process, which provide a higher intrinsic value with 0.7–0.8 V, rather than ZnO nanowires with 0.6–0.7 V for a typical ZnO–TiO₂ core–shell photoelectrode as summarized in Table 4-4. To elaborate, the TiO₂ nanoparticles are more likely to dominant the built-in potential since majority of the photodyes were coating on them. Therefore, the electron–hole pairs were generated from the nanoparticles instead of the nanorod arrays.

Table 4-4. Open-circuit voltages of different photoelectrodes for DSSC.

<table>
<thead>
<tr>
<th>Photoelectrodes</th>
<th>Open-circuit voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO nanorod arrays</td>
<td>0.632</td>
</tr>
<tr>
<td>ZnO-TiO₂ core-shell nanorod arrays</td>
<td>0.697</td>
</tr>
<tr>
<td>ZnO/TiO₂ nanocomposite</td>
<td>0.928</td>
</tr>
</tbody>
</table>

4.3 Electrochemical Impedance Spectroscopy

In order to verify and further understand the observed high open-circuit voltage, electrochemical impedance spectroscopy (EIS) was employed to investigate the electron transport and charge recombination in the ZnO/TiO₂ nanocomposite photoelectrode-based DSSC. It has been applied in order to characterize the internal
resistance and charge-transfer kinetics of composite photoelectrodes in DSSC [44], [69], [70], [95].

Generally, DSSCs have three semicircles in the EIS Nyquist plot, which are assigned to the redox reaction at the Pt counter electrode/electrolyte interface at high frequency range, the electron transfer at the electrodes/dye/electrolyte interface at medium frequency range, and the Warburg diffusion process of I/I₃⁻ in the electrolyte at low frequency range [96], [97]. However, the conventional Warburg diffusion resistance for the redox couple at low frequency, is virtually overlapped by the medium frequency because of the relatively short length for I⁻ ion diffusion caused by the thin spacer, 25 μm, was used.

An equivalent circuit consisting of a series of two parallel RC circuits is shown in Figure 4-10 which was employed to fit the impedance data by using ZView impedance analysis software. The corresponding electron transport parameters are presented as the electron transport resistance ($R_w = r_wL$, L is the thickness of the photoelectrode), the charge transfer resistance ($R_k = r_k/L$), the first-order reaction rate constant for the loss of electrons ($k_{\text{eff}}$), lifetime of an electron in the electrodes ($\tau_{\text{eff}}$), the steady-state electron density in the conduction band of the electrodes ($n_s$), and the effective diffusion coefficient ($D_{\text{eff}}$). The $R_w$ is the transport resistance in the electrodes, and $R_k$ is the charge transfer resistance of the charge recombination between electrons in the electrodes and I₃⁻ in the electrolyte. The values of $\tau_{\text{eff}}$, $n_s$, and $D_{\text{eff}}$ are determined according to the procedure
demonstrated by Adachi et al [98]. $R_s$ is a lumped series resistance at the FTO/TiO$_2$ contact, added to the circuit to account for the nonzero intercept on the real axial of the impedance plot which represents the sheet resistance of TCO. $Z_d$ is the impedance of diffusion of redox species in the electrolyte.

Figure 4-10. An equivalent circuit for dye-sensitized solar cells.

Figure 4-11 shows the Nyquist plots of the ZnO/TiO$_2$ NC photoelectrode and the TiO$_2$ NP photoelectrode for DSSCs, both with a film thickness of 4 μm. The plots present the negative of the imaginary part of the impedance $-Z''$ as a function of the real part of the impedance $Z'$ while the frequency sweeps from 1 Hz to 100 kHz, which includes both the measured data points and the fitted curves. There two cells show a typical double semicircle spectrum for each Nyquist plot which were distinguished in the frequency regime of $10^3$–$10^5$ (small semicircle) and $10^{-1}$–$10^3$ (larger semicircle), from left to right, respectively. The semicircle in the higher frequency range fitted to the electron transfer
resistance \( (R_{pt}) \) and the interfacial capacitance \( (C_{pt}) \) should be ascribed to the process at the electrolyte/Pt counter electrode interface. Furthermore, the semicircle in the intermediate frequency range fitted to the recombination resistance \( (R_{ct}) \) and the chemical capacitance \( (C_u) \) across the electrodes/dye/electrolyte interface.

According to the approach of Adachi et al., several electron transport parameters can be deduced from the Nyquist plot \([98]\). In particular, the charger transfer (recombination) resistance \( (R_k) \) that is related to electron–hole recombination can be determined from the central arc diameter of the intermediate frequency. The size of the semicircle represents the recombination resistance between electrons in the photoelectrode and holes in the electrolyte. It can be seen that the recombination resistance is 128.05 \( \Omega \) for the TiO\(_2\) NP DSSC and 443.27 \( \Omega \) for the ZnO/TiO\(_2\) NC DSSC. The higher recombination resistances of the ZnO/TiO\(_2\) NC photoelectrode cell imply a slower electron recombination process between the injected electrons and the I\(_3^-\) in the electrolyte \([44]\). In other words, less abundant electron interfacial recombination occurred in the ZnO/TiO\(_2\) NC DSSC.
4.4 Improvement of Solar Conversion Efficiency

To validate the potential of further improvement of solar conversion efficiency from the ZnO/TiO$_2$ nanocomposite photoelectrode, the thickness of the dispersed TiO$_2$ nanoparticles' film is extended to 20 μm. Figure 4-12 demonstrates the dependence of (a) short-circuit current and (b) open-circuit voltage on film thickness. Each data value was generated by averaging five samples. The current density had an opposite trend to the open-circuit voltage along with the dependence on film thickness. On one hand, the current density increased continuously with film thickness for the whole range up to 20
μm. This could be due to the fact that ZnO–TiO₂ core–shell nanorod arrays formed a network for the electrons to transport efficiently without suffering the diffusion process through the nanoparticles aggregation which limited the increment of the current density. Phenomena similar to this have been observed from the TiO₂ nanoparticle/nanowire composite photoelectrode [43]. On the other hand, the open-circuit voltage decreased with an increase in the film thickness. The decrease has been elucidated as a consequence of the increased charge recombination and restricted mass transport in thicker films [71]. As mentioned earlier, this ZnO/TiO₂ nanocomposite photoelectrode could provide a high value for $V_{OC}$. Here, even with the continuous decrease along the film thickness, the $V_{OC}$ can still obtain a value above 0.8 V with a film thickness of 20 μm.

![Figure 4-12. Dependence of (a) short-circuit current and (b) open-circuit voltage on film thickness for the ZnO/TiO₂ nanocomposite (NC) photoelectrodes [53].](image)

In the end, the overall conversion efficiency has been calculated. The performance of ZnO/TiO₂ nanocomposite cells were compared with pure conventional TiO₂ nanoparticles cells for a series of film thickness. Figure 4-13 presents the
dependence of the solar conversion efficiency on film thickness for ZnO/TiO₂ nanocomposite (NC) photoelectrodes and conventional TiO₂ nanoparticles (NP) photoelectrodes. Efficiencies from ZnO/TiO₂ NC cells were higher than those from TiO₂ NP cells at the film thickness from 4 to 20 μm. This could be due to the fact that the electron transport rate has been induced with less recombination by the incorporation of the ZnO–TiO₂ core–shell nanorod arrays into TiO₂ nanoparticles films. Thus, the ZnO/TiO₂ NC photoelectrode could provide a relatively higher current density and a much higher open-circuit voltage. The average improvement of the conversion efficiency is around 20% compared ZnO/TiO₂ NC to TiO₂ NP cells. Particularly, when the film thickness became much thicker, one can see that the overall conversion efficiency of TiO₂ NP cells started to saturate; however, ZnO/TiO₂ NC cells do not become saturated. Among all the cells prepared, the highest efficiency was 7.5%, which was achieved from ZnO/TiO₂ NC cells at the film thickness of 20 μm and continued increasing.

The main driving force of employing ZnO–TiO₂ core–shell nanorod arrays is to use them as electron transport trunks so that a thicker layer of dispersed TiO₂ nanoparticles could be harnessed for achieving a higher conversion efficiency. In this case, the thickness of the TiO₂ nanoparticles layer (e.g., 20 μm) can be much thicker than the diffusion length of electrons in TiO₂ nanoparticles (~5 μm).
Figure 4-13. Dependence of solar conversion efficiency on film thickness for ZnO/TiO$_2$ nanocomposite (NC) photoelectrodes and conventional TiO$_2$ nanoparticles (NP) photoelectrodes [53].
Chapter 5

Radiation Detection - Other Works Performed during Ph.D. Study

5.1 Introduction

Because of the wide spread usage of radioactive materials in today’s world, such as in nuclear power plants, radiation detection is critically needed. To minimize the risk of human involvement and radioactive contamination in the environment, it is preferred to detect the nuclear radiation at the standoff distance. Different types of materials and techniques were proposed and developed for detecting different types of radiations. For example, solid-state materials such as scintillation and semiconductor materials have been investigated for gamma radiation detection [99], [100]. The physical mechanism of detection was based on the fact that both electrical and optical properties of the materials experience changes upon the exposure to gamma radiation [101]. For instance, gamma rays can produce a change in the density of charge carriers in semiconducting material, which can be used for detection [102], [103].

Although standoff detection is preferred, it is a challenging job. This is particularly true for alpha radiation detection because of the short penetrating range in air. The conventional detection techniques require bringing a probe within a few centimeters
of the suspect area to operate effectively. Recently, a remote detection technique based on the radiation induced air fluorescence was reported, in which the radiation detection was achieved by detecting the faint light emitted by radiation excited and/or ionized molecules [104]. The air fluorescence is a spontaneous emission which radiates uniformly within an entire $4\pi$ solid angle, so its intensity drops rapidly according to $1/r^2$ law where $r$ is the standoff distance. This intrinsic problem of propagation loss still limits the distance of the standoff detection.

To overcome the above fundamental limitation of $1/r^2$ propagation loss, we report a standoff alpha radiation detection technique by exploring the physical mechanism of excited state absorption of radiation excited/ionized air molecules. Instead of directly detecting the faint light emitted by ionized/excited air molecules, a collimated probe beam with a wavelength matching that of the emitting wavelength of air fluorescence is used to detect the radiation via excited state absorption of air molecules. Since the probe beam is a collimated beam, its propagation does not suffer the fundamental limitation of $1/r^2$ propagation loss. This technology has a potential to realize the long range standoff detection for a stationary environmental monitoring.

5.2 Investigation of Radiation-Induced Air Fluorescence

Generally, radiation can excite and/or ionize air to generate excited state air and the excited state air can generate air fluorescence in all the visible, UV, and IR spectral
range, which includes molecules, atoms, and ions. There are many ways to produce air fluorescence. Here, an exploration on the mechanisms of radiation-induced air fluorescence will be reviewed. Underneath, a systematically investigation of the induced air fluorescence will start with high intensity laser to X-ray radiation, and then to alpha radiation. To further take advantage of this phenomenon, a potential application of radiation detection that utilizes these radiation excited/ionized air fluorescence based on excited state absorption, is discussed.

Radiation-induced air fluorescence is investigated for several different types of radiation sources, including high-brightness laser sources, X-ray radiation sources, and alpha radiation sources. First, the air fluorescence spectrum with three spectral bandpass filters induced by the high intensity laser was analyzed from a spectrometer detector. Second, the air fluorescence intensity induced by different types of radiation are measured using a photomultiplier tube (PMT) detector. Finally, the potential application of radiation induced air fluorescence for the radiation detection, is addressed.

The fluorescent emission results induced by different types, including high intensity laser, X-ray, and alpha radiation sources were measured with an Ocean Optics spectrometer and Hamamatsu photomultiplier tube detectors with three spectral filters in room temperature at one atmospheric pressure. These results may lead to a possible applications of radiation detection.
In the first experiment, we used an Ocean Optics USB2000+ spectrometer to measure the fluorescent emission from high intensity laser-induced air fluorescence, as shown in Figure 5-1. A focused laser beam from an amplified Ti-sapphire laser with a pulse energy of 2 mJ, a pulse duration of 150 fs, and a pulse repetition rate of 1 kHz was focused in order to ionize and excite air to form air fluorescence. To block the exciting femtosecond laser beam, a low pass filter was implemented. To better understanding the air fluorescence spectrum, we added three bandpass filters in front of the spectrometer separately for each measurement. Those spectral filters were centered at 335 nm, 380 nm, and 445 nm, respectively, which correspond to the nitrogen fluorescent peaks. In order to have a better understanding of the induced air fluorescence by using these spectral filters, a Hamamatsu H7827 PMT was used due to its single-photon sensitivity.

Figure 5-1. The experimental setup used to measure the fluorescent emission induced by high intensity laser [105].
Figure 5-2 shows the fluorescent emission spectrum of laser induced air fluorescence by using an Ocean Optics spectrometer. It could be seen that the peaks of the spectrum indeed included the 380 nm and 445 nm passbands, which was consistent with the previously reported results. However, we could not see the peak around 337 nm; we suspect it was due to the limited sensitivity of the Ocean Optics spectrometer.

![Figure 5-2. Experimentally measured fluorescent emission of laser-induced air plasmas by Ocean Optics spectrometer [105].](image)

In order to confirm whether 337 nm passband had air florescence occurred or not, we used a Hamamatsu photomultiplier tube to replace the Ocean Optics spectrometer to measure the air florescence induced by high intensity laser since the PMT had a higher sensitivity than the spectrometer. Indeed, a response at 337 nm was observed. Table 5-1 summarizes the results of the measurements. It can be seen that the PMT has detected the air fluorescence under all three spectral ranges.
Table 5-1. A summary of the experimental result of high intensity laser-induced fluorescent emission [105].

<table>
<thead>
<tr>
<th>Bandpass filter</th>
<th>No</th>
<th>445/20 nm</th>
<th>380/14 nm</th>
<th>335/7 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>wo/ Air plasma</td>
<td>45 mV</td>
<td>5 mV</td>
<td>5 mV</td>
<td>5 mV</td>
</tr>
<tr>
<td>w/ Air plasma</td>
<td>7.5 V</td>
<td>1.1 V</td>
<td>36 mV</td>
<td>24 mV</td>
</tr>
</tbody>
</table>

After the experiment of high intensity induced air fluorescence, we then moved to the air fluorescence induced by X-ray radiation. Figure 5-3 shows the experimental setup of the measurement of X-ray radiation induced air fluorescence with bandpass filters. Since the X-ray radiation could penetrate air that might interfere with the air fluorescence, the PMT detector was shielded with a lead box and a periscope with two UV enhanced aluminum mirrors inside the periscope. In this way, the fluorescent emission signal could pass through but the X-ray signal was blocked so that the direct influence from the X-ray radiation to the PMT detector can be greatly reduced. As shown in Figure 5-3, the X-rays have been focused in front of the periscope system and the fluorescent light reflected off the mirrors and to the detector. Just like the previous experiment, we also used those three bandpass filters to measure the fluorescent emission.
The results of the experiment of X-ray radiation-induced air fluorescence came out to be what we expected as the air fluorescence emission induced by the X-ray radiation could be measureable by the PMT detector. Figure 5-4 shows the experimentally measured fluorescent signal as a function of X-ray energy with different passbands: 337 nm, 380 nm, and 445 nm. There are three different applied voltages along with two different applied currents. For all of the combinations, the intensity of detected signal increases as the X-ray energy increases. It clearly showed the fluorescent emission occurs and could be detected by the PMT detector at all passbands.
Figure 5-4. The experimentally measured fluorescent signal as a function of X-ray energy at different passbands: 337 nm, 380 nm, and 445 nm [105].

Other than air fluorescence induced by high-intensity laser and X-ray radiation, we also measured the fluorescent emission induced by alpha radiation. Unlike the X-ray radiation, the alpha radiation usually travels less than one inch in air and will be stopped within a very short distance in dense media, releasing energy. Figure 5-5 shows the polonium-210 alpha radiation source used in the experiment. This alpha emitter radiation source has a decay energy of 5.3 MeV and a half-life of 138.4 days. The fluence of this alpha emitter is 500 microCuries.

Figure 5-5. The picture of the alpha source, polonium-210, used to measure the fluorescent emission induced by alpha radiation [105].
Figure 5-6 shows the experiment setup used to measure the fluorescent emission induced by polonium-210 alpha radiation. Like the two previous experiments, the PMT detector and three bandpass filters were used to conduct the experiment. Similar to the X-ray radiation experiment, instead of shooting X-rays into the periscope system, the alpha radiation source was placed in front of the tube.

Since we were concerned that the scattered X-rays may have been producing a detector response in addition to the fluorescent emission, we performed the alpha radiation experiment to prove that the PMT detector was actually seeing the light created via nuclear excitation of the air’s electrons. Table 5-2 summarized the PMT measurement results of fluorescent emission induced by the polonium-210 alpha source with and without the spectral bandpass filters. The corresponding voltage signals with the filters are relatively low compared with the background noise without the alpha radiation
source. However, it shows that there are indeed florescent emissions induced by alpha radiation at these three spectral ranges.

**Table 5-2.** A summary of the experimental result of alpha radiation-induced florescent emission [105].

<table>
<thead>
<tr>
<th>Filters</th>
<th>No</th>
<th>445 nm</th>
<th>380 nm</th>
<th>337 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>wo/α</td>
<td>1.5 mV</td>
<td>1.9 mV</td>
<td>1.8 mV</td>
<td>1.9 mV</td>
</tr>
<tr>
<td>w/α</td>
<td>3.5 mV</td>
<td>2.3 mV</td>
<td>2.1 mV</td>
<td>2.3 mV</td>
</tr>
</tbody>
</table>

After observing the results of different types of radiation-induced air fluorescence, we felt there was a potential application for our radiation detection prototype. The theory behind the excited state absorption of air fluorescence will be addressed in the following section. In addition, the preliminary result of the prototype will lead to the discussion of the feasibility of the standoff radiation detection.

### 5.3 Standoff Alpha Radiation Detection via Excited State Absorption of Air

A standoff alpha radiation detection technique based on the physical mechanism of excited state absorption of air molecules was explored and is presented. Instead of directly detecting the radiation via measuring the intensity of radiation-induced air fluorescence, the radiation is detected via the excited state absorption of alpha radiation excited/ionized air molecules. Both theoretical analyses and experimental verifications were conducted. The experimental results confirmed that the radiation could be detected
via excited state absorption of radiation excited/ionized air molecules at a 10 m standoff distance, which was consistent with the theoretical analyses.

It is well known that radioactive materials can generate nuclear radiation including γ-rays, β-particles, and α-particles. These radiations from radioactive materials can excite and/or ionize the air. Depending on the types and energies of the radiation, it may create excited state air molecules, ionized molecular ions, excited state atoms, and ionized atomic ions. The de-excitation from the higher energy excited/ionized states to lower energy states generates air fluorescence, which may cover a broad spectral range from ultraviolet to infrared [106]. Among these different types of emission spectra, the emissions from excited state nitrogen molecules can be employed to detect radiation. First, the main emission lines of nitrogen molecules are within the UV spectral region, which is useful for minimizing the influence of sun light for daylight detection operation [107], [108]. For instance, one of the emission lines from the $C^3\text{II}$ band to the $B^3\text{II}$ band of nitrogen molecules is at a wavelength of 337 nm. Second, the lifetime of $C^3\text{II}$ band is on the order of nanoseconds, which is three orders of magnitude shorter than that of $B^3\text{II}$ band [109] and thus excited state absorption can be easily achieved. This makes it effective to conduct the experiment of excited state absorption. Third, since 337 nm is also the output wavelength of a nitrogen laser, it can be conveniently employed as the source of a collimated probe beam.

Figure 5-7 illustrates the system configuration of the proposed standoff alpha
radiation detection technique based on the excited state absorption of excited/ionized air [105]. In the operation, a collimated UV probe beam with a wavelength of 337 nm from a nitrogen laser is used to pass through an area affected by the radioactive materials. The radiations from the radioactive materials can first excite and/or ionize the nitrogen molecules in the air and pump them from the ground state to the excited states of the B\(^3\) II band and the C\(^3\) II band to generate air fluorescence. Since the radiation-induced ionization is a continuous process, the population of carriers in the upper and lower excited states should be directly proportional to their respective carrier lifetimes, while the populations related to the thermal energy are negligible because the energy levels of both B\(^3\) II band and C\(^3\) II band are much higher than the thermal energy at room temperature. Because of the big difference in their carrier lifetimes, the carrier population density in the B\(^3\) II band should be much higher than that in the C\(^3\) II band. This implies that the population density in the B\(^3\) II band is an indication of the strength of ionization of nitrogen molecules and proportional to the intensity of radiation. As a result, when the UV probe beam passes through the air fluorescence induced by radiation, excited state absorption occurs as the carriers are excited from the lower excited state level to the upper excited state level. We note that the carriers raised to the upper excited state level also go through spontaneous emission back into the lower excited state level. Since the spontaneously emitted photons are incoherent and radiate to the entire 4\(\pi\) solid angle in free space, the intensity quickly drops to an undetectable low level at long standoff.
distances. This should have a negligible influence on measuring the intensity of excited state absorption since the collimated probe beam does not suffer the inverse-square law of propagation loss and should be able to maintain almost the same intensity over the distance. Thus, the amount of excited state absorption can be used to quantitatively detect the radiation intensity at standoff distance by measuring the drop of the intensity of the collimated probe beam. It is important to point out that this proposed detection technique is suitable to monitor the radiation level at the known location. If the location is unknown, a scanning is required. Or, one can detect the backscattered light. However, it will suffer the $1/r^2$ propagation loss for the backscattered returning signal.

Figure 5-7. A conceptual illustration of standoff detection of radiation via excited state absorption of radiation excited/ionized air [105].

To quantitatively analyze the excited state absorption of radiation induced air fluorescence, the rate equations are employed to describe the population densities of the $B^3\; II$ and $C^3\; II$ bands, as given by
where \( N_C \) and \( N_B \) are the carrier densities on the \( C^3 \) II and \( B^3 \) II bands, respectively, \( \chi_{OC} \) and \( \chi_{OB} \) are the carrier excitation rates from the ground energy level to the \( C^3 \) II and \( B^3 \) II bands, respectively, \( \tau_C \) and \( \tau_B \) are the carrier lifetimes of these two energy bands, and \( P_{em} \) is the photon emission rate caused by radioactive transition from \( C^3 \) II band to \( B^3 \) II band. Under the quasi-steady-state mode, \( N_C \) and \( N_B \) are found by setting 
\[
\frac{dN_C}{dt} = \frac{dN_B}{dt} = 0
\]
in Eq. (5.1). Under this circumstance, one can obtain
\[
N_C = (\chi_{OC} - P_{em})\tau_C \quad \text{and} \quad N_B = (\chi_{OC} + \chi_{OB})\tau_B. \quad \text{(5.2)}
\]
Notice that there is a much higher population density expected in the \( B^3 \) II band than that in the \( C^3 \) II band, \( N_B \gg N_C \), primarily due to the fact that carrier lifetime of the \( B^3 \) II band is much longer than that of \( C^3 \) II band, \( \tau_B \gg \tau_C \).

It is worth noting that according to exponential growth function, the power absorption of a probe beam at the transition wavelength between \( B^3 \) II and \( C^3 \) II bands can be expressed as
\[
\frac{P_{out}}{P_{in}} = e^{[-(\sigma_B - \sigma_C)N_C]L}, \quad \text{(5.3)}
\]
where \( \sigma_a \) and \( \sigma_e \) are the absorption cross section of the molecules on the \( B^3 \) II band and the emission cross section of the molecules on the \( C^3 \) II band, respectively. \( N_B \) and \( N_C \) are the population densities of \( B^3 \) II and \( C^3 \) II bands, respectively, and \( L \) is the optical length.
interaction length. Since a weak excitation of the probe beam does not drastically change the population densities, the values of $N_B$ and $N_C$ are mainly determined by the ionization rate and the carrier lifetimes of the energy bands. Also, as mentioned earlier, the lifetime of the $B^3 \text{II}$ band is much longer than the $C^3 \text{II}$ band, $\tau_B \gg \tau_C$, hence, the Eq. (5.3) can be simplified as

$$\frac{P_{\text{out}}}{P_{\text{in}}} = e^{[-N_0 \sigma N L]}.$$  \hspace{1cm} (5.4)

Further solving the Eq. (5.4), one can obtain the following power absorption approximation:

$$\frac{P_{\text{out}}}{P_{\text{in}}} = \left(1 - \eta N_0 \frac{e^2 \lambda^2 f_{ik} L}{4 \varepsilon_0 m_e c^2 \Delta \lambda}\right),$$  \hspace{1cm} (5.5)

where $\eta = \frac{N_B}{N_0}$ represents the ionization ratio at the $B^3 \text{II}$ band that is directly proportional to the intensity of radiation, $e$ is the electron charge, $\lambda$ is the optical wavelength, $f_{ik}$ is the line oscillation strength, $\varepsilon_0$ is the dielectric constant, $m_e$ is the electron mass, $c$ is the speed of light, and $\Delta \lambda$ is the signal spectral linewidth.

Based on Eq. (5.5), we calculated the relationship between the power absorption and ionization ratio. Figure 5-8 shows the normalized power absorption calculated as a function of ionization ratio, $\eta$, with different optical signal spectral linewidths. The calculation was based on a 337 nm wavelength probe beam over a 10 m optical path length with the assumption of the initial total density of nitrogen molecules, $N_0$ of $10^{19}/\text{cm}^3$. One can see that the normalized power ratio increases when the ionization ratio
increases. Thus, from the quantitative relationship between normalized power absorption and ionization ratio, one can quantitatively measure the intensity of radiation by measuring the power absorption. The theoretical detection limit of the presented technology depends on the sensitivity and the signal to noise ratio of the detector as well as detection method. Since a $-60$ dB detection can be achieved by using a lock-in amplifier, one can detect an ionization ratio $10^{-13}$ with a spectral linewidth of 0.2 nm, as illustrated in Figure 5-8. Furthermore, since similar ionization ratios can be achieved by using an alpha source, the effort of this experiment is focused on the alpha radiation detection.

Figure 5-8. The simulation results of optical power transmission ratio for a UV laser at wavelength of 337 nm as a function of ionization ratio with different optical signal spectral linewidths; blue dashed line: $\Delta \lambda = 0.2$ nm, black solid line: $\Delta \lambda = 1$ nm, and red dotted line: $\Delta \lambda = 5$ nm [110].
In the experiment, two tube-shaped polonium-210 alpha sources (Model P-2035, NRD LLC) were used as the radiation sources. Each source had a maximum activity of 40 milliCuries (mCi), a decay energy of 5.3 MeV, and a half-life of 138.4 days. The reasons we chose the alpha source were due to its high ionization ratio, low penetration, and very short stopping distance in dense media. The alpha radiation usually travels about 3.8 cm in air which minimized its influence on the photomultiplier tube (PMT) photodetector. To determine the excited state absorption of air, a UV nitrogen laser manufactured by Spectra-Physics with an emission wavelength at 337 nm, a spectral bandwidth of 0.1 nm, and a pulse width of 4 ns for full width at half maximum (FWHM) was used as the probe beam light source. In order to measure the excited state absorption, a Hamamatsu H7827 PMT was used as a photodetector due to its single photon sensitivity.

Figure 5-9 illustrates the experimental setup used to conduct the excited state absorption of alpha radiation induced air fluorescence. The 337 nm UV nitrogen laser probe beam passes through the air fluorescence region induced by the alpha sources. Due to the meshing nature of the stainless steel protection screen of the alpha source, the UV probe beam was first passed through a circular aperture of 250 μm in diameter so that it passed through the empty central region of the tube-shaped alpha source without being blocked by the protection mesh screen. Inside this region, the air was excited and ionized by the radiation of the alpha source. After that, the UV probe beam passed through a
spectral filter with a central wavelength around 337 nm with a 7 nm pass bandwidth and a transmittance of about $10^{-5}$ in the visible region to block the background visible light, and then detected by the PMT photodetector. To achieve precise monitoring, the PMT photodetector needs to be well aligned with the laser probe beam.

Figure 5-9. A schematic illustration of the experimental setup used to conduct the excited state absorption of alpha radiation induced air fluorescence, including a 337 nm UV laser, two mirrors (M1 and M2), a pinhole (PH), a spectral filter centered at 337 nm, and a photodetector (PMT) [110].

To prove the concept of using excited state absorption of air for the alpha radiation detection, the intensity of the probe beam was measured under different levels of alpha radiation: (1) 0 mCi, (2) 40 mCi (with one alpha source), and (3) 80 mCi (by cascading two alpha sources together). Figure 5-10 depicts the measured light intensity as a function of time under different levels of alpha radiation. The black solid line of Figure 5-10 indicates the measured light intensity without any alpha source. On the same figure, the red dotted line indicates the measured light intensity with one Po-210 alpha source.
(40 mCi) and the blue dashed line indicates the measured light intensity with two cascaded Po-210 alpha sources (80 mCi). One can clearly see that the normalized value of the red dotted line is lower than that of black solid line because of the alpha radiation-induced excited state absorption. In addition, the normalized value of the blue dashed line is even lower than that of the red dotted line due to the increased excited state absorption of air by two cascaded alpha sources. This experimental result confirmed that alpha radiation detection could be achieved through excited state absorption of radiation excited/ionized air. The proposed technique is suitable for measuring the relative intensity of radiation.

Figure 5-10. The experimentally measured excited state absorption of alpha radiation excited air fluorescence as a function of time with different source fluences. Black solid line: without air fluorescence and red dotted and blue dashed lines: with air fluorescence under the alpha source fluence of 40 mCi and 80 mCi, respectively [110].
It should be noted that the magnitude of the response, as shown in Figure 5-10, is not linear because of the following two reasons: first, the two alpha sources used in our experiment were not identical. The radiation level of one alpha source was slightly stronger than the other one. Second, the radiation follows Beer's law. Therefore, even when the two alpha sources are identical, the response is not linear.

To further illustrate the standoff detection capability, the experimental setup, as illustrated in Figure 5-9, was modified to a maximum 10 m distance between the probe beam UV source and alpha radiation source by reflecting the probe beam multiple times via mirrors, as shown in Figure 5-11.

![Figure 5-11. A schematic illustration of the experimental setup used to conduct the standoff detection of alpha radiation via excited state absorption of air, including a 337 nm UV laser, three mirrors (M1, M2, and M3), a pinhole (PH), a spectral filter centered at 337 nm, and a photodetector (PMT).](image)

Figure 5-12 depicts the measured light intensity as a function of time with only one alpha source (40 mCi) for different standoff distances. The black solid line of Figure 5-12 indicates the measured light intensity without any alpha source. Additionally, the red
dotted, blue dashed, and green dash-dot lines indicate the measured light intensities under 40 mCi alpha radiations for 0 m, 5 m, and 10 m standoff distances, respectively. One can clearly see that the detected signal as a function of time is not sensitive to the separation distance between the light source and alpha radiation source. These experimental results confirmed that the detected signal was not influenced by the separation distance between the probe beam light source and alpha radiation because the collimated probe beam did not suffer $1/r^2$ propagation loss where $r$ is the standoff distance. Similarly, it is also true that the detected signal was not influenced by the separation distance between the alpha source and the photodetector. Future development efforts will focus on the evaluation of the sensitivity of the proposed detection technique and increase it by employing an advanced phase-locking system and multiple-path absorptions with a gated PMT photodetector.
Figure 5-12. The experimentally measured alpha radiation as a function of time with one alpha source for different standoff distances. Black solid line: without air fluorescence and red dotted, blue dashed, and green dash-dot lines: with air fluorescence under 40 mCi alpha radiations for 0 m, 5 m, and 10 m standoff distances, respectively [110].

5.4 Summary

In summary, a physical mechanism of alpha radiation detection based on excited state absorption of radiation excited/ionized air was investigated. The detailed description of the technical approach and theoretical modeling were provided. The proposed radiation detection physical mechanism was also confirmed by the experiment. In the experiment, polonium-210 alpha sources were used as the radiation source, a nitrogen laser with an output wavelength of 337 nm was used as the collimated probe beam source, and a PMT photodetector was used to measure the excited state absorption of the probe. Indeed, the experimental results validated that the excited state absorption increased as the fluence of alpha radiation increased. The major advantage of the proposed detection mechanism is the capability of long range standoff detection because the collimated probe beam does not suffer the $1/r^2$ propagation loss. Thus, this proposed detection technique not only advanced the technique of radioactive material detection, but also provided an effective tool to safely and remotely monitor nuclear facilities such as nuclear power plants.
Chapter 6

Conclusion and Future Work

6.1 Conclusion

In this dissertation, ZnO-based photonic nanostructures were fabricated and applied as photoelectrodes for dye-sensitized solar cells (DSSC). In order to achieve a high solar conversion efficiency of DSSC, there are two main challenges: (1) improvement of surface areas for photodye attachment and (2) improvement of the charge transport path for photogenerated carriers.

First, the three-dimensional ZnO nanoforest have been successfully synthesized by a two-step hydrothermal process which can provide large surface areas from the branched ZnO nanowires and an excellent charge transport path from the trunked ZnO nanorods. The experimental results confirmed that the solar conversion efficiency of the 3-D ZnO nanofrest photoelectrode is much higher than the 1-D ZnO nanorod arrays photoelectrode. In addition, our results shows that densely packed, branched ZnO nanowires have been synthesized via a modified sol-gel process.

Secondly, density-controlled ZnO–TiO$_2$ core–shell nanorod arrays were invented and proposed to conventional TiO$_2$ nanoparticles photoelectrode DSSC, which has the feasibility to improve the charge transport path. The ZnO/TiO$_2$ nanocomposite
photoelectrode DSSC obtained a high open-circuit voltage of up to 0.93 V, which is the highest value ever reported. The physical mechanism of high open-circuit voltage was delivered and confirmed with electrochemical impedance spectroscopy. In addition, ZnO/TiO₂ nanocomposite photoelectrodes have indeed further improved the solar conversion efficiency when compared to conventional TiO₂ nanoparticles photoelectrodes because of the fact that recombination loss is greatly reduced from the direct charge diffusion path of the direct grown ZnO nanorod arrays. This dissertation has showed the possibility for further enhancement of the solar conversion efficiency of DSSC which have a feasible application in the renewable energy field.

Last but not least, a radiation detection was investigated. Different types of radiation-induced air fluorescence were first conducted. A physical mechanism of alpha radiation detection based on excited state absorption of radiation excited/ionized air was carried out followed by the experiment. Polonium-210 alpha sources were used as the radiation source and have been detected in a 10 m standoff distance. This detection technique could potentially provided an effective tool to safely and remotely monitor nuclear facilities.

Significant contributions:

- Synthesized high-density, branched ZnO nanowires for the 3-D ZnO nanoforest.
- Synthesized density-controlled ZnO nanorod arrays on the TiO₂ nanocrystal template.
Direct grown ZnO/TiO2 nanocomposite photoelectrodes offer both a high surface area and a direct charge diffusion path to obtain efficient electron transport as a result of the reduced recombination loss.

Achieve a high open-circuit voltage up to 0.93 V (the largest yet reported) for a high-efficiency DSSC from the ZnO/TiO2 nanocomposite photoelectrode.

Improve the solar conversion efficiency (relative 20%) with nanocomposite photoelectrodes.

Successfully realized standoff alpha radiation detection via excited state absorption of air.

6.2 Future Work

The potential of the high-density, branched ZnO nanowires of synthesized ZnO nanoforest has not yet been fully explored. It is believed that optimizing the process parameters will further increase surface areas, resulting in better performance. Also, optimal dye-sensitization condition are required for the ZnO-based DSSC [7], [111].

To date, the highest solar conversion efficiency of ZnO-based DSSC is 7%; this is achieved using multilayer assemblies of high surface area nanowire arrays with a total thickness of 40 μm [112]. One of the key elements of this high efficiency ZnO-based DSSC is the TiO2 coating on the surface of ZnO nanowire arrays, which aids in avoiding ZnO/dye aggregation. As such, we believe that by applying the conformal core–shell
coating of TiO\textsubscript{2} to our 3-D ZnO nanoforest photoelectrodes, conversion efficiency can be improved significantly. This, in turn, would lead to a significant reduction in the thickness of the film.

In addition to the ZnO/TiO\textsubscript{2} nanocomposite photoelectrode, it is worth noting that with the TiCl\textsubscript{4} post-treatment, there still seem to be some spots on the ZnO–TiO\textsubscript{2} core–shell nanorods that are being etched off; this is even though there is a TiO\textsubscript{2} shell covering ZnO nanorod arrays from the core–shell nanostructures. Figure 6-1 presents the FESEM image of the spot being etched off. Although the nanocomposite photoelectrodes had been proven to be able to achieve high open-circuit voltages, we believe that if we can solve the dissolution of ZnO by investigating the proper environment of the TiCl\textsubscript{4} surface treatment, conversion efficiency can be enhanced.

![Figure 6-1. FESEM image of the spot on the ZnO–TiO\textsubscript{2} core–shell nanorod being etched off. Scale bar, 1 \(\mu\text{m}\).](image)
In order to further enhance the performance of DSSCs, we felt that there is a need to investigate the 3-D transparent conductive oxide (TCO) and its application to ZnO nanoforest and ZnO/TiO$_2$ nanocomposite photoelectrodes [113], [114]. In particular, we are interested in the aluminum-doped ZnO (AZO) nanorods as backbones for the two architectures. Since AZO has shown better carrier transport properties, better DSSC performance is expected [115]. So far in preliminary results, AZO nanorods have been synthesized successfully and characterized with the EDS spectrum, as shown in Figure 6-2.

![Figure 6-2. EDS spectrum of the synthesized aluminum-doped ZnO nanorods.](image)

Last, it would be interesting to adapt the ZnO/TiO$_2$ nanocomposite photoelectrode to the perovskite sensitized solar cell, even though it already contains a relatively high open-circuit voltage [116], [117]. This nanocomposite structure could potentially maximize the $V_{OC}$ value by further retarding electron recombination and facilitating efficient electron transport.
Reference


[80] M. K. Nazeeruddin, a Kay, E. Miiller, P. Liska, N. Vlachopoulos, M. Gratzel, C.-Lausanne, and R. April, “Conversion of light to electricity by cis-X2bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium (II) charge-transfer


Appendix

Publications

Journal Papers


Conference Proceedings


VITA

Jimmy Yao

Jimmy Yao received both B.S. and M.S. degrees in the department of electrical engineering from The Pennsylvania State University, University Park, Pennsylvania. In his M.S. thesis work, he focused on the theoretical analysis and simulation of a nonlinear Bragg reflector via coupled wave theory. He enrolled in the Ph.D. program of electrical engineering at The Pennsylvania State University in 2009 while joining Dr. Shizhuo Yin's research lab and worked as a research assistant. During his Ph.D. studies, he is involved in multiple projects, including nanophotonic devices, ultra-fast free-space optical switches, fiber optic beam steering and environmental monitoring. His main research is focused on the development of advanced photonic nanostructures. Moreover, he worked on micro/nanofabrication for material processing and characterization. Furthermore, he has experiences in optoelectronic devices, including designing, fabrication, and characterization. In addition, he has authored and co-authored a number of journal papers and conference proceedings, and is a member of The International Society of Optical Engineering (SPIE), The Optical Society (OSA), and Institute of Electrical and Electronics Engineerings (IEEE).