# An Overview of Nanoscale Techniques for Photovoltaics and Solar Cell Fabrication

# Ramzy R. Obaid

Electrical and Computer Engineering Department, King Abdulaziz University, Jeddah, Saudi Arabia

### rrobaid@kau.edu.sa

Abstract. Over the past decade, research in photovoltaics and solar cell fabrication has boomed worldwide and has been receiving a great attention from researchers in the industry and the academia alike. The trend has recently been towards applying innovative and advanced techniques in fabricating solar cells and also discovering new means of converting the solar energy into electrical energy with improved characteristics compared to conventional silicon-based wafers. This paper describes some of the various new applications of nanotechnology in photovoltaics and the implementation of nanoscale techniques in solar cell fabrication. It describes dye-sensitised solar cells using nanocrystalline Titanium dioxide, TiO<sub>2</sub> DSSC; and illustrates the benefits of using nanoscale materials, such as Silicon nanowires, different types of polymers and organic materials, and quantum dots as means of absorbing the photons and converting them to electrons. In addition to presenting the advantages of incorporating nanoscale techniques in making solar cells, the paper shows how different and scattered the presented methods are. It discusses the essential need to classify these new solar cell fabrication methods and do unbiased comparisons between them in order to determine the best paths for growth in this field.

*Keywords*: Solar Cells, Photovoltaics, Silicon Nanowires, Organic PV, Nanotechnology, Nanocrystalline TiO<sub>2</sub>, DSSC, Organic Photovoltaic cells.

#### 1. Introduction

Since the early 1990's there has been an increased interest among researchers in the field of renewable energy to replace the fossil fuels used to generate electricity <sup>[1]</sup>. In the past ten years, governments, industries, and academic institutions have all been giving a great attention to research in solar energy as one of the main forms of "clean energy". However, over the last five years alone, there has been a huge spike worldwide in research work in the area of photovoltaics and solar cells, especially in the applications, which implement nanoscale techniques. Recent advances in solar cells have shown improved performance and increasing efficiencies, making the research in this area more attractive and promising <sup>[2-4]</sup>. With the drastic increase in Oil prices in the past year, more and more focus will be going towards alternative fuels, and specifically, towards advancing photovoltaics and solar cells.

In spite of the surge mentioned above in original inventions and new advanced techniques to capture the solar energy and convert it to electricity, Silicon remains by far the most used element to manufacture solar cells and produce them commercially. Silicon based wafers still acquire most of the solar cell market worldwide <sup>[1, 3]</sup>.

This paper provides a brief overview of some of the recent and upto-date nanotechnology techniques and methods that are being widely implemented in photovoltaics and solar cell fabrication by researchers around the world. The aim of this paper is to give a general idea of the research work being conducted in some of the laboratories located in different universities and other research facilities sponsored by governments and industries. The paper may provide a general guideline for other researchers interested in tackling the hot field of nanotechnology and its applications in photovoltaics and solar cell fabrication. It illustrates to new researchers where the scope is in this area, thus they would choose the most suitable direction for them in their prospective research in nanotechnology and photovoltaics.

#### 2. Silicon Solar Cells

A Typical solar cell is based on the PV effect, in which light falling on a two-layer semiconductor device produces potential difference between the layers capable of driving a current through an external circuit <sup>[2, 4, 5]</sup>. Original solar cells were generally made of silicon, and consisted of a large-area, single layer p-n junction diode. These cells generate electricity from light sources with the wavelengths of solar light. After that, solar cells based on multiple layers of p-n junction diodes were introduced. Each layer designed to absorb a successively longer wavelength of light, thus increasing the produced electricity <sup>[6]</sup>. Another p-n junction based type is the metal–semiconductor or Schottky junction photovoltaic cell <sup>[7, 8]</sup>. A Schottky junction has rectifying characteristics, which makes it supersede a typical p-n junction with its lower junction voltage and almost nonexistent depletion width in the metal <sup>[9]</sup>. Figure 1 depicts a schematic of a typical physical structure of a Silicon Schottky junction solar cell <sup>[9, 10]</sup>.



Fig. 1. Schematic physical structure of a typical Silicon Schottky junction solar cell. (Sketch adapted from <sup>[9, 10]</sup>).

Newer generations of photovoltaic cells do not rely on the traditional p-n junction to separate photo-generated charge carriers, and are broadly defined as semiconductor devices. Some of these devices, such as silicon nanowires, consist of three layers of silicon forming a p-i-n structure <sup>[11]</sup>.

The performance of a PV cell is gauged by its efficiency. Theoretically, the maximum possible efficiency of silicon solar cells is 25% in non-concentrated sunlight. Traditional wafer silicon solar cells, also called bulk or crystalline silicon, include Monocrystalline and Polycrystalline cells <sup>[12]</sup>. Monocrystalline solar cells are made of thin wafers sliced from meter-long single crystal silicon. They are the most efficient PVs that are commercially available, achieving system efficiencies of 12%. However, they are also relatively expensive and difficult to make. Polycrystalline cells consist of multiple small silicon

crystals. They are less efficient (with typical efficiencies approaching 10%), but are also less expensive to produce than monocrystalline silicon solar cells. A typical silicon solar cell has an area of about  $100 \text{cm}^2$  and produces about 3A at 0.5V <sup>[6, 12]</sup>.

Thin-film PV cells rely on a technology that is different from bulk silicon<sup>[13, 14]</sup>. They are made by depositing one or more thin film coating of photovoltaic material on an underlying substrate, like plastic, metal, or glass <sup>[15]</sup>. Typical thin-film PV cells have only achieved efficiencies of about 5%. Thin-film solar cells offer enormous potential advantages over conventional wafer cells. They can be mass-manufactured economically using an automated assembly line. In addition, because they are light and flexible, they can be easily incorporated into a wide range of surfaces, such as roof tiles, exterior wall panels, and window glass <sup>[15, 16]</sup>. Examples of thin-film PV cells include amorphous silicon and nanocrystalline silicon. Amorphous silicon thin-film cells are based on pi-n structure, and use a very small percentage of the silicon needed for typical crystalline silicon cells <sup>[16]</sup>. Amorphous silicon is non-crystalline allotropic that can be deposited by plasma-enhanced chemical vapor deposition (PECVD), at low temperatures, on different substrates, such as glass and plastic <sup>[10, 17]</sup>. Thus, amorphous silicon thin-film cells can be produced using a roll-to-roll processing technique. Nanocrystalline silicon thin-film PV cells are similar to amorphous silicon cells, except that they have small grains of crystalline silicon within the amorphous phase <sup>[18]</sup>. Because of this, they have higher electron mobility, and increased absorption in the red and infrared wavelengths. Compared to polycrystalline silicon cells, nanocrystalline silicon cells have less electron mobility; however, they have the advantage of being easier to fabricate using PECVD at low temperatures <sup>[19]</sup>.

Other examples of thin-film PV cells include cadmium telluride (CdTe) <sup>[20]</sup>, dye-sensitized solar cells (DSSC), organic polymer cells (OPV), and copper indium gallium selenide (CIGS) <sup>[21]</sup>.

# 3. Titanium Dioxide (TiO<sub>2</sub>) and Dye-Sensitized Solar Cells (DSSC)

Titanium dioxide is a well-known, wide gap semiconductor, which has high light conversion efficiency. It is favored over other semiconductor oxides because it is inexpensive, abundant, and non-toxic <sup>[22, 23]</sup>. A typical dye-sensitized solar cell (DSSC) is composed of an

electrode, dye sensitizers, electrolytes, counter electrode, and transparent conducting substrate <sup>[24, 25]</sup>. The electrode consists of nanocrystalline semiconductor oxide film, such as nc-TiO<sub>2</sub>. The dye absorbs light and transfers excited electrons to the TiO<sub>2</sub>, which acts as an electron acceptor. The electron is then quickly replaced by the electrolyte, which obtains the replacement electron from the catalyst coated counter. The main difference between this type of solar cell and conventional cells is that the dye, which is responsible for light absorption, is separated from the charge carrier transport. In addition, nc-TiO<sub>2</sub> DSSCs are inexpensive, and survive harsh environmental conditions <sup>[23, 24]</sup>.

Another way to construct nc-TiO<sub>2</sub> DSSCs is by replacing the liquid electrolyte with a solid-state analogy, such as polymer electrolyte or a hole conducting material <sup>[26]</sup>. The benefit is that this procedure eliminates practical problems with sealing and degradation. Nc-TiO<sub>2</sub> DSSCs can also be constructed using polymer foil substrate instead of glass <sup>[27]</sup>. This adds more flexibility to the cell, and allows for a continuous roll-to-roll processing. The last two types of cells fall under hybrid organic/inorganic DSSC.

Over the last two decades, there has been an extensive research work on different applications of nanocrystalline  $TiO_2$  in photovoltaics <sup>[28, 29]</sup>. Some work has studied single wall carbon nanotube (SWCNT) architecture, employed as conducting scaffolds in a  $TiO_2$  semiconductor based photoelectrochemical cell <sup>[22, 30]</sup>. It was found that dispersing  $TiO_2$  nanoparticles on SWCNT films improves the photoinduced charge separation and transport of carriers to the collecting electrode surface, and hence, boosts the photoconversion efficiency. Scheme 1 depicts the enhancement of electron transport across nanostructured semiconductor films by nanotube support architectures <sup>[22]</sup>; and Fig. 2 shows SEM of the carbon fiber electrode (CFE) at different stages of modification <sup>[22]</sup>.



Scheme 1. Electron transport across nanostructured semiconductor films: (A) in the absence, and (B) in the presence of nanotube support architecture <sup>[22]</sup>.

Other research work in this area combines CdSe quantum dots with  $TiO_2$  nanoparticles to form a CdSe -  $TiO_2$  composite based PV cell <sup>[31, 32]</sup>. Assembling the CdSe quantum dots onto mesoscopic  $TiO_2$  nanoparticle films offers new opportunities for harvesting light, improving photon-to-charge carrier generation efficiency, and the overall system efficiency <sup>[31]</sup>. Figure 3 shows the structure of a CdSe -  $TiO_2$  composite based PV cell.

#### 4. Organic Photovoltaics OPV

One of the flourishing technologies in fabricating solar cells utilizes organic solid state approaches in making what is known as Organic Photovoltaics (OPV)<sup>[33-35]</sup>. Organic solar cell research has begun more than 30 years ago<sup>[36, 37]</sup>; however, especially in the last decade, the rapid increase in power conversion efficiencies has attracted researchers to focus more on organic materials for photovoltaic applications.



- Fig. 2. SEM of a carbon fiber electrode (CFE) at different stages of modification <sup>[22]</sup>:
  - (A) before surface modification;
  - (B) after modification with TiO2 particles;
  - (C) after electrophoretic deposition of SWCNT;
  - (D) after deposition of TiO2 particles onto SWCNT film.



Fig. 3: (a) Linking CdSe Quantum Dots to TiO<sub>2</sub> Particle with Bi-functional Surface Modifier; (b) Light Harvesting Assembly Composed of TiO<sub>2</sub> Film Functionalized with CdSe QDs on Optically Transparent Electrode (Not to Scale)<sup>[31]</sup>.

OPVs currently have power conversion efficiencies of 3-5% <sup>[38, 39]</sup>. They include small molecule multilayer devices; polymeric mixtures; and hybrid organic/inorganic semiconductor nanostructure mixtures. In all of these types, the efficiency is limited by several factors <sup>[38]</sup>: the absorption coefficient as a function of wavelength, and the transport and collection of the charges by the anode/cathode and the electrode/organic interfaces. The range of the open-circuit voltage and the fill factor of the electrical characteristic also affect the efficiency. In contrast to other types of solar cells, OPVs have numerous attractive features <sup>[40, 41]</sup>. Organic materials can be processed from the vapour phase or from solution at low temperatures. The materials can be processed into large-area devices at low cost. OPV cells are intrinsically light weight and shatterproof. Moreover, organic materials have high absorption coefficient. This requires reduced thickness to absorb light efficiently, which reduces the amount of material needed. These features have paved the way towards low-cost, light-weight, large-area, flexible and conformable solar panels. Another important feature of these materials is that they can be processed into cells by a roll-to-roll process or by using ink-jet printing or screenprinting <sup>[40]</sup>. Organic solar cells are suitable for on grid power generation as well as numerous off-grid applications, such as powering portable electronic devices and sensors. Unlike conventional solar technologies, under low light conditions, like those in offices, homes or conference room settings, OPV could continuously charge a cell phone <sup>[42, 43]</sup>. With paper-thin size, these solar cells are useful for a wide range of new devices and circuits, including radio-frequency identification tags (RFID), and smart monitoring sensors.

The physics of OPV devices is different from that of inorganic solar cells, which are based on p-n junctions. Figure 4 shows a schematic diagram of the typical device structure of a polymer/fullerene bulk heterojunction solar cell <sup>[44]</sup>. OPV cells usually have multilayer or bulk heterojunction structures. In multilayer organic solar cells, p-type and ntype semiconductors are sequentially stacked on top of each other. Figure 5(A) shows a schematic diagram of the typical device structure of a bilayer OPV cell <sup>[44]</sup>. In such structure, exciton diffusion lengths are generally short and smaller than the optical penetration depth needed to absorb all incident radiation. Therefore, the photovoltaic conversion efficiency of multilayer organic solar cells has been limited by this strong exciton binding energy in organics <sup>[38, 42]</sup>. Bulk heterojunction organic devices are based on mixtures or blends of donor- and acceptor-like molecules as depicted in Fig. 5(B). In such junction, the donor-acceptor phase separation is in a 10-20nm length scale, which is within a distance less than the exciton diffusion length from the absorbing site <sup>[44]</sup>. The structure of the organic photovoltaic cell is thin, flexible, and different from the conventional silicon cell; and OPVs, in general, are also referred to as plastic solar cells <sup>[45]</sup>. Figure 6 shows a flexible organic photovoltaic cell <sup>[46]</sup>.



Fig. 4. Schematic device structure for polymer/fullerene bulk heterojunction solar cells. The active layer is sandwiched between two contacts: an indium-tin-oxide electrode coated with a hole transport layer PEDOT:PSS and an aluminum top electrode <sup>[44]</sup>.



Fig. 5: (A) Bilayer configuration in organic solar cells <sup>[44]</sup> .(B) Bulk heterojunction configuration in organic solar cells<sup>[44]</sup>.



Fig. 6. Polymer-Fullerene Bulk Heterojunction Photovoltaic cell [46].

OPVs offer the promise of significant disruption in pricing and aesthetics, as well as impressive efficiencies in low light conditions. OPV materials are also flexible and form-fitting <sup>[36]</sup>. They can potentially be wrapped around or even painted onto various materials, and produced inexpensively by employing roll-to-roll processes <sup>[36, 47]</sup>.

#### 4.1 OPV in the Kingdom of Saudi Arabia

Compared to other nanotechnology techniques for fabricating solar cells, OPVs are the most promising and most appropriate to be conducted and funded in the Kingdom of Saudi Arabia. Organic materials, such as plastics and polymers are common products of Oil, and numerous petrochemical companies produce them in huge amounts in the kingdom. The advancement in such solar cell manufacturing technologies would eventually improve the efficiencies of the cells, the quality of their manufacturing, and reduce their cost of making. The significant reduction in the cost of manufacturing quality solar cells would make the cost of generating electricity from solar power comparable to, if not lower than the cost of conventional thermal generation of electricity through the burning of fossil fuels.

This in turn would lead to the ultimate goal sought by energy scientists worldwide, which is using the solar power as a competitive alternative to fossil fuels, and reserve these fuels for all their other beneficial products besides power generation.

# 5. Silicon Nanowires

Silicon Nanowire has been recently introduced as a new type of solar cell <sup>[48-51]</sup>, aimed to provide an on-chip power for nanoelectronic devices or run microscopic robots. Researchers have produced 200 picowatts of electricity, in lab experiments <sup>[11]</sup>, from a coaxial silicon nanowire solar cell having thickness of about 300 nanometers.

The nanowire consists of three layers of silicon: a positively charged core; a thin intrinsic (neutrally charged) inner shell, and a negatively charged outer shell <sup>[52, 53]</sup>. This p-i-n structure is common in flat photovoltaic devices, now being applied to a coaxial wire. When a photon hits the nanowire, it generates a pair of charges: an electron and a hole. The charges then move radially. Electrons move outward from the center to a contact in the shell and holes move inward to a contact in the core. These contacts send electricity flowing out of the device. The advantage of the circular cross section is that the opposite charges would move across a very short distance (100 nm or less) to reach the contacts, making them less likely to recombine before they are collected <sup>[54]</sup>.

Recombination is when an electron and a hole rejoin instead of exiting the device and produces heat rather than electricity, and is significant in silicon-based solar cells. To decrease the recombination rate, silicon wafers are made relatively thick, which means the carriers have to travel farther <sup>[11, 55]</sup>. And high-quality silicon with few crystal defects is commonly used, which is expensive. However, the coaxial nanowire solar cell is made significantly thin, and uses less pure, and therefore less costly, silicon. Figure 7 shows Schematics and SEM images of the coaxial silicon nanowire solar cell.



Fig. 7. Coaxial silicon nanowire photovoltaic cell <sup>[11]</sup>:
(a) Schematics of device fabrication. Left: pink, yellow, cyan and green layers correspond to the p-core, i-shell, n-shell and PECVD-coated SiO<sub>2</sub>, respectively. Middle: selective etching to expose the p-core. Right: metal contacts deposited on the p-core and n-shell. (b) SEM images corresponding to schematics in a. Scale bars are 100nm (left), 200nm (middle), and 1.5 mm (right).

The efficiency of the coaxial silicon nanowire solar cell is only about 3.4%, which is significantly low compared to commercial solar cells <sup>[52, 54]</sup>. However, such device has numerous advantages in addition to the reduced recombination effect. It does not decrease in function and lasts longer than other nano-scale solar cells. Moreover, additional power could be generated out of a nanowire solar cell by using a lens to concentrate more light onto it; the same approach would quickly destroy an organic solar cell.

Other research work focuses on studying the growth mechanism of cluster formation and vapor-liquid-solid (VLS) for the synthesis of semiconductor nanowires <sup>[56]</sup>. In some processes, laser ablation is used to prepare nanometer-diameter catalyst clusters that define the size of wires produced by VLS growth. Studies suggest that well-established phase diagrams can be used to predict rationally catalyst materials and growth conditions for the preparation of nanowires <sup>[56]</sup>.

### 6. Other Nanoscale Techniques for Photovoltaics

In addition to the techniques presented above, there are numerous other nanoscale techniques and materials, of which researchers around the world have been tackling. Semiconductor nanocrystals are part of the building blocks of nanotechnology that have opened up new ways to make next generation solar cells <sup>[57]</sup>. Recent developments in the utilization of semiconductor quantum dots for light energy conversion include the following three major ways <sup>[58]</sup>: (i) Quantum dot sensitized solar cell, which has been discussed earlier under the TiO<sub>2</sub> section <sup>[59, 60]</sup>. (ii) Nanoscale Metal–semiconductor or Schottky junction photovoltaic cell <sup>[61-64]</sup> having low junction voltage, and almost nonexistent depletion width in the metal. Researchers have observed enhanced photocurrent in cells having depletion layer with a typical thickness of approximately 60nm of the Schottky junction <sup>[61]</sup>. (iii) Polymer – semiconductor hybrid solar cell <sup>[65-71]</sup>, where semiconductor nanorods are used to fabricate readily processed and efficient hybrid solar cells together with polymers <sup>[72]</sup>. The distance on which electrons are transported directly through the thin film device can be controlled by changing the nanorod length <sup>[65]</sup>.

It is evident throughout this overview that many of the discussed techniques are correlated and several methods are nothing but combinations of different nanoscale techniques. Therefore, these techniques are difficult to be classified into certain categories.

# 7. Conclusions

This paper has provided a brief overview of some of the recent and up-to-date applications of nanotechnology in photovoltaics and solar cell fabrication. It has shown how different and scattered the presented methods are. The trend of conducting each presented method follows practices according to schools, companies, or research centers, and each is claiming to present a better technique. The paper has shown how strong the race and competition are between researchers all around the world to advance and found a well-established research program and build a solid name in this new and vastly growing field. The breadth of the presented methods of nanotechnology applications in photovoltaics provides a rich field for other researchers to conduct detailed comparison studies and reviews of these methods. The need is essential to do unbiased comparisons between the new solar cell fabrication methods for efficiency, cost-effectiveness, and practicality in order to determine the best paths for growth in this field.

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#### Ramzy R. Obaid

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عرض لتطبيقات التقنيات النانوية في العلوم الفولت ضوئية وتصنيع الخلايا الشمسية

رمزي رضا عبيد

قسم الهندسة الكهريائية وهندسة الحاسبات، كلية الهندسة، جامعة الملك عبدالعزيز، جدة، المملكة العربية السعودية rrobaid@kau.edu.sa

> المستخلص. إزداد التركبز على أبحاث العلوم الفولت ضوئية وتصنيع الخلايا الشمسية في العقد الماضي، وأصبحت تحظ، باهتمام الباحثين حول العالم في المراكز التعليمية والصناعية على حد سواء. وفي السنوات الأخيرة، أصبح التوجه مكثفا نحو استخدام طرق حديثة، وتقنيات متقدمة، لتصنيع خلايا شمسية ذات كفاءة عالية، وكذلك نحو اكتشاف طرق ووسائط جديدة ومبتكرة لتحويل الطاقة الشمسية إلى طاقة كهربائية بمميزات تفوق خلايا السبليكون الشمسية التقليدية. تعرض هذه الورقة بعضا من التطبيقات المتعددة للتقنيات النانوية في العلوم الفولت ضوئية، واستخدام هذه التقنيات في تحسين أداء الخلايا الشمسية، مثل صبغ وتغطية الخلايا ببلورات نانوية من ثاني أكسيد التايتينيوم. وتعرض الورقة فوائد استخدام مواد بقياس النانومتر كوسائط مبتكرة لامتصاص الأشعة الضوئية وتحويلها إلى إلكترونات، مثل: الأسلاك النانوية من السيليكون، والمبلمرات، والمواد العضوية، وأنابيب الكربون النانوية، والنقاط الكمية. وإضافة إلى إظهار مميزات إدخال هذه التقنيات في تصنيع الخلايا الشمسية، تظهر الورقة مدى تشتت الباحثين في هذا المجال وتنافسهم في السباق على إنتاج خلايا جديدة ذات كفاءة عالية. وتناقش الورقة أهمية تصنيف هذه الطرق