

# Recent advances in Carbon nanotubes incorporated TiO<sub>2</sub> nanostructures as photoanodes in dye sensitized solar cells

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## Abstract

The continuous supply of energy is posing an increasingly major problem as the world's population continues to grow and the cities become more industrialized. Therefore, for a sustainable energy supply chain, the humanity needs to focus its attention on sources other than fossil fuels, which is rapidly drying out. One of the promising alternatives is the solar power which can be harnessed via solar cells to generate electricity. The Dye sensitized solar cells (DSSCs) are an exciting form to generate electricity. In such solar cells, a light absorbing material anchored on a charge extracting material absorbs light and generates charge carriers creating an electric current, which is extracted via an external circuit. By far the most research charge extracting material as a photoanode in the cell is TiO<sub>2</sub> because of well-known properties such as low toxicity, high stability, high efficiency for charge extraction, and its abundance. Carbon nanomaterials are heavily used in solar cell research due to their outstanding electrical characteristics, incredible mechanical and chemical stability, and higher specific surface area. In this review, the incorporation of and contribution of carbon nanotubes with TiO<sub>2</sub> nanostructures for the critical development of dye sensitized solar cells with future research directions are presented and discussed.

*Keywords:* DSSC; CNT; TiO<sub>2</sub>; photovoltaic

## 1. Introduction

The global energy sector faces several issues as fossil fuel resources are being depleted. Renewable energy sources are seen as possible alternatives to this problem because they do not rely on fossil energy sources. Among the technologies that use renewable energy sources include wind, hydro, wave and tidal, solar, etc., the most promising renewable energy technology is photovoltaic (PV) technology since it uses solar energy, which is widely accessible.

Over the years, renewable energy consumption grew at six times the rate of total primary energy and renewable share increased from 29% to 30% of total electricity generation by 2023 (Energy Institute 2023). However, in comparison to the availability of solar power, this percentage of solar energy is insufficient. The main reason for this large disparity is a shortfall in efficiency and costly techniques of solar harvesting.

Solar cells can be considered as the one of the most extensively used solar energy conversion devices. The most developed solar photovoltaic cells are those from the first generation. They are entirely commercial in nature and dominate the market. Examples include single crystalline and multi-crystalline silicon. Then, still in the early phases of development, the second-generation photovoltaic systems are slowly expanding and taking over the market. Lastly, third-generation solar cells, which include organic photovoltaic cells (OPV) and concentrating photovoltaic (CPV) cells, are in the research and development stage or have not yet widely reached a commercial scale. However, the researchers' attention have been drawn due to the affordable production costs. It also includes novel concepts in development. DSSCs have been extensively researched since the first model cell introduced by O'Regan and Gratzel (Ali, Bakr, and Jassim 2016) in 1991. O'Regan and Durrant made notable discoveries regarding the behavior of TiO<sub>2</sub> in DSSCs. Some of them are include,

- In  $\text{TiO}_2$ , more than 90% of the electrons became stuck, with fewer than 10% remaining in the conduction band.
- On average, about 600 dye molecules are accumulated on the surface of an 18nm  $\text{TiO}_2$  particle.
- It was predicted that about 600 electrons per second were emitting into  $\text{TiO}_2$  particles.
- On average, only one dye molecule per 150  $\text{TiO}_2$  particles existed in the oxidized state.
- Surrounding each  $\text{TiO}_2$  particle, there were approximately 1000  $\text{I}^-$  ions and 200  $\text{I}_3^-$  ions.

Compared to solid photovoltaic devices, DSSCs are less expensive, need simpler fabrication methods and promising technology for harvesting solar energy (Sugathan, John, and Sudhakar 2015).

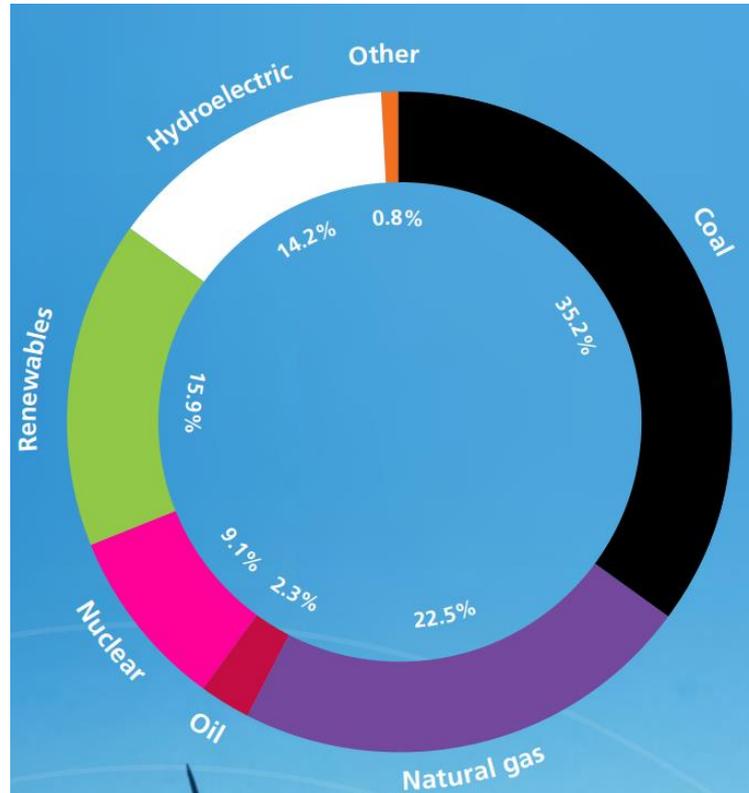


Fig. 1. The total global electricity generation by source in 2023(Energy Institute 2023)

The photoanode in the DSSC is a crucial component to study as it is responsible of the main function of converting sunlight into electrical energy. The overall performance is therefore mainly relied on the photoanode, since the efficient photoanodes can capture more photons from sunlight and generate more electrical current. Therefore, to optimize the efficiency and lower the fabrication cost and make them a competitive alternative to conventional solar cells, researchers continue to investigate novel and more efficient photoanode materials and designs. Photoanodes are usually made of wide bandgap semiconductors, for example titanium(IV) oxide commonly known as titanium dioxide ( $\text{TiO}_2$ ).

## 2. Working Principle of DSSC

A DSSC is composed of a photosensitive dye adsorbed onto a mesoporous semiconducting oxide layer. The photoactive layer is sandwiched between a transparent conducting electrode usually made of Indium Tin Oxide(ITO) or Fluorine Tin Oxide (FTO) and a counter electrode typically made of platinum or carbon.

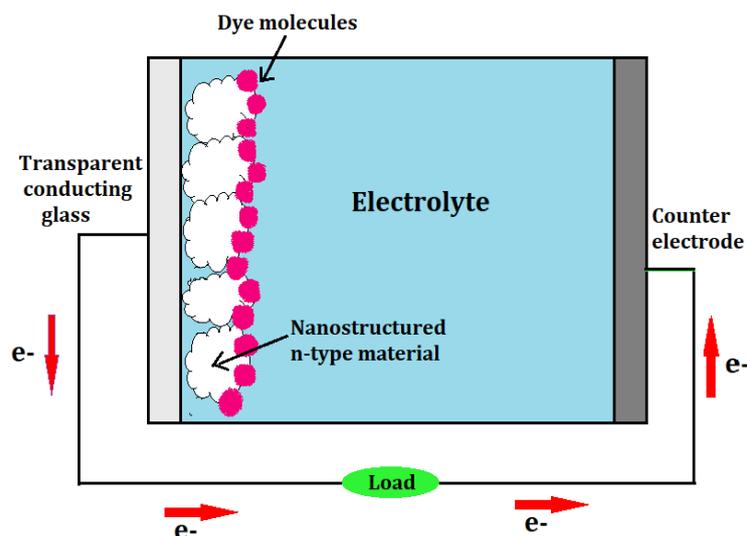


Fig. 2. Working principle of DSSC

The dye molecules are excited when sunlight strikes the transparent anode and flows through. The semiconductor oxide layer, which is often composed of nanocrystalline particles, receives electrons from these excited dye molecules. The effective surface area is increased, and more light can be absorbed across a larger range of the spectrum (from UV to infrared) by using nanocrystalline particles coated with light-absorbing dyes. After that, electrons move from the cathode to the iodide electrolyte via the external circuit. The electrolyte then transfers the electrons back to the dye molecules. The dye in DSSCs undergoes oxidation. An iodide ion donates an electron to the oxidized dye, allowing it to return to its original state. Iodide ions undergo oxidation during this process. Iodide ions are then reduced back to  $I_3^-$  ions by the electron that is returning to the DSSC from the external circuit.

### 3. Photoanode

The photoanode in DSSCs is required to capture photons from sunlight and convert it into power. The photoanode is usually made of wide-bandgap semiconductors with nanoporous structures, like titanium dioxide ( $TiO_2$ ) (Drygala 2021), which gives the dye molecules a lot of surface area to absorb photons. In addition, the photoanode material serves as a binding agent for dye molecules and transport electrons to the semiconductor conduction band (CB) from the sensitizer. The requirements that a photoanode of a DSSC should meet are:

- i. High light absorption: Should be able to absorb most of the sunlight that falls. To achieve this, materials with wide absorption spectrum can be used (Koide et al. 2014).
- ii. Large surface area: Which increases the number attaching dye molecules to the semiconductor material and thereby increase the light absorption (Zhu et al. 2006).
- iii. Suitable band alignment with the sensitizer energy levels (De Angelis, Fantacci, and Selloni 2008).
- iv. Good electron transport (Thavasi et al. 2009).
- v. The photoanode should be stable under the conditions of exposure to light, electrolyte and oxygen (Wang et al. 2003).
- vi. Low cost.

The requirements suggested above indicate that the porosity, thickness, and composition of the photoanode have a major effect on the DSSC's efficiency. Highly porous photoanodes provide higher surface area for excellent dye absorption and also fast charge transmission (Chen et al. 2009). The light absorption and charge transport characteristics of the photoanode are also influenced by its thickness. Thinner films often demonstrate higher

efficiency because of a reduction in charge recombination losses (Kumari et al. 2016). Therefore, it is essential to carefully assess the material, shape, and size of the photoanode in order to ensure that these devices perform at a high efficiency.

### 3.1 Materials used as photoanode.

New photoanode materials with improved surface properties are being researched to overcome the shortcomings of existing materials. Among the most investigated materials are  $\text{TiO}_2$ ,  $\text{ZnO}$  (Sheng et al. 2007) (Xu and Sun 2011),  $\text{Cu}_2\text{O}$  (Madusanka, Pitigala, and Karunarathna 2023),  $\text{Nb}_2\text{O}_5$  (Rani et al. 2014),  $\text{SnO}_2$  (H. Song et al. 2013)  $\text{SrTiO}_3$  (Khan 2015) and  $\text{Zn}_2\text{SnO}_4$  (Sun, Zhang, and Li 2014) (Al-attafi 2019). The performance of DSSCs depends on the structure, morphology and crystallinity of these wide bandgap semiconductor materials. Based on their characteristics and effectiveness in DSSCs, the following commonly used materials are compared:

**$\text{TiO}_2$ :** The most widely utilized semiconductor material in DSSCs is Titanium (IV) oxide because of its stability, high efficiency, and abundance in earth.  $\text{TiO}_2$  can absorb light at a wide range of wavelengths due to its wide bandgap. In addition, it can withstand heat, sunlight, and other climatic conditions without corroding.  $\text{TiO}_2$ -based DSSCs have proven to be highly efficient with reported more than 14% efficiency (Joshy et al. 2022).

**$\text{ZnO}$ :** Zinc (II) oxide is also used as a semiconductor material, which has a relatively wide band gap and high electron mobility. It is also affordable and widely available. DSSCs based on  $\text{ZnO}$  have been shown to be efficient up to 9%. But it also has significant shortcomings such as poor stability and incompatibility with some dyes and electrolytes (Shakeel Ahmad, Pandey, and Abd Rahim 2017).

**$\text{Cu}_2\text{O}$ :** With a smaller band gap than  $\text{ZnO}$  and  $\text{TiO}_2$ , Copper(I) oxide is more suitable for absorbing light with longer wavelengths (Madusanka, Pitigala, and Karunarathna 2023).  $\text{Cu}_2\text{O}$ -based DSSCs have shown efficiencies up to 6%, however less stable compared to  $\text{ZnO}$  and  $\text{TiO}_2$  (Lupan et al. 2021).

**$\text{CdS}$ :** Cadmium (II) sulfide ( $\text{CdS}$ ) has a narrower band gap than  $\text{TiO}_2$  and is therefore more suitable for absorbing visible light (Alkuam and Badrdeen 2018). Efficiency levels of up to 3% (Alkuam and Badrdeen 2018) have been demonstrated by  $\text{CdS}$ -based DSSCs. However,  $\text{CdS}$  is hazardous and poses a risk to both human health and the environment.

**$\text{SnO}_2$ :** Tin (IV) dioxide ( $\text{SnO}_2$ ) has a high electron mobility and a relatively large bandgap. DSSCs based on  $\text{SnO}_2$  have shown efficiencies of up to 7%. However, poor stability and incompatibility with certain dyes and electrolytes are the drawbacks (Pari et al. 2014).

To summarize,  $\text{TiO}_2$  is the most widely used material in DSSCs due to its high stability, efficiency and abundance. Although  $\text{ZnO}$ ,  $\text{Cu}_2\text{O}$ ,  $\text{CdS}$ , and  $\text{SnO}_2$  are potentially interesting materials for use in DSSCs, they have certain disadvantages, including toxicity, low stability, and compatibility issues. To further increase efficiency and reduce the cost of DSSCs, researchers are looking into new materials and designs.

#### 3.1.1 Titanium dioxide ( $\text{TiO}_2$ )

Titanium dioxide ( $\text{TiO}_2$ ), as previously mentioned, has outstanding properties of excellent chemical stability, mesoporous nature and low toxicity, making it an effective candidate for photo-anode materials in DSSC technology (Sensitized et al. 2016) (Liu et al. 2016). Furthermore,  $\text{TiO}_2$  performs better than other transition metal oxides due to its higher surface area, electron affinity, CB edge and dye loading, and thus is the best material to use for the photoanode (Raj and Prasanth 2016). Three primary crystalline forms of  $\text{TiO}_2$  exist: Rutile in the tetragonal crystal structure, Anatase in the tetragonal crystal structure and Brookite in the orthorhombic crystal structure (Dai, Wu, and Sakai 2010). Despite the fact that rutile is thermodynamically more stable, anatase is the best form to use as a

photoanode material than rutile since its increased efficiency in photocatalysis and increased solar energy conversion rate (Shen et al. 2008). According to Zhang et al. (2014) anatase, rutile and brookite have different band gap properties. Rutile and brookite are direct band gap semiconductors, while anatase is an indirect band gap semiconductor. Due to exhibiting an indirect band gap, photoexcited electrons are unable to directly migrate from the CB to the VB of anatase. As a result, anatase has a longer electron lifetime than rutile and brookite. Moreover, all three forms, anatase have light average effective mass of photo-excited electrons. This allows for faster electron transport and a lower electron recombination rate in anatase than in rutile and brookite (Zhang et al. 2014). Park et al. (Frank and Renewable n.d.) and colleagues found that the solar cells fabricated from anatase phase produced higher short-circuit currents but both cell types (anatase and rutile) produced same open-circuit voltage. This is because the small surface area of the rutile film results in less dye absorption and low photocurrent.

As photoanodes, TiO<sub>2</sub> nanostructures such as nanoparticles, nanowires, nanorods, nanotubes, etc. have been recently developed for DSSC applications (Joshy et al. 2022). However, to enhance the efficiency of DSSCs, complex procedures are necessary to fabricate different TiO<sub>2</sub> photoanode morphologies. Exact reaction conditions are needed to control the diameter, length, and thickness of these nanostructures. To develop high-performance DSSCs, carbonaceous material nanocomposites with TiO<sub>2</sub> have been suggested to overcome complex manufacturing processes. High electron mobility, strong stability against electrolytes, and superior electrical conductivity are characteristics of carbon allotropes. Particularly graphene and CNTs have demonstrated potential as photoanode fillers. They have strong electron mobility and light harvesting properties.

#### 4. Carbon Nanotubes

Since their invention in 1991 by Iijima (Michael F. Toney, Jason N. Howard, Jocelyn Richer, Gary L. Borges, Joseph G. Gordon, Owen R. Melroy, David G. Wiesler 1994), CNTs have been extensively researched for many applications, including DSSCs, because of their unique properties. CNTs belong to the Fullerene family. A flat sheet of graphite is rolled into a cylindrical shape to create them; this creates a honeycomb lattice structure with sp<sup>2</sup> hybrid orbitals (Dresselhaus 1996). This structural characteristic gives carbon nanotubes exceptional properties. Some properties are listed below in the Table 1.

Table 1: Properties of Carbon nanotubes

Property	State
Density	Significantly lower than that of steel (Radhamani, Lau, and Ramakrishna 2018)
Surface area	SWCNTs exhibit higher values than MWCNTs (Birch et al. 2013)
Elasticity	Highly elastic (Ruoff, Qian, and Liu 2003)
Tensile strength	100 times greater than steel (Ruoff, Qian, and Liu 2003)
Thermal conductivity	Excellent and range between 2000 – 6000 Wm <sup>-1</sup> K <sup>-1</sup> (Han and Fina 2011)
Electron mobility	Very high and approx. 70-fold higher than silicon (Batmunkh, Biggs, and Shapter 2015)
Electrical conductivity	Higher than many metals including copper and steel (Sivasubramaniyam et al. 2023)
Maximum current density	> 1000 times greater than copper (Batmunkh, Biggs, and Shapter 2015)

The characteristics of CNTs are not always consistent and can differ based on the number of graphite sheets rolled; we usually called the walls of the tube, the defects percentage, the length, the growth techniques, and the concentration. There are various types of carbon nanotubes, including single-walled carbon nanotubes (SWCNTs), which are created

by rolling a single sheet of graphite; double-walled carbon nanotubes (DWCNTs), which consist of a graphite sheet inside another; and multiple-walled carbon nanotubes (MWCNTs), which comprise multiple layers of graphite sheets wrapped around each other.

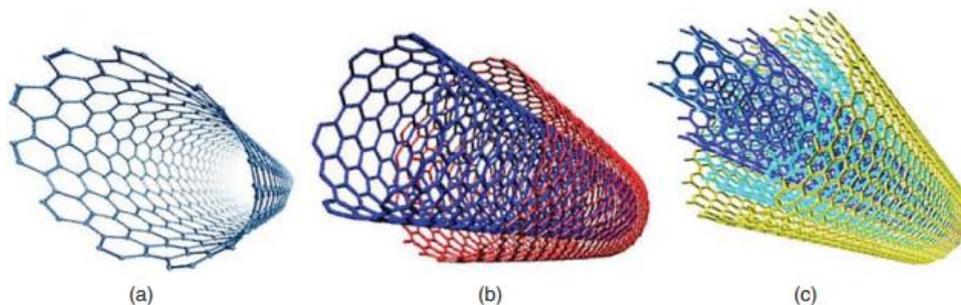


Fig. 3. Structures of (a) SWCNTs, (b) DWCNTs (c) MWCNTs (Cagnani, Joshi, and Shimizu 2019)

SWCNTs typically have a diameter that ranges between 0.8 and 2 nanometers, whereas MWCNTs can have diameters between 5 and 20 nanometers (De Volder et al. 2013). Electronic properties of the CNTs can also be affected by the rolling direction of the graphite sheet (Batmunkh, Biggs, and Shapter 2015). The chiral angle is a measure of the amount of twist in the nanotube which can range between 0 and 30 degrees (Tune et al. 2012). An armchair-shaped carbon nanotube is produced when the chiral angle is 30 degrees, whereas a zig-zag carbon nanotube has a chiral angle of 0 degrees. Chiral carbon nanotubes are defined as any other angle that lies between 0 and 30 degrees (Dresselhaus, Dresselhaus, and Jorio 2004).

The electrical properties of CNTs are mainly influenced by their chiral angle, which can vary from metallic to semiconducting with different bandgaps (Dresselhaus, Dresselhaus, and Jorio 2004)(Tune et al. 2012). Minor variations in the chiral angle of SWCNTs may result in various electrical properties, making them useful in electronic device applications.

MWCNTs are more complicated structures made up of several concentric carbon tubes. The spacing between carbon nanotubes (0.34 nm) and graphite (0.335 nm) is similar. Thus, this complicated structure is a result of Van Der Waals forces and curvature of the tubes. The arrangement of the concentric tubes influences the diameter of MWCNTs, but not their chiral angle, which can vary from conductor to metal-semiconductor layers. Research has shown that the outer layers of MWCNTs are responsible for electronic transport(Cagnani, Joshi, and Shimizu 2019).

#### 4.1 Carbon Nanotubes with $TiO_2$ nanoparticles

Selecting a photo-electrode with efficient electron transport and low charge (electron-hole pair) recombination is critical for achieving high efficiency in DSSCs. This motivated to incorporation of CNTs into the photoanodes of DSSCs (Lee, Alegaonkar, and Yoo 2007). This addition increases the surface roughness, which in turn enhances the capacity for attaching dye molecules and light scattering. The inclusion of carbon nanotubes in the photoanode increased the PCE by 35-50% compared to a bare semiconductor photoanode. Mehmood et al. (2016) demonstrated this improvement by obtaining a PCE of 5.25% in the  $TiO_2$  photoanode which incorporated 0.06 wt% MWCNTs. A 46% increment in the PCE was observed compared to the  $TiO_2$  only cell.

By utilizing the direct mixing technique to create  $TiO_2$ -MWCNT composite films for the working electrode in DSSCs, the device's performance was significantly enhanced compared to conventional DSSCs in 2009 by Sawatsuk et al. (2009). The electrochemical impedance study of the array of manufactured cells was done to examine the role of MWCNTs. The conductivity at the electrolyte/ $TiO_2$ /MWCNT interface and the electrical double layer capacity were

both noticeably enhanced at low MWCNT weight percentage up to 0.025%. When there were more MWCNTs in the composite electrode, he noticed that the performance of the DSSC decreased. This may be caused by the increased optical absorption of the composite electrode and the addition of MWCNTs. Consequently, the double-layer capacitance, electrical conductivity, and optical absorption of MWCNT-incorporated DSSCs have a notable influence in the process of enhancing the overall performance of the cell.

Chang et al. (2009) fabricated a photoelectrode for DSSC using TiO<sub>2</sub>-modified MWCNTs and the natural dye called ipomoea. A self-developed nanofluid system was used to fabricate TiO<sub>2</sub> nanoparticles. These nanoparticles were then mixed with TiO<sub>2</sub>-modified MWCNTs (TiO<sub>2</sub>-CNT), (which was prepared by mixing MWCNTs with pre-prepared titanium tetra-isopropoxide (Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>) sol-gel solution) using sol-gel method. The resulting mixture was deposited onto ITO glass using an electrophoretic deposition method. The results suggested a 30% increment of efficiency which containing 0.001g of TiO<sub>2</sub>/CNT (0.278% to 0.359%) compared to the conventional TiO<sub>2</sub> cell. Also, as a result of enhanced adsorption area and the improved interconnection between TiO<sub>2</sub> nanoparticles and the TiO<sub>2</sub>/CNT, an increase in current density was observed.

Using a direct mixing method of Functionalized MWCNTs and TiO<sub>2</sub> by De Morais et al. (2013) indicated that addition of F-MWCNTs to the TiO<sub>2</sub> photoanode effectively enhanced the conversion efficiency by 3.05% than the conventional porous films for the 0.02% of MWCNT concentration. Also, the device demonstrated an enhancement of J<sub>sc</sub> by 45% due to the improved electron transportation. This is because of the better interconnection between TiO<sub>2</sub> nanoparticles and F-MWCNT composite. However, beyond this concentration of MWCNT, the energy conversion efficiency was decreased due to the low transmittance in the composite films at higher MWCNT loadings and potentially higher charge recombination.

In 2015, Sharma and Mohan (2015) successfully synthesized TiO<sub>2</sub> and TiO<sub>2</sub>/MWCNTs films from the pure anatase form, and it was discovered that the average crystal size of the nanocomposite has reduced. With the addition of MWCNTs to the TiO<sub>2</sub> matrix, the structural and optical properties of the nanocomposite film were enhanced. The TiO<sub>2</sub> and TiO<sub>2</sub>/MWCNTs films were found to be very porous and arranged compactly, according to the SEM analysis. Furthermore, the functionalized MWCNTs with -COOH groups might be able to increase the solar electron collection due to the improvement of the interconnection between TiO<sub>2</sub> nanoparticles and MWCNT. Overall, the results suggest that, compared with conventional TiO<sub>2</sub> nanoparticle photoanodes, MWCNTs can significantly improve DSSC efficiency.

Using MWCNTs - TiO<sub>2</sub> nanocomposites as the photoanode with changing weight percentage of MWCNT and a MWCNT-based Pt-free counter electrode, Younas et al.(2019) fabricated a DSSC. Better light absorption in the visible spectrum, enhanced electron transport, and increased resistance to electron recombination were among the benefits of adding MWCNTs to the photoanode. The photovoltaic efficiency increased when MWCNTs were added to the TiO<sub>2</sub> photoanode. The MWCNT-TiO<sub>2</sub> nanocomposites with 0.06% of MWCNT demonstrated the best photovoltaic efficiency of 7.15% among the four different compositions utilized. This increases the photovoltaic efficiency by 13% compared to the conventional TiO<sub>2</sub> DSSC setup.

Sani et al. (2023) and co-workers investigated the efficiency improvement of DSSC using SWCNT mixed with TiO<sub>2</sub> nanoparticles as active layer introducing TiO<sub>2</sub>@SiO<sub>2</sub> Core-Shell nanostructure for light scattering layer. SWCNT content of 0.04 wt% resulted in higher efficiency due to increased surface area for adsorbing dye molecules. Furthermore, they confirm a significant reduction in resistance due to the SWCNTs resulting in better current flow and improved efficiency up to 5.10%.

By incorporating Graphene-MWCNT nanocomposite into TiO<sub>2</sub> nanoparticles, Mutashar and Al-bahrani (2023) was fabricated a photoanode in DSSC applications. In his research, MWCNTs was incorporated to prevent restacking graphene and to enhance the electron transfer of TiO<sub>2</sub>. Furthermore, he concludes that the MWCNTs act as a bridge

between graphene layers hence increase the surface area and the electrical conductivity of the cell compared to the TiO<sub>2</sub> cell.

There are studies that have used natural sensitizers instead of Ruthenium complexes, however these cells are still low in efficiencies compared to the Ruthenium sensitized cells.

Table 2: Performance of natural dye sensitized solar cells

Photoanode	Dye	Efficiency (%)	Ref.
TiO <sub>2</sub> -MWCNT(0.1 wt%)	ipomoea	0.359	(Chang et al. 2009)
TiO <sub>2</sub> -MWCNT(15 wt%)	Eosin B	1.702	(Mombeshora et al. 2015)
TiO <sub>2</sub> -MWCNT(0.015 wt%)	Curcuma longa	1.653	(You, Be, and In 2019)
TiO <sub>2</sub> -MWCNT(0.03 wt%)	Sandoricum koetjape	0.069	(Sabarikirishwaran, Junluthin, and Unpaprom 2022)

#### 4.2 Carbon Nanotubes with TiO<sub>2</sub> nanotubes

In a study conducted by Yulong et al. (2015) and colleagues in 2015, they examined the effects of adding CNT/graphene/TiO<sub>2</sub> nanoparticles to arrays of TiO<sub>2</sub> nanotubes. The researchers discovered that incorporating 0.1% by weight of CNT-G composite material resulted in increased efficiency. This was due to the improved adsorption of dye and higher electron transport rate. However, the researchers also noted that surpassing the optimal concentration of CNT-G composite material resulted in decreased efficiency. This was caused by electron recombination and light shielding.

#### 4.3 Carbon Nanotubes with TiO<sub>2</sub> nanorods

In their study, Yang and Leung (2013) and his co-worker utilized MWCNTs within TiO<sub>2</sub> nanorods (NRs) using electrospinning method to create a photoanode for DSSC. The diameter of the TiO<sub>2</sub> nanorods were around 70nm and using the SEM and XPS spectra, presence of CNTs inside the TiO<sub>2</sub> nanorods were confirmed. In this study, thickness of the photoanode as well as the weight percentage of the MWCNTs were varied. This incorporation led to a significant enhancement in the charge transport rate, resulting in a high efficiency of 10.24% at a 0.1% MWCNT concentration and a 14.64μm thickness. However, the researchers observed that increasing the MWCNT concentration beyond this point resulted in reduced efficiency and dye loading due to the competition among the sensitizer and the MWCNTs to absorb photons. This enhancement of overall performance was due to the improved fill factor of the MWCNTs incorporated device by 35%.

A novel bilayer photoanode made of TiO<sub>2</sub> nanorods, Mg<sup>2+</sup> doped TiO<sub>2</sub> nanorods and CNT incorporated TiO<sub>2</sub> nanorods was investigated by L. Song et al. (2018) for flexible DSSC application. Films were deposited with small and large nanorods as the under layer and over layer respectively using electrospray deposition method. Among the four cell types, the highest PCE was found in the bilayer cell consisting of small diameter CNT/TiO<sub>2</sub> nanorods (bottom layer) and large diameter Mg<sup>2+</sup>/TiO<sub>2</sub> (upper layer), which was 3.9%. They suggested that this efficiency increase was due to enhanced light harvesting due to the large diameter nanorod scattering layer and faster electron transport with less electron loss due to the different conduction bands of the bilayer nanorods.

#### 4.4 Carbon Nanotubes with TiO<sub>2</sub> nanowires

Young et al. (2013) and coworkers developed a method to make MWCNT-TiO<sub>2</sub> composite nanowires for use in DSSCs. These nanowires were made by electrospinning and contained MWCNTs embedded in TiO<sub>2</sub> nanowires. This combination allowed for fast transport of photogenerated electrons through the nanowires while preventing charge recombination between electrons and the dye or redox couple. When up to 5 wt% of MWCNTs were used, the photovoltaic performance improved significantly for 5.03% and further increment of MWCNTs wt% lead to decrease

in the efficiency. This indicates that MWCNT-TiO<sub>2</sub> composite nanowires can improve the efficiency of DSSCs by promoting efficient light harvesting and electron transfer.

In another study Ahn et al. (2013) and colleagues examined the effect of interfacial boundaries in TiO<sub>2</sub> nanowires as an alternative to TiO<sub>2</sub> nanoparticles by controlling the aspect ratio of the NWs. An electrospinning method with calcination was followed to fabricate TiO<sub>2</sub> NWs rather than the complex processes used in previous studies. The aspect ratio of the NWs was varied only by varying the length of the NWs for a fixed diameter. It was observed that the long TiO<sub>2</sub> NWs compare to the short ones, increase the electron transportation significantly due to the presence of smaller number of interfacial boundaries. Also, the incorporation of MWCNTs into the longer TiO<sub>2</sub> NWs promoted more synergistic effects, resulted in increased efficiency from 2.02% to 5.16%.

## 5. Summary and Future Prospect

The development of DSSCs has gained considerable interest over the last two decades in an effort to reach the efficiency of traditional silicon cells. The photoanode is regarded as the prominent section of the DSSC since it takes part in the most fundamental events that occur in the operation of the device, including photon absorption, recombination, and electron transport. Being non-toxic and having a feasible functional architecture, TiO<sub>2</sub> is more desirable than other semiconductors due to its proper band alignment with the sensitizer (dye) and the resulting charge transport properties. As photoanodes for DSSC applications, a wide range of TiO<sub>2</sub> nanostructures, including nanoparticles, nanowires, nanorods, and nanotubes, have recently been investigated. However, to reach higher efficiencies, complex and complicated processes are required to synthesize different morphologies of TiO<sub>2</sub> photoanodes. The photoanode is made by combining carbon nanotubes with TiO<sub>2</sub> nanostructures, mainly the TiO<sub>2</sub> nanorods, enhance the electron transportation properties and reduces the recombination of dye molecules, resulting in efficient dye-sensitized solar cells. Incorporation of CNTs to the TiO<sub>2</sub> nanostructures is becoming a developing field of research. However, increasing the MWCNT concentration beyond optimal point, resulted in increasing the charge transport resistance. This is due to the reduced dye adsorption of the photoanode and resulting lower efficiencies.

The addition of CNTs to the conventional TiO<sub>2</sub> cells enhances the overall performance of DSSCs, however they are not able to compete with silicon solar cells. Therefore, efforts are needed to improve the performance of CNT-based photoanodes. Introducing new methods to incorporate CNTs instead of widely used direct mixing methods, using different core-shell nanostructures as light-scattering layers, and fine-tuning of CNTs are expected to enhance the performance of the devices.

Despite all the optimistic features, DSSCs inherit a significant drawback, which arises directly from their design, and the problem is fundamental. It uses a liquid electrolyte and under illumination, the liquid film tends to evaporate due to light's heat, placing more stringent conditions for sealing the cell. Therefore, extensive research are ongoing to develop solid-state cells. Incorporating CNTs into the development of solid-state cells therefore would not only be a breakthrough in solar cell technology but also facilitate more efficient and sustainable energy harvesting methods.

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