CHAPTER III

TITANIUM DIOXIDE AS ACTIVE LAYER

Titanium Dioxide

Titanium dioxide (TiO_2) is a widely used and well-studied material that has been used in many applications, including photo catalysis, sunscreens and solar cells. TiO_2 exhibits remarkable properties, such as high chemical stability, strong absorption in ultraviolet (UV) and a wide band gap. In this section, the structure of TiO_2, its phases and its use in solar cells has been discussed.

Structure and Phases of TiO_2

TiO_2 exists as a crystalline material in different crystal structures, or phases. The most common phase is the Anatase phase, which is a tetragonal crystal structure. This is the most active phase for photocatalytic reactions, due to its high surface area providing more active sites and efficient charge separation. Anatase TiO_2 is used in the production of pigments, coatings and cosmetic products (Gao et al. 2019).

Another phase of TiO_2 is the Rutile phase, which has a more compact and ordered crystal structure than Anatase. Rutile TiO_2 is often used in applications where high chemical resistance and high mechanical stability is required, such as in the production of ceramic materials and dental implants. Rutile TiO2 is used in the production of white pigments, due to its high refractive index and opacity (Diosa et al. 2021).

There is also a third phase of TiO_2, known as Brookite, which has a orthorhombic crystal structure (Wang et al. 2022). Brookite TiO_2 is often found in mineral specimens and is the least stable of the three phases.

Anatase phase is most suitable for application in solar cells.

Use of TiO_2 in Solar Cells

TiO_2 is a key material used in the production of Dye-Sensitized Solar Cells (DSSCs), which are a type of thin-film solar cell that has gained significant attention in recent years due to their potential for their low-cost and low power applications.

In a typical DSSC, a layer of TiO_2 nano particles is coated onto a conductive glass substrate, forming the photoanode. The TiO_2 layer is then sensitized with a dye molecule, which absorbs light and generates electron-hole pairs. The excited electrons get injected into the TiO_2 conduction band, get collected by the electrode and generate an electrical current.

TiO_2 plays a critical role in the performance of DSSC's, as it provides a high surface area for dye absorption and efficient charge separation. Additionally, the bandgap of TiO2 is well-matched to the solar spectrum, allowing for efficient absorption of sunlight (Chen et al. 2021).

There are several factors that influence the performance of TiO_2 in DSSCs, including the thickness of the TiO_2 layer, the size and shape of the TiO_2 nanoparticles and the degree of dye coverage. Researchers have investigated various strategies to optimize the performance of TiO_2 in DSSCs, such as surface modification with metal nanoparticles, doping with other elements and the use of alternative sensitizing dyes (Masuda & Kato 2009).

TiO_2 can also be used in other types of solar cells, such as perovskite solar cells and quantum dot solar cells. In perovskite solar cells, TiO_2 is used as the electron transport layer, while in quantum dot solar cells, TiO_2 is used as the scaffold for the quantum dots.

METHODS OF PREPARATION OF TiO_2

SOL-GEL METHOD:

The sol-gel method is a widely used technique for the preparation of TiO_2. This method involves the hydrolysis and condensation of a Titanium Alkoxide precursor in a solvent to form a sol, which is then dried and calcined to form TiO_2. The reaction can be summarized as follows:

$$Ti(OR)_4 + 2H_2O \rightarrow TiO_2 + 4ROH \quad (R = (-CH(CH_3)_2))$$

The sol-gel method offers several advantages, such as the ability to control the size and morphology of the particles as well as the ability to incorporate dopants into the structure. However, it also has some disadvantages, such as the requirement for a lengthy preparation time and the need for careful control of the processing conditions to obtain the desired properties (Gao et al. (2023).

HYDROTHERMAL METHOD:

The hydrothermal method involves the reaction of a Titanium precursor in an aqueous solution at high pressure and temperature. This method is particularly useful for the preparation of TiO_2 nanoparticles with a high degree of crystallinity and purity. The process can be summarized as follows:

$$Ti(OR)_4 + 2H_2O \rightarrow TiO_2 + 4ROH$$

The hydrothermal method offers the same advantages as the above method. However, it also has some disadvantages, such as the requirement for high pressure and temperature, apart from the need for careful control of the processing conditions (Mahmood et al. 2010).

SOLVOTHERMAL METHOD:

The solvothermal method involves the reaction of a Titanium precursor in an organic solvent at high pressure and temperature (Zhao et al. 2022). This method is particularly useful for the preparation of nanoparticles with a high degree of crystallinity and purity. The process can be summarized as follows:

$$Ti(OR)_4 + nROH \rightarrow TiO_2 + nH_2O$$

The advantages and limitations remain the same as above.

FLAME SPRAY PYROLYSIS METHOD:

The flame spray pyrolysis method involves the combustion of a Titanium precursor in a high-temperature flame. The chemical process can be summarized as follows:

$$TiCl_4 + 2O_2 \rightarrow TiO_2 + 2Cl_2$$

Titanium dioxide (TiO_2) is commonly used in organic solar cells as a key component in the device architecture. It serves as an electron transport material and plays a crucial role in facilitating efficient charge extraction and transport within the solar cell.

There are two primary ways in which TiO_2 is employed in organic solar cells:

a. **ELECTRON TRANSPORT LAYER (ETL):** TiO_2 is commonly used as an ETL in inverted organic solar cell architectures. In this configuration, TiO_2 is deposited on top of the active layer, forming a selective contact for electrons. It enables efficient transfer of electrons from the active layer to the electrode, while blocking the transport of holes in the opposite direction. This selective transport helps to minimize charge recombination and enhance the overall device performance.

b. **MESOPOROUS SCAFFOLD:** TiO_2 can be used as a mesoporous scaffold in certain types of organic solar cells, such as dye-sensitized solar cells (DSSCs) and perovskite solar cells. In these devices, TiO_2 nanoparticles are assembled into a porous network, providing a large surface area for the deposition of light-absorbing materials and facilitating charge separation and transport. The porous structure of TiO_2 allows for efficient diffusion and collection of photogenerated electrons, while the electrolyte or hole transport material fills the voids to facilitate hole transport.

The use of TiO_2 in organic solar cells offers several advantages:

a. **HIGH ELECTRON MOBILITY:** TiO_2 exhibits good electron mobility, which is beneficial for efficient charge extraction and transport. It helps to minimize electron trapping and recombination, leading to improved device performance and higher power conversion efficiency.

b. **STABILITY:** TiO_2 is chemically stable and compatible with organic materials, making it suitable for long-term device operation. It can withstand the harsh environmental conditions that organic solar cells may be exposed to without significant degradation.

c. **LOW COST:** Titanium dioxide is an abundant and relatively inexpensive material, contributing to the cost-effectiveness of organic solar cell production. Additionally, TiO_2 can be easily synthesized and processed, allowing for scalable manufacturing methods.

d. **VERSATILITY:** TiO_2 can be incorporated into various device architectures and interfaces due to its compatibility with different organic semiconductor materials. It can be used in both single-junction and tandem configurations, as well as in different types of organic solar cells, including polymer-based, small-molecule, and perovskite solar cells.

While TiO_2 offers many advantages, there are also some challenges associated with its use in organic solar cells. One limitation is its relatively high energy bandgap, which results in limited light absorption. This can be addressed by incorporating light-absorbing materials with complementary absorption spectra or by using tandem device architectures to extend the spectral response (Chen & Burda, 2008).

Furthermore, TiO_2 films typically require a high-temperature annealing process, which may not be compatible with flexible substrates (Daghrir et al., 2013). The high-temperature treatment can limit the choice of substrates and hinder the scalability of organic solar cell manufacturing.

Researchers are exploring alternative materials and processing techniques to mitigate these challenges and improve the overall performance of organic solar cells (Hanif et al., 2022).

EXPERIMENTAL:

PREPARATION OF TiO_2 USING HYDROTHERMAL METHOD:

Anatase TiO_2 was prepared by hydrothermal method. 20 ml of Ti-isopropoxide was diluted in 5 ml of isopropanol (Solution A). Another solution was made by mixing 0.5 ml of H_2O and 0.5 ml of HNO_3 (Solution B). Solution B was added drop wise into Solution A. Then the mixture was stirred at room temperature on a magnetic stirrer. After 30 minutes alcogel was obtained. The obtained alcogel was transferred into stainless steel autoclave and kept in an oven for 24 h at 240°C. The precipitates were filtered and washed first with distilled water and then isopropanol. The precipitates were of anatase TiO_2.

XRD ANALYSIS OF TiO_2

XRD was taken on Bruker D8 Advance X-ray diffractometer. XRD analysis reveals a clear crystalline structure of TiO_2. Figure 16 shows the XRD pattern of hydrothermally prepared TiO_2. The peaks are sharp and broad. The peaks match with the characteristic peaks of Anatase phase of TiO_2. (Le et al., 2021)

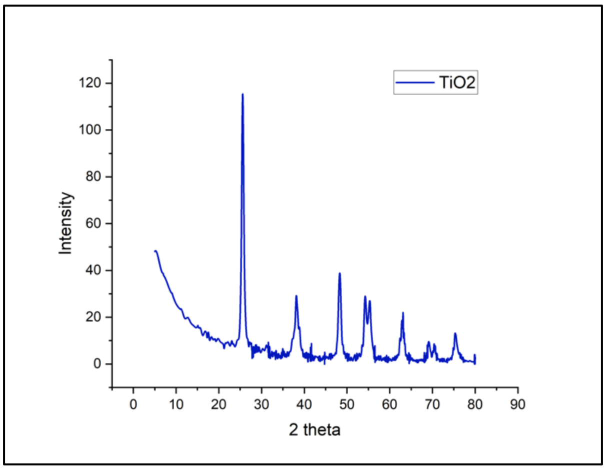
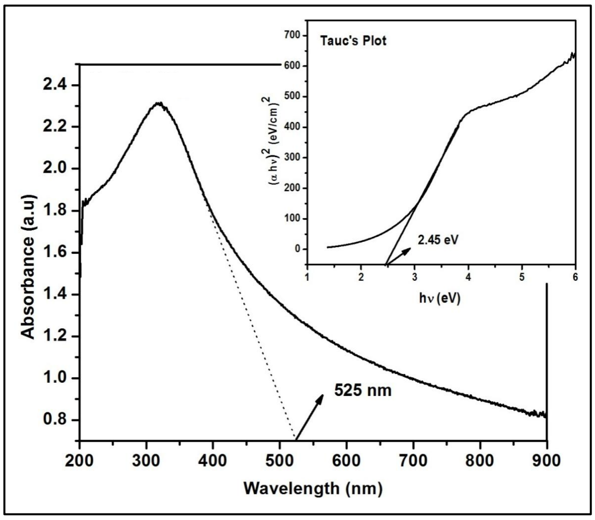


Figure 15: XRD Analysis of TiO_2

The d values of the peaks match very closely with those reported in JCPDS file 21-1272 and 21-1276 corresponding to the anatase phase. The most intense peak at 2θ value of 25.36° is the characteristic peak of (101) plane. (Bodson et

UV-VIS ANALYSIS OF TiO_2

UV-visible absorption spectra was recorded on Thermo Scientific (Evolution 600 UV-Vis) in wavelength range of 200 nm to 900 nm. The absorbance peak is observed at 340 nm that corresponds to characteristic absorbance of TiO_2. Band gap determined using Tauc's relation was found to be around 2.45 eV. (Zhang et al., 2014)



The synthesized TiO_2 was spin coated for use as active material.