Synthesization and optical characterization of photovoltaic materials for perovskite solar cell application

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Abstract. The performance of Perovskite solar cells (PSCs) has rapidly increased over the last decade. The power conversion efficiency (PCE) of 25.2% has been reported. Drastic and rapid change in PCE of PSCs has attracted a lot of attention toward this alternative photovoltaic technology that can be manufactured using simple and low cost processing techniques, over the traditional silicon solar technology. Here in this work, we have synthesized Molybdenum trioxide (MoO₃) and Titanium dioxide (TiO₂) for charge transport materials application in PSC application. The analysis of materials has been carried out by photoluminescence and absorbance spectra. The results signify that MoO₃ has absorbed at the visible region around (600-800) nm and the absorbance of TiO₂ tuned at 400 nm. Due to high absorption range (600-800) at visible region MoO₃ is suitable for Hole Transport Material (HTM). The widely used Electron Transport Material (ETM) TiO₂ is also synthesized and characterized.

1. Introduction

In current era, most of the electricity is produced by using fossil fuels including coal, oil and Petroleum gases. The energy produced by fossil fuels is not green because it contains pollutant gases like (CO₂, S, C, N etc). The byproduct of fossil fuels is directly affected to our environment [1]. Clean, green and sustainable energy is best alternative for future energy, which is produced by solar technology. One other issue related to fossil fuels are its availability, it is limited in stocks and to be finished within some year and also it has unbalanced distribution in the earth [2]. Solar energy is a one of the best promising alternative energy source for today energy requirement. The solar cell poses the ability to act as a savior in the current scenario. On the basis of absorber materials there are variety of solar cells are available and classified from 1st to 4th generation. 1st generation’s cells are mainly based on Silicon technology, which have very high temperature processing and costly. The advancement of Si technology, the various cells such as single crystalline silicon (c-Si), multi-crystalline silicon and amorphous silicon (a-Si) were used with different cell architecture [3, 4]. Hydrogenated amorphous silicon (a-Si:H), Cadmium Telluride (CdTe), copper indium diselenide,
(CuInSe$_2$) and its related alloys like Copper Indium Gallium diselenide, CuIn$_x$Ga$_{1-x}$Se$_2$ (CIGS) are second generation solar cell, used in place of Si to reduce the cost of Si solar cell, with reported efficiencies of CIGS and CdTe 20% and 17%, respectively [5, 6]. Silicon (Si) processing cost is very high so the overall cost of device is also high; to reduce the cost and increases the efficiency of solar cells 3rd generation thin film solar technology was invented. Organic photovoltaic solar cells (OPVs) technology employs conducting polymers as low cost materials; ease of fabrication and tunable bandgap suitable alternatives to inorganic semiconductors (Si, CIGS and CdTe). The highest reported power conversion efficiencies for dye-sensitized and polymer single cells using chlorinated acceptor are relatively ~ 14% and 16% [7, 8]. The 4th generation solar cells are combination of organic and inorganic materials, which are basically perovskite materials. In 2009, perovskite material was first used in photovoltaic application by Miyasaka and his co-workers [9, 10]. The perovskite material has a highest reported efficiency of ~28.2% in tandem architecture [11]. The limiting factor of this technology is instability in environment and toxicity due to incorporation of lead (Pb).

1.1. Perovskite material structure

Perovskite meanwhile, the mineral is composition of Calcium, Titanium and Oxygen in the form CaTiO$_3$. The generic form of perovskite structure is ABX$_3$ and the same crystallographic structure as the mineral [12]. The perovskite lattice structure and morphology arrangement is shown in figure 1.

![Figure 1](image)

**Figure 1.** (a) Perovskite structure and larger A-cation occupied in cubo-octahedral site, showing (BX$_6$) octahedral, (b) Cubic CH$_3$NH$_3$PbI$_3$ perovskite Unit cell, Ref [12].

The generic form to think about a perovskite (positively-charged) is as a large atomic or molecular cation of type A in the centreof a cube. The positively-charged B cations are occupied at the corners the cube and the faces of the cube are occupied by a smaller atom X with negative charge (anion). The cation A can be an organic material such as Methylammonium CH$_3$NH$_3^+$ [MA], Formamidinium NH$_2$CH=NH$_2^+$ [FA] or inorganic material such as Cs$^+$ ion [13, 14].

1.2. Perovskite Solar Cell

Organometal halides compound shortly named as perovskite represent an emerging active layer materials for photovoltaic technology. In recent years, perovskite shows capability of developing high performance
photovoltaic devices with higher efficiency at a low cost. In 2009, first perovskite solar cell was discovered with reported PCE of around 3.81%. The current highest PCE was reported around 25.2% for single junction PSCs. Perovskite name comes from a Russian mineralogist L. A. Perovski and was discovered by Gustav Rose in 1839 in Ural mountains of Russia [15]. Organo metal halide CH$_3$NH$_3$BX$_3$ was discovered by Weber in 1978, the material that is responsible for the main part of perovskite solar cells. Here, B represents the metal elements and X substitutes for halide elements [16]. CH$_3$NH$_3$BX$_3$ has an oriented crystal structure arranged in ABX$_3$ formula, where (X can be oxygen or halogen, in PV application X is halogen). The cubic-octahedral site shared with twelve X anions, attached with larger A cation. B cation is stabilized in an octahedral site shared with six X anions. New and advanced thin film deposition techniques were adopted which led to the modification of the performance of the cell [16-18]. Methylammonium free stable and more efficient perovskite solar cell has been reported in 2020, with 20.5 % power conversion efficiency [19]. A new breakdown approach has been developed to replace the organic-inorganic composition to all inorganic materials, which shows 15.6% power conversion efficiency [20].

2. Experimental

2.1. Preparation of Titanium dioxide (TiO$_2$)
Sol-Gel method is used for synthesis of Titanium dioxide (TiO$_2$); here Titanium tetra isopropoxide (TTIP) material is dissolve in the mixture of Ethanol and Acetic acid in proper molar concentration. Titanium tetra isopropoxide [Ti(OCH(CH$_3$)$_2$)$_4$, from Sigma Aldrich, 97% pure], and iso-propanol [(CH$_3$)$_2$CHOH, from Sigma-Aldrich, 99.7% pure], is dissolved in mixture of ethanol (C$_2$H$_5$O) and acetic acid (CH$_3$COOH) to form TiO$_2$ liquid solution. The mixture of ethanol and an acetic acid undergoes constant steering for 50 minutes at 60ºC. After 50 minutes, titanium tetra isopropoxide is mixed in prepared solution and the resultant solution is stirred for 5 minutes at same temperature, leading the synthesis of TiO$_2$ solution. The formation process along with deposited film is shown in figure 2.

![Figure 2](image1.png)

(a) (b)

**Figure 2.** Synthesis and deposition of (TiO$_2$), (a) Preparation of TiO$_2$ solution, (b) Deposition of (TiO$_2$), on ITO.

2.2. Chemical Compounds for MoO$_3$ synthesis: Using Ethanediol, Isopropanol and Hydrogen Peroxide
In this work, Isopropanol basically Isopropyl alcohol with the chemical formula CH$_3$CHOHCH$_3$ is used.
Isopropyl alcohol (IUPAC name propan-2-ol) flammable and colorless with chemical formula C₃H₈O is used. It poses strong odor. Isopropyl group linked to a hydroxyl group, to make the simplest example of a secondary alcohol, where the alcohol carbon atom is attached to two other carbon atoms. Basically it is a structural isomer of 1-propanol. Hydrogen peroxide is a chemical compound with the formula H₂O₂, in its pure form; it is a pale blue, clear liquid, and slightly more viscous than water. Hydrogen peroxide is unstable by chemical nature and slowly decomposes in the presence of base or a catalyst [21].

2.3. Synthesization of blue color (MoO₃) Molybdenum solution
The synthesis of MoO₃ is based on the preparation of Molybdenum solution with the treatment of ultrasonic reaction. Firstly, the ethanediol and isopropanol were mixed in a proper volume (in ratio of 1:9; ethanediol to isopropanol), then MoO₃ powder is mixed in the complex solvent, 30% aqueous H₂O₂ was added to enhance the chemical reaction. The total solution was ultrasonicated for around 30 minutes. At last, the thermal treatment at around 200ºC is provided with the help of hydrothermal method. Finally, a dark black colour MoO₃ solution is formed and proceeded for one day freezing, the colour of MoO₃ solution have been changed to dark blue as shown in figure 3.

![Figure 3. Dark blue color; Molybdenum oxide (MoO₃) synthesized solution.](image)

3. Result and Discussion

3.1. MoO₃ Absorbance analysis
High conductivity of MoO₃ materials varies from 10⁻⁹ to 10⁻⁵ (Ω cm)⁻¹ [22] which raises the free charge carrier concentration and also increases the carrier mobility of the material. The high work function (6.7 ev) [23] and energy levels of MoO₃ (5.3 to 2.3) matches with perovskite materials [24], making it suitable choice for carrier extraction (electron blocking as well as hole transporting) material to promote carrier transport and reduce the carrier recombination. Interface state of MoO₃ and perovskite is low, that helps reduce the recombination at the interface and it builds an ohmic contact with the metal electrode, and also provides the mechanical strength to devices. Apart from that the nontoxicity and environmental stability of MoO₃ is made suitable candidate for HTL in perovskite solar cell. Spectrophotometer model ELICO SL 159UV-VISIBLE is used for the measurement of the ultraviolet and visible spectrum of the prepared solutions. Firstly, the UV-VISIBLE measurement is performed on the molybdenum solution in the room temperature then at increased temperature up to 200°C. The obtained results are shown in figure 4. At the annealing temperature of 200°C, the small broad spectra ranging from 600nm to 800nm is absorbed, and it becomes more evident.
and this fascinating phenomenon may be attributed to the free electron being trapped in the oxygen vacancies in MoO₃, which results MoO₃ to act as hole transport layer as well as Electron Blocking layer.

**Figure 4.** MoO₃ Absorbance analysis: Spectra of synthesized MoO₃ at room temperature and 200°C.

3.2. *Titanium dioxide (TiO₂) Absorbance and Thickness Spectrum analysis*

TiO₂ thin film prepared by Sol-Gel method and deposited by using spin coater over the surface of ITO substrate has been investigated by UV-VIS Spectrophotometer at 400nm. The absorbance peak is obtained in range (600-800) nm, the absorption spectra is evident that TiO₂ is suitable for charge transport application. The thickness measurement has been done by using Spectroscopic Ellipsometer, the measured thickness of deposited TiO₂ is around 53.2nm.

**Figure 5.** TiO₂ spectrum analysis (a) Absorbance spectra of prepared TiO₂, (b) TiO₂ thickness spectra.

### 4. Conclusion

In this work, the synthesis and characterization of MoO₃ and TiO₂ film has been carried out. The MoO₃ film is synthesized by sol-gel method followed by ultrasonic reaction and deposited using spin coater on ITO...
substrate. Results suggest that the MoO$_3$ and TiO$_2$ affect the performance of the device, at the wavelength window from 600nm to 800nm a growing small broad spectrum is absorbed for the MoO$_3$ at annealing temperature 200°C. Due to high temperature annealing process, the small broad spectra becomes more evident and this fascinating phenomenon may be attributed to the free electron being trapped in the oxygen vacancies in MoO$_3$, which result MoO$_3$ serve as hole transport layer as well electron blocking layer. Absorbance spectra of TiO$_2$ thin film (53.2nm) prepared by Sol-Gel method deposited on ITO substrate has been investigated by UV-VIS Spectrophotometer. At 400 nm, the absorbance is high (~ 70%) and which tends to decrease from visible to IR region of solar spectrum. In this work the results suggest that MoO$_3$ can be used as eminent HTL material. This material is capable of enhancing the charge transportation of the device, prevents charge recombination, and also increases the carrier mobility of the cell, and prevents the active materials from the external environments (i.e. moisture, rain, air and temperature).

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