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A Review on the development of TiO2 photoanode for Solar Applications

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***Abstract* - Recently perovskite solar cell (PSC) have emerged as a new class of light absorbers, achieving exceptional progress in solar cell performance. Typically, A PSC consists of a photoanode, absorber and a hole transport material whereas the Photoanode plays a crucial role by efficiently transporting electrons as well as simoutenously blocking holes towards the Perovskite absorber. Titanium dioxide (TiO2) is the most common n-type semiconductor used as photoanode in PSCs because of its chemical stability, ability to moderate charge transport and ease of synthesis process. It has been well evaluated that the performance of PSCs is greatly influenced by the charachteristiscs of the TiO2 nanostructures. The key properties of the TiO2 photoanodes are exemplified by particle size, morphology crystallinity, phase content and chemical composition. In this review paper, we discuss the key mechanisms of TiO2 photoanodes and elaborate on the effect of its incorporation in perovskite solar cells. Dye-sensitized solar cells (DSSCs) have appeared as a promising source to meet the energy demand as an environmentally friendly alternative.**

Keywords-* *perovskite solar, Titanium dioxide, Dye-sensitized solar cell , DSSC.

I. INTRODUCTION

A solar cell or photovoltaic cell is a device that converts solar energy into electricity by the photovoltaic effect[1],[2],[3]. Photovoltaic is the field of technology and research that studies the application of solar cells used to convert sunlight into electricity[2],[3]. Although traditional solar cells based on silicon have reasonable energy conversion efficiencies up to 20%, they require high-purity silicon and skilled manufacturing techniques. This increases the cost and hence restricts their use. As such, organic solar cells or Dye-sensitized solar cell (DSSC) appear to be a highly promising and cost-effective alternative for the photovoltaic energy sector [4],[5],[6]. A typical Dye-sensitized solar cell (DSSC) is a combined sandwich structure of: (a) semiconductor materials such as TiO2, ZnO, SnO2 nanoparticles (photoanode) [7] deposited on a conducting glass substrate, (b) counter electrode and (d) electrolyte. In a single layer DSSC anode, titania is generally used as a base material for its high absorptivity of the photon absorbing dye[8],[6]. Among these DSSC components, the photoanode plays a vital role in determining the DSSC performance. So far, a titanium dioxide (TiO2) is one of the most commonly used photoanode materials, and it is a promising material for a DSSC because of its low cost, ease of fabrication, relatively high energy conversion efficiency, high specific surface area, and non-toxicity[8],[9]. The recent emergence of efficient solar cells based on organic/inorganic lead halide perovskite absorbers tends to transform the fields of dye-sensitized, organic, and thin film solar cells. Therefore,solid perovskite solar cells (sPSC) can be considered as a robust candidate for commercialization[10]. Perovskite solar cells are one of the most promising alternatives to conventional photovoltaic devices, and exhaustive studies focused on device optimization to further improve their performance[11]. Since it was first reported in 2009, the perovskite type CH3NH3PbX3 solid solar cell has recently been marked with over 15% efficien [10],[12]. In general, perovskite solar cells are configured as a sandwich structure. Explicitly, a mesostructured TiO2 layer on FTO serves as the photoanode, which is filled up with perovskite CH3NH3PbX3 as the PV active layer is followed by capping with a hole transport material layer (HTM) and a metal counter electrode[12]. However, TiO2 activity is reduced to the region of UV light (wavelength around 360 nm) [13]. The need for a green and more environmentally friendly energy production has led to recent research of using natural products in the production photovoltaic cells.The extracted dye materials were characterized by using UV and IR methods after which they were used in developing DSSCs. The dyes containing carboxyl and hydroxyl functional groups showed weak to large absorption under the visible light irradiation.[14]. Several attempts have been made to enhance the electron transport and prevent charge recombination, including the surface modification of TiO2 by doping with metals and nonmetals. This study will review some of those solutions and possibility of using surface modification of TiO2 by doping with metals and nonmetals to increase the solar cells efficiency.

II. SEMICONDUCTOR PHOTOANODE

The photoanode is a thin porous film of metal oxide semiconductor supported on to a transparent conducting oxide (TCO) glass. Extensive research in this field has revealed the photophysics of semiconducting electrodes like TiO2, ZnO and SnO2 etc. Selection of metal oxide for this purpose relies on crystallinity, particle size, thickness of the film, surface area, dye affinity and porosity[15]. Oxides such as TiO2, ZnO, SnO2 and chalco- genides have been thoroughly studied due to the wide application in energy storage and environmental remediation of photoelectrodes. Among all oxide materials, TiO2 is cheap, non-toxic and also has good stability.[7] In contrast, oxide semiconductor materials, especially TiO2, have good chemical stability under visible irradiation in solution[16],[7],[17],[18]. Zinc Oxide (ZnO) is an important and versatile n-type direct wide bandgap (3.37 eV) semiconductor, with a large exciton-binding energy (~60 meV) at room temperature. ZnO has wide-ranging applications in electronic and optoelectronic devices, such as piezoelectric sensors, ultraviolet (UV)/blue light-emitting diodes, transistors, field emission displays, gas sensors, UV detectors, trans- parent conductive films, hybrid solar cells, etc. ZnO is also inexpensive, relatively abundant, chemically stable, easy to prepare, and nontoxic[19]. The bandgap energy and the electron affinities of ZnO are similar to TiO2, but its higher electron mobility compared to TiO2 may overcome higher electron recombination in the TiO2 based-dye sensitized solar cells (DSSCs), which is beneficial for solar cell performance[20]. It has been found that TiO2 is a stable photoelectrode in photo- electrochemical systems even under extreme operating conditions. It is cheap , readily available, and non-toxic. Its conduction band edge coincides well with the excited electronic level of anthocyanin containing dyes which is an important condition to be satisfied for the injection of electrons from the dye molecule to the semiconductor[16]. The semiconductor electrode is usually a layer of nanocrystalline titanium dioxide (TiO2), a thin film deposited on conducting glass film with the thickness ca. 5–30 µm, which plays an important role in both the exciton?? dissertation and the electron transfer process[21]. The photoelectric conversion efficiency (η) of DSSCs has reached greater than 11% using anatase TiO2 such as the photoanode materials[18].

III. TITANIUM DIOXIDE (TIO2) NANOMATERIALS

Titanium dioxide is a semiconductor which exhibits catalytic properties, exits in three natural forms namely anatase, rutile and brookite, with band gaps of 3.2, 3.02, and 2.96 eV respectively [13],[22]. It is widely used in environmental applications such as the use of a photocatalyst for oxidation reactions of organic compounds in alcohol thermal decomposition reactions, photocatalytic decomposition of water for hydrogen production, and in photovoltaic cells [13]. Two allotropic forms of TiO2 are important, anatase and rutile. Anatase appears as pyramid-like crystals and is stable at low temperatures whereas needle-like rutile crystals are dominantly formed at high temperature processes. Single crystals of TiO2 also have rutile structure and the densities are 3.89 g/cm3 and 4.26 g/cm3 for anatase and rutile respectively. Rutile absorbs 4% of the incoming light in the near-UV region, and band gap excitation generates holes that act as strong oxidants reducing the long-term stability of the dye-sensitized solar cells. Anatase is dominant in low temperatures (< 800 oC)[15],[22]; however rutile is at the equilibrium phase for any temperature[21]. Though rutile form is more stable, anatase is perceived to be more chemically active when used in dye-sensitized solar cells. Anatase is metastable? and tends to convert to rutile upon heating[21]. Hence, the phase constituents are greatly influenced by the synthesis processing method.Anatase TiO2 is considered to be the active photocatalytic component based on charge carrier dynamics, chemical properties and the activity of photo- catalytic degradation of organic compounds[22].

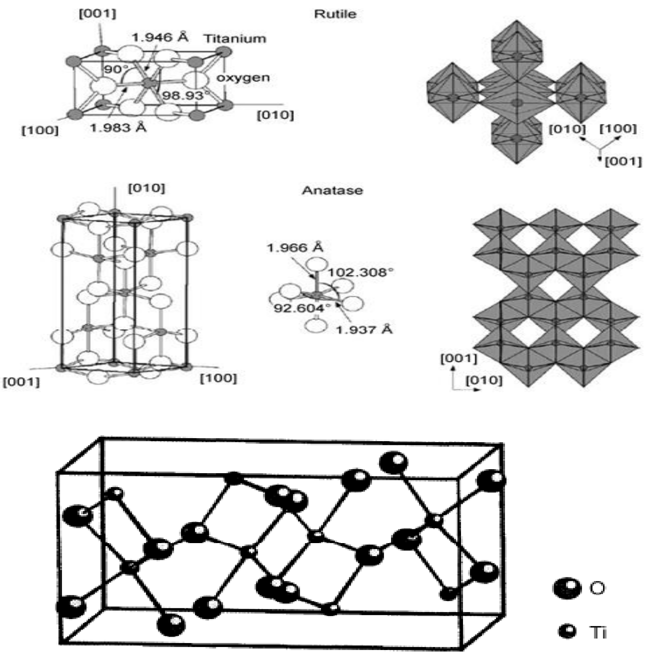


Fig. 1 .Crystal structures of the rutile and anatase and brookite phases of TiO2 [22].

IV. MECHANISM OF PHOTOACTIVITY OF PURE TIO2 ELECTRODES

The photocatalytic mechanism is initiated by the absorption of the photon hν1 with energy equal to or greater than the band gap of TiO2 (~3.3 eV for the anatase phase)[23],[24] producing an electron hole pair on the surface of TiO2 nanoparticle. An electron is promoted to the conduction band (CB) while a positive hole is formed in the valence band (VB)[24]. Excited-state electrons and holes can recombine and dissipate the input energy as heat[16], get trapped in metastable surface states, or react with electron donors and electron acceptors adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles. After reaction with water, these holes can produce hydroxyl radicals with high redox oxidizing potential. Depending upon the exact conditions, the holes, OH radicals, O2 -, H2O2 and O2 itself can play important roles in the photocatalytic reaction mechanism. As a photocatalyst, TiO2 can act as sensitizers for light – reduced redox processes due to their electronic structure, which is characterized by a filled valence bad and an empty conduction band. When the photon with an energy of hν1 exceeds the bandgap, Eg, of the semiconductor, an electron e- is promoted from the valence band, VB, into the conduction band, CB, leaving a hole HVB behind[13]. The visible light photoactivity of metal-doped TiO2 can be explained by a new energy level produced in the band gap of TiO2 by the dispersion of metal nanoparticles in the TiO2 matrix. An electron can be excited from the defect state to the TiO2 conduction band by the photon with energy equaling to hν2. An additional benefit of transition metal doping is the improved trapping of electrons to inhibit electron-hole recombination during irradiation. The decrease of charge carriers recombination results in an enhanced photo- activity[24].

One of the major challenges for the scientific and industrial community involved in photocatalytic research is to increase the spectral sensitivity of TiO_2-based photocatalysts to visible light. A major area of future research would be the development of new dopants, a new method of dopant incorporation into a TiO_2 structure as well as the new application for the environmental technology.The most important challenge which faces titania-based catalysis is stable TiO_2 with predictable photoactivity in UV and visible light.

V. MODIFICATIN OF TIO2

A. *Doping of TiO_2:*

Some of the major problems associated with photocatalysis are rapid charge recombination, back reaction, and an inability to use visible light efficiently. Addition of electron donors can enhance photocatalytic activity by irreversibly reacting with valence band holes to prevent charge recombination. By addressing these issues, many attempts have been made to enhance the photocatalytic activity of TiO2 nanostructures via improving the electron–hole separation and extending the optical absorption to the visible-light region by surface modification, structure optimization, and doping of noble metal or nonmetal elements[25]. Doping of TiO2 can inhibit charge recombination and expand its photoresponse to the visible region through the formation of impurity energy levels[22]. Doping of TiO2 is an important approach in band gap engineering to change the optical response of semiconductor photocatalysts. The main objective of doping is to induce a bathochromic shift, i.e., a decrease of the band gap or introduction of intra-band gap states, which results in the absorption of more visible light. Doping may lead to photocatalytic systems that exhibit enhanced efficiency. It is desirable to maintain the integrity of the crystal structure of the photocatalyst while changing its electronic structure by doping[22].

It has been reported that a hydrothermal synthesis of iron and europium codoped TiO2 materials under mild conditions. The photocatalytic activity for the degradation of phenol was improved under both visible and UV light by codoping[22].TiO2 (anatase) has wide band gap, Eg≈3, 2eV, thus only light below 400 nm is absorbed and capable of forming the e-/h+ pair[13]. Several approaches for TiO2 modification have been proposed: metal-ion implanted TiO2 (using transition metals: Cu, Co, Ni, Cr, Mn, Mo, Nb, V, Fe, Ru, Au, Ag, Pt) , reduced TiO2 photocatalysts , and doping of TiO2 with nonmetal atoms, (N, S, C, B, P, I, F) especially Nitrogen which attracted significant interest in the past decade as a promising way to reduce the TiO2 absorption from the Uv to the visible region[24]. Also the doping of TiO2 as photocatalyst by mono-rare earth either elements, such as Gd, La , Yb ,Er, or Ce enhances the separation of photogenerated electron–hole pairs or extends absorption wavelength span of TiO2. By combining TiO2 base with bi-rare earth elements, the limits of mono-doping issues can be efficiently compensated[25].

UV-Vis diffuse reflectance spectra presented slight shift to longer wavelengths and enhances the absorption in the visible region (>400 nm)for the Fe doped TiO2 nanoparticles, compared to the non-doped powder. The implanted Fe ions could decrease the band gap of the TiO2 to enable the absorption in the visible light[13]. However, when metal ions or oxides are incorporated into TiO2 by doping, the impurity energy levels formed in the band gap of TiO2 can also lead to an increase in the rate of recombination between photogenerated electrons and holes. Photo- catalytic reactions can only occur if the trapped electron and hole are transferred to the surface of the photocatalyst. This means that metal ions should be doped near the surface of the photocatalyst to allow efficient charge transfer. In the case of doping at a high concentration, metal ions can behave as recombination centers[22].

The light scattering, harvesting, and adsorption effects in dye-sensitized solar cells (DSSCs) are studied by the preparation of coated carbon nanotubes (CNTs) with TiO2 and Zr-doped TiO2 nanoparticles in the forms of mono- and double-layer cells. X-ray diffraction (XRD) analysis reveals that the phase composition of Zr-doped TiO2 electrode is a mixture of anatase and rutile phases with major rutile content whereas it is the same mixture with major anatase content for coated CNTs with TiO2. Furthermore, the average crystallite size of **Zr-doped** TiO2 electrode is slightly decreased with Zr introduction. Field emission scanning electron microscope (FE-SEM) images show that the porosity of Zr-doped TiO2 electrodes is higher than that of undoped electrode enhancing dye adsorption. UV–visible spectroscopy analysis uncovers that the absorption onset of Zr-doped TiO2 electrodes is slightly shifted to longer wavelength (the red-shift) in comparison with that of the untapped TiO2 electrode. Moreover, the band gap energy of TiO2 nanoparticles is decreased by Zr introduction enhancing light absorption. It is found that electron injection of monolayer TiO2 electrode is improved by the introduction of 0.025mol% Zr, resulting in the enhancement of its power conversion efficiency (PCE) up to 6.81% compared to 6.17% for pure TiO2 electrode. Moreover, electron transport and light scattering are enhanced by incorporation of 0.025 wt% coated CNTs with TiO2 in the over-layer of double layer electrodes. Therefore, double layer solar cell is composed of 0.025mol% Zr-doped TiO2 nanoparticles since the under-layer and mixtures of these nanoparticles and 0.025wt% coated CNTs with TiO2 and that the over-layer shows the highest PCE of 8.19%[26].

Well-crystallized TiO2 and neodymium (Nd)-doped TiO2 nanoparticles with various doping levels were synthesized by hydrothermal method and utilized as the photoanode of nanostructured solar cells. The results indicated that Nd-doping was caused the absorption spectra shift to higher wavelength while the morphology and surface area were unchanged. As a result, by employing 0.4mol% Nd in the TiO2 photoelectrode, the overall conversion efficiency of the cell reached 9.08% ,which is 26% higher than pure one. Based on the photo-electrochemical characterizations, the improvement is a consequence of electrons injection increment from dye to TiO2 conduction band, charge collection efficiency enhancement, and trap states density reduction in the Nd-doped photoanode[27].The common method to fabricate nanoporous TiO2 film is to screen-print TiO2 nanoparticles (NPs) paste over TCO surface followed by annealing to burn out the polymer binders. The paste is made up of TiO2 nanoparticles (NPs) synthesized by hydrothermal process starting with titanium-based precursor. In general, a good TiO2 photoanode should possess a high electrical conductivity and a tight chemical bonding with dye, and match the dye's lowest unoccupied molecular orbital (LUMO). To further improve the performance of TiO2 electrode, the incorporation of metal (Er, Yb, Zn, Co, Nb) as a dopant in TiO2 has been reported to be used as a favorable electron-transfer mediator in photovoltaic devices[28].

Titanium dioxide (TiO2) thin films had been deposited with various substrate temperatures by spray pyrolysis technique onto ITO substrates. All films exhibited polycrystalline nature with the preferred orientation along (101) plane. At the substrate temperature 450 ˚C, the film favored the formation of anatase phase. The higher substrate temperature (475 ˚C) favored the appearance of rutile structure. The efficiency of anatase TiO2 photoelectrode deposited at the substrate temperature 450 ˚C based cell was much higher than the efficiency of TiO2 photoelectrode deposited at the substrate temperature 475 ˚C based-cell[29].

A cost-effective way to prepare Nb-doped TiO2 nanoparticles (NPs) as the photoanode of DSSCs is simply done by mixing TiO2 paste with Nb2O5 sol gel. This synthesis method is suitable for mass production. After screen printing and annealing, Nb was successfully doped into anatase TiO2 lattice to form Nb5+-O bonds based on XRD, Raman and XPS investigations. By Nb doping into TiO2, the Ti3+ 3d1 and Nb5+ 4d0 levels existing in the nanocrystals make a positive shift of conduction band minimum (CBM) to enhance the driving force of electron injection, and the increase of electron concentra- tion improves the electron conductivity. The DSSCs with 2.0 mol% Nb-doped TiO2 electrode improve both Jsc and Voc to achieve a high photoconversion efficiency of 8.44%, which is 18.9% improvement as compared with the standard DSSCs[28].

Tak Kim and Sang Ho Kim (2011) found that the performance of DSSCs can be enhanced by both O2 plasma treatment and over-layer coating, dipped in saturated Ba(NO3)2 solution, and coated onto TiO2 electrodes and plasma treatment. The efficiency of (Barium nitrate coated onto TiO2 plasma treatment) solar cell increased up to 6.76% from 5.27%. That is to say, the improvement of (uncoated TiO2 electrode no plasma treatment) is about 28.3% and the current density (JSC) increased from 11.01mA/cm2 to 13.71mA/cm2. Likewise, O2 plasma treatment increased the Ru dye absorption. The effect of various over-layers and plasma treatment on the TiO2 electrodes was investigated and confirmed by X-ray diffraction (XRD) and electrochemical impedance spectroscopy (EIS) measurements. The UV–Vis absorption spectra of the TiO2 electrodes showed that the absorption of N719 dye was increased by over-layer coatings and by O2 plasma treatment[30]. Another approach reported by Wang et al (2014) to enhance the efficiency is the maximum efficiency (η, 3.17%),Jsc =12.18(mA/cm2), Voc=0.93 (V) through which a compact layer (CL) of TiO2 is introduced between fluorine-doped tin oxide (FTO) electrode and TiO2 nanoparticle layer in peroveskite-based solar cells[31].

VI. RECENT DEVELOPMENTS TIO2 PHOTOANODES IN PEROVSKITE SOLAR CELL

In 2013, a new milestone for solid-state mesoscopic TiO2 solar cells sensitized with lead iodide perovskite (CH3NH3PbX3) was reported to achieve an exciting power conversion efficiency of more than 14%[10], with expected future values reaching 20%[32]. The instability against humidity and UV light, reproducibility, lack of uniformity of perovskite layer on TiO2 surface are a challenging task to obtain high performances PSCs for commercial market[33]. To overcome these limitations, a systematic study was carried out on the device architectures such as interface properties between photoanode (e.g. TiO2) and Perovskite absorber layer, the surface morphology of mesoporous TiO2 layer, understanding the rule of electron transport and recombination process etc. This paper will review the current state and recent developments in the field of TiO2 photo anode, for perovskite sensitized solar cells (PSSCs) .

Qiu et al. (2013) show that the a novel organometal halide perovskite (CH3NH3PbI2Br) is synthe- sized and used as a visible light absorber to sensitize one-dimen- sional (1D) TiO2 nanowire arrays (NWAs) for all-solid-state hybrid solar cells. It achieved a power conversion efficiency (PCE) of 4.87% and an open circuit voltage (Voc) of 0.82 V, whereby both of which are higher than those of its analogue CH3NH3PbI3. The 1D TiO2 NWAs were grown on seeded fluorine-doped tinoxide (FTO) substrates via a hydrothermal process[34].

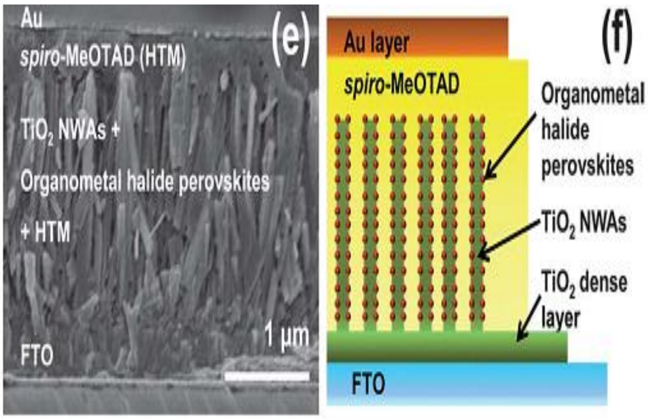


Fig.2. (e) Cross-sectional SEM image of the TiO2 NWAs/ perovskite sensitizer/spiro-MeOTAD hybrid photovoltaic cell. (f) Schematic illus- tration of the hybrid solar cell[34].

Wang et al. (2014) show that a compact layer(CL) of TiO2 was introduced by spray pyrolysis deposition between fluorine-doped tin oxide (FTO) electrode and TiO2 nanoparticle layer in peroveskite-based solar cells. A series of solar cells were fabricated wherein (CL) .

of TiO2 of varying thickness (0–390nm) to three different device structures,FTO/CL/nc- TiO2/Perovskite/HTM (classical cell) which showed optimal photovoltaic performances when the thickness of CL is 90nm. the maximum efficiency (η, 3.17%),Jsc =12.18(mA/cm2), Voc=0.93 (V) and FF=0.279. FTO/CL/nc-TiO2/ Perovskite (omitting HTM) and FTO/CL/Perovskite/HTM (omitting nc-TiO2)[31].

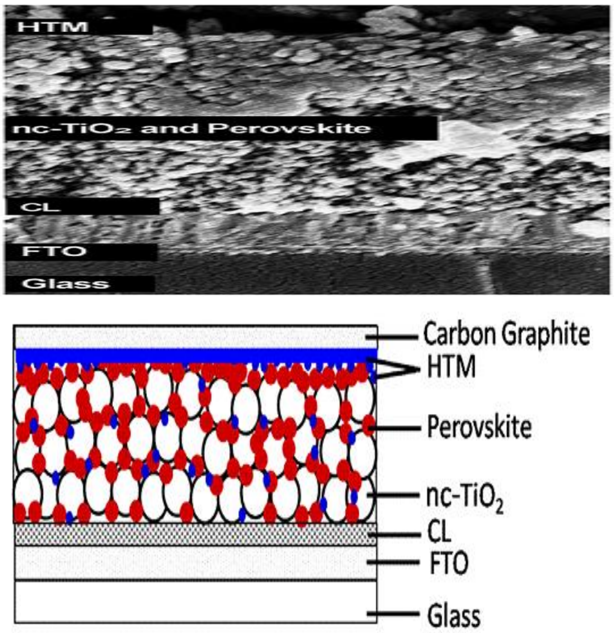


Fig.3. Cross section and schematic representation of the perovskite-based solar cell. nc-TiO2=TiO2 nanoparticle[31].

Ku et al. (2013) developed the mesoscopic methylammonium lead iodide (CH3NH3PbI3) perovskite/TiO2 heterojunction solar cell with low-cost carbon counter electrode (CE) and full printable process. With carbon black/spheroidal graphite CE, this mesoscopic heterojunction solar cell presents high stability and much higher performance (Voc = 0.878 V, Jsc = 12.4 mA/cm2, FF= 0.61, and a PCE of 6.64%) which is higher than that of the flaky graphite-based device, comparable to the conventional Au version. The mesoscopic CH3NH3PbI3/TiO2 heterojunction solar cells are fabricated by spray pyrolysis methods[35].

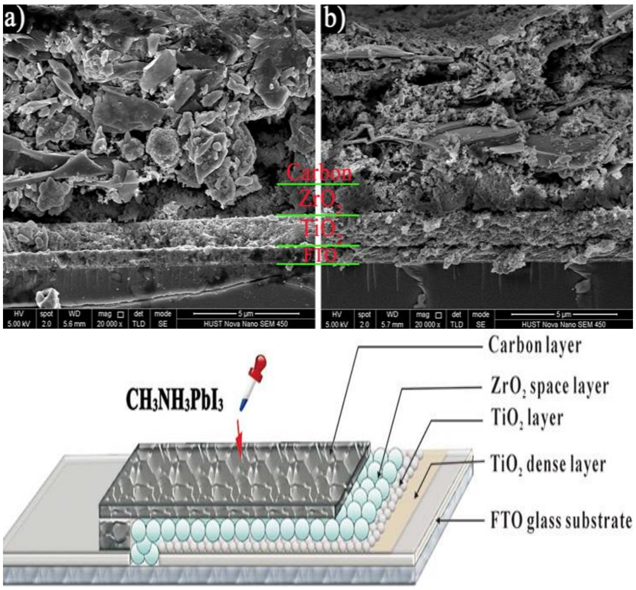


Fig 4. - Cross-sectional structure of the devices. (a) Spheroidal graphite (SG) based monolithic device. (b) Flaky graphite (FG) based monolithic device. And a schematic structure of a carbon based monolithic device[35].

According to H. Kim et. al (2013), fabricated solar cell are based on a submicrometer (~ 0.6 μm) rutile TiO_2 nanorod sensitized with $CH3NH3PbI_3$ perovskite nanodots and a substitution of liquid redox electrolytes with (HTMs). Rutile nanorods were grown hydrothermally and their lengths were varied through the control of the reaction time. Infiltration of perovskite-adsorbed submicrometer-thick rutile TiO2 nanorod films with spiro-MeOTAD yielded a strikingly high PCE of 9.4% under AM 1.5G illumination. With increasing the nanorod length, Jsc and Voc decrease with a corresponding decrease in [PCE] from 9.4% (0.56 μm) to 7.3% (0.92 μm) and to 5.9% (1.58 μm). The study also made it clear that the results from (Jsc) of 15.6 mA/cm2, (Voc) of 955 mV and fill factor of 0.63. IPCE of over 50% are observed at almost entire wavelength range from 400 to 750 nm with a maximum of 71% attained at wavelengths between 420 and 500 nm. That was under the simulated AM 1.5G one sun illumination,and (0.56 μm) Length[36].

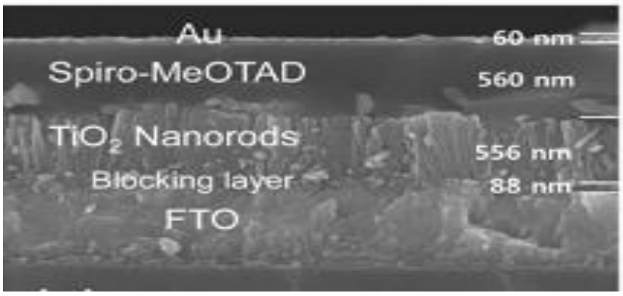


Fig 5. - Cross-sectional SEMimages of solid state DSSCs based on perovskite CH3NH3PbI3-sensitized rutile TiO2 nanorod photoanode, the spiro-MeOTAD hole transporting layer, and the Au cathode[36].

Etgar et. al (2012) prepared solid state DSSCs based on CH3NH3PbI3 perovskite/TiO2 heterojunction solar cell using anatase nanosheets with dominant (001) facets exemplified by the electron collector and CH3NH3PbI3 simultaneously as an absorber and hole-transporting material. A gold film was evaporated on top of the CH3NH3PbI3 as a back contact. This simple mesoscopic heterojunction solar cell achieved a remarkable photovoltaic performance with short-circuit photocurrent (Jsc) = 16.1 mA cm−2, a fill factor (FF) = 0.57, and open-circuit voltage (Voc) = 0.631 V corresponding to a light to electric PCE = 5.5% under standard AM 1.5 solar light of 1000 W/m2 intensity. At a lower light intensity of 100W/m2, a PCE of 7.3% was measured.The fact that the perovskite is stable in dry ambient air and can be deposited by low-cost solution processing opens up new avenues for future development of high-efficiency[37].

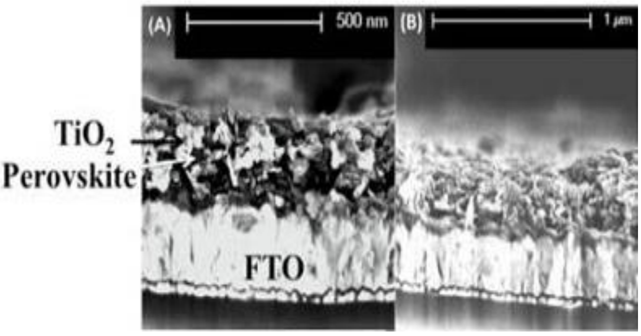


Fig. 6. - (A) High-resolution scanning electron microscopy (HRSEM) picture of the cross section of the CH3NH3PbI3/TiO2heterojunction solar cell. The dark areas can be attributed to the CH3NH3PbI3 which penetrates into the mesoporous TiO2 film. (B)HR-SEM of the cross section of the TiO2 nanosheets film alone[37].

Liu and Kelly (2013) reported on the use of a thin film of ZnO nanoparticles as an electron-transport layer in CH3NH3PbI3-based solar cells. In contrast to mesoporous TiO_2, the ZnO layer is substantially thinner and requires no sintering. They took advantage of these facts to prepare flexible solar cells with a V_{oc} of 1.03 V, a J_{sc} of 13.4 mA cm^{-2}, a fill factor of 73.9% and power-conversion efficiencies in excess of 10%. The use of ZnO also results in improvements to device performance for cells prepared on rigid substrates. Solar cells based on this design exhibit power-conversion efficiencies as high as 15.7% when measured under AM1.5G illumination making them some of the highest-performing perovskite solar cells until this day[38].

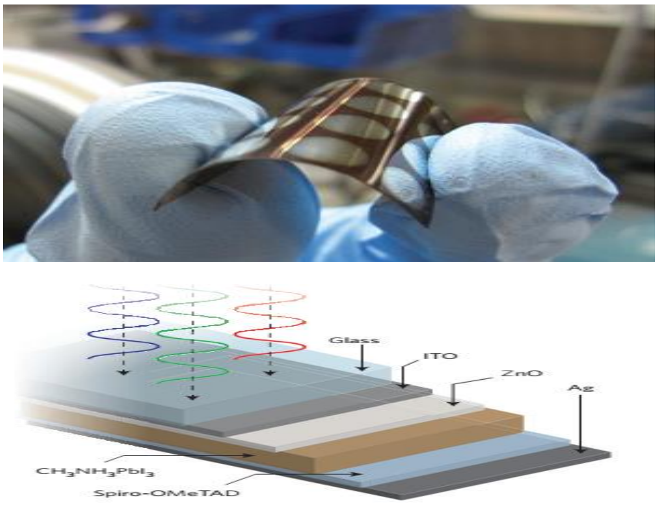
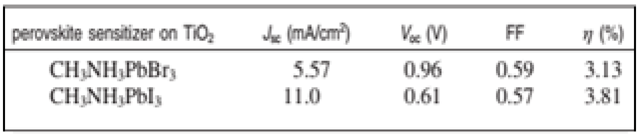


Fig .7. Photograph of an ITO/ZnO/CH3NH3PbI3/spiroOMeTAD/Ag device prepared on a flexible poly(ethylene terephthalate) PET substrate and Device architecture of the ITO/ZnO/CH3NH3PbI3/spiro-OMeTAD/Ag cells tested in this study[38].

Kojima et. al (2009) have studied the photovoltaic function of the organic-inorganic lead halide perovskite compounds CH3NH3PbBr3 and CH3NH3PbI3 as visible-light sensitizers in photoelectrochemical cells. They show a photovoltaic function of the perovskite nanocrystalline particles selforganized on TiO2 as n-type semiconductors and assume that the origin of the high Voc is the bromide employed as a redox partner to couple with the perovskite bromide which electrochemically has more positive potential of bromide compared with iodide which expands the range of photovoltage. Solar energy was converted with an efficiency of 3.8% on a CH3NH3PbI3-based cell, while a high photovoltage of 0.96 V was obtained with a CH3NH3PbBr3 -based cell[39].

Table 1.Measured with an effective incident area of 0.24 cm^2 under 100 mW/cm^2 AM 1.5 simulated sunlight irradiation[39].



perovskite sensitizer on TiO_2	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
$CH_3NH_3PbBr_3$	5.57	0.96	0.59	3.13
$CH_3NH_3PbI_3$	11.0	0.61	0.57	3.81

Burschka et. al. (2013) have prepared mesoporous TiO_2 (anatase) films by spin-coating a solution of colloidal anatase particles onto a 30-nm-thick compact TiO_2 underlayer. The underlayer was deposited by aerosol spray pyrolysis on a transparent conducting-oxide-coated glass substrate acting as the electric front contact of the solar cell. Lead iodide(PbI_2) was then introduced into the TiO_2 nanopores by spin-coating a 462mg ml^{-1} (~1 M) solution of PbI2 in N,N dimethylformamide (DMF) kept at 70˚C. They derive values of 20.0 mA cm^{-2}, 993 mV and 0.73 for Jsc, Voc and the fill factor, respectively, yielding thereby a PCE of 15.0% measured at a light intensity of Pin 5 96.4 mW cm^{-2}[40].

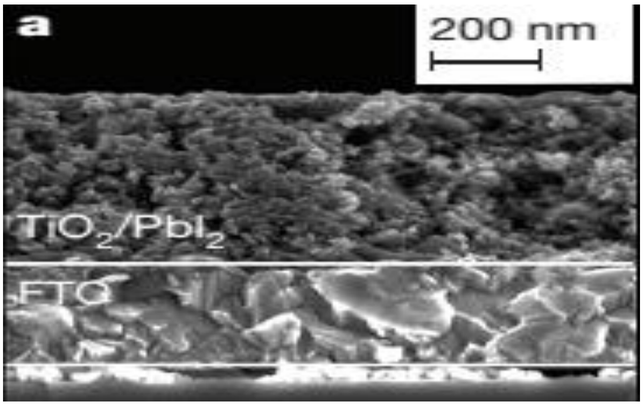


Fig.8. Transformation of PbI2 into CH3NH3PbI3 within the nanopores of a mesoscopic TiO2 film. a,Cross-sectional SEM of a mesoporous TiO2 film infiltratedwith PbI2.FTO, fluorine dopedtinoxide[40].

According to Aharon et. al (2014), a synthesis of CH3NH3PbI3 on the TiO_2 surface was carried out by a two-step deposition technique, but with several modifications. At the beginning, PbI_2 was dropped onto the TiO_2 film and spin-coated after various waiting time periods (1 min, 1.5 min, 3 min, or 5 min) followed by annealing at 70 ˚C for 30 min. In the second step, the cell was dipped into 10mg/ml of CH3NH3I solution at 70 1C for 20 s, and then annealed at 70 ˚C for another 30mins.During the dip and annealing, CH3NH3PbI3 was formed, indicated by the dark brown color of the electrode. Finally, the back contact was deposited by evaporating 50 nm of gold under a pressure of 5×10^{-6} Torr. The active area was 0.09 cm^2. The best PCE Device achieved was 10.85% with a Voc of 0.84 V, a FF of 68% and a Jsc of 19 mA cm^{-2} [41].

Docampo et al. (2014) show that the perovskite crystal orientation can be modified by the temperature of the immersion solution, and they found out that a high degree of oriented crystals is necessary for efficient operation. The device architecture for planar heterojunction perovskite solar cells used in this study is composed of $FTO/TiO_2/MAPbI_3$/Spiro-OMeTAD/Au. The TiO_2 layer is non-porous and acts as the electron selective contact, while spiro-OMeTAD is used as the hole collecting contact. The perovskite film was deposited via a two-step deposition/conversion process, wherein a layer of PbI_2 was first deposited via spin-coating, followed by conversion to the perovskite phase in the second step through immersion in a solution of methylammonium iodide and chloride in isopropanol at varying temperature degrees. However, devices fabricated at lower temperatures exhibit much lower short circuit currents than those fabricated at higher temperatures. For example, at 30 ◦C, the short circuit current approaches 19 $mAcm^{-2}$, while at 60 ◦C this value exceeds 22 $mAcm^{-2}$. Correspondingly, the device efficiency for 60 ◦C is the highest in this set of experiments, standing at 14.3% [42].

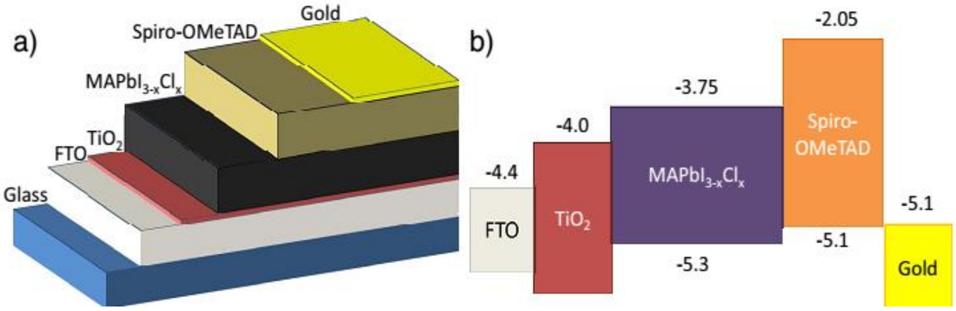


Fig. 9. (a) Schematic of the device architecture. (b) Energy level diagram with respect to vacuum for all the layers comprising the solar cell (numbers in eV) [42].

VII. CONCLUSION

In general, the photoanode is a thin porous film of metal oxide semiconductor supported on to a transparent conducting oxide (TCO) glass . there are several requirements to be met by the photoelectrode material such as : (1) it must be transparent and have high surface area for light harvesting; (2) it should have high charge carrier mobility and charge recombination resistance for more efficient photoelectron collection;Extensive research in this field has revealed the photophysics of semiconducting electrodes like titanium dioxide TiO2 and ZnO. Recently perovskite solar cell have emerged as a new class of light absorbers, achieving exceptional progress in solar cell performance.(TiO2) is the most common n-type semiconductor used as photoanode in perovskite solar cell because of its chemical stability, ability to moderate charge transport and ease of syntheis process. Also TiO2 is a relatively cheap, abundant, nontoxic, biocompatible. The perovskite solar cell technologies, TiO2 photoanodes are attractive options due to their ease of syntheis process and availibility. The performance of photoanodes depends on the TiO2 nanostructures including properties of the TiO2 such as particle size and morphology crystallinity, phase content, chemical composition (doping) , which have been extensively studied and shown to have a significant effect on the overall perovskite solar cell efficiency. In this review, we elaborate on the detail mechanism of TiO2 photoanode and the effect of its incorporation in perovskite solar cells. Dssc nowday are widly regarded as the promossing third gerenration of the PV solar technology. These solar cells can be considered the closest mankind has come to replicating nature’s photosynthesis.

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