The Effect of Photoanode TiO$_2$/ZnO Ratio in Perovskite Solar Cell and Its Photosensitivity and Solar Cell Performance

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Abstract. Perovskite Solar Cell (PSC) CH$_3$NH$_3$PbI$_3$ has attracted interest due to a high potential for cheap and high-efficiency solar cell. The PSC mainly consists of three components that are an electron transporting material (ETM), perovskite layer, and hole transport material (HTM). The ETM layer quality plays an important role for electron transport, acts as a selective collection of electron and hole blocking layers that have an important influence on photovoltaic performance. TiO$_2$ and ZnO are the most common materials used in ETM. TiO$_2$ has a good photo activity, high stability, and non-toxicity. Meanwhile, ZnO has good anti-reflecting properties that make electron more easy to transfer from valence band to conduction band. In this research, the formation of TiO$_2$ and ZnO was composited as ETM to combine the advantages of both with the variations of TiO$_2$/ZnO mass ratio. The ETM films were synthesized by screen printing methods, whereas the perovskite layer and HTM of Cu$_2$O were coated by spin coating and chemical bath deposition (CBD) respectively. The samples were characterized by XRD and UV-Vis spectrometer. The photosensitivity and solar cell performance were measured by electrometer and solar simulatores. The TiO$_2$/ZnO composition of ETM showed a different efficiency and photosensitivity. The sample with higher TiO$_2$ indicated stable photosensitivity but less in the solar cell efficiency and vice versa.

Keywords: TiO$_2$, ZnO, PSC, ETM, HTM, photodetector

1. Introduction
The availability of fossil fuels used for most electricity sources is currently running low. Therefore, many researchers have been interested in developing renewable energy sources. One of the renewable energy sources is solar energy that can be converted to electricity by photovoltaic device [1]. Photovoltaic devices are semiconductor materials consisting of n-type and p-type allowing electron and hole flow (current) by sunlight photon absorption [2]. The most well known solar cell is a silicon-based solar cell, but its disadvantages are high cost, rigid, and low-efficiency [3]. Recently, perovskite solar cell (PSC) that has a great interest is perovskite solar cells (PSC) due to one of the most promising candidates for obtaining cheap; it can be grown on flexible substrate, transparent and easy fabrication [4,5]. PSC has attracted much attention of photovoltaic technology in recent years [6]. This is based on the capability of the solution process, high carrier mobility, good optical properties, and large absorption.
coefficients [7]. Organic-inorganic perovskite (hybrid perovskite) halide hydrides have developed rapidly over the last few years with exceptional performance [8]. The material is essentially a liquid so that the manufacture of the solar cell can be a simple method such as spin coating or dip coating.

A hybrid perovskite solar cell has the potential to offer low-cost solar energy conversion. In general, hybrid perovskite contains particularly of methyl (M), ammonium (NH$_3$), a metal such as Sn or Pb, and halide (Cl, Br, and I). This perovskite is suitable for solar cells due to the bandgap in the range of 1.3 eV to 2.9 eV, and the band gap can be tuned by using different metal ions, halide cations, and doping in both[4]. In the PSC architecture, the compact layer quality plays an essential role in the transport of electrons in perovskite devices [9]. The compact layer acts as a selective collection layer of electrons and a blocking layer of holes in solar cells that have an essential influence on the performance of photovoltaics [10,11]. Now, many attentions are focusing on electron transport layer materials to obtain films with high carrier mobility, suitable conduction bands and good compact morphology [6].

In general, PSC consists of three parts of layers which include ETM, perovskite, and HTM. The criteria of ETM are having good electron mobility, a wide bandgap, and compatible energy levels of both conduction band minimum (CBM) and valence band maximum (VBM) with perovskite [12]. Several electron transport layers (ETM) have been studied such as TiO$_2$ and ZnO [11,13]. TiO$_2$ has an electron mobility of 1 cm$^2$/V.s with a CBM of 4.2 eV which is relatively 0.3 eV lower than the perovskite. Therefore, TiO$_2$ is an efficient hole-blocking ability which facilitates the injection of photogenerated electrons from a perovskite light absorber to ETM. ZnO has electron mobility higher than TiO$_2$, that is 200 cm$^2$/V.s. The CBM of ZnO is also higher than TiO$_2$ but still lower than perovskite light absorber; hence ETM of ZnO is expected to have high efficiency of electron extraction and electron transport [12]. The combination of ZnO/TiO$_2$ might have the advantage of both ETM. However, the study of TiO$_2$/ZnO composite as ETM is rarely reported. Therefore, In this study, we investigated the TiO$_2$/ZnO ratio to the performance of photosensitivity and solar cell. The hole transport material (HTM) used in this PSC was Cu$_2$O synthesized by chemical bath deposition.

2. Methods

2.1. Materials
TiCl$_3$, HCl, distilled water, NH$_3$, zinc acetate dihydrate, NaOH, Na$_2$S$_2$O$_3$, PEG 6000, sodium dodecyl sulfate (SDS), Asethyl acetone, CuSO$_4$, DI water, ITO glass.

2.2. Methods

2.2.1. TiO$_2$ powder synthesis
The TiO$_2$ powder was synthesized by co-precipitation method from TiCl$_3$. 10 ml of TiCl$_3$ and 0.3 ml of HCl were dissolved in 4.7 mL distilled water then stirred for 5 minutes. It was added with 30 ml HCl 32% and stirred for 10 minutes then dropwised slowly by 180 ml of NH$_3$ and the TiO$_2$ solution was formed. The solution was left for 24 hours to form a precipitate. The residue was then washed by distilled water until the pH became neutral and filtered. The TiO$_2$ powders were heated at 100 °C and annealed at 450 °C for 2 hours.

2.2.2. ZnO powder synthesis
Zn acetate powder was dissolved in distilled water and stirred until homogenous. NaOH 3M was added slowly to the solution until the pH 13, and the solution became milky. The solution was washed several times by distilled water and ethanol and filtered. ZnO powders were heated at 100 °C and annealed at 550 °C for 2 hours.
2.2.3. Screen printing methods
The solution for making TiO$_2$/ZnO paste was prepared by dissolving SDS and PEG 6000 into distilled water and then stirred until homogeneous. In the homogeneous solution, acetylacetone was added, and the solution was stirred until homogeneous. The TiO$_2$/ZnO nanoparticles were then spilled with the prepared solution, and the ETM coating was made by screen printing using an FTO substrate. The TiO$_2$/ZnO film was calcined at 450 °C for 2 hours.

2.2.4. Perovskite synthesis
Perovskite CH$_3$NH$_3$PbI$_3$ solution was made by mixing CH$_3$NH$_3$I powder, PbI$_2$ powder, DMF, and DMSO, and then stirred for 1 hour. The solution was deposited on the ETM TiO$_2$/ZnO layer using a spin coating method. The film was then preheated for 60 seconds at a temperature of 40 °C and heated at 100 °C for 30 minutes.

2.2.5. Cu$_2$O synthesis
Cu$_2$O coating began by heating the first solution of 1M of NaOH at a temperature of 70 °C and then mixing a second solution consisting of 1M of CuSO$_4$ with 1M of Na$_2$S$_2$O$_3$. The FTO substrate was immersed in the first solution and the second solution alternately for 20 s in each solution.

2.3. Characterization
The samples were characterized by means of XRD to know the crystal structure. Uv-Vis was to measure optical properties and bandgap energy. The solar cell performance of PSC was measured by solar simulator with PEC-CEL software.

3. Results and Discussion

3.1. X-ray diffraction pattern
Figure 1 shows the diffraction pattern of ZnO nanoparticles (NPs), TiO$_2$ NPs, and PSC with the variation of the ZnO/TiO$_2$ ratio as ETM. The XRD TiO$_2$ NPs patterns match with the results of previous studies by Lee et al. [14]. The XRD patterns are in accordance with research previously reported by Ahamed et al. [15]. The peak intensity of ZnO was higher compared to TiO$_2$ indicating that the crystallinity of ZnO was better than TiO$_2$. The peaks width of TiO$_2$ was wider compared to ZnO showing that TiO$_2$ NPs had smaller size rather than ZnO NPs although both TiO$_2$ and ZnO were still in the nanometer range. Furthermore, Figure 1 also shows the PSC pattern containing perovskite and ETM layers. The perovskite layer was successfully synthesized by a one-step spin coating method. The XRD pattern of perovskite layer match with the XRD result reported by Fan et al. [16] and showed good crystallinity. The others PSC peaks related to ZnO or TiO$_2$ and no impurities phases were observed from XRD Patterns.
Figure 1. X-Ray diffraction patterns of ZnO NPs, TiO$_2$ NPs, and PSC with the variation of TiO$_2$/ZnO ratio as ETM

3.2. UV-Vis measurement
The Absorbance and bandgap energy of PCS are shown in Figure 2. All samples had the peak at the wavelengths below 400 nm which were the peaks of TiO$_2$ and ZnO. Thus, the results are in accordance with the previous report by Rao (2016), where the peak of TiO$_2$ shown at 354 nm [17] and ZnO had the peak at 366 nm [18] which means that it exhibited a good absorbance at UV region [19]. The absorbance and wavelength were then converted to $(\alpha h\nu)^2$ and $h\nu$ to calculate the bandgap energy using touch plot method [20]. The bandgap showed the energy separation between the highest energy orbitals that had free electron pairs (HOMO) and the lowest energy to excite electrons (LUMO) which was analogous to the valence band and conduction band. The bandgap energy of PSC at different TiO$_2$/ZnO (TZ) mass ratios are as follow: TZ 1:0 was 3.15 eV, TZ 0:1 was 3 eV, TZ 1:1 was 3.25 eV and TZ 1:3 was 3.05 eV. These bandgaps are related to ZnO bandgap [20]. In this study, the bandgap of perovskite was not clearly observed where the ideal bandgap value of perovskite layer was about 1.3 to 1.4 eV as reported by Yang et al. [4].
Figure 2. Optical properties of the PSC with the variation of TiO\textsubscript{2}/ZnO ratio

3.3. Solar simulator

Figure 3 shows the graph of current versus voltage (J-V) of PSC with the variation of TiO\textsubscript{2}/ZnO ratio. The J-V measurement was performed by a solar simulator with the PECCELL software using LED lights with an intensity of 173.206 W/m\textsuperscript{2}. The PSC samples combined with Cu\textsubscript{2}O film were coated in ITO substrate as HTM materials to be complete device solar cell. The performance of solar cell could be extracted from J-V curve by using by nonlinear fitting with Equation 1. Based on this equation, the efficiency of solar cell was affected by several parameters such as short circuit current density ($J_{SC}$), open circuit ($V_{OC}$) voltage, and fill factor (FF).

$$\eta = FF \frac{V_{OC}J_{SC}}{P_{in}}$$ (1)

The efficiency was proportional to $J_{SC}$, $V_{OC}$, fill factor, and inversely to the Input power ($P_{in}$). Therefore, the higher $J_{SC}$, $V_{OC}$ and fill factor would give high-efficiency value. The parameter of PSC with the variation of TiO\textsubscript{2}/ZnO ratio is summarized in Table 1. The efficiency of PCS samples is affected by the composition of TiO\textsubscript{2}/ZnO. The PSC sample with the composite of TiO\textsubscript{2}/ZnO had a greater efficiency compared to PCS sample without TiO\textsubscript{2}/ZnO composite. The samples of TZ 1:1 and TZ 1:3 showed that the greater ZnO had the greater efficiency due to the greater $J_{SC}$ and fill factor.
Figure 3. J-V curve of perovskite solar cell with the variation of TiO$_2$/ZnO ratio of: a) TZ 1:0, b) TZ 0:1, c) TZ 1:1, d) TZ 1:3

Table 1. The parameters PSC with the variation of TiO$_2$/ZnO ratio

| Parameter  | TZ 1:0 | TZ 0:1 | TZ 1:1 | TZ 1:3 |
|------------|--------|--------|--------|--------|
| $I_{sc}$/mA | 0.06   | 0.03   | 0.05   | 0.07   |
| $J_{sc}$/mA cm$^{-2}$ | 0.03   | 0.03   | 0.05   | 0.07   |
| $V_{oc}$/V   | 1.64   | 2.02   | 3.72   | 1.90   |
| Fill Factor | 0.31   | 0.45   | 0.31   | 0.47   |
| Efficiency/% | 0.17   | 0.29   | 0.53   | 0.60   |
| $P_{max}$/mW | 0.03   | 0.03   | 0.05   | 0.06   |
| $I_{max}$/mA | 0.03   | 0.02   | 0.03   | 0.05   |
| $V_{max}$/V  | 1.10   | 1.84   | 1.77   | 1.12   |
| $R_s$/ohm    | 12736.79 | 23884.98 | 11940.21 | 1492.50 |

3.4. Photoresponse
Hybrid perovskite has a good optical and electronic properties, so this material is a promising candidate for Photodetectors (PDs) [21]. In this study, the photodetector performance was investigated by applying on/off light irradiation and measuring the current using electrometer. The stability of photosensitivity was investigated by switching on and off at every 20 second interval times. The PSC samples combined
with Cu$_2$O films were coated on ITO substrate as HTM. Figure 4 shows the time dependence of photocurrent in applying on/off light irradiation. The PSC sample with pure TiO$_2$ showed better and stable photosensitivity rather than others PSC samples. Whereas, the PSC sample containing ZnO showed decreasing photosensitivity by increasing time and switch on/off cycling. Therefore, PSC sample with TiO$_2$ is a good candidate for the photodetector.

**Figure 4.** Photosensitivity of PSC samples with the variation of TiO$_2$/ZnO ratio

4. Conclusion
The ETM films with the variation of TiO$_2$/ZnO ratio have been successfully synthesized by a screen-printing method. The XRD result showed that PSC samples had perovskite phase in combination with TiO$_2$ or ZnO phase, and no impurities phase was observed. The bandgap of the PSC samples was between 3 eV to 3.25 eV originated from TiO$_2$ or ZnO. The PSC sample with the higher ZnO had a good solar cell performance but less photosensitivity. In contrast, The PSC sample with the higher TiO$_2$ had good and stable photosensitivity but less in solar cell performance. In general, the low solar cell efficiency is due to the instability of the perovskite structure. The PSC sample with TiO$_2$ as ETM is a good candidate for the photodetector.

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