An Effective TiO₂ Blocking Layer for Perovskite Solar Cells with Enhanced Performance

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High performance perovskite solar cells (PSCs) based on organolead halide perovskite CH$_3$NH$_3$PbI$_3$ were fabricated by employing magnetron sputtered TiO$_2$ (MS-TiO$_2$) blocking layer with high compactness. Coating effect of the MS-TiO$_2$ to F-doped SnO$_2$ grains was confirmed by electrochemical analytical tools. 10.23% power conversion efficiency of the solar cell was obtained with the structure of FTO/TiO$_2$ blocking layer/CH$_3$NH$_3$PbI$_3$/P3HT/Ag.

Energy shortage and environment pollution have become the emergent problems around the world in the 21st century. Countries are exploring sustainable and pollution-free new energy sources. Solar cells based on photoelectric conversion technology are effective ways to convert solar energy to energy sources. Solar cells based on photoelectric conversion technology are effective ways to convert solar energy to energy sources.

As a result, attention of researchers was attracted to PSCs in the past two years. Recently, Seok group have certified the practical application. In 2009, Miyasaki group adopted CH$_3$NH$_3$PbI$_3$ to act as the sensitizer, and invented a novel structure of solar cells, dye-sensitized solar cells (DSSCs). The dye played a key role in the structure, serving as the light-absorber and then producing excited photoelectrons. In recent years, Yamashita and Hua groups developed new types of dyes and enhanced the ability of light absorbing, and therefore the performance of DSSCs was improved. However, the range of light absorbance of the dyes is still narrow. The power conversion efficiency (PCE) of the devices is consequently limited. In 2014, DSSCs got the highest PCE of 13% after the development for more than 20 years. The relatively low PCE of large area DSSC modules is still a big obstacle for the industrial application.

In 2009, Miyasagi group adopted CH$_3$NH$_3$PbI$_3$ to act as the sensitizer in DSSCs-like solar cells and got the PCE of 3.8%. Then, Park group developed the device of perovskite solar cells (PSCs). The device was based on the organic lead halides or mixed halides perovskite, e.g., CH$_3$NH$_3$PbI$_3$ or CH$_3$NH$_3$PbI$_3$Cl$_3$. Soon after, Grätzel and Snaith groups developed the fabrication processes of PSCs with different methods and promoted the PCE to about 15%, respectively. As a result, attention of researchers was attracted to PSCs in the past two years. Recently, Seok group have certified the PCE of 20.1% for PSCs. Additionally, about the reproducibility of the cell fabrication process, Wakamiya et al. identified the crucial role of the water content in the starting material of PbI$_2$. PSCs have shown their prospect towards the practical application.

In the structure of PSCs, compact TiO$_2$ blocking layers are indispensable and play critical roles in preventing the carrier recombination at the interface of fluorine doped tin oxide (FTO) and perovskite layer and avoiding short-circuit. So, high quality TiO$_2$ blocking layers contribute significantly to the reduction of carrier recombination. As far as we know, atom layer deposition (ALD) conducting in a layer-by-layer style, can provide a compact TiO$_2$ layer acting as high quality blocking layer. However, the thermal post-treatment on ALD layers might lead to thermal shrinkage and leave electronic pinholes. The costly equipment is also prohibitive to the large-scale application. Spray pyrolysis is widely used in solid-state DSSCs for the deposition of TiO$_2$ blocking layer, but a high temperature is required. Consequently, the process is relatively energy-consuming. Sol-gel method truly provided convenience for the preparation of the blocking layer, and 15.9% PCE was obtained with a low-temperature TiO$_2$ nanoparticles sol. However, it is difficult to avoid pinholes in the surface of the blocking layer. Therefore, new methods are required to satisfy the needs of easy access and pinhole-free compact TiO$_2$ blocking layer. Magnetron sputtering method provided a balanced approach to fabricate compact TiO$_2$ blocking layer and lowered the cost, which showed great potential for large-scale application. The method exhibits a similar process as ALD and spray pyrolysis for TiO$_2$ nanoparticles, being compact to coat on F-doped SnO$_2$ grains of FTO layer. Ke et al. sputtered Ti nanoparticles and then thermally oxidized them to TiO$_2$ nanoparticles. The approach provided inspiration for high performance and low-cost blocking layer. However, the thermal oxidation process might cause the residues of Ti nanoparticles, and consequently increase the recombination of charges.

In the letter, we employed TiO$_2$ target to achieve an excellent TiO$_2$ blocking layer. The as-prepared TiO$_2$ nanoparticles were coated on the surface of F-doped SnO$_2$ grains of FTO layer compactly. Then the magnetron sputtered TiO$_2$ blocking layer was introduced to fabricate high performance PSCs with the structure of FTO/TiO$_2$ blocking layers/CH$_3$NH$_3$PbI$_3$/P3HT/Ag. For comparison, the blocking layer through titanium isopropoxide sol-gel method was also prepared according to the literature reported method. Surface-smooth and high quality CH$_3$NH$_3$PbI$_3$ thin film was synthesized via subliming-assisted in situ gas-solid reaction method.

Figure 1 shows the X-ray diffraction (XRD) pattern of the as-prepared CH$_3$NH$_3$PbI$_3$ thin film. It indicates a high crystallinity with featured peaks at 14.12°, 28.44°, 31.88° and 43.23°, which are highly consistent with that reported by Chen.

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et al.22 There is a weak peak at 12.6°, indicating some impurity of PbI₂ due to the decomposition of CH₃NH₂PbI₃ during annealing.23

Figure 1. XRD pattern of the as-prepared CH₃NH₂PbI₃ thin film.

Field emission scanning electron microscopy (FE-SEM) is used to characterize the surface morphology of CH₃NH₂PbI₃ thin film, as is shown in Figure S1. Highly compact perovskite thin film is composed of large nanoparticles with sizes of 150-500 nm. The grain boundaries are largely eliminated. Consequently, the separation of electrons and holes becomes easier than that of the solution methods with rough surface24 and rich grain boundaries.25 Thus, the charge recombination rate is lowered to some extent.

Figure 2. Top-view ((a), (b)) and cross-section ((c), (d)) FE-SEM images of TiO₂ blocking layers prepared by magnetron sputtering (MS-TiO₂) and sol-gel (SG-TiO₂) methods, respectively, (The black circle stands for the gap at the valley between FTO layer and TiO₂ blocking layer), and (e) schematic diagram of the transportation processes of electrons in the MS-TiO₂ and SG-TiO₂ blocking layers.

Figure 2 is the top-view and cross-section FE-SEM images of the TiO₂ blocking layers prepared by magnetron sputtering method (MS-TiO₂, (a) and (c)) and sol-gel method (SG-TiO₂, (b) and (d)), respectively. For the cross-section images, CH₃NH₂PbI₃ thin films were deposited on the blocking layers. Obviously, MS-TiO₂ nanoparticles present a good coating property to F-doped SnO₂ grains. Even in the valleys between F-doped SnO₂ grains, MS-TiO₂ nanoparticles are also filled, leaving no gap, as is shown in Figure 2(a). The thin TiO₂ layer replicates the morphology of the underlayer FTO substrate. Therefore, direct and full-range contact between MS-TiO₂ and F-doped SnO₂ grains contributes greatly to the fast and effective transportation of electrons, resulting in the so-called “coating effect”. As a result, the charge collection capability enhances substantially with the MS-TiO₂ blocking layer. For the SG-TiO₂ blocking layer, a flat surface is also exhibited on the surface of FTO glass. However, TiO₂ nanoparticles just spread on the surface of FTO glass, leaving unfilled interstices among F-doped SnO₂ grains. The bad contact between SG-TiO₂ particles and FTO substrate can be found in Figure 2(d) (the black circle). The large gaps at the valleys of F-doped SnO₂ grains prolong the transportation distance of electrons to some extent, which is harmful to the charge collection. In Figure 2(e), the schematic diagram of the transportation processes of electrons along the cross-section also depicts the issue.

Figure 3. (a) Schematic diagram of the Tafel test mold, the electrode was immersed in the 0.1M I⁻/I³⁻ electrolyte, (b) Tafel plots of FTO layers/TiO₂ blocking layers (the square stands for the MS-TiO₂ blocking layer, and the circle stands for the SG-TiO₂ blocking layer), (c) Schematic diagram of the home-designed test mold for electrochemical impedance spectrum (EIS), and (d) Nyquist plots of the MS-TiO₂ and SG-TiO₂ blocking layers (A and B in the Nyquist plots were due to the flaw of the test equipment at the given frequency).

We then characterize the electrochemical properties of the MS-TiO₂ and SG-TiO₂ blocking layers. Figure 3(a) is the schematic diagram of the Tafel test. Tafel plots of the FTO layers/TiO₂ blocking layers are described in Figure 3(b). We can find that MS-TiO₂ blocking layer shows a higher potential than that of SG-TiO₂ blocking layer because of MS-TiO₂ blocking layer combining with F-doped SnO₂ grains compactly. However, for FTO layer/SG-TiO₂ blocking layer, the gaps at the valleys between F-doped SnO₂ grains serve as the active sites for the back reaction of electrons. Therefore, a part of the electrons participate in the reaction and the charge collection is hindered. As a result, the performance of the SG-TiO₂ blocking layer is decreased.
Figure 3(c) diagrams the home-designed test method of electrochemical impedance spectrum (EIS) of MS-TiO2 and SG-TiO2 blocking layers. Resistance of SG-TiO2 blocking layer is definitely larger than that of MS-TiO2 blocking layer. As a result, the transportation obstacle of electrons between the MS-TiO2 blocking layer and the FTO substrate is eliminated and the lifetime of electrons is prolonged. 

Figure 4. I-V curves of PSCs with MS-TiO2 (red circle), and SG-TiO2 (black square) blocking layers. The masked active area is 0.159 cm².

In Figure 4, the photovoltaic properties of CH3NH3PbI3-(P3HT). The photoelectric performance of the MS-TiO2 to F-doped SnO2 grains, leading to better charge collection. The PCE of the MS-TiO2 blocking layer-based PSCs is 10.23%, compared to 7.42% of the SG-TiO2 blocking layers. Resistance of SG-TiO2 blocking layers is definitely larger than that of MS-TiO2 blocking layer. As a result, the transportation obstacle of electrons between the MS-TiO2 blocking layer and the FTO substrate is eliminated and the lifetime of electrons is prolonged. 

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References and Notes
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