Modern Physical Chemistry Research (2024)
Clausius Scientific Press, Canada

DOI: 10.23977/mpcr.2024.040112
ISSN 2616-1702 Vol. 4 Num. 1

Research Progress on Modified-Titanium Dioxide Electron Transport Layers in Perovskite Solar Cells

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Keywords: Perovskite solar cells (PSCs), Titanium dioxide (TiO_2), Doped, Modified

Abstract: Perovskite solar cells (PSCs) have emerged as the most promising solar cells due to their high efficiency and environmentally friendly characteristics. Additionally, titanium dioxide (TiO_2), with its excellent properties, has become the optimal choice for the electron transport layer (ETL) in perovskite devices. However, issues such as energy level mismatch between TiO_2 and perovskite light-absorbing materials have limited the efficiency of these devices. Therefore, this review primarily introduces the application of TiO_2 in PSCs and discusses the use of modified TiO_2 as ETL in perovskite devices. Finally, the existing problems and future research directions of TiO_2 in PSCs are proposed.

1. Introduction

Since the beginning of the 21st century, with industrial development, the issues of energy shortages and environmental pollution have become increasingly severe. Renewable clean energy has gradually attracted people's attention. Solar energy, as an inexhaustible and endlessly available green energy source, has extremely high application prospects. Therefore, developing high-efficiency, low-cost, and long-term stable solar cells is a current research hotspot.

In recent years, perovskite solar cells (PSCs) have gradually replaced organic photovoltaics and dye-sensitized cells due to their advantages, such as high light absorption coefficient, good charge mobility, and tunable direct bandgap. PSCs have become one of the most promising types of solar cells for future development.

In PSCs, the properties of the electron transport layer (ETL) exert a significant influence on the structure and electrical performance of PSC devices. Titanium dioxide (TiO_2) is an important material widely used in ETLs; however, due to its mismatched conduction band offset, it hinders electron extraction and transport between the perovskite film and the ETL, and its electron mobility is not high enough. These drawbacks affect the long-term stability of PSCs and limit the further improvement of device efficiency. Therefore, enhancing the performance of TiO_2 as an ETL to develop more efficient PSCs has become a current research focus. This article introduces the research status and progress of modified TiO_2 ETL applied in PSCs.

2. Application of TiO_2 in PSCs

PSCs are third-generation solar cells that utilize perovskite-type organic metal halide semiconductors ($MAPbX_3$) as the light-absorbing material. The prevalent transparent conductive electrodes in conventional (n-i-p) type PSCs are ITO and FTO. The perovskite material is deposited on the ETL, the hole transport material is deposited on the perovskite material, and finally, a metal electrode is plated on top.

The ETL is a crucial component in PSCs, primarily forming an interface with the perovskite layer. It receives electrons transferred from the perovskite layer and efficiently blocks holes. Electron transport materials (ETMs) are typically n-type semiconductor materials with high electron affinity and ionization potential. For effective PSCs, the ETL should have a good energy level alignment to facilitate effective charge transfer and hole blocking. Its conduction band minimum should be lower than that of the perovskite material to facilitate electron reception and transport to the transparent conductive electrode. Charge transfer between the perovskite material and the ETM occurs through a mechanism involving directional drift of electrons and holes due to the internal electric field and scattering caused by thermal excitation in inorganic semiconductors.

For n-i-p structured PSCs, metal oxides are the most commonly used choice for ETLs, with TiO_2 being the preferred material due to its excellent electrical properties. The first PSCs using TiO_2 as a photoelectrode were successfully fabricated in 2009, achieving an efficiency of only 3.8%. However, with continuous optimization of TiO_2, its certified efficiency has now reached 25.02%, and it is expected to improve further in the future.

3. Common Methods for Preparing TiO_2 Films

The commonly used methods for preparing TiO_2 films mainly include the sol-gel method, chemical vapor deposition (CVD), and magnetron sputtering [1-5].

(1) Sol-Gel Method

The sol-gel method, proposed by French chemist J.J. Ebelmen in 1846 based on the principle of polycondensation reactions, is a commonly used technique for preparing TiO_2 films. This method can effectively control the hydrolysis and polycondensation reactions to form a stable sol system. Then, by using spin coating or spraying methods, a layer of sol is applied to the substrate surface, followed by drying and heat treatment to produce TiO_2 films. The sol-gel process is based on the formation of sol and gel through typical reactions, represented by the following equations:

$$Ti(OR)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4ROH \tag{1}$$

$$Ti(OH)_4 + Ti(OR)_4 \rightarrow 2TiO_2 + 4ROH \tag{2}$$

$$2Ti(OH)_4 \rightarrow 2TiO_2 + 4H_2O \tag{3}$$

$$Ti(OC_4H_9)_4 + 2H_2O \rightarrow 2TiO_2 + 4C_4H_9OH \tag{4}$$

The traditional sol-gel method involves the hydrolysis and polycondensation of inorganic or metal alkoxides to form a solid oxide or other compound after solution, sol, and gel formation followed by heat treatment. For the preparation of TiO_2, this mainly involves the hydrolysis and polycondensation of titanium (IV) butoxide. This method requires precise chemical control and a long reaction process.

(2) Chemical Vapor Deposition (CVD)

CVD involves retaining volatile substances in a solid state on the sample surface under high-temperature conditions. The advantage of this method is the high crystallinity and strong stability of the prepared films. However, the reaction conditions require high temperatures, which can lead to energy waste.

(3) Magnetron Sputtering

Magnetron sputtering is an important physical preparation method. In this process, gas is ionized in an electromagnetic field, producing charged particles that bombard the target, causing it to sputter and adhere to the substrate, forming a thin film. This method is widely used for material surface modification due to the uniform thickness of the films produced.

4. Application of Modified TiO_2 as ETL

TiO_2 is currently one of the most commonly used ETMs, but its application in perovskite ETLs is limited due to its strong absorption of ultraviolet light, significant oxidative effect on perovskites, and relatively low electron mobility. Therefore, doping and modifying pure TiO_2 has become a major focus of research for many scientists. Advanced preparation techniques and metal doping can effectively enhance the optical properties and conductivity of TiO_2, as well as improve the compatibility between ETL and the light-absorbing layer.

Xiao et al. prepared TiO_2 nanorod arrays using a hydrothermal method, and the resulting PSCs exhibited a maximum photoelectric conversion efficiency (PCE) of 15.93%[6]. Yella et al. used a chemical bath deposition method to prepare TiO_2-based ETLs for PSCs, achieving an optimized PCE of 13.7%[7]. Md. Shahiduzzaman et al. employed electrostatic inkjet printing to deposit TiO_2 as an ETL, achieving a PCE of 13.19% under low-temperature processing, which suggests the potential for fabricating low-temperature processed perovskite devices[8]. Wang used a sol-gel method, adding titanium acetylacetonate as a titanium source and acetic acid to adjust the pH, followed by annealing at 150 ℃ to create a dense TiO_2 ETL, achieving a PCE of 15.5%[9]. Patricia S.C. Schu Lze employed electron beam evaporation to process the TiO_2-dense layer and UV treatment for the mesoporous layer, ultimately obtaining a PCE of 18.2%[10]. Li et al. proposed a solvothermal method based on a ketone-HCl system to adjust the quality of TiO_2 nanorod array films, resulting in a device efficiency of 18.22%. This structure avoids direct contact between the TiO_2 nanorods and the hole transport layer (HTL) [11].

Doping semiconductors with metal ions of different valence states can enhance their optical properties and alter the positions of the conduction band and valence band, enabling electrons and holes to be transported in their respective matched bands [12]. However, the effects of doping with different metal ions vary. Some dopants can form lattice traps that suppress ineffective recombination, while others may accelerate recombination. Only metal ions whose electronic structures and ionic radius match the crystal structure and electronic system of TiO_2 can have a positive impact when used as dopants.

Zhou et al. used yttrium-doped c-TiO_2 as the ETL in PSCs, which promoted charge extraction at the ETL interface [13]. In 2016, Gao et al. prepared La^{3+}-doped TiO_2 ETL, showing that La^{3+} doping improved the device's voltage and fill factor (FF) and reduced series resistance [14]. Since then, metal doping modification of TiO_2 has become increasingly popular. In 2017, Liu D et al. used Li-doped TiO_2 as the ETL, resulting in a 2.9% efficiency increase. Li doping passivated surface defects in TiO_2, increased its conductivity, and significantly reduced electron trap density without negatively affecting optical properties[15]. Also, in 2017, the Institute of Atomic and Molecular Physics at Jilin University used La-doped TiO_2 as the ETL. La doping made the TiO_2 film surface smoother, inhibited particle agglomeration, reduced interface charge transfer resistance, and effectively increased recombination resistance, improving efficiency by 4.8%. In 2018, Sidhik et al. used Co-doped TiO_2 as the ETL, which exhibited lower charge transfer resistance and a matching work function, resulting in a 3.24% efficiency increase [16]. That same year, Shuo Wang et al. used Ru-doped TiO_2 as the ETL, finding that the low carrier transport rate in undoped TiO_2 led to low overall device efficiency, which improved by 3.52% after modification [17]. In 2018, Shih-Hsuan Chen et al. studied Ag^{+}-doped TiO_2 as the ETL, showing that Ag^{+} doping optimized the band structure between the ETL and the perovskite layer, increasing efficiency by 3.41% compared to undoped TiO_2 [18]. Also in 2018, Xiaotao Liu's research group used Zn^{2+}-doped TiO_2 as the ETL, with various characterizations showing that Zn^{2+} could elevate Fermi level and reduce carrier loss, resulting in a 4.21% increase in PCE [19]. In

2019, Xu et al. used Ce^{3+}-doped TiO_2 as the ETL, demonstrating that Ce^{3+} doping facilitated electron transport at the perovskite layer interface, improving device efficiency by 5.75% [20]. In 2020, Yoshitaka Sanehira et al. used Nb-doped TiO_2 as the ETL, finding that Nb doping effectively improved the conduction band gap of TiO_2 and increased the conversion efficiency of perovskite devices [21]. In 2022, Xiamen University of Technology prepared 1.5 mol% Ta-TiO_2 ETL using atomic layer deposition, achieving a PCE of 19.62%. Table 1 summarizes the changes in PCE with different metal-doped TiO_2 as the ETL, indicating that metal doping can effectively alter the photovoltaic conversion efficiency of PSCs.

Table 1: Change in PCE after Doping TiO_2 with Different Elements.

Dopped Element	TiO_2 Preparation Method	Pure TiO_2 PCE	ModifiedTiO_2 PCE
Li-TiO_2	Spray Pyrolysis Deposition	14.2%	17.1%
La-TiO_2	Spray Pyrolysis Method	12.4%	17.2%
0.3mol%Co-TiO_2	Sol-Gel Method	14.92%	18.16%
Ru-TiO_2	One-Step Spray Pyrolysis	14.83%	18.35%
1.00mol%Ag-TiO_2	Sol-Gel Method	14.29%	17.7%
4.5mol%Zn-TiO_2	Chemical Vapor Deposition	13.39%	17.6%
0.009mol%Ce-TO_2	Chemical Bath Deposition	10.43%	16.18%
5 mol % Nb-TiO_2	Spray Pyrolysis Method	16.56%	21.3%
1.5 mol%Ta-TiO_2	Atomic Layer Deposition	16.87%	19.62%

5. Conclusion

TiO_2, as a traditional electron transport material, requires comprehensive and extensive research for its modification and enhancement. Identifying suitable elements for doped and modified PCE is a current research focus. In addition to studying the energy level matching of various functional layers in PSCs, the modification process must also consider the material's stability. Ensuring efficiency while exploring large-scale production methods will expedite the commercial application of PSCs. In the future, PSCs are expected to be a prominent direction in the energy sector.

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