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Ordered porous structures and photocathode enhancements in dye-sensitized solar cells

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Abstract. Dye-sensitized solar cells (DSSCs) have garnered significant attention as a promising alternative to traditional silicon-based photovoltaic devices. This paper provides an overview of the latest advancements in DSSCs, with a particular focus on the incorporation of ordered porous structures and improvements in the photocathode material, titanium dioxide (TiO_2). The paper starts by emphasizing the background of DSSCs as renewable energy technology and the challenges associated with enhancing their efficiency. It further explores the application of ordered porous structures in DSSCs, specifically in semiconductor thin films and electrode materials, to enhance their performance. The paper delves into various optimization techniques employed to improve the properties of the photocathode material, TiO_2, including doping strategies and other enhancements. These approaches aim to improve charge transfer kinetics, light absorption, and overall device efficiency. The significance of this paper lies in discussing the potential of ordered porous structures and improved photocathode materials in addressing the limitations of DSSCs and enhancing their overall performance. By providing a comprehensive overview of these advancements, the paper offers insights into future research directions and opportunities for the development of more efficient and cost-effective DSSC.

Keywords: DSSCs, photocathode material, ordered porous structures.

1. Introduction

80% of the energy consumed by human beings comes from the combustion of fossil fuels! The burning of fossil fuels emits harmful gases, pollutants, and CO_2, with excessive CO_2 emissions leading to the greenhouse effect and melting ice caps. Therefore, it is crucial to search for an environmentally friendly, cost-effective, and renewable energy source. Solar energy has tremendous potential in meeting the demand for renewable energy.

Solar cells include first-generation, second-generation, and third-generation solar cells, with the third generation comprising DSSCs and organic photovoltaics, among others. Among them, third-generation solar cells have lower costs and can directly convert light into electricity. However, there is still significant room for improvement due to the short lifespan and low power conversion efficiency (PCE) of DSSCs.

In the DSSC structure, semiconductors undergo three consecutive processes: light absorption, charge separation, and charge collection. Dye sensitizers are excited by light, and an electron is injected into the conduction band (CB) of the photoanode upon illumination. Dyes absorb photons, causing electrons

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(S') in the highest occupied molecular orbital (HOMO) of various dyes to transition into the lowest unoccupied molecular orbital (LUMO), rapidly losing energy and reaching energy levels higher than LUMO, generating a current. When an excited electron is injected into the CB of the photoanode, the sensitizers in the dye undergo reactions [1]. In this process, PE plays a critical role in DSSC, and its material ranges from single TiO_2 nanoparticles to doping TiO_2 with other substances. This paper analyzes the research progress of photoanode materials in DSSCs, starting from the basic structure and working principle of DSSC. It explores the existing challenges in performance optimization and offers insights into the development trends of photoanode materials in DSSCs.

2. Application of ordered mesoporous structures in DSSCs

2.1. Semiconductor thin films based on ordered porous structures

The main function of semiconductor thin films is to load dye sensitizers and transport photo-generated electrons. In general, semiconductor thin films are composed of TiO_2 particles with a size of approximately 20 nm. Ordered porous structures can not only be used as dye sensitizers in semiconductor thin films but also serve as scattering layers, leveraging their excellent optical properties to enhance the utilization efficiency of incident light in solar cell devices.

Using TiO_2 ordered porous structures as scattering layers on the photoanode is an effective method to improve device efficiency. By using a TiO_2 thin film as a substrate and employing a templating method to fabricate TiO_2 ordered porous structures, a dual-layered photoanode is constructed. Compared to alternative approaches, the photovoltaic performance parameters of the battery device are enhanced, effectively increasing the photoelectric conversion efficiency. TiO_2 ordered porous structures, acting as scattering layers, can scatter incident light and exhibit a mirror effect, thereby enhancing the device's response to longer wavelength incident light. Furthermore, there are studies reporting a spectroscopic technique for investigating the electron transport properties in dye-sensitized solar cells based on TiO_2 ordered porous structures, indicating that they can increase electron recombination lifetime and improve electron collection efficiency.

TiO_2 nanotube photonic crystals can also be applied as another type of ordered porous structure in dye-sensitized solar cells. Placing TiO_2 nanotube photonic crystals on the surface of TiO_2 thin films serves the main purposes of Bragg scattering and diffuse scattering, effectively enhancing the capture efficiency of incident light and increasing the short-circuit current density of the battery device.

In dye-sensitized solar cells, TiO_2 order porous structures are intelligently utilized. A typical device structure consists of conductive glass/TiO_2 ordered porous structure/TiO_2 particle thin film, forming a "sandwich" structure. There is a strong interaction between the TiO_2 ordered porous structure and the TiO_2 particle thin film, exhibiting multiple scattering effects on incident light and significant slow light effects, effectively improving the absorption efficiency of the device for longer wavelength incident light. As a result, the short-circuit current density of the battery device based on TiO_2 ordered porous structures is increased by 26%. This study attempted to introduce TiO_2 ordered porous structures on the surface of TiO_2 thin films and investigated their impact on the photovoltaic performance of the battery device. Through reviewing relevant literature, it was found that the photoelectric conversion efficiency of the device based on TiO_2 ordered porous structures is 5.35%, higher than that of the device based on TiO_2 thin film (3.95%), resulting in a 35.4% increase in the photoelectric conversion efficiency. The experimental results demonstrate that TiO_2 ordered porous structures play a significant role in enhancing the photoelectric conversion efficiency of the battery device [2]. Additionally, this study reveals that the ordered nature, pore size, type, and structural parameters such as defects of TiO_2 ordered porous structures all have a certain influence on the incident light.

2.2. Electrodes for sensitized dye solar cells based on ordered porous structures

Platinum is commonly used as an electrode material due to its excellent conductivity and catalytic activity. However, its limited reserves and high production costs have limited its industrial applications. To overcome these challenges, researchers have been exploring cost-effective and highly efficient non-

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platinum electrode materials. Carbon materials, conductive polymers, inorganic compounds (such as sulfides and selenides), and alloy materials (including platinum alloys and cobalt-nickel alloys) are among the non-platinum electrode materials that have been discovered in recent years [3].

Among these materials, sulfur-based compounds have shown several advantages as electrode materials, including low cost, simple preparation methods, and good chemical stability. They have also demonstrated outstanding electrocatalytic performance. Researchers have used reverse constant potential electrodeposition to prepare transparent cobalt sulfide films on conductive glass. By optimizing the pH value of the electroplating solution and the number of electrodeposition cycles, nanoscale sheet-like cobalt sulfide films have been effectively constructed under pH=7.2 conditions [4]. Dye-sensitized solar cells assembled with cobalt sulfide-based electrodes exhibited higher photoelectric conversion efficiency (7.26% compared to 6.94%) compared to platinum-based electrode devices.

In addition, researchers have utilized electrochemical deposition techniques and solvothermal techniques to prepare nickel-based metal-organic frameworks, followed by selenization to obtain NiSe2 films. Testing revealed that $NiSe_2$ exhibited excellent electrocatalytic performance as an electrode and achieved a photoelectric conversion efficiency of 7.63% in the corresponding solar cell devices, surpassing the efficiency of platinum-based electrode devices (7.21%) [5]. Moreover, researchers have used reverse constant potential electrodeposition to prepare S | CoSex and S | NiSex films on conductive glass. By adjusting the S/Se molar ratio in the electrodeposition solution, they optimized the S | CoSex (S | NiSex) films with abundant edge sites and strong electron transfer capabilities, significantly enhancing their electrocatalytic activity. The efficiency of the solar cell devices increased from 6.38% to 7.44% (7.54%) compared to platinum-based electrode devices.

In summary, sulfur-based compounds offer promising electrode materials for dye-sensitized solar cells, featuring advantages such as low cost, simple preparation, and excellent electrocatalytic performance, providing an alternative to replace the noble metal platinum. Researchers have also explored the use of ordered mesoporous structures in electrode materials for dye-sensitized solar cells. Fluorine-doped tin oxide (FTO) ordered mesoporous structures loaded with platinum nanoparticles have shown excellent electrocatalytic activity, improving the efficiency of solar cell devices. Additionally, the use of two-dimensional cobalt sulfide nanocup arrays and ordered mesoporous structures of different materials has demonstrated enhanced photovoltaic performance in dye-sensitized solar cells [6]. These findings highlight the potential and application prospects of ordered mesoporous structures in electrode materials, showcasing their excellent electrocatalytic activity and improved photovoltaic performance in dye-sensitized solar cells.

3. Improvement methods for the photoanode of DSSCs

The DSSC is a third-generation solar cell technology known for its high efficiency and low cost. Among them, the photoanode is one of the core components of DSSC, and its performance directly affects the efficiency and stability of the entire cell. To enhance the performance of DSSC, researchers have been exploring various improvement methods, among which element doping and morphology modification have been proven to be effective strategies.

3.1. Doping with other chemical elements

In the research on metal doping in the photoanode, researchers have found that by doping Cu into mixed-phase TiO_2 photoanodes, the external surface of the photoanode remains unchanged while the porosity increases, accelerating the ability of the dye to absorb electrons. The impact of Cu doping on the performance of DSSC was analyzed, and it was found that the open-circuit voltage, short-circuit current density, and PCE of DSSC all increased with increasing Cu doping concentration. However, as the Cu doping concentration increased, the charge transfer resistance also increased, leading to a decrease in PCE. Therefore, the doping concentration of the metal needs to be determined based on different parameters and should not be excessive or insufficient [7]. Furthermore, researchers also investigated the doping of tin (Sn) into TiO_2. Sn-doped materials with Sn mole fractions ranging from 0.25% to 1% were synthesized using a hydrothermal synthesis method. The study found that the best effect was

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achieved at 0.5% Sn doping, and the efficiency of the photoanode was improved compared to pure TiO_2. Additionally, there have been reports on the synthesis of molybdenum (Mo)-doped TiO_2 nanotube arrays using anodization and magnetron sputtering [7]. It was found that Mo doping reduced the bandgap to 3.16 eV and increased the photocurrent [8]. Dong et al. also doped nickel (Ni) into TiO_2 nanotubes using anodization and prepared DSSC photoanodes through annealing at 550 ℃ [9]. The doped nanotubes showed enhanced light absorption and water splitting capabilities after annealing, facilitating the separation of photo-generated electrons and holes.

Regarding non-metal doping, studies have shown that it does not hinder the electron coupling between Ti atoms and dye molecules, enhancing the adsorption capacity and electron injection efficiency. Fluorine (F) as an excellent dopant has minimal impact on the conduction band gap of TiO_2 and can effectively inhibit electron recombination. In contrast, metal doping can alter the bandgap of TiO_2, enabling it to absorb longer-wavelength light, but the post-doping bandgap change is not significant, and the thermal stability and PCE are lower. Non-metal doping, on the other hand, can enhance photocatalytic activity, increase dye loading, reduce ion recombination, and enhance capacitive performance [10].

Considering the favorable conditions of both metal and non-metal doping, co-doping of metals and non-metals has been proposed to improve thermal stability. Various methods of co-doping metals and non-metals have been reported, such as Cu/N, Cu/S, Al/N, N/S, Ag/S, N/F/S, etc [11]. Co-doping of metals and non-metals can extend the absorption range to visible light, adjust the bandgap energy, and enhance the performance of DSSC [11,12].

3.2. Modification of the morphology of the photoanode

Nanostructured TiO_2 can be achieved with various nanostructures, including nanowires, nanotubes, nanorods, and hollow spheres, by controlling the synthesis conditions and methods. These nanostructures provide direct electron transport pathways, accelerating electron transfer speed, and enhancing charge collection efficiency.

Mesoporous TiO_2 refers to TiO_2 materials with mesoporous structures, which can be single-layered, double-layered, or multi-layered. Mesoporous materials have larger pore sizes (2-50 nanometers) and high surface areas but lower conductivity as they lack built-in electric fields [13]. Studies have shown that synthesizing double-layered structures by combining two different-diameter single-layer TiO_2 nanofibers as the photoanode in DSSC can enhance the conversion efficiency by up to 10%. Rough and porous rutile TiO_2 nanowires prepared via hydrothermal methods can easily load dye molecules and achieve a photoconversion efficiency of approximately 9.4% under simulated sunlight conditions (AM 1.5). Additionally, aligned TiO_2 nanowires synthesized through hydrothermal processes can achieve a photoconversion efficiency of 3.43%. By preparing porous nanowire structures, the lifetime and PCE of the photoanode can be improved [14].

TiO_2 nanostructures can also be fabricated into nanotube structures (NTs), which significantly influence the efficiency of DSSC. Proper dimensions, wall thickness, and length of NTs can accelerate electron transfer and reduce recombination reactions. The length of nanotubes should be shorter than the electron diffusion length to enhance charge collection efficiency. TiO_2 nanotubes with their increased surface area can improve dye adsorption and thus increase the photoconversion efficiency [15].

Hollow spherical TiO_2 structures belong to three-dimensional structures. Fabricating hollow spheres enhances light scattering ability, charge collection efficiency, and optical performance. By preparing N-doped hollow spherical TiO_2 structures via solvothermal methods and using them as scattering layers on the photoanode of DSSC, larger surface areas and a photoconversion efficiency of up to 8.08% can be achieved.

Electrospinning can produce layered nanorod-branched TiO_2 nanofibers, which can transform nanofibers into nanorod structures, thereby improving the performance of DSSC. By combining electrospinning with hydrothermal methods, smooth-surfaced nanofiber structures can be prepared, and subsequent hydrothermal treatment can create layered nanofiber structures with branching or porous features. These improved structures can enhance the efficiency of DSSC to approximately 6.26% [16].

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In conclusion, by controlling the synthesis conditions and methods, various nanostructured TiO_2 can be fabricated, and these structures play crucial roles in enhancing the efficiency of DSSC, such as accelerating electron transfer speed, enhancing charge collection efficiency, and improving light scattering ability.

4. Conclusion

DSSCs are a type of solar cell technology that utilizes dye molecules to absorb light energy and convert it into electricity. In this paper, the research progress and improvement methods of photocathode materials in DSSC are discussed, with emphasis on the application of ordered mesoporous structures in DSSC. The electrode of sensitized dye-based solar cells based on ordered porous structure is also discussed. Finally, the improvement methods of DSSC photoanodes, including element doping and morphological modification, are introduced.

However, there are still challenges to overcome in the future development of DSSC. One of the challenges is improving the photovoltaic conversion efficiency. Currently, the efficiency of DSSC has exceeded 10%, but there is still a gap compared to silicon solar cells. Therefore, further enhancing the photovoltaic conversion efficiency will be a focus of future research. DSSCs also need to address durability and stability issues. Long-term stability and durability are crucial for the commercialization of the cells. Researchers need to find methods to improve the lifespan and stability of the cells to ensure their reliability in practical applications. Future development may also involve the exploration of new materials. Currently, commonly used dye sensitizers, such as organic dyes (e.g., sulfide dyes), may be limited by the degradation and stability of the dye molecules. Therefore, the search for new sensitizers and materials may enhance the performance and stability of the cells. Additionally, compared to other solar cell technologies, DSSCs still hold a smaller market share. Further research and engineering improvements are needed to drive their commercialization, improve production efficiency, and reduce costs.

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