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Strategies to improve the performance of metal-free dye-sensitized solar cells

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ABSTRACT

In recent years dye-sensitized solar cells (DSSCs) have attracted more and more attention due to many advantages such as high molar absorption coefficient, facile molecular tailoring and simple fabrication process as compared to conventional silicon devices. High-energy conversion efficiency is one of the most important factors for the large-scale commercialization. However, the maximum reported DSSCs efficiency of 12.3% is still short of the performance of silicon devices (above 25%) and other commercialized technologies. Even lower efficiency for metal-free organic dyes as sensitizers in DSSCs have been reported. Therefore much work is required to reach optimal efficiency. Improving performance of metal-free DSSCs is a great challenge to the academic research community and for industrial applications scientists. The purpose of this review is to highlight the recent progress in improving the performance of metal-free DSSCs based on the chemical design of the sensitizer and interface molecular engineering principles.

1. Introduction

Human society is facing a global energy problem, which is closely related to three ever-growing issues such as: the increasing energy demand to support economic growth, the gradual depletion of fossil fuels, and the greenhouse effect caused by fossil fuel combustion. In order to reduce environmental pollution and adverse climate change as a result of traditional fuel use, the European Union in its Energy Roadmap 2050 plans to reduce greenhouse gas emissions to 80–95% by 2050 [1]. At present, development of clean energy alternatives to fossil fuels technology has become one of the most important tasks undertaken by modern science. Solar energy is regarded as one of the perfect energy sources due to its huge reserves, in exhaustibility and pollution-free character. Different technologies in photovoltaics, such as crystalline silicon, semiconductor based cells, thin-film solar cells, organic bulk heterojunction solar cells, perovskite solars and dye-sensitized solar cells (DSSCs) coexist to complete the future market. Among them, the DSSCs have been considered as a promising generation of photovoltaic technology due to their biomimetic operating principle, short energy payback time and a realistic approach towards market energy source such as BIPV (Building Integrated PhotoVoltaics).

One of the key elements in DSSCs is the sensitizer, separating the electron and the hole upon excitation by light. Since the applied nano-sized TiO_2 proposed by Grätzel's group [2], many transition metal complex dyes as the sensitizer have been reported [3]. Until now, the state-of-the art DSSCs based on the zinc metal complexes, hold the record of the overall efficiencies up to 12.3% under standard test condition (STC) [4]. The maximum theoretical power conversion efficiency of a single junction solar cell is limited to around 32% [5]. For DSSCs the main deviation from this ideal limit is through the loss-in-potential, which can be defined as the difference between the optical bandgap for the sensitizer divided by the charge of an electron and the open-circuit photovoltage (V_{oc}). However DSSC requires relatively large over-potentials to drive electron injection to the semiconductor from the excited state of the dye and regenerates the oxidized sensitizing dye. For the record efficiency of 12.3% the total loss-in-potential was around 775 mV [4].

Expensive ruthenium dyes have some limitations in the practical application for DSSC. The first and foremost problem is the rarity of the ruthenium metal in the earth's crust. The second drawback is that their synthesis needs tedious purification process, which hampers the large-scale production of these complexes [6]. Recently, metal-free organic dyes have attracted increasing attention due to their high structural flexibility, high molar extinction coefficient, low toxicity, environmental friendly materials and facile synthesis [7,8]. Recent reviews have discussed different aspects of DSSCs. Some of them have highlighted the recent trends in metal-free dyes as photosensitizers and their anchoring to the semiconductor [3,9–13]. The research effort of the solid-state and quasi-solid DSSCs has been also discussed [14]. Apart from that the progress of photoanode modifications [15], the fabrication of nanostructured photoanodes [16] and effect doping, morphology and film thickness of photoanodes [17] have been

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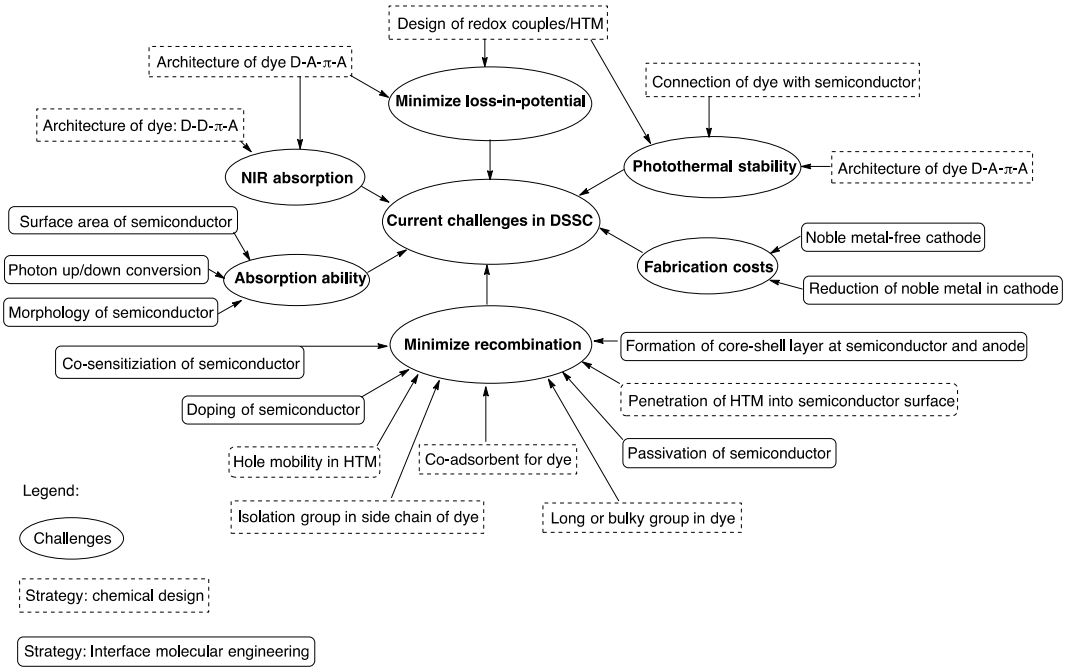

Fig. 1. Technical challenges (ellipses) in DSSC and corresponding strategies (boxes) to address them.

comprehensively summarized. What's more the special features and performance, advantages and disadvantages, preparation, characterization, mechanisms and development histories of various counter electrodes has been presented [18,19].

This review highlights the recent progress in improving the performance and cost-effectiveness of metal-free dye-sensitized solar cells based on the chemical structures of the sensitizer and interface molecular engineering principles. There are several main challenges in which the efficiency and cost-effectiveness of DSSCs can be improved: (i) minimize loss-in-potential, (ii) extend the light absorption into the near-infrared region, (iii) increase absorption ability, (iv) minimize recombination of charges, (v) increase photothermal stability and (vi) decrease fabrication costs (Fig. 1). In this review several strategies to realize the foregoing challenges are presented (Fig. 1).

2. Structure and operational principles of dye-sensitized solar cells

DSSCs are devices that convert visible and infrared electromagnetic radiation into electricity and are based on a mesostructured thin film of a wide-band gap semiconductor oxide modified by dye molecules. A typical DSSC consists of the following parts (Fig. 2): (1) the photoanode which is composed of (i) a transparent glass sheet covered with a transparent conductive oxide layer, which allows light to pass through and electron transport; (ii) a mesoporous semiconductor oxide layer (e.g. TiO_2 or ZnO) deposited on the substrate to transfer electrons; (iii) a monomolecular layer of dye molecules adsorbed on the surface of the mesoporous oxide layer to harvest sunlight; (2) an electrolyte (usually I_3^-/I^- redox couple) for the recovery of dye and the regeneration of the electrolyte itself during operation; (3) a counter electrode (cathode) made of a transparent conductive oxide layer glass sheet coated with a catalyst (typically, platinum) to catalyze the redox couple regeneration reaction and collect electrons from the external circuit [20].

A schematic and energy level diagram showing the operation of a DSSC is shown in Fig. 2. Upon absorption of light, an electron is injected from excited state of the dye (LUMO) into the conduction band (E_{CB}) of the semiconductor oxide layer (e.g. mesoporous TiO_2). The rate of this electron injection is ultrafast (in the range 100 fs to 10 ps). Meanwhile, there are two competitive reactions in the process. One is that the electrons in the semiconductor layer are captured by the oxidized dye (D^+), resulting in the recombination of electrons. The other is that the electrons in the semiconductor film are captured by the oxidized form (Ox) of the redox couple, also leading to the recombination of electrons. The injected electron percolates through the semiconductor, and is thought to move by a "hopping" mechanism driven by a chemical diffusion gradient and is collected at a transparent conductive oxide glass electrode (TCO), on which the semiconductor film is formed. When electrons are in TCO there is competitive process, during which the electrons are captured by the oxidized form (Ox) of the redox couple, resulting in the recombination of electrons. After passing through an outer circuit, the electron is reintroduced into the solar cell at a counter electrode, where the oxidized form (Ox) is reduced to the reduced form (Red) of the redox couple. The reduced form (Red) then regenerates the oxidized dye (D^+), thereby completing the circuit with no net chemical change. Dye regeneration must be fast, but recombination of electrons in the semiconductor with the oxidized form (Ox) must be very slow. To ensure the unidirectional charge flow all elements of DSSCs should posses the appropriate level of energy.

The parameter, which expresses the sunlight-to-electric power conversion efficiency is external quantum efficiency (EQE), called incident photon to current conversion efficiency (IPCE). It is the photocurrent density produced in the external circuit under monochromatic illumination of the cell divided by the photon flux that strikes the cell.

$$IPCE = \frac{J_{sc}}{P} \cdot \frac{1240}{\lambda} \cdot 100\ [\%]$$

where, J_{sc} is the photocurrent density produced in the external circuit [$mA \cdot cm^{-2}$]; P is the incident light [$mW \cdot cm^{-2}$]; λ is the wavelength [nm]. IPCE values provide practical information about the monochromatic quantum efficiency of a solar cell. Generally the efficiency of a DSSC device is also determined by its photocurrent density (J_{sc}), open-circuit photovoltage (V_{oc}), and fill factor (*FF*) [21].

3. Improvement of DSSCs by means of strategy based on chemical design of sensitizer

The sensitizer in DSSCs plays a crucial role in gaining higher solar-to-electricity conversion efficiency. The performance of DSSC strongly