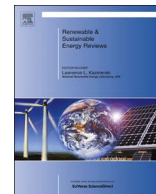




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Zinc oxide based dye-sensitized solar cells: A review

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ABSTRACT

Zinc oxide (ZnO) is the closest alternative to TiO₂ as the semiconductor material in a dye-sensitized solar cell (DSSC). This is to be attributed to the facts that both TiO₂ and ZnO have same electron affinities and almost the same band gap energies, and ZnO has much higher electron diffusivity than TiO₂, a high electron mobility, a large excitation binding energy, is available at low-cost, and stable against photo-corrosion. The article provides a broad survey of ZnO based DSSCs, and highlights the potential of utilizing a ZnO photoanode in the place of a TiO₂ photoanode in a DSSC. The merits of a ZnO photoanode, over against those of a TiO₂ photoanode, are discussed in detail, associated main problems are mentioned, and their solutions are suggested. Parameters to improve the performance of a DSSC are revealed and solutions to optimize them are suggested. Discussions are made on ZnO based flexible, quasi-solid state, and solid state DSSCs. The advantages and disadvantages of ZnO as semiconductor material in DSSCs are weighed. All architectures reported till date are cited, and the techniques used to achieve such hierarchical structures are mentioned. A thorough discussion is made on the dyes used for ZnO based DSSCs. Organic dyes and metal-free dyes are found to be most suitable for such DSSCs. Optimum particle size of ZnO, its stability, its suitable facet for the application in a DSSC, and the best redox couple for a ZnO based DSSC are discussed with evidences. Great emphasis is given on ZnO films that are doped with various materials. The review also discusses miscellaneous works on ZnO based DSSCs. A hitherto never discussed concept of usage of MOFs in a ZnO based DSSC concludes the review.

1. Introduction

Dye-sensitized solar cells (DSSCs) are important power devices, as they are expected to provide an answer to many environmental and energy problems. It is well known that a typical dye-sensitized solar cell (DSSC) consists of three adjacent thin layers: a mesoporous TiO₂ film, a dye such as a ruthenium bipyridyl derivative adsorbed on the TiO₂ film and is sensitive to sunlight, and an organic liquid electrolyte, essentially containing iodide and triiodide ions as the redox couple [1]. These three layers are sandwiched together between two conducting glasses, one covered with a thin buffer layer of TiO₂ and the other with a platinum layer. Zinc oxide has been considered as the best alternative to TiO₂ for DSSCs since the inception of research on TiO₂-based DSSCs; this trend is to be attributed to the facts that both TiO₂ and ZnO have same electron affinities and almost the same band gap energies, i.e., ~3.2 eV and ~3.3 eV, respectively, and ZnO has much higher electron diffusivity than TiO₂ [2], has a high electron mobility of 115–155 cm² V⁻¹ s⁻¹ [3], which is favourable for efficient electron transport in the semiconductor and for reduction of recombination rate. A DSSC with ZnO is expected to show reduced recombination

reactions, compared to a DSSC with TiO₂. In fact, ZnO was the first oxide semiconductor material used for the photoanode of a DSSC [4]. Subsequently, Grätzel and co-workers became the pioneering group for fabricating a DSSC with TiO₂. Zinc oxide has a large excitation binding energy (60 eV), is available at low-cost, and is stable against photo-corrosion. ZnO showed, indeed, the first experimental evidence of irreversible electron injection from organic molecules into the conduction band of a wide band gap semiconductor [5] and [6]. Moreover, by virtue of the diverse morphologies of ZnO, probably richer than those of metal oxides known today, several designs of photoanodes can be expected with it for DSSCs. Unlike the crystalline structure of TiO₂, the crystalline structure of ZnO is conducive to anisotropic growth [7], making it a prime candidate for DSSCs with photoanodes consisting of nanorods, nanowires or nanosheets.

The power conversion efficiency (η) of a DSSC is defined as:

$$\eta = V_{oc} \times J_{sc} \times FF / P_{inc}, \quad (1)$$

where V_{oc} , J_{sc} , and FF are the open-circuit voltage, short-circuit current density and fill factor of the DSSC, and P_{inc} is the incident light power on the semiconductor electrode of the DSSC. The values of V_{oc} and J_{sc}

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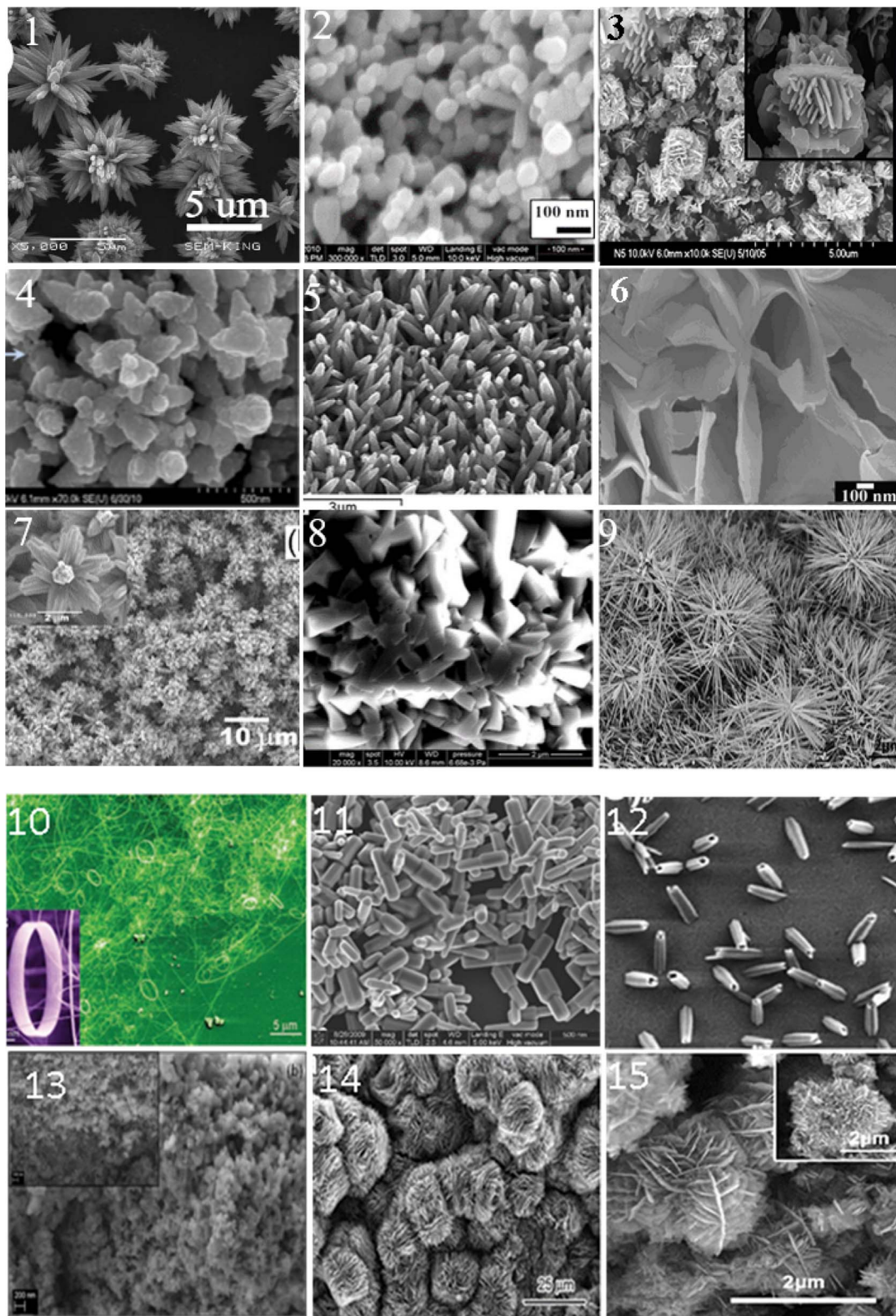
are measured experimentally and the value of FF is calculated by using the following equation:

$$FF = [V_m \times J_m] / [V_{oc} \times J_{sc}], \quad (2)$$

where J_m and V_m represent the current density and voltage at the maximum power output, respectively.

The highest reported light-to-electricity conversion efficiency (η) has been 7.5% [8] for a pure ZnO based DSSC, using liquid electrolyte;

this value of η is much lower than that of a TiO_2 -based DSSC (12.3%) [9]. In the case of a ZnO based DSSC using quasi-solid state electrolyte, Tingli Ma et al. have achieved an efficiency as high as 6.46%, through a solid-state synthesis of the ZnO nanostructure [10]. In a rare case, a ZnO compact layer prepared by a sol-gel method was introduced into the photo electrode at the interface between fluorine-doped tin oxide (FTO) substrate and a mesoporous ZnO layer [11] and [12]. There were scarce reports on solid state ZnO based DSSCs [13], [14] and [15]; the



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