

Efficient Materials for Dye-Sensitized Solar Cells

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Abstract— Dye-sensitized solar cells (DSSCs) have attracted considerable attention in recent years as they offer the possibility of low-cost conversion of photovoltaic energy. Recently, DSSC has reached an efficiency of 13% using porphyrin as sensitizer, Co(II/III) as redox couple in volatile organic solvent. However, almost all components of the device has to improved for device durability and leading to commercialization of the technology.

Keywords— Sensitizer, redox couple, metal oxide, conduction band, durability.

1. INTRODUCTION

‘Energy’ is identified as one of the topmost problems that humanity faces over the next 50 years.¹⁻³ To overcome this problem the scientific community had already started working on various issues (to save, convert or create energy by utilizing existing resources). As a result, the *solar energy conversion* has become one of the major alternatives to the conventional fossil fuels, considering their drastic depletion over the last few decades. A solar cell is any device that directly converts the light energy into electrical energy through a photovoltaic process. Solar cells are broadly divided into three generations.³ The first two generations of solar cells are based on either single-crystal silicon or thin-film (amorphous silicon (a-Si), Cd-Te, Ga-As, GaInAs etc.) technologies. The first two generations of solar cells are highly efficient, but their applications are limited due to either cost ineffective or hazardous materials used in these technologies. Therefore, considering the necessity and for the tapping of solar energy, in recent years excitonic solar cells, known as third-generation solar cells, have been shown considerable attention due to their interesting and promising conversion efficiencies. The excitonic solar cells are broadly divided into nanocrystalline dye-sensitized solar cells (DSSCs) and organic/polymer solar cells. Of these DSSCs are on the verge of commercialization.

Nanocrystalline Dye-Sensitized Solar Cells (DSSC)— The first observation of injecting electrons by a dye molecule into the conduction band of the semiconductor substrate was reported in 1960’s.⁴ From then on the concept of dye sensitization developed gradually. But, the efficiency of the device was very low until 1991, when Prof. Michaël Grätzel of EPFL, Switzerland reported that the sensitization of nanocrystalline TiO₂ using a ruthenium(II) polypyridyl complex with an efficiency of (η)7.1%.⁵ This approach of generating electricity from

sunlight has many advantages over first and second generation solar cell technologies. The DSSC devices are easy to fabricate when compared to crystalline silicon solar cells. They can be made in transparent modules to integrate into windows and sunroofs. They maintain their performance even in shaded conditions and higher temperatures unlike silicon solar cells. Though various other wide band gap semiconductors such as NiO, ZnO, SnO₂, WO₃ etc. were studied, TiO₂ has many advantages including its long term thermal and photo stability. It is low-cost, abundant, non-toxic, biocompatible and widely used in healthcare products (e.g. toothpaste) and paints.

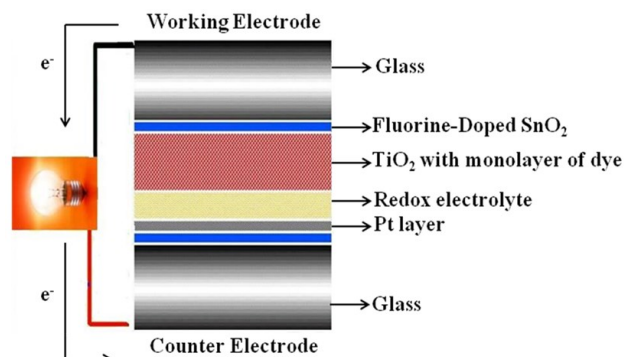


Fig. 1: Schematic structure of DSSC device

Typically the device composed of a porous layer of TiO₂ nanoparticles, covered with a molecular dye (usually a ruthenium(II) polypyridyl complex) absorbs sunlight like chlorophyll in green leaves. The TiO₂ is immersed under an electrolyte solution, above which a platinum-based catalyst is placed. Similar to a conventional alkaline battery, an anode (the titanium dioxide) and a cathode (the platinum) are placed on either side of a liquid conductor (the electrolyte). Detailed device fabrication and working principle of a DSSC are well documented in our earlier reports. Since 1991, many affords have been paid to improve the power conversion efficiency. Moreover, it does not take much time to the scientific community to prove them (DSSCs) as alternative for the conventional

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first & second generation silicon and other thin film solar cells. Interestingly, the DSSC technology works well even in the diffused light conditions, which are unlike in first and second generations of photovoltaic devices.

Almost all the elements of the DSSC device need to further improvement before commercialization of this technology. The main components in DSSC device are (a) Sensitizer (b) Semiconducting nanostructured metal oxides and (c) Redox electrolytes.

a) **Sensitizer**— Among various components of DSSC device, the sensitizer is one of the key components in achieving high efficiency and durability. The most successful charge transfer sensitizers employed so far in DSSCs are, *cis*-dithiocyanatobis-(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) (together with its various protonated forms), its modified forms (N3 & N719) and trithiocyanato 4,4'4''-tricarboxy-2,2':6',2''-terpyridine ruthenium(II) (the black dye), yields conversion efficiencies up to 11% under air mass (AM) 1.5 solar conditions with liquid redox electrolyte.⁶ Nevertheless, substantial amount of research work is still needed to fill the gap between today's benchmark conversion efficiency 32% (the Shockley-Queiser limit predicted for a single junction cell). This can be achieved only through proper molecular designing of sensitizer. A great variety of

ruthenium(II) complexes have been reported in the literature in order to further improve the efficiency and durability of the device. Even though the ruthenium(II) polypyridyl complexes are more dominant in today's DSSC research, they are very expensive due to the rarity of the metal. Moreover, they are less durable due to the presence of two or three -NCS groups in its molecular structure. But, to date Ru(II) polypyridyl complexes are dominating as sensitizers.⁷ In order to commercialize the technology one has to reduce the cost of the device. In this regard other class of sensitizers such as metal-free organic sensitizers, tetrapyrroles that includes porphyrins, phthalocyanines and corroles. Metal-free organic sensitizers have crossed an efficiency of 10%. Recently, porphyrin based sensitizers using an organic molecules as co-sensitizer has crossed an efficiency of 13%.⁸

b) **Semiconducting Nanocrystalline Metal Oxides**— The semiconductor, which provides a surface area for the adsorption of the dye, accepts electrons from the excited dye and conducts them to the external circuit to produce an electric current. The electron transport rate, which highly depends on the crystallinity, morphology, and the surface area of semiconductors, affects the efficiency of DSSCs. Metal oxides like titanium oxide (TiO₂), zinc oxide (ZnO), and stannic

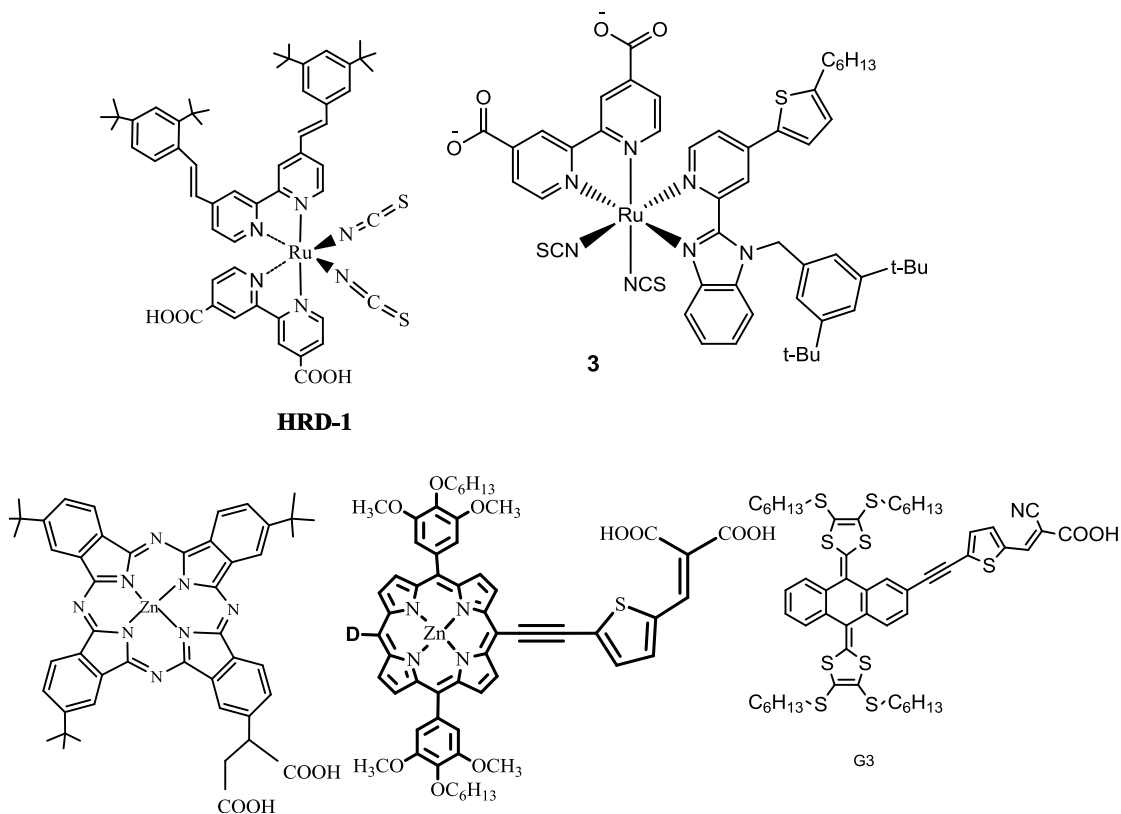


Fig. 2: New efficient sensitizers.

oxide (SnO₂) have been used as the semiconductor material. However, experiments show that DSSCs based on ZnO and SnO₂ yield a lower efficiency in comparison to those based on nanocrystalline TiO₂. The latter has been considered as an ideal semiconductor material for DSSCs since 1991 due to this and its better morphological and photovoltaic properties when compared to other semiconductors. Of the two crystalline forms of TiO₂, anatase and rutile, the former is preferred because of its high conduction band edge energy (3.2 eV) when compared to rutile (~3 eV). High band gap energy makes anatase chemically more stable. The electron transport process in rutile is also slow when compared to anatase due to the high packing density. Short circuit photo current of an anatase-based DSSC is 30% more than that of a rutile-based DSSC with the same film thickness. Owing to the smaller surface area per unit volume, rutile absorbs less dye and therefore rutile-based DSSCs are less efficient.

- c) **Redox Electrolyte**— The most successful redox couple in these devices are I⁻/I₃⁻ in an organic solvent. The efficiency is high when liquids were used due to better interfacial contacts but, durability of the device is less due to leakage and evaporation problems. Though I⁻/I₃⁻ redox couple have shown very good efficiency, but it has certain constraints. The drawbacks of I⁻/I₃⁻ redox couple competitive light absorption by the triiodide and by the inability of I⁻/I₃⁻ to regenerate far-red absorbing dyes. Moreover, the scale up and the module stability of the DSC are hindered by the high vapor pressure of liquid I⁻/I₃⁻ electrolytes, and the corrosiveness of I⁻/I₃⁻ towards most metals and sealing materials. In this regard, we found Co(II/III) redox couples are found to be best alternatives to iodide redox couple. The electron recombination reactions for these one-electron redox couples have been indeed

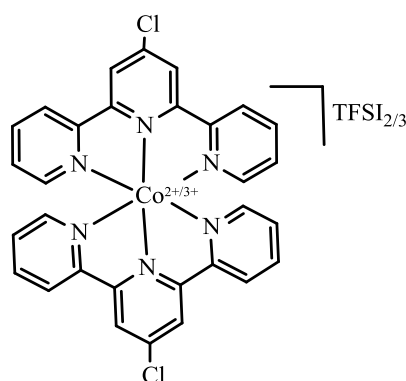


Fig. 3: Co(II/III) redox couple.

shown to be faster than those for I⁻/I₃⁻ systems, even though the insulating long alkoxy chains or co-adsorbent incorporated in these systems are expected to retard electron recombination reactions at the TiO₂/dye/electrolyte interface. The much more positive

potentials of these one-electron redox couples still strongly compensate the larger electron recombination losses, resulting in the gains of open-circuit voltages (*V_{oc}*). Due to the facile tuning of their redox potential of cobalt complexes, which can be adjust to match the oxidation potential of the sensitizer, minimizing energy loss in the dye regeneration step, and to enable maximum open circuit voltages. Numerous cobalt complex-based electrolytes have been reported with bi-dentate and tri-dentate polypyridyl ligands.⁹

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