

Dye-Sensitized Solar Cells-A Review

Faizan Baig¹, V.N. Kshirsagar²

²Assistant Professor

^{1,2}G. H. Raisoni College of Engineering, Nagpur - 440016

Abstract- *The dye-sensitized solar cells (DSC) provides a technically and economically credible alternative concept to present day p-n junction photovoltaic devices. In contrast to the conventional systems where the semiconductor assume both the task of light absorption and charge carrier transport the two functions are separated here. Light is absorbed by a sensitizer, which is anchored to the surface of a wide band semiconductor. Charge separation takes place at the interface via photo-induced electron injection from the dye into the conduction band of the solid. Carriers are transported in the conduction band of the semiconductor to the charge collector. The use of sensitizers having a broad absorption band in conjunction with oxide films of nanocrystalline morphology permits to harvest a large fraction of sunlight. Nearly quantitative conversion of incident photon into electric current is achieved over a large spectral range extending from the UV to the near IR region. Overall solar (standard AM 1.5) to current conversion efficiencies (IPCE) over 10% have been reached. There are good prospects to produce these cells at lower cost than conventional devices. Here we present the current state of the field, discuss new concepts of the dye-sensitized nanocrystalline solar cell (DSC) including heterojunction variants and analyze the perspectives for the future development of the technology.*

I. INTRODUCTION

Photovoltaic devices are based on the concept of charge separation at an interface of two materials of different conduction mechanism. To date this field has been dominated by solid-state junction devices, usually made of silicon, and profiting from the experience and material availability resulting from the semiconductor industry. The dominance of the photovoltaic field by inorganic solid-state junction device is now being challenged by the emergence of a third generation of cells, based, for example, on nanocrystalline and conducting polymers films.

These offer the prospective of very low cost fabrication and present attractive features that facilitate market entry. It is now possible to depart completely from the classical solid-state junction device, by replacing the contacting phase to the semiconductor by an electrolyte, liquid, gel or solid, thereby forming a photo-electrochemical

cell. The phenomenal progress realized recently in the fabrication and characterization of nanocrystalline materials has opened up vast new opportunities for these systems. Contrary to expectation, devices based on interpenetrating networks of mesoscopic semiconductors have shown strikingly high conversion efficiencies, which compete with those of conventional devices. The prototype of this family of devices is the dye-sensitized solar cell, which realizes the optical absorption and the charge separation processes by the association of a sensitizer as light-absorbing material with a wide band gap semiconductor of nanocrystalline morphology.

II. OPERATION PRINCIPLE OF THE DYE-SENSITIZED NANOCRYSTALLINE SOLAR CELL (DSC)

A schematic presentation of the operating principles of the DSC . At the heart of the system is a mesoporous oxide layer composed of nanometer-sized particles which have been sintered together to allow for electronic conduction to take place. The material of choice has been TiO₂ (anatase) although alternative wide band gap oxides such as ZnO [2], and Nb₂O₅ [3] have also been investigated.

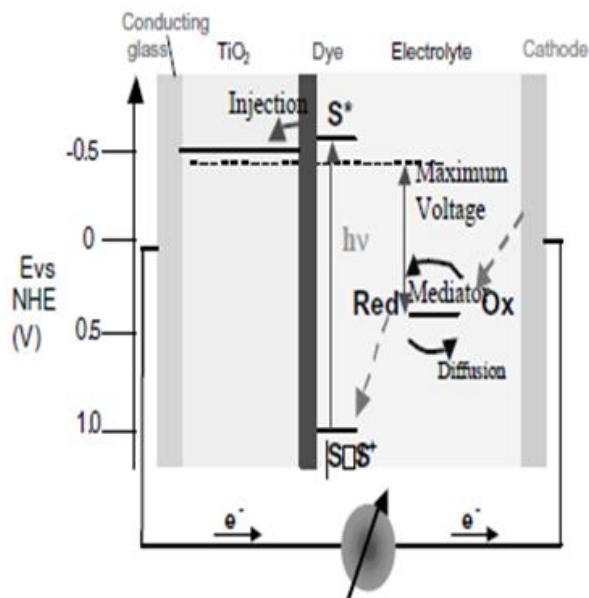
Attached to the surface of the nanocrystalline film is a monolayer of the charge transfer dye. Photo excitation of the latter results in the injection of an electron into the conduction band of the oxide. The original state of the dye is subsequently restored by electron donation from the electrolyte, usually an organic solvent containing redox system, such as the iodide/triiodide couple. The regeneration of the sensitizer by iodide intercepts the recapture of the conduction band electron by the oxidized dye.

The iodide is regenerated in turn by the reduction of trii-odide at the counter electrode the circuit being completed via electron migration through the external load. The voltage generated under illumination corresponds to the difference between the Fermi level of the electron in the solid and the redox potential of the electrolyte.

Overall the device generates electric power from light without suffering any permanent chemical transformation. Fig shows the scanning electron micrograph of a typical TiO₂

(anatase) film deposited by screen printing on a conducting glass sheet that serves as current collector.

The film thickness is typically 5–20 μm and the TiO_2 mass about 1–4 mg/cm^2 . Analysis of the layer morphology shows



the porosity to be about 50–65%, the average pore size being 15 nm. The prevailing structures of the anatase nanoparticles are square–bipyramidal, pseudocubic and stablike. A recent alternative embodiment of the DSC concept is the sensitized heterojunction usually with an inorganic wide band gap nanocrystalline semi conductor of n-type polarity as electron acceptor, the charge neutrality on the dye being restored by a hole delivered by the complementary semiconductor, inorganic or organic and of p-type polarity.

III. THE DILEMMA OF LIGHT HARVESTING BY SURFACE IMMOBILIZED MOLECULAR ABSORBERS

A monolayer of dye on a flat surface absorbs at most a few percent of light because its size is much larger than its optical cross section.

Compact semiconductor films need to be n-doped to conduct electrons. As a consequence there is energy transfer quenching of the excited sensitizer by the electrons in the semiconductor.

IV. LIGHT HARVESTING BY NANOCRYSTALLINE TiO_2 FILMS

Light is absorbed by a dye derivatized mesoporous film made of a network of undoped (insulating) TiO_2 nanocrystallites

- The sensitizer is grafted onto the TiO_2 surface through suitable anchoring groups, e.g. carboxylate, phosphonate or hydroxamate.
- Light induced electron injection from the adsorbed dye into the nanocrystallites renders the TiO_2 conductive.

The best photovoltaic performance both in terms of conversion yield and long-term stability has so far been achieved with polypyridyl complexes of ruthenium and osmium. Sensitizers having the general structure $\text{ML}_2(\text{X})_2$, where L stands for 2,2'-bipyridyl-4,4'-dicarboxylic acid M is Ru or

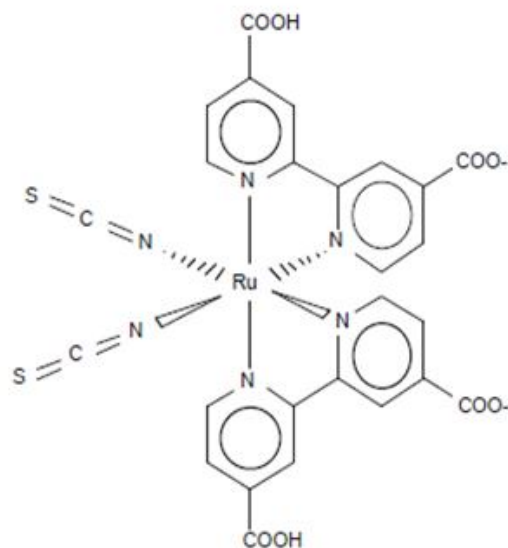


Fig. 4. Chemical structure of the N3 ruthenium complex used as a charge transfer sensitizer in dye-sensitized solar cells.

Os and X presents a halide, cyanide, thiocyanate, acetyl acetonate, thiocarbamate or water substituent, are particularly promising.

Thus, the ruthenium complex $\text{cis-RuL}_2(\text{NCS})_2$, known as N3 dye, shown in Fig. 4 has become the paradigm of heterogeneous charge transfer sensitizer for mesoporous solar cells.

The complex emits at 750 nm the lifetime being 60 ns. The optical transition has metal-to-ligand charge transfer (MLCT) character: excitation of the dye involves transfer of an electron from the metal to the orbital of the surface anchoring carboxylated bipyridyl ligand from where it is

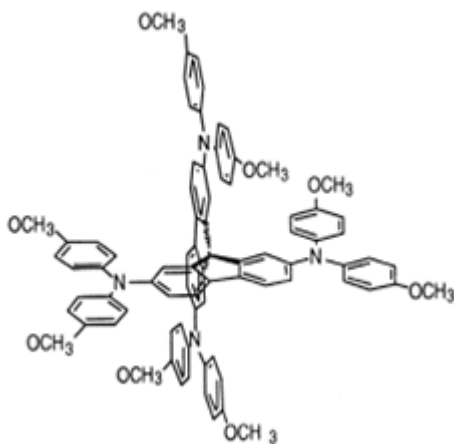
released within femto- to picoseconds into the conduction band of TiO₂ generating electric charges with unit quantum yield.

V. PHOTOVOLTAIC PERFORMANCE STABILITY

A photovoltaic device must remain serviceable for 20 years without significant loss of performance. The stability of all the constituents of the nanocrystalline injection solar cells, that is, the conducting glass the TiO₂ film, the sensitizer, electrolyte, the counter electrode and the sealant has therefore been subjected to close scrutiny. The stability of the TCO glass and the nanocrystalline TiO₂ film being unquestionable investigations have focused on the four other components.

VI. SOLID-STATE DYE-SENSITIZED SOLAR CELLS

One alternative which offers itself to confront the sealing problem is the replacement of the redox electrolyte by a solid p-type semiconductor inter penetrating the nanocrystalline TiO₂ structure which would permit the charge neutralization of dye molecules after electron injection by its hole transport properties.



The sensitizing dye itself does not provide a conducting functionality, but is distributed at an interface in the form of immobilized molecular species, it is evident that for charge transfer each molecule must be in intimate contact with both conducting phases. It is evident that this applies to the porous wide bandgap semiconductor substrate into which the photo-excited chemisorbed molecules inject electrons. It is also evident that in the photo-electrochemical format of the sensitized cell the liquid electrolyte penetrates into the porosity, thereby permitting the intimate contact with the charged dye molecule necessary for charge neutralization after the electron loss by exchange with the redox system in solution. It is not immediately evident that an interpenetrating

network of two conducting solids can so easily be established that an immobilized molecule at their interface can exchange charge carriers with both. However results are promising.

VII. CONCLUSIONS

The dye-sensitized nanocrystalline electrochemical photovoltaic system has become a validated and credible competitor to solid-state junction devices for the conversion of solar energy into electricity. It is the prototype of a series of optoelectronic and energy technology devices exploiting the specific characteristics of this innovative structure for oxide and ceramic semiconductor films. Recent developments in the area of sensitizers for these devices have led to dyes which absorb across the visible spectrum leading to higher efficiencies. The recent development of an all solid-state heterojunction dye solar cell holds additional potential for further cost reduction and simplification of the manufacturing of dye solar cells.

REFERENCE

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