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Recent theoretical progress in the organic/metal-organic sensitizers as the free dyes, dye/TiO_2 and dye/electrolyte systems; Structural modifications and solvent effects on their performance

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A B S T R A C T

Here, we review the effects of the structural modifications, dye/TiO_2 absorption modes, solvent effects and dye/electrolyte interaction on the performance of the DSSCs. The expansion of the quantum chemistry perspective on this field has shown different aspects of the molecular properties and charge transfer processes which are important in solar cell designing from the chemistry viewpoint. Also, the quantum chemistry reactivity indices are proper descriptors for better analyzing the performance of the sensitizers. For this purpose, a reasonable selection of the proper functionals and basis sets, for calculation of the ground and the excited states are important. Structural modification of the organic and metal-organic dyes, efficient substitution of the donors, π-bridges and acceptors as well as the role of the solvent on the solar cell efficiency are analyzed. Also, the presence of different ions in the solvent, the nature of the electrolyte, the interactions of the dye/TiO_2 and dye/electrolyte, which affect strongly the efficiency, are discussed.

1. Introduction

In the 21st century, the generation of the renewable energies is the main topic of the most of the researches from the scientific and technological viewpoints. The population growth in the world makes this topic more critical in all fields [1]. Also, based on the U.S. Energy Information Administration, a rapid growth in the electricity section is observed and it is predicted that the worldwide electricity consumption follows an upward trend to 35.2 trillion kW h in 2035, while it was estimated to be 19.1 trillion kW h in 2008 [2]. Moreover, the development of the renewable energies is useful to decrease the fossil fuel consumption and its environmental problems.

After discovery of the photoelectric effect by Edmond Becquerel, researchers and engineers have followed the topics about the conversion of light into the electricity and chemical fuels [3]. Their goal was access to the free energy for generating electricity or fuels such as hydrogen. Photovoltaic property is related to the incidence of the photons to a conductor/semiconductor and the generation of the electron-hole pairs, creating an electric potential difference across the interface of two different materials.

Solar cell is one of the safe devices in electricity generation that will be one of the main renewable sources of energy in the future [4–6]. Solar cell is a photoelectrochemical cell which converts the solar energy into electricity. Recently, DSSCs have attracted high attention due to their good efficiency, simple construction and low cost [7–10]. But there are challenges for the DSSCs consist of the low dye stability, low absorption capacity of the dye, caused by weak bonds between the dye molecules and TiO_2 surface, and small quantity of dye molecules on the TiO_2 surface [11]. Advantages and disadvantages of the DSSCs are presented in Scheme 1.

A modern DSSC, the Grätzel cell [12], contains a conductive mechanical support, a mesoporous semiconductor metal oxide film, a sensitizer (dye), an electrolyte and a counter electrode. Fig. 1 shows a schematic working plane of a DSSC. When sunlight passes through the

Abbreviations: DSSC, dye-sensitized solar cells; LUMO, lowest unoccupied molecular orbital; HOMO, highest occupied molecular orbital; FF, fill factor; V_{OC}, open circuit voltage; J_{SC}, short-circuit photocurrent density; ΔG_{inj}, free energy change of electron injection; ΔG_{reg}, free energy change of dye regeneration; LHE, light harvesting efficiency; EBE, excited binding energy; IPCE, incident photon to current conversion efficiency; APCE, absorbed photon-to-current conversion efficiency; DFT, density functional theory; TD-DFT, time-dependent density functional theory; CT, charge transfer; λ_{max}, absorption maximum wavelength; NBO, natural bond orbital; PCM, polarized continuum models; TPA, triphenylamine; FTO, fluorine doped tin oxide; TM, transition metal; τ, life time; PIB, particle in box; EQE, external quantum efficiency; CIS, configuration interaction single; LANL, Los Alamos National Laboratory; RASPT2, second-order perturbation theory restricted active space; MLCT, metal to ligand charge transfer; DFTB, density functional tight-binding; NPs, nanoparticles; BB, bridged bidentate; M, monodentate; EL, electrostatic; γ, dye's surface concentration

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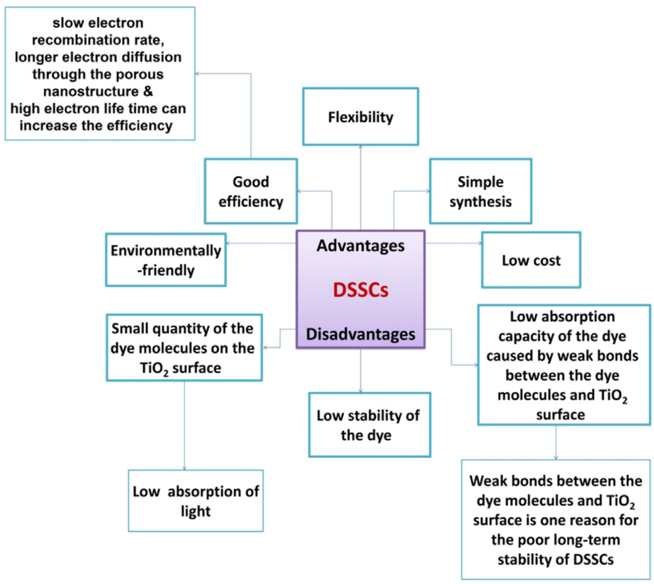

Scheme 1. Advantages and disadvantages of the DSSCs.

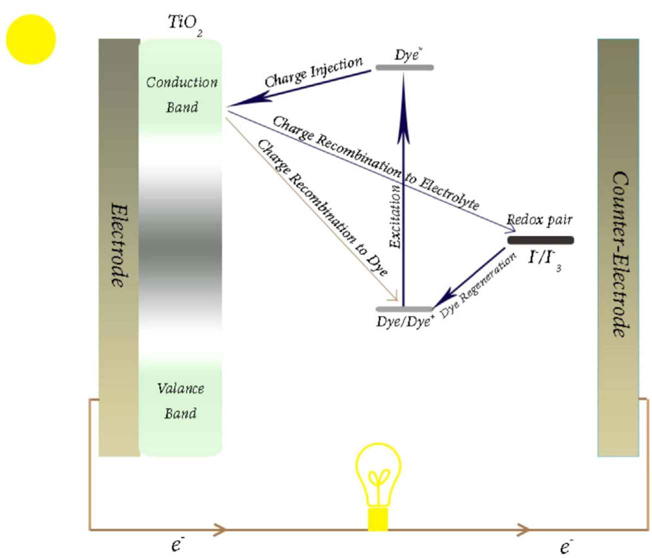

Fig. 1. Schematic working plane and main processes of a DSSC.

transparent electrode into the sensitizer anchored to the surface of the TiO_2 semiconductor nanocrystals, the excited electrons flow into the titanium dioxide coated FTO electrode, Eqs. (1) and (2), respectively. The electrons flow toward the electrode and after passing through the external circuit, they contact a metal or graphite electrode on the opposite side and then reach to the electrolyte. The electrolyte transfers the electrons to the sensitizer for regenerating of the dye to its original state, Eq. (3) [13,14]. In turn, the circuit is completed by the reduction of triiodide to iodide at the counter electrode, Eq. (4). However, there are some undesirable reactions which reduce the cell efficiency such as the recombination of the injected electron with the oxidized sensitizer, Eq. (5), or recombination with the oxidized redox couple at the TiO_2 surface, Eq. (6) [15,16].

$$\mathrm{Dye_{ads.}} + h\nu \rightarrow \mathrm{Dye^{*}_{ads.}} \tag{1}$$

$$\mathrm{Dye^{*}_{ads.}} \rightarrow \mathrm{Dye^{+}_{ads.}} + \mathrm{e^{*}_{inj.}} \tag{2}$$

$$\mathrm{Dye^{+}_{ads.}} + 3/2\,\mathrm{I^-} \rightarrow \mathrm{Dye_{ads.}} + 1/2\,I_3^- \tag{3}$$

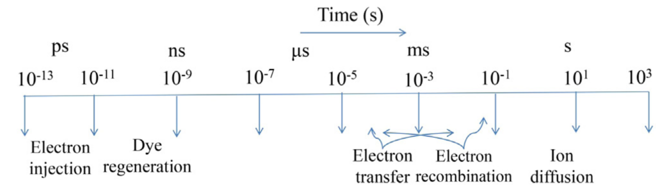

Fig. 2. The comparison of different process time scales in the DSSC.

$$\mathrm{I_3^-} + 2\mathrm{e^-(cathode)} \rightarrow 3\mathrm{I^-(cathode)} \tag{4}$$

$$\mathrm{Dye^{+}_{ads.}} + \mathrm{e^-(TiO_2)} \rightarrow \mathrm{Dye_{ads.}} \tag{5}$$

$$\mathrm{I_3^-} + 2\mathrm{e^-(TiO_2)} \rightarrow 3\mathrm{I^-(anode)} \tag{6}$$

The competition of the opposite chemical reactions with different rate constants determines the performance of the DSSC. Whatever the rate constant of the desirable reactions is higher and mutually it is lower for undesirable reactions, the efficiency will be developed. Fig. 2 shows the time scale of different processes for a conventional DSSC based on Ru-complex dye. This figure shows that the favorable processes, electron injection, and dye regeneration are faster than the unfavorable processes such as recombination processes [17]. Kinetic studies of the photovoltaic processes in DSSCs are helpful to design the efficient DSSCs.

Therefore, some factors, such as the type of the photoelectrode, semiconductor nanoparticles, electrolyte and different properties of the dye such as molecular structure, anchoring group, morphology and self-assembly of the dye affect the performance of the dye-sensitized solar cell.

The n-type semiconducting nanoparticles are widely used materials in the DSSCs. TiO_2 is usually applied, but ZnO [18–20] and other oxides such as SnO_2 [21], CdSe [22], $CuInS_2$ [23], PbS [24] and $SrTiO_3$ [25] are used, too. Nickel(II) oxide is used in the p-type cells based on the hole transfer due to its good stability and transparency. This type of the solar cells and related studies are rare in the literature [26–28]. Different morphologies and modifications of other semiconductor photocatalysts such as WO_3 [29,30], Fe_2O_3 [31], $BiVO_4$ [32,33] and CdS [34,35] have been investigated and developed. Photocatalysts absorb the light, yielding the electron-hole pair separation and charge transfer. The modifications of the semiconductor surface structures and their properties affect the photocatalytic processes [36]. The imbalance of the interfacial CT of the electrons and holes cause charge recombination which reduces the overall photocatalytic activity. Because of a good ability in CT, semiconductor photocatalysts are of great interest, especially in two main purposes:

1) Environmental applications such as purification of the polluted water and air.

2) Solar energy storage through the production of solar fuels such as H_2 production from the water splitting, CO_2 conversion to hydrocarbons.

Among the variety of the semiconductors, TiO_2 is a proper chemical, which represents a good photocatalytic activity and excellent stability in a vast pH range under both dark and irradiation conditions [37]. However, there are various methodologies to eliminate the limitations of the other semiconductors and even TiO_2, such as applying low-dimension nanostructures [38], isotropic nanomaterials [39], surface treatment [40], coupling two semiconductors together [41], core-shell [42] and metal-semiconductor nanocomposites [43].

As mentioned earlier, one of the important factors in the solar cell performance is the electrolyte and its components [44]. The electrolyte surrounds the dye acting as a compensatory for the lost electrons. There are three states for the electrolytes consist of the solid-state, quasi-solid-state or liquid [45,46]. Liquid electrolytes consist of an additive and a redox couple, which play a key role in the dye regeneration and charge transfer between two electrodes. The electrolyte which contains I^-/I_3^-