Description of the thesis

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ab-initio investigation of factors impacting the performance of nanostructured solar cells

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by

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This dissertation entitled "*ab-initio investigation of factors impacting the performance of nanostructured solar cells*" aims to analyze dye-sensitized solar cells (DSSCs) efficiency improvement through a computational approach. In this regard, Density functional theory (DFT) and its time-dependent extension (TD-DFT) are employed to characterize the electronic and optical properties of several recently synthesized chromophores and dye/semiconductor interfaces to clarify mechanisms behind efficient energy harvest under operational conditions of DSSC devices. The thesis is composed of five chapters as follows;

Chapter 1 deals with introductory and discusses sustainable energy resources as well as their indisputable role in the development of human societies. In the following, this chapter provides a chronological overview of four different generations of photovoltaic devices and the main challenges in enhancing their yields. At the end of this introduction, DSSCs are introduced as promising candidates to supply renewable energy.

In chapter 2, components, the mechanisms behind the efficient operation, and the energetics of DSSCs have been discussed in-depth to a great extent. The dyes development process, metal oxides, and electrolytes as the main constituents are reviewed individually. On the other hand, mechanisms behind efficient energy conversion have been argued in terms of the forward and backward reaction paths. The energetic section discusses level alignment changes at the interface of dye and semiconductors. The effect of level alignment on both open-circuit voltage and short circuit current was studied closely. Finally, different scenarios to improve the efficiency of solar cells were reviewed while the device's structure, mechanisms, and energetics were considered.

Chapters three and four are devoted to the basics of DFT and TDDFT, respectively. Born-Oppenheimer approximation, Hartree-Fock, and configuration interaction methods

were briefly reviewed in chapter three. The main part of the third chapter deals with the basics of DFT and solving Kohn-sham equations within PW and local basis sets. In chapter four Runge-gross theorem as a building stone of TDDFT was presented. The Casida approach to solving the linear-response TDDFT equation is reviewed in the following.

The result section is subdivided into four sections; I)Modeling the TiO2 nanoparticles, II) The effect of organic co-adsorbents, III) Organic D-pi-A dyes, IV) Heteroleptic Ru-complexes. The first section is focused on the electronic structure of anatase TiO2 employing both slab and cluster models. The next section is devoted to the geometrical arrangement of oleic acid as a promising co-adsorbents. In the third section, we have theoretically studied the electronic and optical properties of the two recently synthesized coadsorbents Y1 and Y2, which were aimed to enhance the efficiency of the black dye-sensitized solar cells. To determine the solvatochromic shifts, both the implicit and mixed implicit–explicit models have been used. The connection between the solvatochromic shifts and the changes in dipole moments in the excitation process is discussed. The difference in excitation charge transfer is utilized to explain the experimentally observed difference in Jsc for Y1 and Y2. Investigating the interactions of I2 molecules in the electrolyte solution with the coadsorbents showed that with Y1 the recombination loss was weakened by decreasing the I2 concentration near the TiO2 surface, whereas with Y2 it was increased. As a result, the higher values of both Jsc and Voc with the Y1 coadsorbent explain its experimentally observed higher efficiency. In the last section of our results, we have investigated the electronic structure and absorption spectra of newly synthesized Ru-complex dyes and compared the results to those of well-known N3 dye to describe the variations of the properties due to molecular engineering of the ancillary ligand. We have shown that the calculation results of the absorption spectra for these dyes using the PBE0 for the exchange-correlation functional are in better agreement with the experiment than using B3LYP or range-separated CAM-B3LYP. We have also derived a

formula based on the DFT and used it to visually describe the level shifts in a solvent. The higher J_{sc} observed in these new dyes is explained by the fact that here, in contrast to N3, the excitation charge was effectively transferred to the anchoring ligand. Furthermore, we have shown that the difference between dipole moment vectors of the ground and excited states can be used to determine the charge-transfer direction in an excitation process. On the other hand, different electron lifetimes observed in these dyes are explained by investigating the adsorption geometries and the relative orientations of iodine molecules in different "dye$\cdots$I2" complexes.

In summary, research conducted gives an atomistic explanation for the changes in DSSC performance and the mechanisms behind device operation as a function of constituents. This study sheds light on how to design and engineer newer coadsorbents, dyes, and electrolytes for higher efficiencies.

Related Publications:

1- Theoretical description of efficiency enhancement in DSSCs sensitized by newly synthesized heteroleptic Ru complexes
YT Azar, M Payami
Physical Chemistry Chemical Physics 17 (44), 29574-29585

2- Efficiency enhancement of black dye-sensitized solar cells by newly synthesized D–π–A coadsorbents: a theoretical study
YT Azar, M Payami
Physical Chemistry Chemical Physics 16 (20), 9499-9508

3- First-principles calculation of electronic energy level alignment at electrochemical interfaces
YT Azar, M Payami
Applied Surface Science 412, 335-341