Abstract

Thanks to the pioneering work of Grätzel (*Nature* 353 (1991) 737), dye-sensitized solar cells (DSSC) are becoming more and more popular due to the possibility of cheap conversion of solar radiation into electricity. An oxide semiconductor, such as titanium dioxide (TiO_2), in DSSC cells forms an anode on which dye molecules are adsorbed, absorbing light in the visible range. The ability to convert light into electricity depends on the electron properties of the semiconductor and dye as well as the type of their connection. Component compatibility affects the photovoltaic properties of the hybrid material. The proper selection of dyes for a particular semiconductor can be made by employing computer simulations of their electronic and optical properties. Determining the method of electron transfer between the dye and the semiconductor gives the possibility of a well-thought-out selection of photovoltaic components.

The aim of the work was to create a methodology for computer simulations to predict the electron and optical properties of hybrid materials based on ruthenium dye/TiO_2 nanostructure. This allowed us to determine the mechanism of electron transfer between the dye and the semiconductor.

Quantum-chemical calculations of the electron properties of TiO_2 with oxygen vacancies and doped with zirconium (Zr), copper (Cu), manganese (Mn), nickel (Ni), and nitrogen (N) ions in the form of a bulk crystal, thin films, and nanostructures were performed. The impurity ions were selected based on performed experimental studies. A DFT-based method to calculate the structural and electron properties of semiconductor materials was developed using appropriate Hubbard parameters. It has been proven that the use of Hubbard's corrections gives computational results in agreement with the experimental data of both structural and electron parameters. The influence of individual ions and the role of oxygen vacancies in the TiO_2 structure on the charge transfer process in DSSC cells was determined. It was found that the Zr impurities stabilize the anatase form of the TiO_2 nanostructures and generate oxygen vacancies, which is conducive to photoconductivity. It has been proven that doping of the TiO_2 with other ions lowers the band gap of the semiconductor, but only donor levels with high energy dispersion favor photoconversion processes. The results of the performed research indicate that the type of admixture and its content has a significant impact on the charge transfer in DSSC cells.

Quantum-chemical calculations of electron and optical properties of two groups of ruthenium dyes were carried out. In the first group there were dyes with one trisbipyridine

center in the molecule, and in the second - dendrimer dyes with two trisbipyridine centers each. The dyes differed in the position and number of anchor groups (-COOH) and in the construction of the separator between the trisbipyridine and the anchor. It was shown that the intramolecular electron transfer capability depends on the position of the anchor group. Dyes with an anchor in the meta and para position adsorb on the TiO_2 surface in a similar amount, but the efficiency of cells sensitized with para-substituted dye is higher. It was found that the additional anchor group placed in the para position to the metallic center improves the charge transfer. It was shown that the replacement of the ethynyl π-linker with the phenyl one in the dye weakens the intramolecular electron transmission capacity but increases the lifetime of the free charges, which has a positive effect on the operation of DSSC cells.

An innovative method of modeling the geometry of hybrid systems was developed, consisting in substituting a dye in place of the anchor and separator, which made it possible to preserve the structure of trisbipyridine groups. Three types of possible connections between the dye and the semiconductor have been identified. The stability of the resulting hybrid systems and the quantitative charge transfer between the hybrid components were analyzed. Using the method of computer simulations and the results of experimental studies, the mechanism of electron transfer in the studied systems was explained. It was found that two-step dye/semiconductor transitions make the main contribution to the photoconversion process.

The presented work completes the state of the art regarding charge transfer processes in dye cells. The presented results are important for the search for new sensitizers and may be a starting point for further research beyond the field of photovoltaics.

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