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"Hybrid materials for dye-sensitized solar cells applications – investigating the influence of TiO_2 modifiers and structure of anchoring ligands in sensitizers molecules on the charge transfer mechanism"

Over the years, unreasonable human activity has severely damaged the nature of our planet. Humanity's main problem today is global warming, which requires immediate prevention of its effects and consequences. First, new solutions should be invented in the energy field to replace conventional energy sources emitting greenhouse gases. One of them is photovoltaics (PV) - an area of science and technology that studies and uses the phenomenon of converting light energy into electricity. This dissertation deals with a specific type of solar cell called dye-sensitized solar cells (DSSC).

The main goal of this doctoral thesis - explaining the phenomena and mechanisms occurring during the operation of DSSC based on TiO_2 nanomaterials doped with transition metal ions, as well as sensitizers with a modified structure of anchoring ligands - has been fully accomplished. Therefore, it should also be emphasized that the intention of the work was not to obtain a cell with record photoconversion efficiency. In order to achieve the above goal, thirteen TiO_2 nanomaterials doped with Zr^{4+}, Cu^{2+}, Mn^{2+}, and Ni^{2+} cations with different percentages of modifiers (including unmodified oxide) were synthesized by the sol-gel method, which does not require the application of extreme synthetic conditions. The structural and optical properties of the synthesized oxides were characterized in detail before they were used to prepare a semi-finished product for producing working electrodes. Moreover, some analyses were repeated after the nanomaterials' calcination in the form of thin layers on the conductive glass surface to determine eventual changes in their structure. In fact, it was found that the nanoparticles on the photoelectrodes surface are slightly smaller than those in the corresponding powders. In this Ph.D. thesis, various types of dyes were used to sensitize working electrodes, depending on the research stage - during the analysis of doped TiO_2:Zr^{4+}/Cu^{2+}/Mn^{2+}/Ni^{2+} nanomaterials, a commercial dye N3 was used. In contrast, in the last part of the study, the influence of the anchoring ligands structure in synthesized for this purpose complex compounds from the BX series (X = 1/2/3) on the charge transfer mechanism in DSSC was investigated. Solar cells based on the obtained nanomaterials and the standard P25 oxide were also characterized by plotting their current-voltage curves and using EIS and IPCE spectroscopy. It should also be mentioned that the experimental results were supported with quantum-chemical calculations to understand better the charge transfer processes between the sensitizer and the semiconductor. The above research strategy was used at all three stages of the doctoral dissertation in which the assumed research hypotheses were proven.

Therefore, the first stage of research work concerned a series of TiO_2 nanomaterials doped with Zr^{4+} ions. In the beginning, it was proved that the synthetic procedure was correct, which ensured obtaining the polymorphic type of titanium(IV) oxide with the nanoparticle's size not exceeding 20 nm. As a result, the experimental data were as close to theoretical calculations as possible. The structure and morphology of the obtained oxides were characterized using XRF, XRD, TEM techniques, Raman spectroscopy, and nitrogen adsorption-desorption analysis. The above research determined the materials' percentage composition, crystalline phase, crystallite morphology, and textural parameters. FTIR spectroscopy and TGA analysis were performed to confirm the correctness of applying the temperature of 450°C to annealing the working electrodes (quantitative and qualitative determination of post-synthetic residues). Then, nanomaterials' optical and physicochemical properties were analyzed using DRS, XPS, UPS, and EPR spectroscopy. It should be emphasized that the experimental data were supported with quantum-chemical calculations in both parts of the characteristics (structural and physicochemical). Thus, incorporating Zr^{4+} cations in the TiO_2 matrix and simultaneously forming structural defects in the form of oxygen vacancies was proved. These modifications significantly impacted the DSSCs' operation mechanism, as the resulting oxygen vacancies contributed to the shift of the Fermi level of TiO_2 nanomaterial doped with 3,7% Zr^{4+} ions towards higher energy values. As a result, an optimal energy difference was obtained between the semiconductor's conduction band level and the dye's LUMO, which increased the driving forces of the electron injection process. According to the author's knowledge, the photoconversion process efficiency measured for a cell based on a titanium(IV) oxide with a content of 3,7% of Zr^{4+} cations, equal to 8,63%, is the highest value obtained so far in the scientific literature related to zirconium-doped titanium(IV) oxide systems.

The second stage of the work was related to a group of nanomaterials doped with Cu^{2+}, Mn^{2+}, and Ni^{2+} ions. Again, the experimental data were supported with theoretical calculations, which was justified, especially since the sizes of nanoparticles obtained in this experiment also did not exceed 20 nm. Analogously to the characteristics of TiO_2:Zr^{4+} nanomaterials, similar research techniques were used to determine the structural properties, additionally expanded with SEM analysis. Thanks to the conducted analyses, the successful incorporation of bivalent metal ions in the TiO_2 structure was proved, contradicting the numerical data of cell parameters obtained by quantum-mechanical simulations. Nevertheless, the dopant concentration was lower than planned, which resulted from the type of metal ion precursor in the form of nitrate(V) salts used in the synthesis. Therefore, it was decided to compare nanomaterials with 0,4% Cu^{2+}/Mn^{2+}/Ni^{2+} ions mainly and to characterize the remaining oxides to show a broader context of the research. Optical and physicochemical properties were determined using DRS, XPS, and EPR spectroscopy. The substitution of Ti^{4+} cations in the oxide matrix by doping ions was proved again, and the presence of oxygen vacancies was found to compensate not only for lattice distortions related to differences in the size of ionic radii but also discrepancies in their charge values. In contrast to the Zr^{4+} ions, it was found that the bandgap width was reduced, and the conduction band

shifted towards higher energy values. The results of measurements of photovoltaic cells made of TiO_2 nanomaterials: Cu^{2+}/Mn^{2+}/Ni^{2+} were confronted with the energy gaps structures of defected and doped oxides obtained by theoretical calculations. Such a holistic approach to the subject made it possible to determine the influence of individual ions in the structure of titanium(IV) oxide on the charge transfer process in DSSCs. The cells with the highest efficiency, equal to 7,98%, were obtained for 0,4% Ni^{2+} doped nanomaterials, which is also the highest efficiency obtained so far for this type of material (TiO_2 doped with Ni^{2+} ions). Each selected doping ion influenced the modified titanium(IV) oxide bandgap structure differently. The flattened intermediate band located just below the conduction band in the TiO_2:Cu^{2+} structure caused a destructive effect on the charge conductivity in the nanomaterial, while the TiO_2:Ni^{2+} specific bandgap structure ensured fast and efficient charge transfer. Simultaneously, in the case of TiO_2:Mn^{2+}, the position of the conduction band related to the LUMO level of the dye was unfavorable, causing the increased contribution of recombination processes.

In the last stage of work, the anchoring ligands' structure influence in BX dyes on the semiconductor-dye interfacial charge transfer process was investigated. The complex compounds differed in the number of carboxyl groups and a type of π-linker in the anchoring ligands. The influence of the modification on the electronic properties was investigated using UV-Vis spectroscopy, based on which, among others, the values of their molar absorption coefficients were determined. Moreover, using the CV technique, the values of the anode and cathode potentials of the signals related to the oxidation and reduction processes were determined, based on which the energy levels of HOMO and LUMO were calculated. The experimental data were supported by quantum-chemical calculations concerning individual dyes' energy levels and their dipole moments for more comprehensive characterization. Then, BX dyes were used to sensitize working electrodes made of standard P25 oxide and selected nanomaterials, i.e., unmodified TiO_2 and doped with 1,2% Zr^{4+} and 0,124% Ni^{2+} ions, synthesized during this Ph.D. project. The analysis of the photovoltaic parameters of cells based on hybrid structures BX_P25 proved to improve the charge transfer between LUMO of the dye and the conduction band of titanium(IV) oxide after the introduction of the second anchor group substituted in the *para* position to the metal center (in the B2 dye). Nevertheless, it was also associated with a shift of the TiO_2 Fermi level towards positive energy values, which increased the contribution of recombination processes. Simultaneously, replacing the ethynyl with phenyl linker (in the B3 dye) caused an increase in the open circuit potential and a significant dye's LUMO level shift towards negative energy values (according to the NHE). As a result, the driving forces of the charge injection process were increased with a reduced contribution of recombination processes, leading to the highest photoconversion efficiency in the BX series, equal to 0,42%. When the cells utilizing synthesized nanomaterials were made, their efficiency was increased, reaching 0,53% for unmodified TiO_2 sensitized with B2 dye. In the case of oxides doped with Zr^{4+} (1,2%) and Ni^{2+} (0,124%) ions, a decrease in the efficiency was observed, confirming the need for the appropriate adjustment of the nanomaterial energy gap structure to the HOMO-LUMO levels of the dye.

Apart from the implementation of the main goal of the study, the assumed research hypotheses concerning the influence of oxygen vacancies and the bandgaps' construction on the charge transfer mechanism in cells made of TiO_2 nanomaterials modified with $Zr^{4+}/Cu^{2+}/Mn^{2+}/Ni^{2+}$ were also confirmed. The relationship between the structure of the dye's anchoring ligands and the process mentioned above was also investigated. The results of the first and second stages of work on modified oxides were presented in two international scientific publications with a total impact factor equal to 11,14. An additional effect of the doctoral dissertation was obtaining two nanomaterials showing cells' record-breaking efficiency in their categories. It is worth noting that the results of this doctoral dissertation supplement the current state of knowledge related to DSSC cells' operation mechanisms and may also constitute a starting point for further research beyond the field of photovoltaics.