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Kraków, 22 August 2023

Review of the PhD thesis „Photoactive hybrid structures based on TiO_2 for photovoltaic applications – a computational approach”

by Oleksandr Korolevych

The PhD dissertation *Photoactive hybrid structures based on* TiO_2 *for photovoltaic applications – a computational approach* was prepared by Oleksandr Korolevych under the supervision of prof. dr hab. Małgorzata Makowska-Janusik, Head of the Chair of Photoinduced Phenomena at the Faculty of Science and Technology of the Jan Długosz University in Częstochowa. The computational research involved the collaboration with several experimental groups from the Adam Mickiewicz University in Poznań, Gdańsk Technical University, and the Le Mans University in France.

The work was devoted to computational studies of titanium dioxide/dye structures of potential interest for applications in photovoltaic cells. For obvious reasons such a subject attracts large scientific attention. To meet the goals set for the reduction of carbon dioxide emissions, with still growing power demands of the modern society, contribution of renewable resources, including solar energy, has to increase substantially. Although the technology of silicon-based photovoltaics has been very successful, a constant search for cheaper, environment-friendly, and easy to fabricate devices is continuing. Dye-sensitized solar cells (DSSCs) emerged as a promising alternative. An archetypal example of a DSSC is titanium dioxide (TiO_2) sensitized with a ruthenium complex. However, with the use of a dye based on expensive and toxic metal (Ru), another expensive noble metal for the electrode (Pt) and a liquid electrolyte, such a cell is neither cheap, nor environment friendly, nor easy to assembly and its energy conversion performance is significantly lower than that of silicon devices. Therefore much effort in invested in research on DSSCs with improved properties. As usual in science, the best results are obtained when theory supports and supplements experiments. Theoretical modeling on modifications of two vital components of a DSSC, the metal oxide and the sensitizing molecule was in the focus of the presented work, which is therefore a timely contribution.

The thesis was prepared in a standard way, as a classical dissertation comprising nine chapters. Chapter 1 is a brief introduction, providing some background information on three generations of solar cells and on the concept of DSSCs and the principles of their operation. Next two chapters present current state of research (mainly experimental) on DSSC components. Chapter 2 focuses on metal oxides, and on TiO_2 in particular, discussing properties of

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its polymorphs and the possibility of modifications by dopants. Sensitizers are described in Chapter 3; ruthenium complexes in Ch.3.1, followed by information on selected metal-free dyes in Ch.3.2. Chapter 4 is an introduction to the computational methods used in the work. Typical methodologies of solid state physics and quantum chemistry are applied in the thesis to solve the electron structure of investigated systems and to calculate their optical properties. Accordingly, described methods are the standard approaches of quantum chemistry: Hartree-Fock, Density Functional Theory (DFT) and semi-empirical, with variants adapted to systems with translational symmetry. I think that also the quantum-chemical methods used to study optical excitations (time-dependent HF/DFT, configuration interaction with single excitations) should have been described in this chapter, because they were widely used in Chapters 7 and 8. At this point I should underline that the use of quantum-chemical methods is non-surprising, even though the thesis has been submitted for the degree in Physics. At the atomic level, chemistry and physics become unified, sharing common methodologies and the distinction between the two is quite often merely a matter of terminology. Probably it would be better to change the sequence of Chapters 4 and 5, that is, first define the problem and then present the methodology to solve it. Nevertheless, the methods are adequate to the aims of the thesis outlined in the next chapter.

Objectives of the work are briefly defined in two-page Chapter 5. These comprise investigations of band structure of TiO_2-based materials with dopants and defects, studies on optical properties of modified dye molecules and on the oxide-dye coupling relevant to charge transfer. Altogether, there objectives constitute an original problem. The obtained results are described on almost 140 pages in three next chapters.

Structural and electron properties of TiO_2 are discussed in Chapter 6. The study starts with finding an appropriate method (parameters of Hubbard potential) to model the bulk anatase crystal. As the aim of this part of the work was to investigate several modifications of the oxide by defects and dopants, breaking the translational symmetry, a model supercell was used for further calculations. Relaxed geometries, band structure/band gaps and effective masses of charge carriers were computed for a series of systems with Ti atoms substituted by other metals (Zr, Ni, Cu or Mn), doped with N atoms and/or containing vacancies. Next, similar investigations were performed for thin layers of neat TiO_2 and its selected modifications. Finally, UV-vis absorption spectra were calculated for small clusters of TiO_2 with hydrogen terminating atoms using semi-empirical PM6 method; these calculations were aimed at selecting the cluster size and the modeling method for the modeling of nanocluster-dye structures. Computational results are supplemented in Chapter 6.4 by experimental studies on the structure (X-ray diffraction, Raman spectra) and optical properties (optical absorption spectroscopy) of TiO_2 films. Experiments were performed by the Author of the thesis during his visit to the Prof. Kassiba's group at the Le Mans University. Whereas supplementing of an experimental work with computations is quite common nowadays, performing experiments in addition to a mostly theoretical dissertation is rather unusual and shows that the Author is open to new challenges and learning new skills. Thorough the Chapter 6, several other theoretical results obtained for studied systems (or similar) are referenced in comparison to the Author's data. It would have been therefore helpful for the reader if the novelty of the current research had been better underlined. In my understanding, the innovation is in presenting a common methodology of electron structure calculations for neat and modified TiO_2 nanostructures, allowing the results for different structures to be compared within a single computational framework.

Chapter 7 is focused on investigations of dye molecules used (or proposed for the use) in DSSCs. The size of studied systems became a factor limiting the possibility of performing calculations (in particular, computations of optical transitions). Therefore a large part of this chapter describes the efforts to find suitable combinations of methods and basis sets for geometry relaxation and calculations of excited states, yielding satisfactory agreement with existing experimental data at a reasonable computational cost. UV-vis spectra were calculated for optimized structures and compared to experiments, where available. Analysis of the spectra was based on the determination of the parentage of calculated transitions and the orbitals involved in the excitation – with relation to the possible mechanism of electron transfer to the electrode. Although the absorption spectra were the primary subject thorough the chapter, for one selected dye, named RuLp, also the electroabsorption (EA) spectrum was calculated (presumably as a difference of two absorption spectra computed at zero and non-zero electric field – this was not stated explicitly). There are only few reported cases of direct quantum-chemical calculations of EA spectrum. Obtaining the differential spectrum is a challenging task, requiring a good reproduction of the two underlying spectra. Therefore this result is particularly interesting and should have been better exposed.

The dyes investigated in Chapter 7 are mainly the ruthenium complexes, starting with the $[Ru(bpy)_3]^{2+}$ and three its derivatives with carboxylic anchoring groups in different positions. Then the discussion continues to four complexes containing two Ru(II) moieties; experimental results exist for three of these structures. Finally, in Ch.7.3, two series of derivatives of commercially available dyes were studied with modifications aimed at improving the oxide-dye interactions by changing the anchoring part of the molecule. These dyes were purely organic molecules, therefore interesting as a possible alternative to Ru-based dyes. Unfortunately, the results of the modeling predict no significant improvement of the properties relevant to photovoltaic applications.

In Chapter 8, the knowledge about titanium dioxide clusters and on sensitizing dyes gained in preceding sections of the thesis is combined in an investigation of TiO_2/dye complexes. The size of the systems (nanocluster+dye) restricted the applicable quantum-chemical methods to low-level or semi-empirical. Even the full geometry optimization of the whole structure was not feasible, therefore in the study of dye anchoring to TiO_2 (Ch.8.1) a small molecule was used in nanocluster relaxation as an anchoring template which was finally substituted by the separately optimized dye molecule. The complexes investigated in Chapter 8 used the mono- and bi-ruthenium dyes selected in Chapter 7. Electron structure and optical spectra calculations were used to compare the UV-vis spectra to the measured data and to analyze the frontier orbitals involved in optical excitations and charge transfer.

Introductory chapters and the description of results are supplemented by references to scientific literature; providing background to the applied methodology, information on the current state of the research in the field and references to experimental data and relevant computational results. The list of references is comprehensive, with some minor deficiencies mentioned in the following part of the report. References are presented at the end of each chapter, therefore it is not easy to estimate the total count of unique citations; depending on the length of the chapter, the number of references is between 20 and 80.

Final conclusions of the thesis and some perspectives for future studies have been formulated in short Chapter 9. Overall, the work demonstrated the performance of computational modeling for oxides and dyes used in DSSCs. The approach developed in the thesis is useful mainly in supporting and elucidating experimental data. The results have no direct technological importance, but this cannot be expected from a basic research. Costs of calculations caused by the size of studied systems forced the Author to select the computational method for each part of the system based on comparisons with experimental data. This limits the predictive power of the methodology when completely new systems were considered. Nevertheless, the thesis is an interesting and valuable contribution to the field. The results obtained by Mr. Korolevych have been partially published in four papers [2 papers in *Materials* (IF_{2022}=3.4, 140 pts), 1 paper in *Solar Energy Materials and Solar Cells* (IF_{2022}=6.9, 140 pts) and 1 paper in *Applied Surface Science* (IF_{2022}=6.7, 140 pts)], another paper has been submitted.

After reading the thesis, I have several questions or comments, listed here in the order of appearance, not by their significance:

- The value of the Hubbard parameter U had to be adjusted in the calculations for TiO_2, which is a commonly used procedure. Of key importance is the parameter used in the band structure calculations, giving the correct band gap – and this is well described in the text. I wonder how the value used for geometry relaxation was set: according to Table 6.1, the best agreement of lattice periods is obtained for U=0. The Author apparently considers that not the lattice parameters themselves, but rather their ratio is more important – why? This ratio improves with increasing U value, so why U=6 was chosen, instead of the same value as for electron structure calculations, yielding even better *c*/*a* ratio?
- What was the initial structure for geometry relaxation of TiO_2 – the known crystal structure? How much the band structure for neat TiO_2 depends on the geometry, that is, whether the value of U used in structure relaxation really matters for the electron structure?
- How large the band gaps of TiO_2 and ZrO_2 would be, if the crystal structures (without geometry relaxations) were used for band structure calculations?
- What was the accuracy of the electron structure calculations, accordingly, how precisely the system could be classified as a direct or an indirect gap semiconductor? For example, in Fig. 6.4 a direct gap is shown for ZrO_2, but the energy of the valence band at the M point is close to the energy at the Γ point and the energy at the A point seems even higher. How much the energies (and accordingly direct/indirect gap assignments) are affected by the parameters of calculations (e.g. the grid size)?
- In Ch.6.1.2 (page 103) it is stated that the band gap for TiO_2 doped by Ni is 2.50 eV and "It is in agreement with data presented in Fig. 6.9 where the

Ni impurities are accompanied by v(O)" - but the band gap shown in Fig. 6.9 is 3.33 eV.

- It is unclear how the results were rescaled (page 110).
- What was the charge/spin state of TiO_2 clusters investigated in Chapter 6.3? Neutral clusters with an odd number of H atoms must have an odd number of electrons – so how could the restricted HF formalism be used?
- Page 121: "Without saturating hydrogens the obtained spectra do not agree with experimental results" – a reference to the experimental data is necessary (and a brief comment on the differences between the calculations and the experiment would be helpful).
- According to Fig. 6.26, there are several excited states calculated in the range 300-360 nm. How these states were selected to be shown in Table 6.5 – according to the largest oscillator strength? Table 6.5 would have been more informative if the orbitals involved in the excitations had been labeled with their contribution to the transition – this comment regards also many other plots in Chapters 7 and 8. Perhaps showing the Natural Transition Orbitals would be instructive in the cases where many orbital pairs contribute to the transition.
- Page 131: "Table 6.2 presents the statement that the 2×2×1 $TiO_2:N_O$ structure has better stability than structures with Ni and Mn impurities" – but it is stated in page 128 that "the N impurities introduced substitutionally destroyed the TiO_2 lattice structure". Therefore these statements possibly refer to two different structures?
- Page 131: "doping of TiO_2 with Zr^{4+} ions … generates oxygen vacancies" – how this conclusion was drawn – vacancies were just introduced to the initial structure of the system.
- Page 144: "The better geometry of the $[Ru(bpy)_3]^{2+}$ was achieved when the molecule is in the neighborhood of the $(PF_6^-)_2$" – how the goodness of the geometry was assessed? Anyway, it is not surprising that for a charged complex better results are obtained when counterions are present and a solvent model is used.
- A general question regarding several calculations with an implicit solvent: why dimethylformamide was used, although the experimental spectra were measured in alcohols or acetonitrile? The choice of the solvent would probably have a marginal impact on the results, but why not to choose the solvent used in experiments?
- How the positions of PF_6^- anions were optimized in the structure? I guess that there are several local minima for different anion positions. Does the calculated UV-vis spectrum depend on the location of counterions?
- In Fig. 7.11 frontier orbitals involved in the transition are localized mainly on the one of two dye moieties (especially in vacuum). As the B_1 molecule is symmetric, one may expect that there should be another transition involving the other part. Can it be found in the data? This may be an example of a more general problem: several transitions with similar energies are calculated but only one of the them is analyzed in more detail.
- Page 165: A band at 325 nm was reported for B_1 molecule and the Author writes "In the next part of the work, I will try to explain the nature of this peak". I have not found such an explanation in the text. Moreover, the said peak, noticeable in the spectrum of B_1 in Fig. 7.10, disappeared in the experimental spectrum in Fig. 7.19 – why?

- Page 170: what is the structural instability of B_4 observed during relaxation, and what geometry was used in that case to obtain the spectrum in Fig. 7.15?
- Page 185: Positions of the first absorption peak measured in solution for D102 and D149 are 503 and 532 nm, respectively. Why these wavelengths are compared to the values 447 and 489 nm calculated in vacuum, instead to 508 and 549 nm obtained in the solvent?
- Page 185: "The DMF solvent increases the polarizability of all molecules" – but no polarizability is presented in Table 7.15. Did the Author mean "dipole moment" instead?
- The clusters used in oxide/dye structures in Chapter 8 are distorted from the TiO_2 structure what could affect their electron properties. What does it mean that "freezing the atoms on the surface of the cluster does not give good results" (page 200)? Why to freeze the atoms on the surface? A reasonable approach seems to be the opposite: allowing the surface to adapt its geometry to the anchoring atoms of the dye while imposing constraints on the atoms in lower layers to keep the structure possibly close to bulk TiO_2.
- How the charge of the clusters with anchored molecules was balanced? – after the deprotonation of the COOH group, the molecule becomes an anion.
- Page 203/Table 8.3 – what are the binding energies of anchoring templates and B_n molecules? Calculated values are presented only for RuLx dyes.
- Unfortunately, no orbitals were labeled in the plots in Chapter 8, therefore we do not know if the LUMO is shown in any of the panels of Fig. 8.12. Nevertheless, the difference to Fig. 8.9 is presumably not due to the choice of a particular orbital (I think that LUMO+x behaves similarly to the LUMO), but it is rather the effect of the cluster size. And this difference is even qualitative: in Fig. 8.9 LUMO is located on the oxide part, whereas the unoccupied orbitals displayed in Fig. 8.12 are located on the dye molecule. With such a huge dependence on the cluster size/shape, the results obtained in Chapter 8 and the conclusions about possible charge transfer may be rather questionable.
- A general comment regarding the discussion on the unoccupied orbitals with respect to charge transfer. LUMO was considered when the principles of operation of DSSCs were described in Chapter 1. However, as shown in Chapters 7 and 8, the target orbital in the optical excitation is not necessarily the LUMO, but it may be one of higher orbitals as well. Accordingly, LUMO+x and not the LUMO is then relevant to the charge injection process.

I have also found several mistakes or inconsistencies in the text; some of them are listed below.

- Some abbreviations are incorrectly defined (and used in the text): CB is conduction band (not "conductional"); HOMO is not "higher" but the highest occupied molecular orbital; LUMO stands for the lowest unoccupied molecular orbital (not "lower"); PF_6^- is hexafluorophosphate; RPA (not PRA) is used for random phase approximation.

- There is no dihexafluorophosphate $(PF_6)_2$ (Fig. 3.3). PF_6^- is a hexafluorophosphate anion and two anions are required to balance the charge of the ruthenium complex. But they do not form dimers.
- The anchoring template used in Chapter 8 is not benzene but benzoic acid and phthalic acid (or rather benzoate and phthalate anions).
- In chemistry, "molecule" is used for a neutral species. A charged molecule becomes an ion (anion or cation). Accordingly, PF_6^- are anions and $[Ru(bpy)_3]^{2+}$ is a cation (not a molecule).
- Unfortunately, quite a common misconception regarding the relation of frontier orbitals to the ground and the excited state appears repeatedly thorough the text. HOMO and LUMO orbitals (more general HOMO-x and LUMO+x) are the orbitals of the ground state of the system. In the orbital picture, an excitation is described by the electron transfer from an occupied orbital to an unoccupied orbital (e.g. HOMO → LUMO), but neither HOMO is the ground state, nor LUMO is the excited state! Both are the orbitals describing the ground state.
- TDHF is not used to calculate the frontier orbitals (Table 7.4). Orbitals result from ground state HF calculations. TD formalism is needed to find the energies of optical transitions.
- In the text, the wavelength of the MLCT transition in N749 is 920 nm (page 42), but 620 nm in Table 3.1 (page 41).
- Page 161: I have some doubts about the labels in Fig. 7.8. According to the text (page 152), the second MLCT transition is experimentally observed at 245 nm and it was red-shifted by 30 nm in TD/PM6 calculations. But in Fig. 7.8 the band at about 375 nm is assigned (arrow b) to a pair of orbitals looking like they are involved in a metal-to-ligand transfer.
- Pages 173-174: "HOMO energy is not affected by solvent". According to Fig. 7.18, this is not true: changes of the HOMO energy are similar to the changes of LUMO levels. Otherwise, the statement "The solvent does not change the E_g of the B_x molecule significantly compared with vacuum-calculated data" could not be true. Similarly, the sentence: "Because LUMO is associated with orbitals located far from the Ru atom it is sensitive to the nature of the environment" seems to disagree with what was stated on the preceding page: "the LUMO energies are in better agreement with the ones calculated in vacuum".
- Page 192: "the molecules B_3 and B_4 are rather good candidates for photovoltaic applications". How can B_4 be a good candidate although its synthesis was unsuccessful and even the calculations indicated instability of this compound?
- There are numerous misspelled words in the text, even some well-known names, e.g. Koch-Sham (p. 67), Kohn-Shame, Bassel (p. 74) or Beck (p. 71). I'm not the right person to assess the quality of the language; certainly there are errors in grammar and style, but the text can be understood. Nevertheless, I could not figure out what was the intended meaning of the word "although", apparently not being used as a conjunction.

Overall, these critical comments do not affect my positive opinion on the work.

Final conclusions

The work proves that the Author has knowledge of the current research on the DSSCs, on its background and on the recent literature as well as shows the understanding of computational methods used to solve electron structure problems in solid state physics and quantum chemistry. The Author has demonstrated the skills to define a scientific problems and to use the methodology to analyze and to solve it. The work presented in the thesis has contributed new knowledge to the research on DSSCs.

I conclude that the PhD thesis of Mr. Oleksandr Korolevych meets the customary and the formal requirements according to the Law on Higher Education and Science (Dz. U. 2018, poz. 1668, with later amendments). Therefore, I recommend the admission of Mr. Korolevych to further stages of the proceeding.

I suggest also considering the possibility of awarding the PhD with distinction. The reasons are the following:

- The computational work was performed in a close collaboration with several research groups and supported the experiments.
- Some experimental research has been performed by the Author, in addition to computations.
- There are some quite original results in the work, e.g. the electroabsorption spectrum calculated from first-principles.
- Results have been published in four papers, two of these in journals with IF > 6.

Therefore, I think that the distinction should be discussed, according to the rules implemented at the J. Długosz University.

Wnioski końcowe

Po zapoznaniu się z pracą doktorską p. Oleksandra Korolevycha stwierdzam, że spełnia ona wymagania stawiane rozprawom doktorskim, zarówno zwyczajowe jak i formalne określone przez Ustawę Prawo o Szkolnictwie Wyższym i Nauce (Dz. U. 2018, poz. 1668, z późniejszymi zmianami). W związku z tym wnoszę o dopuszczenie p. Korolevycha do dalszych etapów postępowania o nadanie stopnia.

Jednocześnie sugeruję rozważenie możliwości wyróżnienia rozprawy, zgodnie z kryteriami przyjętymi na Uniwersytecie J. Długosza. Uzasadnienie podaję wyżej, w angielskojęzycznej części recenzji.

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