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Chapter 8

DFT-based Theoretical Simulations for Photocatalytic Applications Using TiO_2

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http://dx.doi.org/10.5772/intechopen.68976

Abstract

TiO_2 has been shown to be a potential candidate for photoinitiated processes, such as dye sensitized solar cells and water splitting in production of H_2. The large band gap of TiO_2 can be reduced by functionalizing the oxide by adsorbing dye molecules and/or water reduction/oxidation catalysts, by metal/nonmetal doping, and by mixing with another oxide. Due to these methods, several different TiO_2-based complexes can be constructed having different geometries, electronic structures, and optical characteristics. It is practically impossible to test the photocatalytic activity of all possible TiO_2-based complexes using only experimental techniques. Instead, density functional theory (DFT)-based theoretical simulations can easily guide experimental studies by screening materials and providing insights into the photoactivity of the complexes. The aim of this chapter is to provide an outlook for current research on DFT-based simulations of TiO_2 complexes for dye sensitized solar cells and water splitting applications and to address challenges of theoretical simulations.

Keywords: density functional theory, ab-initio molecular dynamics, photocatalyst, TiO_2, dye sensitized solar cells, water splitting

1. Introduction

Emergent technologies and the demand for alternative energy sources, which do not produce greenhouse gases as a byproduct lead to a growing awareness in using those renewable sources already provided by nature, such as sunlight. The ideal goal is to emulate the photochemical process with which the plants convert H_2O and CO_2 into O_2 and carbohydrates by absorbing photons in the energy range between 3.3 and 1.5 eV (visible spectrum). Scientists then aim at designing new catalysts that can employ the easily available sunlight and convert it into chemical energy, without depending on the activation energy generated by traditional fuels.

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In 1938, for the first time, Goodeve and Kitchener [1] demonstrated the photocatalytic activity of the TiO_2 surface, which can produce oxygen by absorbing UV light thus leading to the photobleaching of dyes. This study has initiated many others toward discovering photocatalytic reactions that can be catalyzed by TiO_2. The success of this material is also justified by its high stability, low cost, no side effects on humans and environment, and ease in large-scale usage. In spite of the promising properties of TiO_2, the photocatalytic activity of the bare surface is not optimal, due to the too large energy gap [2]. This limits the photons' absorption and induces the fast recombination of the photogenerated carriers [3]. While these drawbacks significantly hinder the effective application of the pristine material, several possible solutions have been envisioned by considering surface modifications, such as composite semiconductor coupling, metal/nonmetal doping, and functionalization by means of different types of adsorbates [4]. For instance, Zn-porphyrin adsorbed on the TiO_2 surface reduces the threshold for the photons' absorption, and by allowing the fast electron injection toward the substrate, slows down the charge recombination process [5].

Among many photocatalytic applications of functionalized TiO_2 surface, water splitting for H_2 production and dye sensitized solar cells (DSSCs) are among the most widely studied topics. Although the increasing number of promising studies is going to build photocatalytically efficient and robust several TiO_2-based materials, in this field, the support of the theoretical approach to explore the properties of possible candidate materials is essential. The investigation of proper atomistic models of the systems of interest, possibly including the electronic structure characterization and reproducing the relevant processes, can significantly help the screening of materials. In particular, it is necessary to understand the nature of the adsorbate-substrate interaction, and providing insights into the photoactivity prior to extensive experimental efforts. The aim of this chapter is to review the current progress and challenges in density functional theory (DFT)-based simulations of functionalized TiO_2 surfaces, including rutile, anatase, and TiO_2 nanoparticles, with respect to the applications in photocatalytic water splitting and DSSCs.

2. Overview on density functional theory

DFT is developed by Hohenberg, Kohn, and Sham [6, 7] in 1964 as a minimization problem of the ground state energy as a function of electron density. The approach is to solve any fully interacting problem by mapping it to a noninteracting problem introducing exchange-correlation functional, see Eq. (1).

$$E = T_s[\rho(r)] + J[\rho(r)] + \int v_{ext}(r)\,\rho(r)\,dr + E_{xc}[\rho(r)] \tag{1}$$

where $T_s[\rho(r)]$ is the kinetic energy of the noninteracting system, $J[\rho(r)]$ is the classical Coulomb repulsion energy, $\int v_{ext}(r)\,\rho(r)\,dr$ is the interaction of the external potential acting on the electrons, and $E_{xc}[\rho(r)]$ term is the exchange and correlational energy. All of these terms are called functionals and they depend on the electron density $\rho(r)$, i.e., the number of electrons per unit volume.

Electron density can be expressed in many ways [8]; however, Gaussian and plane wave formalism is shown to be significantly efficient for the description of the orbitals [9]. A localized Gaussian basis set positioned at each atom is used to expand the Kohn-Sham orbitals and an auxiliary plane wave basis set is used to describe the electron density, thus improving the computational performance in the calculation of the Coulomb interactions. This scheme is shown to be a suitable choice for large-scale DFT simulations [10, 11].

Although the achievement in introducing electron density depends on the total energy instead of the electron wave function formalism and providing simple, universal, and self-consistent-field description of the ground-state electronic structure, any practical usage of DFT requires an accurate description to the exchange and correlational effects, $E_{xc}[\rho(r)]$, see Eq. (2).

$$E_{xc}[\rho(r)] = (V_{ee}[\rho(r)] - J[\rho(r)]) + (T[\rho(r)] - T_s[\rho(r)]) \tag{2}$$

where $T[\rho(r)]$ is the kinetic energy of the interacting system and $V_{ee}[\rho(r)]$ is the nonclassical interaction between electrons. Although the exact analytic expression of the exchange-correlation functional is not known, approximations to these terms have been demonstrated to be able capture most of the physical/chemical properties of many systems from the solid state to the liquid state.

Many methods have been proposed to calculate exchange-correlation contribution to the total energy [12]. One of the most commonly used ones is the generalized gradient approximation (GGA), where the exchange and correlation energy depends on both electron density and its gradient [13]. This method includes semiempirical functionals that consist of one or more parameters fitted to experimentally observed quantities. Perdew-Burke-Ernzerhof (PBE) [14] and Becke exchange/Lee-Yang-Parr correlation (BLYP) [15] are the most popular semiempirical functionals. These functionals are successfully applied to many systems from metals to 2D self-assemblies [16]. However, it is shown that they fail to reproduce some of the experimentally observed properties of oxides accurately, due to the incorrect description of electronic localization by standard DFT [17]. The problem is the incomplete cancellation of the Coulomb self-interaction in GGA functionals, which leads to stabilization of electron delocalization [18]. For instance, PBE density functional is shown to be quite good to capture structural properties of both bulk phase and the surface of TiO_2; however, band gap of bulk TiO_2 is predicted as 1.74 eV [19] which significantly underestimates the experimentally measured band gap of 3.2 eV [20]. Therefore, for electronic structure analysis and band alignment of oxides one should go beyond GGA [21].

One of the commonly applied methods to overcome the failure of GGA is to use hybrid density functionals that mix exact exchange from Hartree-Fock exchange [22] and correlation from GGA. Applying hybrid functionals removes some of the self-interaction error and favors localized electronic states by reducing the barrier to the localization [23]. Including orbital analogue of exchange formalism in hybrid functionals often improves the accuracy of the simulations; however, computational cost increases by at least an order of magnitude with respect to the pure GGA formalism. The most popular hybrid functionals are, e.g., HSE06 [24] and PBE0 [25]. The band gap of the bulk TiO_2 is calculated to be 4.21 eV [26] and 3.35 eV [21]

by PBE0 and HSE06, respectively. Although larger band gaps are obtained for semiconductors using hybrid functionals, one should carefully choose the exchange-correlation formalism since significantly larger band gaps can also be obtained, e.g., PBE0.

For most of the photocatalytic applications of TiO_2, a photosensitizer or an active catalyst is adsorbed on the surface in which case both chemical and physical interactions play a role on the adsorption geometry or stability of the complex. For instance, it is shown that cis/trans coordination of the ligand with respect to anchoring group adsorbed on anatase TiO_2 (110) surface affects binding mode of the dye which likely arises due to the dispersion interactions [27]. It is well known that the exchange-correlational functionals suffer for a poor description of dispersion interactions or van der Waals interactions. To increase the accuracy of the simulations the missing dispersion interactions can also be incorporated into DFT. One way is to add dispersion energy correction term, Grimme-D3 [28], which calculates pairwise interactions between atomic species and shows usual $1/r^6$ asymptotic behavior, on top of the total energy obtained by DFT.

Using DFT, one can optimize structures, determine the most stable adsorption geometries, calculate corresponding adsorption and interaction energies, and extract electronic properties. Electronic structure can be analyzed by calculating projected density of states, which also provides energy band gaps, schematic representation of molecular orbitals, charge distribution maps, and charge density difference maps. On the other hand, the exploration of the conformational space at finite temperature is obtained by running ab-initio molecular dynamics simulations (AIMD) [29] through the generation of trajectories of several picoseconds. Phase-space trajectories are generated via numerical integration of equations of motion. Due to the advances in the electronic structure calculations, forces can be derived directly from the electrons without any empirical parameters. Within the Born-Oppenheimer approximation [30], electrons are fully decoupled from the nuclear motion at each MD step. Nuclei is subsequently propagated according to the forces obtained from the electronic structure calculation from timestep to timestep.

Although there are significant contributions to the modeling of materials/devices using many simulation methods, such as time-dependent density functional theory (TD-DFT) [31] or quantum mechanics-molecular mechanics (QM/MM) [32], it is beyond the scope of this chapter to give a complete overview of all studies with different simulation techniques. Therefore, the following sections will focus on theoretical simulations of DSSC and water splitting using DFT, sometime in combination with AIMD.

3. Theoretical simulations for photocatalytic applications of TiO_2

The photoinitiated reactions can be performed using TiO_2 as a substrate-like film having 2–3 μm thickness with 4–10 μm surface area [33], supported on another material, or in the form of nanoparticles ranging from 10 to 300 nm [34] depending on the preparation conditions [35]. There are three main stable crystal phases of TiO_2 rutile, anatase, and brookite, that being interested in heterogeneous catalytic processes. We consider the interactions at the TiO_2 surfaces, and that the most stable surfaces, i.e., the exposed surfaces of TiO_2 films or nanoparticles are the rutile (110) and anatase (101) surfaces [36]. Among these surfaces, the most stable one is known

to be the rutile and this is also the reason why it is easier to grow high quality single crystal thin films of rutile exposing the (110) surface [37]. Regarding the electronic structures, the band gaps of rutile and anatase are very similar, ≈3.2 eV; in the case of nanoparticles, some effects due to the finite size might appear, for example, the band gap increases slightly and becomes 3.35 eV [38].

For photocatalytic applications of TiO_2, the anatase phase is often preferred to the rutile phase because of its higher activity [39]. This characteristic is attributed to the its larger conduction band (CB) edge energy [40]. On the other hand, the comparison of DSSC performance of rutile and anatase films shows that their voltage and current characteristics are very similar. The overall solar energy conversion efficiency of rutile is only a few percentage lower than the efficiency of the anatase cell [41]. Given the relatively small difference in activity, rutile and anatase phases are the most widely explored phases of TiO_2. Therefore, in the following sections, we are going to consider only the anatase and rutile TiO_2 polymorphs.

3.1. Dye sensitized solar cells

3.1.1. Historical overview

DSSCs are obviously an important and promising application area of TiO_2, converting photon energy to electric energy. The very first examples of DSSCs have been developed in 1954 by Rappaport and coworkers [42]. Gallium arsenide (GaAs)-based p-n junctions, which are formed by joining n-type and p-type semiconductors, were proposed providing a solar energy conversion efficiency of 6%. The main drawback of such a system has always been its high fabrication cost on a large scale, thus preventing its commercialization. In 1991, O'Regan and Grätzel [43] proposed the today's known modern photovoltaic cell based on a n-type highly porous layer of TiO_2 film coated with a monolayer of dye molecules. This system can be produced at a much lower cost and it mimics photosynthesis providing a photon energy conversion efficiency of 7% under sunlight and 12% under diffuse natural light. Dye molecules absorb photons in the visible light region, while TiO_2 nanoparticles are employed to harvest the excited electrons from the dye's conduction band. The large band gap of TiO_2 is overcome by anchoring the dye to the TiO_2 exposed surfaces by means of properly chosen linking groups, dyes to the device are chemically stabilized on oxide nanoparticles by anchoring groups, for instance by carboxylates. Another advantage with respect to the GaAs-based photovoltaic cells is the extremely thin layer of dye molecules on a TiO_2 substrate which facilitates photosensitization and the electron injection into the TiO_2 conduction band with an efficiency of close to unity [44]. The early discovery of these interesting features and of the advances obtained by the efficient combined dye/TiO_2 systems, the research in this area has been strongly supported and it has led to significant progress in the field of photovoltaics.

3.1.2. Working principle of DSSC

A schematic representation of the most common TiO_2-based DSSC is shown in **Figure 1(a)** where the working principle of DSSC is also illustrated. A transparent conductive oxide (TOC) layer, commonly treated with a glass sheet, is the anode that is exposed to photons in the visible spectrum [45]. A mesoporous layer of TiO_2 nanoparticles is deposited over the TCO layer. In order to facilitate the photosensitization, dye molecules having relatively small band gap are

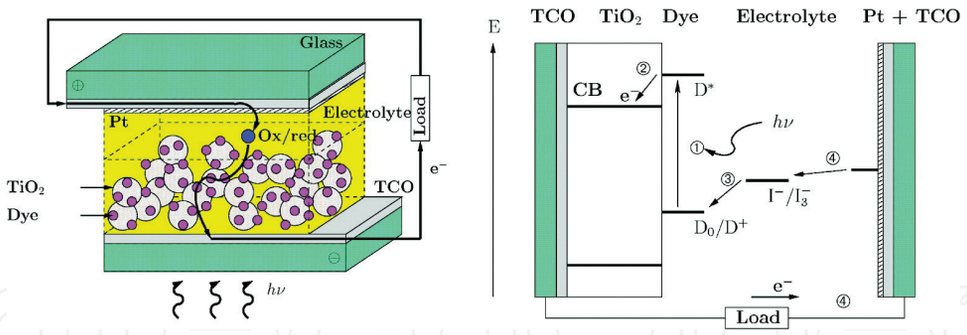

Figure 1. DSSC schematic (left) structure and (right) working principles. TCO stands for transparent conducting oxide. Reprinted with the permission from Ref. [46]. Copyright (2012) American Chemical Society.

chemically bonded to the surface of TiO_2 nanoparticles. The environment is filled with an electrolyte solution, typically consisting of acetonitrile as a solvent and iodine/triiodide (I^-/I_3^-) as a redox couple. The electrolyte is responsible for the regeneration of the dye molecules. The cathode part consists of TOC and an effective catalyst, generally Pt, to collect electrons from the anode.

Exposure to sunlight leads to charge separation in the dye molecules, thus generating excited electrons (e^-) in the conduction band (CB) and electron vacancies, holes (h^+) in the valence band (VB) of the dye. The photogenerated electrons are injected into the TiO_2 CB, thanks to the characteristic ultrafast electron transfer (fs timescale) [47]. Through the oxide, the electrons can be transferred to the TOC at the anode part [48]. This is known as the indirect mechanism. The direct electron injection from the VB of dye into the CB of TiO_2 is also possible which is reported to be faster than an indirect mechanism [49]. Transferring electrons from the anode to the cathode creates an electric current. The photogenerated holes in dye molecules combine with the electrons in $3I^-$, oxidizing $3I^-$ to I_3^-. The electrons at the Pt cathode reduce I_3^- to $3I^-$ so that regeneration of the electrolyte solution is also completed. Thanks to this working principle, solar energy is converted to an electric current in a complete cycle.

In order to be efficient, the described devise has to satisfy some essential conditions. The absorption spectra of the photosensitizers should have a good overlap with the whole solar light spectrum and some of the near-infrared regions. Moreover, the dyes should have high molar extinction coefficient, which is a measure of how strongly a substance absorbs light at a given wavelength per molar concentration. The dye's chemical stability is an another important feature, which affects the lifetime of the device. This can be achieved by chemically linking dyes and semiconductors using anchoring groups. In addition to the chemical stability, properly chosen anchoring groups might also strengthen the degree of coupling between the dyes and oxides thus enhancing the electron injection into the semiconductor CB [50].

It is necessary for a photosensitizer to promote electron injection into TiO_2 layers efficiently. The dye's LUMO has to be aligned correctly if the anchoring group is present, then also its LUMO alignment matters, in particular it has to be energetically close to the dye's LUMO and probably partially overlapping. Besides, the LUMO of the dye should be higher than the CB edge of the oxide to make the electron injection possible. To achieve proper regeneration of the dye, its highest occupied molecular orbital (HOMO) should be below HOMO of the redox mediator, see **Figure 1(b)** for illustration of the complete charge transfer mechanism.

3.1.3. Insights on DSSC components

Dye molecules are relatively well understood with respect to the complex surface structures of TiO_2 phases. The commonly used photosensitizers are either metal-free organic donor-acceptor dyes, such as polythiophenes [51], polypyrroles [52], azobenzene, catechol, and anthraquinone [53] or transition-metal based ligand complexes, such as Ru-polypyridyl molecules [54]. The metal-free organic dyes have large π conjugation leading to π-π^* transitions following the photon absorption. Higher extinction coefficients can be obtained by functionalizing metal-free organic dyes using different donor-acceptor groups, introducing heteroaromatic groups, or changing the number of double bonds in the dye structure thus enabling absorption spectra tuning [33]. Recent advances in designing purely organic dyes adsorbed on nanocrystalline TiO_2 result in achieving solar to power conversion efficiency of 9.5% using indoline dye by Ito et al. [55] and 9.8% using thienothiophene conjugated chromophore by Zhang et al. [56]

Transition metal-based dyes show higher efficiencies with respect to their fully organic counterparts. This is attributed to their capability of absorption in large spectrum range from the visible to the near-infrared regime. The ligand system, i.e., polypyridyl-based or phthalocyanine-based, can be complexed with a chosen transition metal, i.e., Ru, Zn, Mg, and Co. The possibility of long-lived metal-to-ligand (MLCT), d-π^*, or ligand-to-ligand (LLCT), π-π^*, charge transfer once exposed to solar light makes them promising candidates for DSSC applications. However, all these advantages come with a cost, such as the presence of expensive transition metal, i.e., Ru, and rather difficult synthesis and purification steps. Nontoxic and cheap natural dyes that are already present in vegetables and fruits are another possibility to consider. However, unlike synthetic dyes, their recorded efficiency is only around 2% [57].

As already stated, dye molecules are bound to the TiO_2 surface by anchoring groups to enhance chemical stability of the complex. The anchoring groups should be well chosen, since the presence of water in electrolyte solution may weaken the binding strength of the anchors to the TiO_2 surface thus leading to desorption of the dye molecules. Phosphonate groups have been proposed for anchoring Ru-dye/TiO_2 complex and shown to be better candidates than carboxylates [58]. Formic acids are another common example of anchoring groups used in DSSCs [59]. In addition to chemical stability, anchoring groups also affect the degree of coupling between the dye and the semiconductor, which promotes/hinders electron injection into oxide CB. It is shown that strong coupling between Ru-based dyes and TiO_2 nanoparticles anchored by carboxylates leads to an electron injection on femtosecond timescale. On the other hand, SnO_2 and ZnO thin films having lower density of states coupled to a dye/anchoring group have much slower electron injection time with respect to TiO_2 [60].

3.1.4. Simulation studies for DSSC

Up to date, Ru-based dyes such as N3 and N749 are the most widely investigated dyes with recorded efficiency of 11.4% [61]. Labat et al. [62] studied the electronic and structural properties of N3 dye on anatase (101) surface using DFT. As depicted in **Figure 2** while computed orbitals of the HOMO and HOMO-1 are centered on N3 dye and correspond to a $t_{2g} - \pi^*$ interaction between Ru and the ligand, the LUMO is distributed over anatase slab. This picture

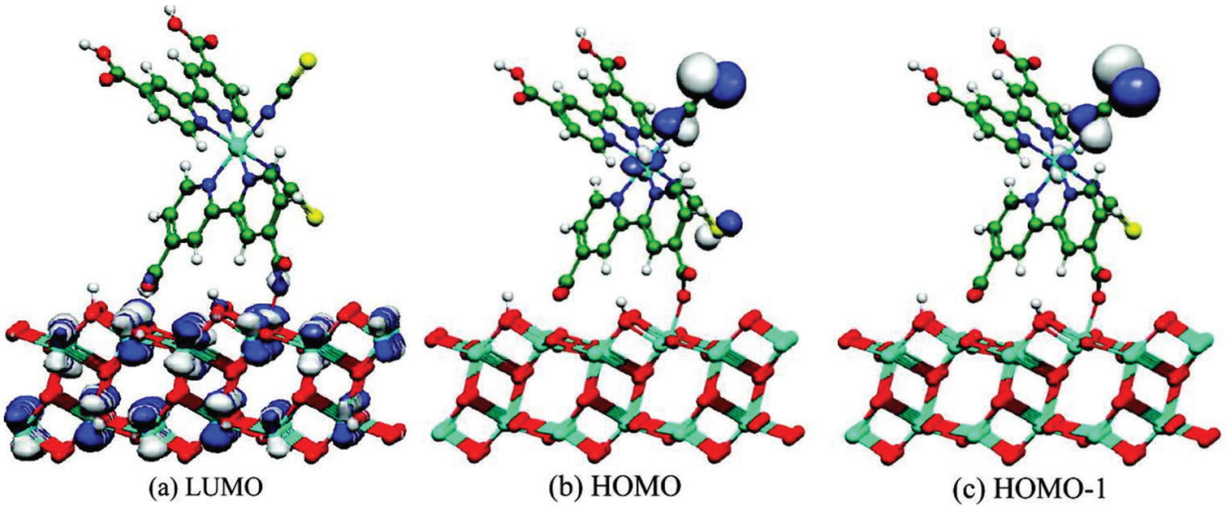

Figure 2. Calculated (a) LUMO, (b) HOMO, and (c) HOMO-1 crystalline orbitals for the bridging adsorption mode of N3/TiO_2\rm_2_2. Isovalues: |0.040| and |0.007| for HOMOs and LUMOs, respectively. Reprinted with the permission from Ref. [62]. Copyright (2010) American Chemical Society.

suggests a favorable electron transfer from the HOMO of the dye to the LUMO of the TiO_2. Schiffmann et al. [27] modeled N3, N712, and N719 dyes adsorbed on anatase (101) surface in the presence of solvent acetonitrile using AIMD. Results indicate that the dyes that are doubly bound to the pristine anatase surface have higher stability. On the other hand, addition of surface protons changes adsorption geometry and mixed bidentate and monodentate binding modes become more favorable. Similarly, the modeling of protonated/deprotonated different N749/$(TiO_2)_{28}$ structures shows that the complexes with deprotonated dye molecules are more favorable with higher adsorption energies [63]. Lundqvist et al. [50] investigated the effects of several spacer unit and anchoring group combinations on the interfacial electronic coupling between a set of Ru^{II}-$(tpy)_2$ dyes and $(TiO_2)_{46}$ nanocrystal. Calculations show that while the strongest coupling is observed using a carboxylic acid anchoring group without a spacer unit, the weakest coupling is observed with the combination of the phosphonic acid anchor group and phenylene spacer group. A good comparison of the calculated structural and electronic characteristics of several Ru-based dyes and their interactions with TiO_2 is available in a recent review [64].

Although Ru-based photosensitizers are very often explored in the literature because of their specific photophysical characteristics and their better performance [65, 66], there are other studies which try to replace expensive Ru metal with cheaper transition metals, such as Fe, Cu, and Co. The experimental study of Ferrere and Gregg [67] investigating Fe(II)bipyridine molecule adsorbed onto nanocrystalline TiO_2 films reveals the substandard performance of Fe-based dyes. The low performance of Fe-based dyes is attributed to the weaker ligand field which prevents MLCT state populations. While the strong ligand field in Ru-based dyes results in having nanoseconds to microseconds lifetime of excited states, excited state lifetime in Fe(II)bipyridine is shown to be only around ps timescale. In spite of the lower performance of the cheaper transition-metal deposited dyes, there are several theoretical studies investigating structural and electronic properties of the most promising ones.

Guillemoles et al. [68] modeled the Os-based polypyridyl dyes with different linker groups (CN^- vs. NCS^-) and in different environments (gas vs. aqueous solution). Their study shows the effects of linker groups and environment on the structural and electronic properties of the dyes. Although in the gas phase the Os-CN^- distance becomes shorter than Os-NCS^- due to the better electron donation character of CN^-, aqueous solution leads to contraction of Os-CN^- (Os-NCS^-) bonds and increases the Os-pyridine distances. Calculated HOMO has contribution from both Os and the linkers, while the LUMO is located on the bipyridyl ligand with π^* character. Shalabi et al. [69] compared the optimized structures of Zn-based porphyrin (ZnPor) and porphyrazin (ZnPz) macrocycles and their energy gaps using DFT. They showed that band gap becomes narrower for ZnPz with respect to ZnPor by more than 0.8 eV, which suggests that light harvesting efficiency can be increased by replacing porphyrin ligand with porphyrazin. Lu et al. [70] compared the electronic structures of several polypyridyl-based dyes with Cu and Ru metal centers. HOMO-LUMO gaps of all considered Cu-based dyes are within the range of 2.41–2.93 eV providing properly aligned energies of the HOMO and LUMO with respect to the electrolyte solution and the CB of TiO_2, respectively. The optical characteristics of Cu and Ru-based dyes are shown to be similar in this study thus providing motivation for the future works on abundant metal-centered dyes.

Fully organic dyes are the alternative of the transition metal deposited ones. One of the widely studied metal-free dyes is catechol. The band gap of catechol, ≈4.2 eV, is larger than the TiO_2 band gap; however, it is shown that the absorption spectra of the catechol/TiO_2 complex have an intense band at 2.95 eV [71]. This observation is explained by a direct electron injection into the CB of TiO_2 from the catechol VB [72]. A DFT study by Persson et al. [73] attributes the reason of direct electron injection to the occupied π level of the catechol at the lower end of the anatase band gap. In terms of adsorption geometry, it is shown that two possible stable catechol monolayer structures present on the rutile TiO_2 (110) surface are monodentate only or mixed monodentate-bidentate configurations [74].

Oprea et al. [75] investigated several coumarin-based dyes adsorbed on different sizes of anatase (101) nanoparticles. Preferential adsorption mode of the coumarin dyes is determined as bidentate bridging which results in localization of the HOMO state on the dyes and the LUMO on the substrate. De Angelis et al. [76] modeled squaraine dye adsorbed on anatase (101) slab in water environment using AIMD. They showed that adsorption mode of squaraine changes from bridged bidentate to a monodentate as simulation time evolves. After 6 ps, however, squaraine is desorbed from the surface due to the strong solvent reorganization which weakens the binding strength of the anchoring group, carboxylic acid.

3.2. Photocatalytic water splitting

Molecular hydrogen has the highest specific energy content as compared to other energy carriers such as electricity and biofuels, conventional fuels such as coal and oil or renewable energy sources as, for example, wind and biomass. Dihydrogen is also environmentally friendly because, the waste product after its reaction with pure dioxygen is only water. These features make H_2 a potential candidate for energy carrier in the near future. One of the dihydrogen generation methods is photochemical water splitting [77]. Several transition metal

deposited catalysts such as porphyrin-derived molecules [78], cobaloximes [79], pyrphyrins [80], and molecules with polypyridine ligands [81] have been used for hydrogen evolution in homogeneous environment. Alternatively, to prevent photogenerated charge recombination and stabilize the system and reaction intermediate heterogeneous systems have been widely investigated.

Water splitting on the bare TiO_2 surface is thermodynamically allowed; however, due to the large overpotential for both H_2 and O_2, the reaction is kinetically hindered. Therefore, the pristine TiO_2 surface is inactive for water splitting and needs to be functionalized with metals/nonmetals, large macrocyclic molecules, or mixed with other types of oxides. Several studies deduce the design criteria for an efficient overall water splitting devise based on TiO_2 which can be summarized, as its valence band maximum should be more positive than the oxidation potential of water and its conduction band minimum should be more negative than the reduction potential of a proton [82].

In 1972, Fujishima and Honda [83] carried out the successful and inspiring experiment of water splitting using TiO_2 as a photoanode. In a closed circuit photoelectrochemical cell, photogenerated electron and hole pairs move to the TiO_2 surface where water molecules are oxidized to generate O_2 and resultant protons are combined with electrons at the cathode, Pt, to generate H_2. The correlation has been observed between the band gaps of the photoanode and its water splitting activity. If the band gap becomes closer to the free energy of the water splitting reaction, 1.23 eV, then the efficiency of the photoelectrochemical cell becomes relatively high, around 41%. Efficiency drops to 18% for a band gap of 2 eV. Further increase in the band gap, 3 eV, results in dramatic decrease in the efficiency of the cell, 0.05% [84]. These results engender band gap tuning of TiO_2 by taking advantage of several methods, as discussed below.

An alternative to the photoelectrochemical cells proposed by Fujishima and Honda [83], two other widely explored methods of water splitting using TiO_2 have been recommended. One method is to use transition metal-deposited TiO_2 nanoparticles together with another metal oxide. An example is depicted in **Figure 3(a)** where photon absorption is followed by charge

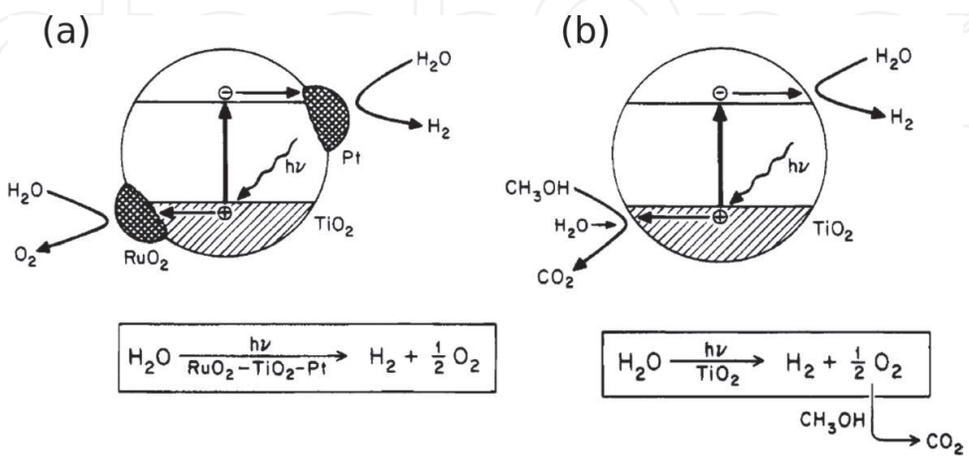

Figure 3. (a) Photosplitting of water on a composite catalyst. (b) Photosplitting of water: sacrificial donor effect. Reprinted with the permission from Ref. [85]. Copyright (1995) American Chemical Society.

separation in TiO_2 and photogenerated electrons and holes are transported into Pt for H_2 generation and RuO_2 for O_2 evolution, respectively. This design results in a substantial decrease in overpotential of the reaction [85]. Another proposed method is to use sacrificial agents to remove one of the photogenerated products. An illustration is shown in **Figure 3(b)** where CH_3OH is used as a sacrificial specie. While photogenerated holes are injected into CH_3OH which afterwards oxidizes water, excited electrons in TiO_2 CB reduces water to H_2 [85]. This system focuses on half reactions, either water reduction via sacrificial electron donor or water oxidation via sacrificial electron acceptor [86].

Prior to reviewing theoretical studies of water splitting on functionalized TiO_2 surfaces, it is useful to first give a closer examination of the interactions between water molecules and the pristine TiO_2 surface. It is shown that water molecules prefer to adsorb on oxygen vacancies of the rutile (110) surface [87]. Water adsorption is followed by a proton transfer to the adjacent two-coordinated surface oxygen thus leading to a formation of hydroxy radical on the surface [88]. Zhao [89] calculated adsorption and decomposition energies of water molecules on different rutile surfaces, such as (110), (100), and (001) using DFT. While dissociative adsorption of water is more favorable on the (110) surface, the activation energy of the water dissociation is largest on the (100) surface. Calculations by Hahn et al. [90] showed that the employed adsorbate coverage affects the favored adsorption mechanism of water molecules. While at low coverage water molecules tend to dissociate on the rutile (110) surface, increasing coverage leads to an associative adsorption. Investigating interactions between water and bare TiO_2 surface is a fundamental research; however, for photocatalytic water splitting TiO_2 surface has to be functionalized, as stated earlier.

Adsorption of large macrocyclic water reduction/oxidation catalysts on the TiO_2 surface is shown to be a promising way of achieving the water splitting reaction. In this regard, Monti et al. [91] proposed a model system of Ru-based catalyst/antenna/TiO_2 complex for water splitting and investigated proton coupled electron transfer dynamics of the catalyst in water solution using AIMD. Results show that a water molecule binds to the Ru center and after 1.9 ps of simulation, time proton transfer from the attached water molecule to the closest one in the solution is achieved. Gurdal et al. [21] modeled adsorption of co-deposited pyrphyrin (CoPyr), a water reduction catalyst [80], on the rutile TiO_2 (110) surface using DFT. The band gap of the complex is decreased by more than 1.5 eV with respect to the bare surface. Additionally, the catalytic properties of CoPyr are preserved upon adsorption since the adsorption process does not lead to strong modifications of the electronic structure at the Co(II) active center.

Alternative complexes, metal/nonmetal deposited TiO_2 structures, are investigated by many groups. Phase stabilities of Fe, Al, Si, and F deposited rutile and anatase phases of TiO_2 are compared using DFT [92]. Results show that while cationic dopants in Ti lattice sites stabilize anatase slightly more than rutile, anionic doping with F substantially reduces the phase stability of the anatase. Modeling Pt, Ru, and Co ions doped anatase TiO_2 (001) surface shows that band gaps of the complexes decrease in the order of deposition of Co (by 1.8 eV), Ru (by 1.7 eV), and Pt (by 0.4 eV) [93]. Nucleation and growth mechanism of Ru clusters on the anatase TiO_2(101) surface reveals that in addition to decrease in the band gap, an electron accumulation at the metal/oxide interface is observed due to the electron flow from Ru to TiO_2 [94].

There are also other studies that focus on designing water splitting systems by mixing TiO_2 with another metal oxide. Graciani et al. [95] modeled water adsorption on the Ce_2O_3 doped rutile TiO_2(110) surface. Results show that the proposed mixed-metal oxide has a promising ability to dissociate water exposing an exothermic dissociation energy of −0.7 eV with a small activation barrier of 0.04 eV. A relatively larger system is investigated by Pastore and De Angelis [96] who modeled TiO_2/Ru-dye/IrO_2 complex using DFT. In the designed complex Ru polypyridyl dye, acting as a linker between the oxides, is attached to both the anatase TiO_2(101) and IrO_2 surfaces via phosphonic acid and malonate groups, respectively. **Figure 4** shows the orientation of the Ru-dye with respect to the oxides. Electronic structure analysis shows that both the HOMO and LUMO are located on IrO_2 showing a metallic-like character. While the occupied molecular orbitals of the dye are located within the IrO_2 VB, its unoccupied orbitals are distributed over the CB of both IrO_2 and TiO_2.

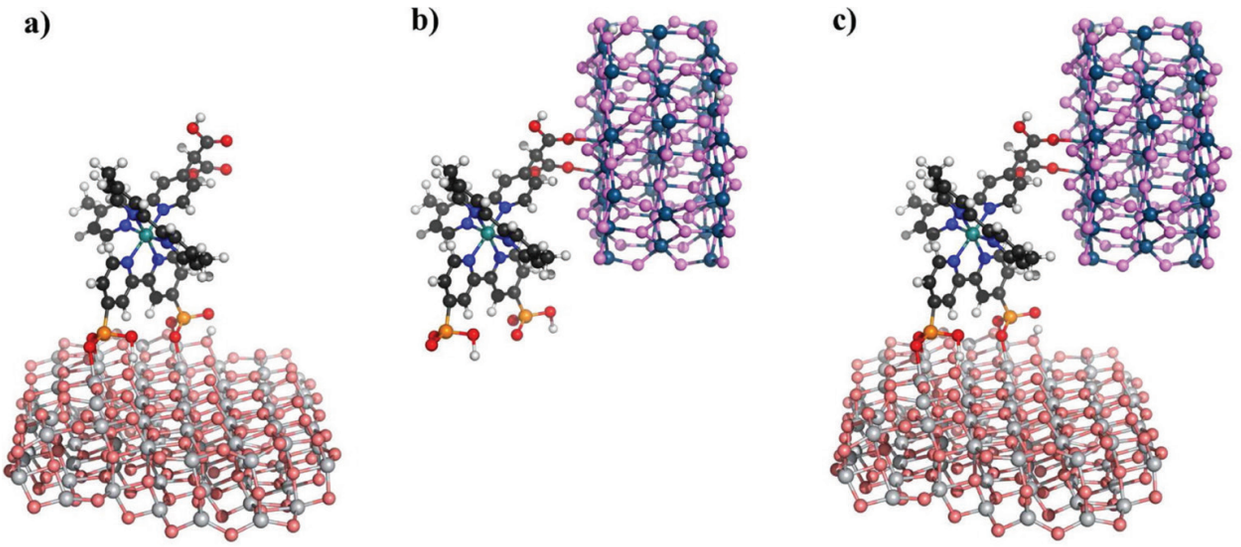

Figure 4. Optimized molecular structure of Ru-dye in its partially deprotonated form, grafted to the $(TiO_2\backslash rm_2_2)_2\backslash rm_\{82\}_2$ cluster (a), to the $(IrO2_2\backslash rm_2_2)_2\backslash rm_\{56\}_2.2H_2\backslash rm_2_2O$ nanoparticle (b), and tethered across the $TiO_2\backslash rm_2_2$ and $IrO_2\backslash rm_2_2$ systems, (c). Reprinted with the permission from Ref.~\cite{pastore2015} Copyright (2015) American Chemical Society

4. Challenges of DFT-based simulations

In order to understand the physical properties of TiO_2 complexes and develop photocatalytically active and efficient devices, one has to use adequate theoretical methods. Although DFT is a powerful tool to analyze and screen TiO_2-based complexes for photocatalytic applications, it also has some limitations. Accurate results can be obtained by increasing system size, i.e., increasing layers of the TiO_2 slab. While the thickness of the slab has to be sufficient to reproduce the correct behavior at the surface and increase the calculated accuracy, increasing system size also increases computational effort. In the case of AIMD runs required computational source becomes even more expensive than DFT calculations. Therefore, one needs to find a compromise between the accuracy and the computational cost. In this regard, Harris

and Quong [97] proposed a method named "25% rule" to determine the sufficient slab thickness that should be used in the simulations.

As already stated, the other issue is the uncertain forms of the exchange-correlation functionals which limit the accuracy and cause a dilemma in trusting obtained results. Though, several methods beyond DFT are developed and successfully used to increase the accuracy of the calculations, such as random phase approximation and Green function theory [98, 99].

In spite of several limitations, in both the accuracy of the DFT description and the size of feasible models, this approach seems to be the most appropriate one so far. Constant improvement in computational algorithms together with rapidly increasing computer power, DFT, and AIMD are robust methods used to gain preliminary knowledge on the systems and supervise experimentalists to build promising materials for photocatalytic applications.

5. Conclusions

Search for renewable energy sources leads scientists to benefit from sunlight and convert photon energy to chemical/electric energy using TiO_2-based materials. Although photocatalytic water splitting and DSSC applications are accomplished using TiO_2 surface, large band gap of the oxide limits absorbing photons in the visible spectrum thus hindering device efficiency. Therefore, functionalizing TiO_2 surface by adsorbing photosensitizers and/or water reduction/oxidation catalysts, by metal/nonmetal deposition, or by mixing with other oxides, the optical response of the complex can be shifted from UV to the visible region. This is the crucial requirement in designing promising, robust, and scalable photocatalysts toward water splitting and DSSC applications.

Together with the improvement in the computational power, today, DFT is an important tool to obtain optimized geometries of the complexes, analyze electronic structures, model many spectroscopic techniques, determine intermediate states of the reactions, and so on. In particular, it is powerful for modeling several TiO_2-based materials and testing their physical/chemical/optical characteristics for photocatalytic applications. Although there are some limitations in DFT, several new exchange-correlation density functionals and van der Waals correction schemes have been proposed to increase the flexibility and accuracy of the model. Using DFT, all phases of TiO_2 surfaces, i.e., rutile, anatase, and TiO_2 nanoparticles can be modeled. The outcome of the simulations serves as an initial knowledge on the systems for scientists without experimental effort.

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