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Theoretical calculations of strontium titanate for application to hydrogen production from photocatalytic water splitting under visible light irradiation.

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DEDICATIONS

I dedicate this thesis to:

My lovely parents

My aunt Mahjouba and my uncle Said (God rest her soul)

My lovely wife

My children (Silya and Salim), my life light

My brothers Ismail, Yassine, Abdelghafour and Zakaria

My sisters Fatima, Malika, Zhour and Meryame

Abstract

This thesis reports the results of first principles theoretical studies of the electronic, optical and photocatalytic properties of monodoping (with Mn, S, Se, and Te) and codoping (with S/Mn, Se/Mn and Te/Mn) of SrTiO_3 based on density functional theory (DFT) within the generalized gradient approximation (PBE-GGA) for the exchange-correlation potential. Electronic properties calculations contain, band structures, density of states, charge density distributions. Investigation for the optical properties, cover detailed analysis for several optical parameters like absorption coefficient, refractive index, extinction coefficient, energy loss function, reflectivity and optical conductivity in both parallel and perpendicular directions of electric field. Our results show that monodoping with Te decreases the effective band gap energy of SrTiO_3 significantly (by about 1.04 eV), and codoping with Te/Mn narrows further the band gap (by about 1.61eV), leading to enormous absorption spectrum red-shifting. Besides, our findings show that the conduction band and valence band positions of SrTiO_3 are optimized through Te/Mn codoping, in a way that improves significantly the ability of pure SrTiO_3 , towards the photocatalytic hydrogen production from water splitting using sunlight.

Keywords: SrTiO_3 ; doping; DFT; visible light; photo-catalytic hydrogen production; water splitting.

Résumé

Cette thèse rapporte les résultats *ab initio* de l'étude théoriques des propriétés électroniques, optiques et photocatalytiques du monodopage (avec Mn, S, Se et Te) et du codopage (avec S/Mn, Se/Mn et Te/Mn) de SrTiO_3 basant sur la théorie de la fonctionnelle de la densité (DFT) dans l'approximation du gradient généralisé (PBE-GGA) pour le potentiel d'échange-corrélation. Le calcul des propriétés électroniques contient les structures de bande, la densité d'états, les distributions de densité de charge. L'étude des propriétés optiques couvre l'analyse détaillée de plusieurs paramètres optiques tels que le coefficient d'absorption, l'indice de réfraction, le coefficient d'extinction, la fonction Eloss, la réflectivité et la conductivité optique dans les directions parallèles et perpendiculaires du champ électrique. Nos résultats montrent que le monodopage avec Te diminue l'énergie de la bande interdite effective de SrTiO_3 de manière significative (d'environ 1,04 eV), et le codopage avec Te/Mn réduit de plus la bande interdite (d'environ 1,61 eV), conduisant à un énorme déplacement du spectre d'absorption vers les longues longueurs d'onde. En outre, nos résultats montrent que les positions des bandes de conduction et de valence du SrTiO_3 sont optimisées grâce au codopage Te/Mn, d'une manière qui améliore considérablement la capacité du SrTiO_3 pur à produire de l'hydrogène photocatalytique à partir de la décomposition de l'eau en utilisant la lumière du soleil.

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Abbreviations

- BO: Born-Oppenheimer approximation
- DFT: Density Functional Theory.
- DOS: Density Of States.
- E_{xc} : Exchange-Corrélation energy.
- FP-LAPW: Full Potential Linearized Augmented Plane Wave
- GGA: Generalized Gradient Approximation.
- GGA+U : Generalized Gradient Approximation combined with Hubbard term
- HF: Hartree-Fock.
- KS: Kohn and Sham.
- APW : Augmented Plane Wave
- FP : Full Potential
- LAPW: Linearized Augmented Plane Wave
- LO: Local orbital
- LDA: Local Density Approximation
- LSDA: Local Spin Density Approximation.
- mBJ: Potentiel Modified Becke-Johnson.
- MT: Muffin-Tin.
- RMT: Radius of Muffin-tin.
- SCF: Self-Consistent Field
- TB-mBJ: Tran-Blaha modified Becke Johnson Potentiel.
- TDOS/PDOS: Total / Partial density of states.
- CB : Conduction band
- CBM : Conduction band minimum

- VB : Valence band
- VBM : Valence band maximum
- BZ : Brillouin zone
- E_F : Fermi energy
- UV : ultraviolet
- IR: Infrared
- SP : Spin polarized
- α : absorption coefficient
- E_g : Energy band gap
- NHE: Normal Hydrogen Electrode
- e^- -- h^+ : electron-hole

List of publications

1. Bentour, H., El Yadari, M., El Kenz, A. Benyoussef, A. : DFT study of electronic and optical properties of (S–Mn) co-doped SrTiO₃ for enhanced photocatalytic hydrogen production. Solid State Communications.312, 113893 (2020). <https://doi.org/10.1016/j.ssc.2020.113893>
2. Bentour, H., El Yadari, M., El Kenz, A. Benyoussef, A. : *DFT study of Se and Te doped SrTiO₃ for enhanced visible-light driven photocatalytic hydrogen production*. Optical Quntum Electronics. 53, 589 (2021). <https://doi.org/10.1007/s11082-021-03214-1>
3. Bentour, K. Belasfar, H., El Yadari, M., El Kenz, A. Benyoussef, A. : DFT study of Se/Mn and Te/Mncodoped SrTiO₃for visible light-driven photocatlytic hydrogen production (Submitted to Optical Materials Journal)

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Action	Manuscript Number	Title	Initial Date Submitted	Status Date	Current Status
Action Links	OM-D-21-02500	DFT study of Se/Mn and Te/Mn codoped SrTiO ₃ for visible light-driven photocatalytic hydrogen production	Oct 09, 2021	Nov 11, 2021	Under Review
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4. En preparation “ DFT-mBJ study of SrTiO₃/BaMnO₃ heterojunction for visible light photocatalysis”.

Introduction

Abstract

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Introduction entails the background about the need for alternative fuels, focuses on the route of photocatalytic H₂ production from water splitting, and the definition of the problem, aims and objectives adopted for this study. Besides, it presents the structure of this thesis.

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1. General context

Fossil energies are important sources for human society. They include coal, petroleum, natural gas, oil-sand, and oil-shale. Recently, the entire world has realized the importance of energy resources as a main enabler for welfare and economic development of a society. However, the rate of fossil fuels consuming is extremely high, particularly in developed and rapidly developing economies. According to the report of International Renewable Energy Agency in 2020, under the Planned Energy Scenario, primary energy demand increases from around 600 exajoules (EJ) in 2020 to 710 EJ by 2050 [1]. Consequently, the expected lifetimes of the known reserves are alarmingly short. Meanwhile, the emissions of greenhouse gases and other toxic pollutants associated with fossil energy are environmentally unacceptable. Hence, it is an urge to develop clean and sustainable sources of energy to handle the circumstance [2]. In this context, renewable energy resources have an ability to complete the world's energy demand, protect the environment, and provide energy security, and it is expected that will be one of the important sources for achieving sustainability in the energy sectors in both developing and industrialized countries, both in rural and urban areas; this can be explained by the following main reasons: less environmental impact, continuous supply (with careful utilization), decentralization, local and flexible solutions [3].

Generally, renewable energy sources replenish themselves naturally without being depleted in the earth; they include bioenergy, hydropower, geothermal energy, solar energy, wind energy and ocean (tide and wave) energy [4]. Among the various types of sustainable energy resources, solar energy is considered to be promising due to its inexhaustible supply, universality, high capacity, and environmental friendliness. It is known that the amount of solar energy incident on the earth's surface is approximately 1.5×10^{18} KWh/year, which is about 10,000 times the current annual energy consumption of the entire world, and the density of power radiated from the sun (referred to as solar energy constant) is 1.373 kW/m^2 [5]. However, the natural solar irradiation is decentralized, intermittent and fluctuates constantly. Therefore, effective utilization of solar energy in a clean, economic, and convenient way remains a grand challenge [6]. Thus more researchers are trying to convert it into a more available renewable energy sources. Hydrogen is considered to be the most ideal alternative clean energy because of its high calorific value, zero pollution, and storability, and it is widely considered to be the future clean energy carrier in many applications, such as energy production, storage, and distribution, electricity, domestic heating, and cooling for buildings and households, the industry, transportation, environmentally friendly vehicles, stationary

power generation, and the fabrication of feedstock [7]. Among the promising methods to transform the scattered, inexhaustible solar energy into the highly concentrated and clean hydrogen energy, the water splitting process using a powder photocatalyst is considered one of the most attractive methods to address the environmental problems and produce sustainable fuels in the future; this is due to divers advantages of this method over other methods [8,9,10]: (i) this strategy is founded on photon (or solar) energy and water, which is a clean, perpetual, and renewable source of energy; (ii) it is an environmentally friendly technology without harmful by-products and pollutants; and (iii) the photochemical conversion of solar energy into hydrogen can effectively deal with the intermittent character and seasonal variation of the solar influx. In particular, hydrogen gas has a high energy capacity (143 MJ.kg^{-1}) and releases no toxic emissions [11]. Therefore, an efficient and immediate photocatalytic hydrogen-generation route is urgently needed. In fact, since the pioneering work, of Honda and Fujishima [12], significant progress has been marked in this field, and various photocatalytic materials and water-splitting systems have been developed. For example, SrTiO_3 crystal has received a great attention, due to its chemical stability, low cost and safety. However, this photocatalyst is not effective in absorption of visible-light due to its wide band gap, which reduces its photocatalytic ability. Nevertheless, many experimental theoretical studies expected that SrTiO_3 perovskite will be able to split water efficiently under visible light irradiation; This prompted researchers to study and search the possible ways to shifting its absorption into the visible light region, which will be able to boost its photocatalytic performance.

2. Aims and outline of this thesis

As outlined above, the photocatalytic water splitting reaction employing SrTiO_3 , has received a wide attention. However, this photocatalytic semiconductor has a wide band gap, therefore it cannot use visible light and only makes use of ultraviolet (UV) light which occupies less than 5% of the solar spectrum [13]. This is a major limitation to its application. Thus, the aim of the majority of photocatalytic scientists is to extend its absorption of light to the visible region. Therefore, the aim of this work is to modify SrTiO_3 by foreign elements doping to increase the efficiency of photocatalytic water splitting in the visible light region. The objectives of this thesis are:

- To investigate the effect of monodoping with Mn, S, Se and Te on the stability, electronic, optical and photocatalytic properties of SrTiO_3 ;

- To study the influence of codoping with S/Mn, Se/Mn and Te/Mn on the as mentioned properties of SrTiO_3 and their utility in enhancing the charge carriers separation;
- To relates the studied properties of SrTiO_3 to its ability for photocatlytic hydrogen production from water using solar energy.

3. Thesis structure

This thesis has been categorized in the following chapters:

The **Chapter 1** is dedicated to present the basic principle of photocatalytic water splitting. Also, the main modifications techniques for improving the photocatalytic performance of semiconductors like introducing foreign elements, nanostructures and heterostructures fabrication, and cocatalysts utilization are discussed. Finally, a short bibliographic study about ideal perovskites, particularly cubic SrTiO_3 is presented.

In **Chapter 2**, we explained the foundations of Density Functional Theory. First, the Schrödinger Equation and the general many-body problem are presented. Then the approximations to the many problems, as the Born-Oppenheimer, Hartree and Hartree-Fock approximations are investigated. Subsequently, the theoretical backbone of DFT, the Hohenberg-Kohn theorems and the Kohn Sham equations are reviewed.

In **Chapter 3**, we presented the methodology used in the calculation of our work. We explain how the exchange correlation potential can be treated through various approximations (LDA, GGA and GGA+U), also the modified becke-johnson potential (mBJ) is submitted. Then, we presented the fundamental concepts of the linearized /augmented plane wave plus local orbitals (L/APW+lo); and we showed the different versions of (L/APW+lo) and their main developing steps in terms of linearization, full potential, local orbitals and mixed basis sets. Finally the wien2k code is spresented.

The **Chapter 4** is devoted to investigate the effects of Manganese and chalcogenides (sulfur, selenium and tellurium) atoms doping on the stability, electronic, optical, and photocatalytic properties of strontium titanate (SrTiO_3) bulk through DFT calculations. Defect formation energies, band structures, density of states, electronic density distributions, optical absorption spectra and imaginary part $\epsilon_2(\omega)$ of the dielectric function $\epsilon(\omega)$, for undoped, Mn doped, S doped, Se doped and Te doped SrTiO_3 , were thoroughly studied using DFT in its GGA approximation. Band alignments were calculated with the purpose of ensuring the thermodynamic validity of the studied compounds for water splitting reaction. The abilities of

systems, towards the photocatalytic hydrogen production from water splitting were discussed in the basis of obtained results.

In **Chapter 5**, we turned to the study of the modified SrTiO_3 photocatalyst with codoping strategy. Specifically, we illuminated the advantages of codoping in improving the photocatalytic performance of SrTiO_3 . We studied the influence of S/Mn-, Se/Mn- and Te/Mn-codoping on the stability of SrTiO_3 and its electronic, optical and photocatalytic properties.

Finally, the obtained results in this thesis are summarized and recommendations and perspectives for photocatalytic water splitting improving are provided.

Part I

Background information

Chapter 1

Literature review

Abstract

=====

Water splitting for hydrogen evolution under light irradiation is an ideal system to provide renewable energy sources and to reduce global warming effects. Even though numerous attempts have been made to perform photo-catalysts that function not only under UV light but also under visible-light illumination to efficiently utilize solar energy.

In this chapter, the basic principle of photocatalytic water splitting is presented. The main modifications techniques for improving the photocatalytic performance of semiconductors like introducing foreign elements, nanostructures and heterostructures fabrication, and cocatalysts utilization are discussed. Finally, a short bibliographic study about ideal perovskites, particularly cubic SrTiO_3 is presented.

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1. Introduction

Nowadays, researchers are paying more attention to the development of green and renewable energy sources [14;15]. Photocatalytic hydrogen generation has been considered as one of the most potential technologies using solar energy and generating new energies. Since Fujishima and Honda first proposed the use of TiO_2 electrode to split water for hydrogen production under ultraviolet-light irradiation, various photocatalysts have been explored and applied to many photocatalytic fields [12], and one of the main issues is, finding high-performance photocatalytic materials. Up to now, several semiconductor materials, such as oxides, sulfides, phosphides and nitrides have been developed for photocatalytic hydrogen generation [16]. Particularly, the perovskite type (ABO_3) materials have been dealt with big interest due to their abundance, non-toxicity, and chemical stability [17]. Unfortunately, a satisfactory system under visible light irradiation has not been obtained yet, due to the wide band gap energy and the lower efficiency of the photo-induced charge carriers separation which limit the practical applications of existed photo-catalysts, under visible light irradiations. Lots of strategies have been exploited to overcome these obstacles, such as constructing nanostructures, constructing heterojunctions, cocatalyst loading and ions doping. Among the perovskite photo-catalysts the strontium titanate SrTiO_3 has gained remarkable attentions due to its superior physicochemical properties. The long lifetime on e^- - h^+ pairs, high chemical and thermal stability, and strong catalytic activity have become the advantages of SrTiO_3 [18].

2. Current and future status of global hydrogen production

Hydrogen is the simplest and most abundant element on earth—it composed of only one proton and one electron. As it can deliver a clean and restorable, alternative energy source, it is also an important part of future energy systems as countries over the world drive towards zero carbon economies. Hydrogen is an energy carrier, not an energy source, with an energy density more than twice that of natural gas. Hydrogen can be used in fuel cells to generate electricity, or power and heat.

The global hydrogen production demand has progressively increased over the last few decades, due to the global economic growth, the increase in the population, and advances in technology [19]. Hydrogen can be produced from diverse resources; however, extracting it from fossil fuels is considered as easiest and cheapest method to meet the demand. For example, for hydrogen production from natural gas, the cost ranges from USD 0.5 to USD 1.7 per kilogramme (kg), due to the regional differences in gas price. Introducing CCUS (carbon

capture, utilization and storage) technologies to reduce the CO₂ emissions from hydrogen production lead to an increase of the levelised cost to the range of USD 1 - USD 2 per kg. Using renewable electricity to generate hydrogen costs USD 3 to USD 8 per kg. **Fig. 1. 2.** illustrates the current routes for production of hydrogen according to the report of International Energy Agency in 2021[20].

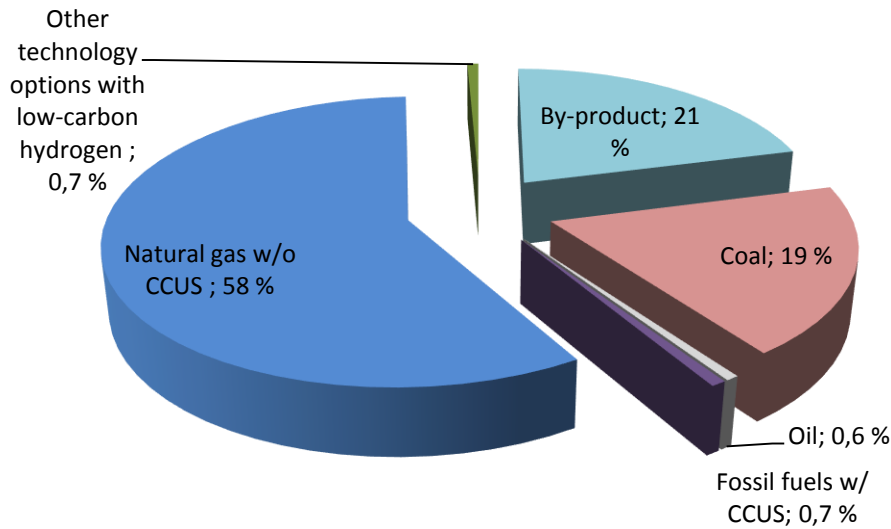


Fig. 1.1. The current routes for the production of hydrogen

Since 1975, global hydrogen demand has grown more than quadruple, reaching more than 80 million tonnes per year in 2020. (**Fig. 1. 1.**) [20; 21].

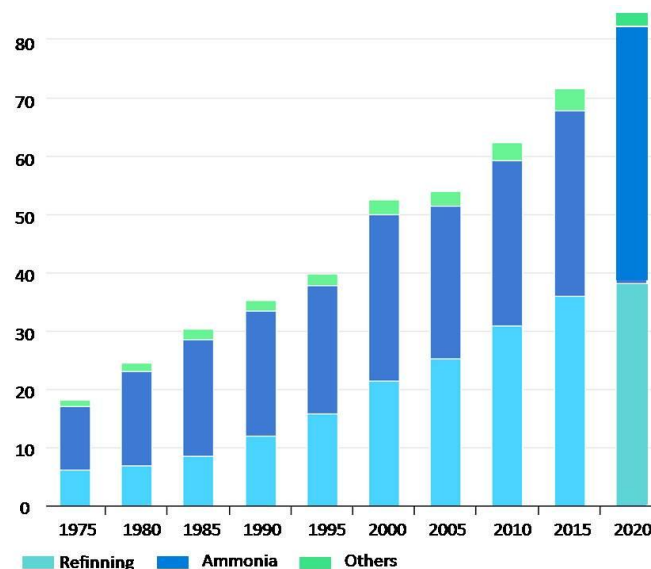


Fig. 1.1. Global annual demand for hydrogen since 1975.

To meet growing hydrogen demand, some players in the sector are thus planning large-scale development in the world with a doubling of the demand for hydrogen by 2030 and by

six by 2050; besides the adoption of cleaner technologies for hydrogen production in the Net Zero Emissions Scenario (NZE), is expected to enable avoiding up to 60 Gt CO₂ emissions in 2021-2050 (**Fig. 1.2**) [20; 21].

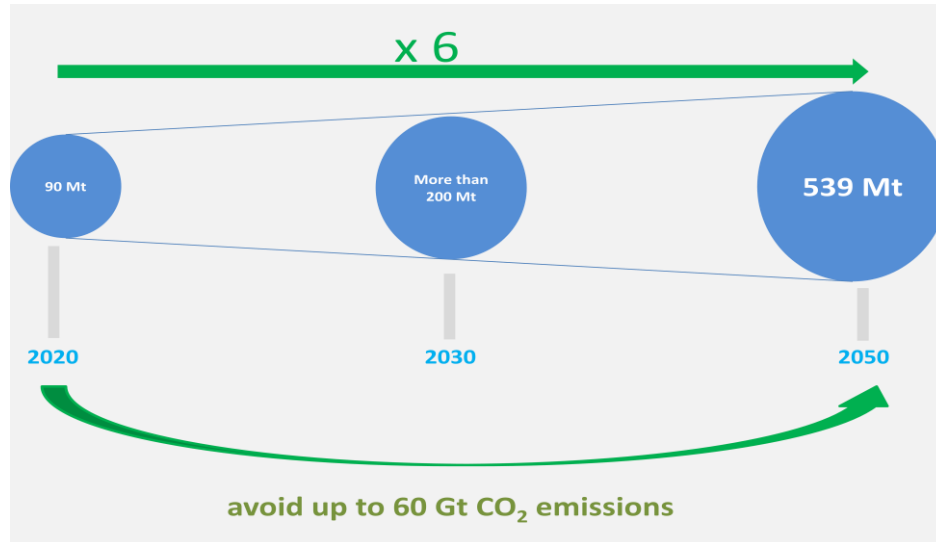
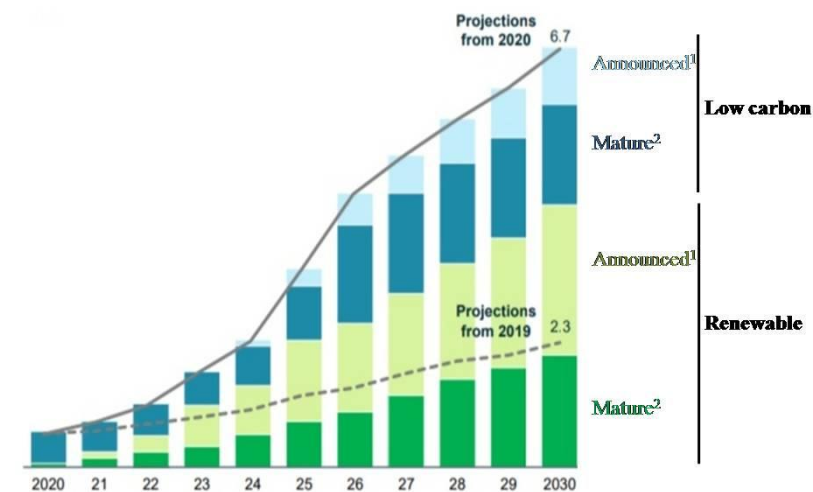


Fig. 1.2. The Projected total hydrogen production for the period 2020-2050

Due to the growing interest in hydrogen production and sustainability, the announced production capacity for clean hydrogen increases year over year; for example between 2019 and 2020, this capacity for 2030 increased to 6.7 million tons a year from 2.3 million tons previously. In other words, players have announced two-thirds of the clean hydrogen production capacity over the course of the past year (**Fig. 1.3**) [22].



1. Includes projects at preliminary studies or at press announcement stage
2. Includes projects that are at the feasibility study or front-end engineering and design stage or where a final investment decision (FID) has been taken, under construction, commissioned or operational

Fig. 1.2. Photoelectrochemical cell for Fujishima and Honda.

In addition, hydrogen is considered an important part of the Net Zero Emissions Scenario by 2050 (NZE). The sources of hydrogen production in this scenario are presented in **Fig1.1**, 2020-2050

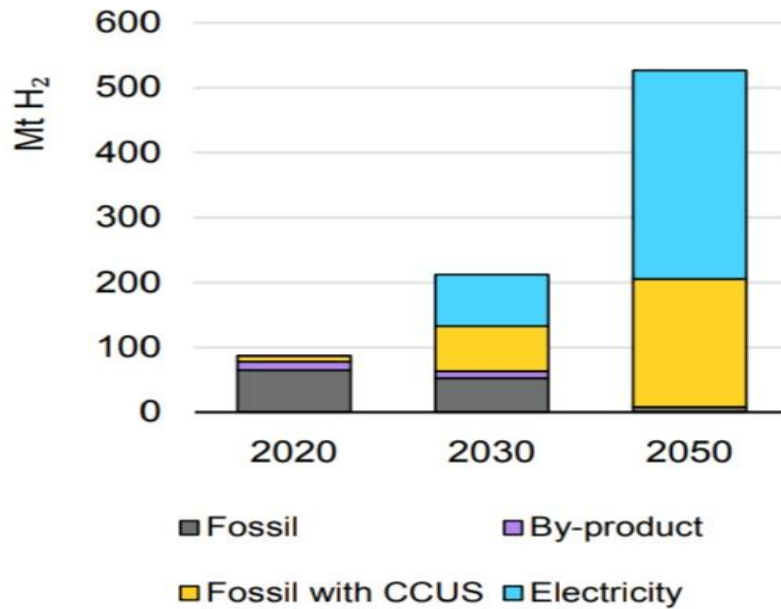


Fig. 1.3. Sources of hydrogen production in the NZE, 2020-2050. [20]

The current and future uses of hydrogen [20; 21] are presented in **Fig. 1.5**. The largest use of hydrogen occurs in petroleum refining as hydrogen is used to crack heavier oils into lighter oils for use as petroleum, and in agriculture where it is used to produce ammonia for fertilizers (by combining hydrogen with nitrogen). The remaining part is directed towards food, metals, electronics, and methanol industries.

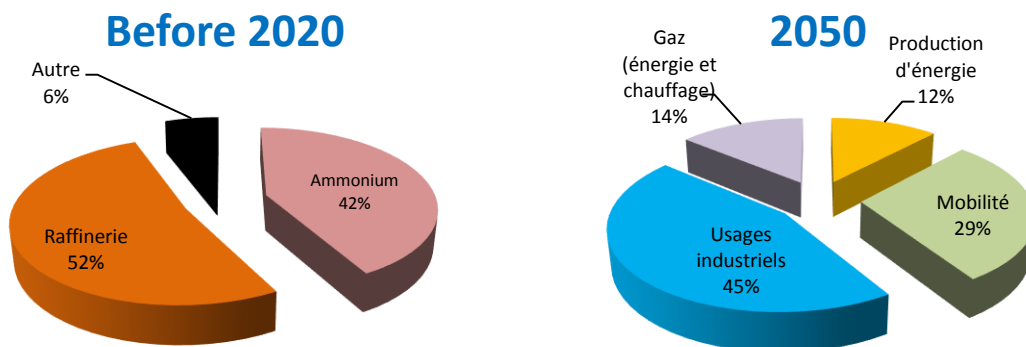


Fig. 1.4. The current (before 2020) and future (in 2050) uses of hydrogen.

3. The basic principle of photocatalytic water splitting

Since the pioneering work for photo-dissociation of water with assistance of Pt and TiO₂ electrodes under UV light, done by Japanese scientists Fujishima and Honda in 1972 (**Fig. 1.1.**), many efforts have been proved on different semiconductors to generate hydrogen under visible light irradiation. Photocatalytic hydrogen production is a thermodynamically uphill reaction accompanied by positive Gibbs free energy change (ΔG^θ) (238 kJ/mol or 1.23 eV) [23]. The decomposition of H₂O into H₂ and O₂ occurs as the following reaction:



Direct thermal decomposition involves a temperature exceeding 2000°C, or over 900°C with the assistance of a Pt/Ru catalyst [24].

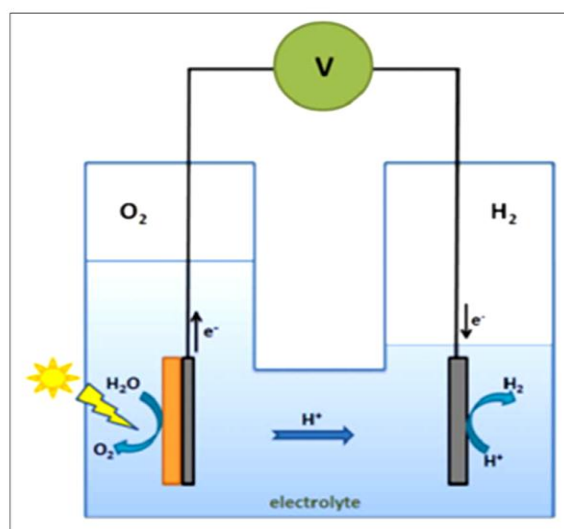


Fig. 1.1. Photoelectrochemical cell for Fujishima and Honda. Adapted from Ahmad et al., (2015) [25].

Any semiconductor photocatalyst used for water splitting should have band gap energy (E_g) over 1.23 eV. Moreover, from thermodynamic point of view, an efficient photo-catalyst for water splitting must have the CB edge above the water reduction level (H^+/H_2) (0 V vs. NHE) and the VB edge below the water oxidation level (O_2/H_2O) (1.23 V vs. NHE). Under illumination with a photon energy equivalent to or larger than the band gap energy of semiconductor photocatalyst, electrons migrate from the VB to the CB, leaving holes in the VB. Then, the electrons reduce H^+ to H_2 and the holes simultaneously oxidize H_2O to H^+ and O_2 , leading to the overall water splitting as shown in **Fig. 1.2.** The requirements for UV-light-driven photocatalysts are: **1)** suitable valence band (VB) and conduction band (CB) edge

potentials and 2) good chemical stability in the photocatalytic reactions, whereas visible-light-driven photocatalysts have to meet the third qualification 3) band gap energy less than ca. 3.0 eV [26].

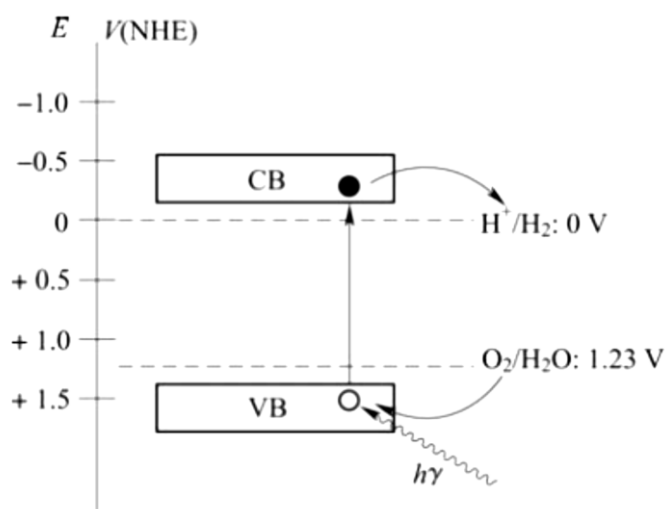


Fig. 1.2. Energy diagram for H_2 production from the photocatalytic water decomposition.

Photocatalytic water-splitting systems can be divided into one step excitation system (based on a single particulate photocatalyst) and two-step excitation system (based on a coupled two individual particulate photocatalysts) (See Fig. 1.3.) [27]

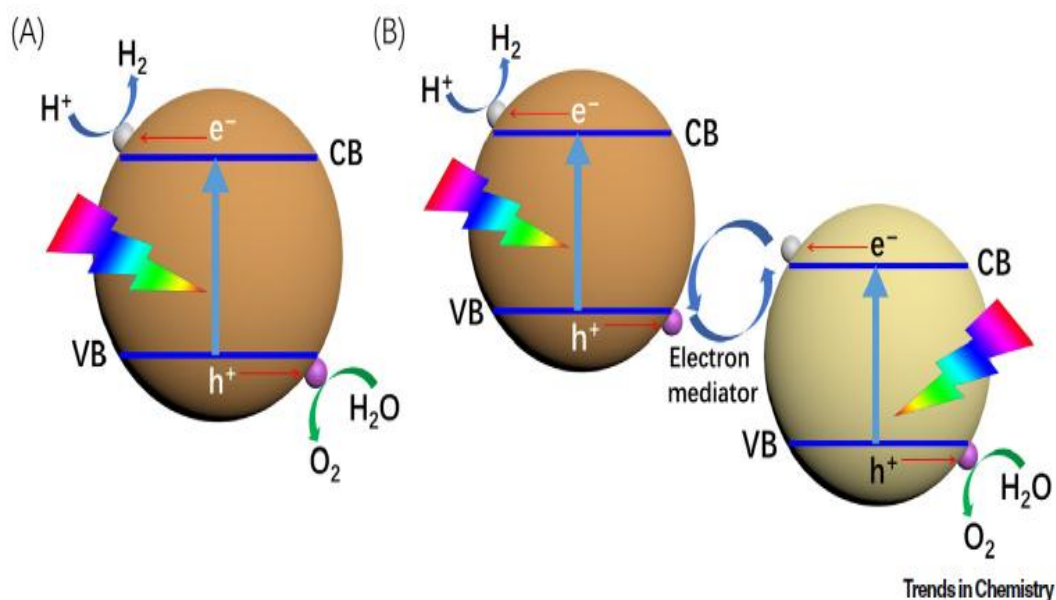


Fig. 1.3. Types of photocatalytic water-Splitting Systems. **(A)** One-step-excitation water splitting. **(B)** Two-step-excitation water splitting.

4. Modifications techniques for enhancing the photocatalytic performance of semiconductors

3.1. Fabrication of unique nanostructures

As mentioned above, the photocatalyst should efficiently benefit from the solar energy to stimulate electron - hole pairs, and the generated excitons are requested to be diffused on a short time scale to the surface of materials where the oxygen evolution reaction and hydrogen evolution reaction reactions will take place. It have been reported that the particle size and microstructure influence the diffusion length and subsequent lifetime of charge carriers [28]. In this context contrary to the bulk materials, nanostructures materials have shorter paths for exciton diffusion [29]. This makes the nanostructured materials fabrications and uses more interesting in the research field of photocatalytic hydrogen production, and many reported studies on water splitting of the semiconductor can be found in recent literature.

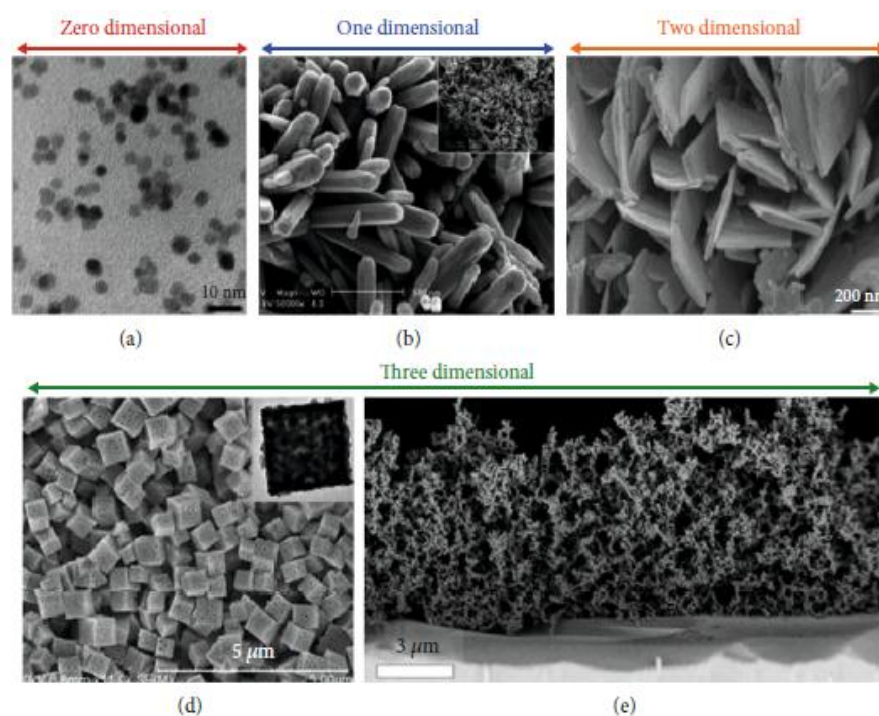


Fig. 1.4. (a) Typical TEM image of ZnO quantum dots (QDs) obtained through a wet synthesis method. (b) SEM images of ZnO nanorods. (c) SEM image of ZnO nanosheets formed through a simple mixed hydrothermal synthesis method. (d) SEM images of acid-washed porous SnO₂ microcubes after calcinations at 900°C for 2 h. Inset: TEM image of the as-prepared porous SnO₂ microcubes. (e) ZnO ultra porous film made by flame spray pyrolysis. Adapted from [30].

Nanostructures or - synonymously - nanophase materials, nanocrystalline materials or supramolecular solids, refer to materials or structures which have a nanometer scale sizes at least in one dimension typically between 1 and 100 nm range [31]. There are various kinds of nanostructures with different dimensions which range from zero-dimensional (0D) (nanoparticles), one-dimensional (1D) (nanorods, nanotubes, nanofibres and nanowires), two-dimensional (2D) (nanosheets and films), three-dimensional (3D) (polycrystals and ultraporous nanostructures, and nanoscaffolds) [32] as illustrated in **Fig. 1.4**.

3.2. Heterojunctions

Unlike the single photo-catalysts, heterojunction semiconductors are a better system for electron-hole separation and can decrease the energy lost from electron-hole recombination, which leads to enhanced photocatalytic activity [25].

Generally, a semiconductor-based heterojunction photocatalyst is done by coupling the semiconductor photocatalyst by another photocatalyst (or a co-catalyst). Subjecting to the band gap of VB and CB potentials of photocatalysts, the heterojunctions is arranged into 3 classes, which are, straddling gap (Type I), the staggered gap (Type II), and the broken gap (Type III) as illustrated in **Fig. 1.5**.

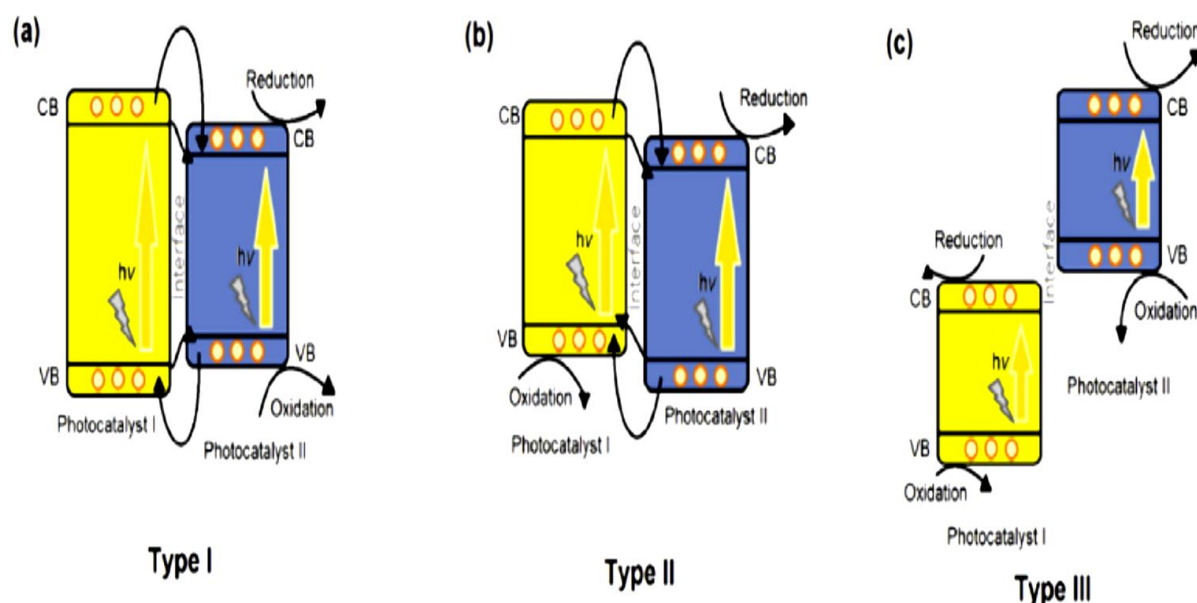


Fig. 1.5. Schematic diagram of types of heterojunctions. Adapted from Ref [33].

- For the straddling gap band alignment, the potential of both VB and CB of the narrower band gap photocatalyst are confined within the wider band gap

photocatalyst. Thus, when the sufficient light energy is irradiated, photogeneration of e^-h^+ pairs take place, and resulted in the transfer and accumulation of all charge carriers in a single component within a hybrid structure owing to the band edge positions.

- For staggered gap, the band edges potentials are staggered between the first photocatalyst and second photocatalyst. As a result of chemical potential between both semiconductors, and the upwards or downward band bending was formed, leading to the transfer of charge carriers in the opposite direction. This can improve the e^-h^+ pairs spatial separation on various parts of heterojunction to slow down the charge recombination so that able to prolong the lifetime of e^-h^+ pairs.
- Meanwhile, the second photocatalyst edges of both VB and CB are located above the CB potential of the first photocatalyst without crossing each other for the Type III (broken gap) heterojunction [34].

The two photocatalysts with matching electronic band structures can importantly improve the separation of photogenerated electrons (e^-) and holes (h^+), thereby substantially improving the photocatalytic ability [35]. For example, Ahmed et al. [36] synthesized the $AgIO_4$, and studied their properties via: high resolution transmission electron microscopy (HRTEM), X-ray Photoelectron Spectroscopy (XPS), Diffuse Reflectance Spectra (DRS), Photoluminescence (PL), Energy-dispersive X-Ray Spectroscopy (EDS) and X-Ray Diffraction (XRD) methods. They found that the incorporation of $AgIO_4$ into SnO_2 leads to an extending of photocatalytic reactivity into the visible light region, and an improving of the quantum efficiency of charge carriers separation. Besides they obtained a good rate (50 times better than that of pure SnO_2 single phase) of photocatalytic hydrogen evolution, for an amount of 5 wt% of $AgIO_4$ in the synthesized heterojunction. They explained that by a Z-scheme mechanism in which the electrons and holes of nearby CB and VB are recombine, while those in distant CB and VB are preserved, which improves the electrons-holes separation efficiency and raises the oxidative and reductive power of the photogenerated carriers. Liang et al. prepare a type-II $g-C_6N_6/g-C_3N_4$ heterojunction which improves the effective separation of electron-hole pairs [37]. In a theoretical study Wang et al. predict that the $CdS/g-C_6N_6$ heterojunction possesses suitable band edges for overall water splitting processes and shows strong absorption in visible light region [38]. It is noteworthy that the construction of heterojunction not only incorporates the advantages of constituent components, but also displays novel properties, which has been considered as an effective way for materials to

widen the optical absorption and enhance photocatalytic ability in visible light domain [39]. Sun et al [40], systematically investigate the stability, electron properties and optical absorption of g-C₆N₆/GaS heterojunctions by density functional theory (DFT) calculations. They study the potential capacity of g-C₆N₆/GaS on water splitting. Their results indicate that g-C₆N₆/GaS shows a type-II band alignment with a narrower band gap, and the electrons are spatially separated from the holes. The build-in electric field at the interfaces further promote the separation of photogenerated electron-hole pairs. Besides, the g-C₆N₆/GaS exhibits a higher optical absorption in the visible light region, which indicates the suitability of the type-II g-C₆N₆/GaS heterojunction for photocatalytic water splitting and solar energy conversion. Through facile aqueous synthesis and hydrothermal method, Han et al [41] synthesized CdSe/SrTiO₃ nanocomposites and obtained an effective heterojunction structure through modifying the CdSe QDs on the surface of SrTiO₃ nanoparticles. Their structure showed a good visible light absorption and significant photocatalytic hydrogen efficiency compared to the pristine SrTiO₃ nanoparticles.

3.3. Engineering with Cocatalysts

The cocatalysts investigation is a topic of interest in the scientific endeavours to improve the solar conversion efficiency. In fact, suitable cocatalysts loaded on the surface of photocatalyst can speed up the rate of photocatalytic reactions. However, to combine between a photocatalyst and a cocatalyst, the energy levels and electronic structures of these two materials must be carefully tuned. That is, the work functions or band levels of the cocatalysts should be in accordance with the Fermi-levels or electronic structures of the photocatalyst semiconductors. This permits the formation of a desirable junction (an Ohmic-type or Schottky-type contact) that enables photogenerated charges to migrate from semiconductor to the cocatalysts through the interface [42]. **Fig. 1.6.** shows the charge transfer for metal/semiconductor under light irradiation due to the formation of the Schottky junction.

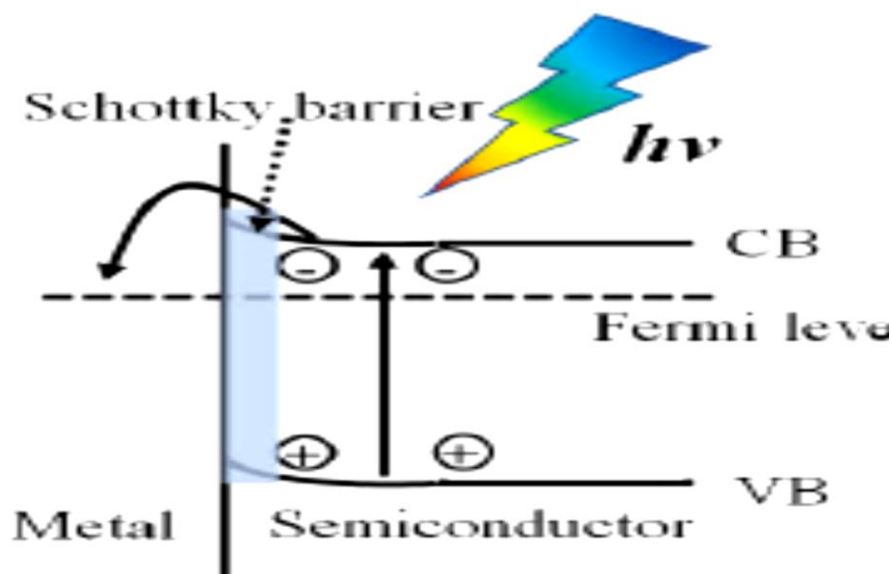


Fig. 1.6. Schematic of a Schottky junction [43]

In fact, when a metal is put in direct contact with a semiconductor, a so called Schottky barrier can be formed, leading to a band bending in the semiconductor at the interface of the contact. This occurs both when the semiconductor is n-type (p-type) and its work function is smaller (larger) than the work function of the metal. In this case, the electrons must have a higher energy to overcome the barrier. The photogenerated electrons will pass from the CB of the semiconductor to the metal through the Schottky barrier until their Fermi levels are similar, and the holes will hold in the VB of the semiconductor, thereby achieving effective separation of electron-hole pairs.

In the photocatalytic H_2 production system, the cocatalysts have four crucial roles in improving the activity of the semiconductor photocatalysts (**Fig. 1.7.**) [44] which are:

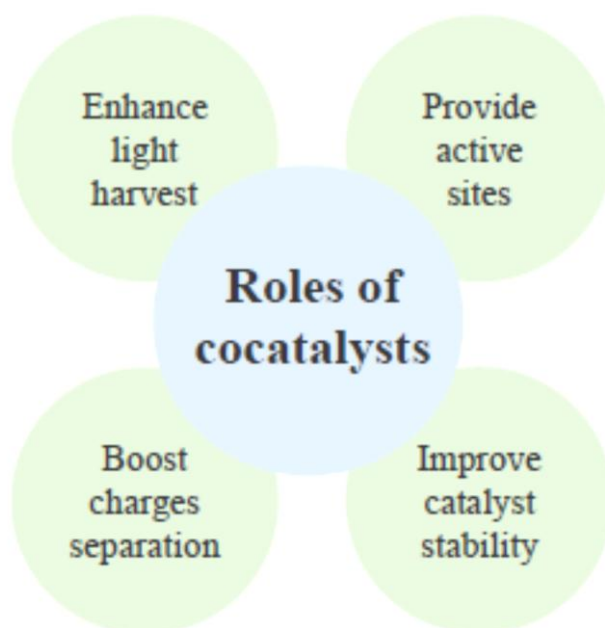


Fig. 1.7. Functions of cocatalysts in photocatalytic H₂ production.

- i) Cocatalysts can enhance the light harvesting.
- ii) Cocatalysts can be effective in facilitating the separation of electron-hole pairs, through the contribution of the interfacial electric field induced by the layered region formed between the cocatalyst and semiconductor. This electric field is a driving force for the separation of the photogenerated electrons and holes.
- iii) Cocatalysts can provide active sites that promote H⁺ reduction and H₂O oxidation by lowering the respective activation energies.
- iv) Cocatalysts can timely eliminate the photogenerated charges from the surface of the semiconductor and subsequently avoid the photocorrosion and enhance the stability of the photocatalysts.

Moreover, various developed bimetallic cocatalyst systems retard the backward recombination of H₂ and O₂ seen with some metallic promoters [42]. In general, cocatalysts for water splitting can be classified into three categories: H₂ evolution cocatalysts, O₂ evolution cocatalysts, and dual cocatalysts. Commonly, metals such as Pt, Rh, Ru, Ir and Ni can function as H₂ evolution cocatalysts, whereas oxides of Co, Fe, Ni, Mn, Ru and Ir work as O₂ evolution cocatalysts [45]. **Fig. 1.8.** shows the processes of charge transfer between host photocatalyst and cocatalyst, for water splitting on **(a)** H₂ evolution cocatalyst, **(b)** O₂ evolution cocatalyst and **(c)** Dual cocatalyst [46].

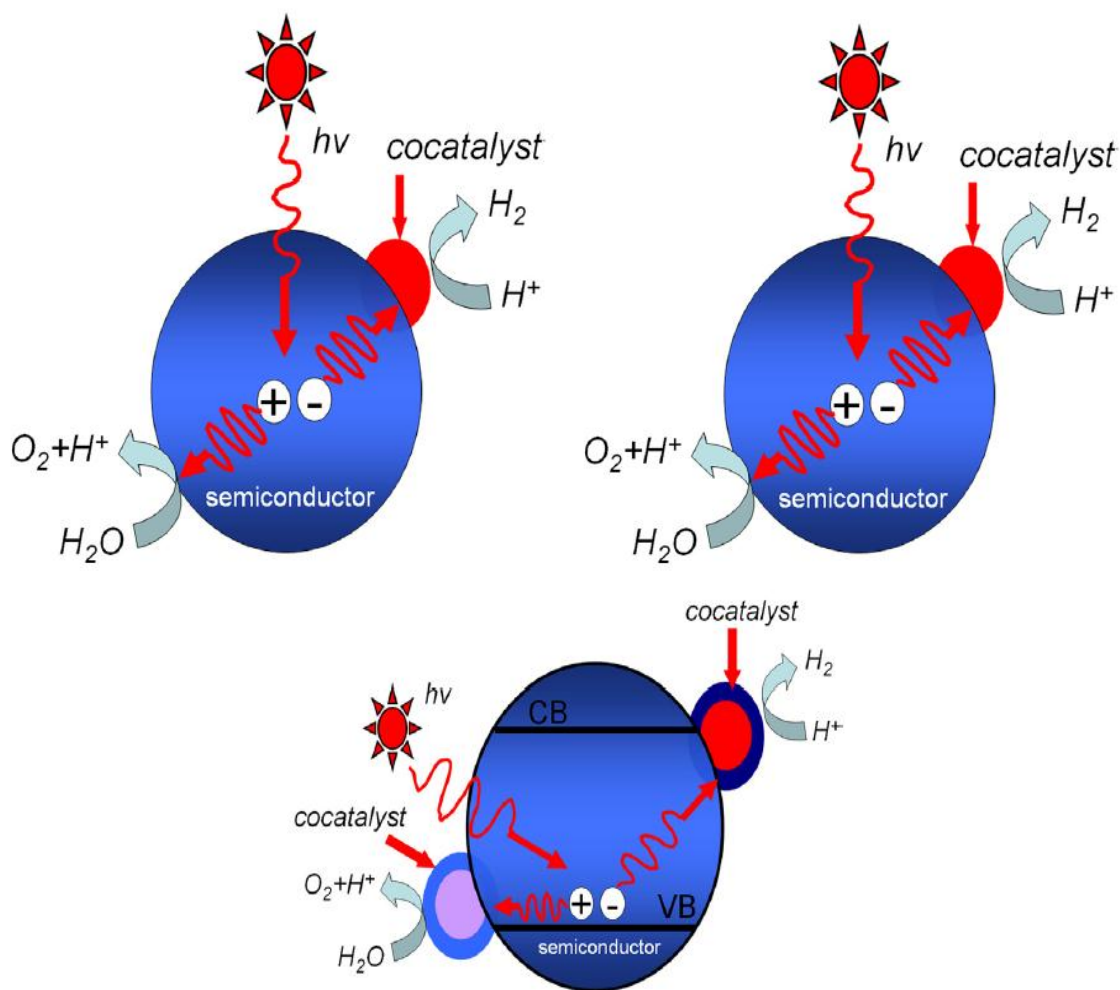


Fig. 1.8. processes of charge transfer between host photocatalyst and cocatalyst, for water splitting on (a) H_2 evolution cocatalyst, (b) O_2 evolution cocatalyst and (c) Dual cocatalyst.

3.4. Ions doping

Numerous studies showed that modifying semiconductors through doping has proved to be easy, effective, and successful path way to shift their absorption spectrum into the visible light region, which may increase their activity in visible light and improves their photocatalytic performance. For example, KNbO_3 ($E_g=3.14$ eV) and NaNbO_3 ($E_g=3.08$ eV) absorb only UV radiations due to their wide band gap, however adequate adjustments of the band structure have led in visible light photocatalysis [47]. N doped NaNbO_3 is a recognized visible light photocatalyst for the degradation of 2-propanol [48]. Nitrogen doping in KNbO_3 has been investigated for water splitting as well as organic pollutant degradation [49]. The n-type Nb-doping of SrTiO_3 in the Ti site, demonstrates high absorption and high photocatalytic activity in the visible light region [50]. Also, in order to evolve the SrTiO_3 photocatalyst for photodegradation of Rhodamine B solution, Wang et al [51] examined the

photocatalytic properties of SrTiO₃ powders doped with Eu³⁺ ion. The study detected a band gap reducing owing to the hybridization of Eu d-state with the Ti 3d or O 2p orbitals, which leads to a significant enhancement of light absorption ability in the visible light domain for the doped system compared to the undoped one. The energy band gap of TiO₂ is in the range 3.0 eV (rutile) to 3.5 eV (anatase) corresponding to wavelengths of 385 and 410 nm respectively, which allows the absorption of light in ultraviolet range only [52]. Nonmetal-doped TiO₂ is reported as the most promising photocatalysts candidates [53]. Among all the nonmetal-doped TiO₂ photocatalysts, nitrogen doped TiO₂ is the most studied material [54]. In addition, several other visible-light active materials, such as carbon C, F and S, doped TiO₂ were reported [55]. Thanh et al. [56] studied the influence of Mn doping on the structural, optical and magnetic properties of SrTi_{1-x}Mn_xO₃ (x = 0.0–0.1) synthesized by a solid-state reaction method. They found that an increasing of Mn concentration in the host material, leads to a significant band gap narrowing, which shifts the absorption spectrum of SrTiO₃ to the longer wave length region, and increases its photocatalytic performance.

In general, doping strategy enhances the photocatalytic properties of semiconductors through narrowing the band gap by lowering the CB, raising the VB, and/or inducing midgap states [57]. However, it is found that inducing mid-gap states associated with some types of monodoping, minimizes the photoconversion efficiency by trapping the photogenerated charge carriers. For example, In a theoretical study Modak et al. [58] reveal that the dopant elements (N, Mo and W) individually can reduce the band gap of KTaO₃ either by introducing localized unoccupied states or occupied states in between valence band and conduction band. Unfortunately, these localized states in combination with charge compensating vacancy defects may reduce the photoconversion efficiency. Also, Chen et al. [59] studied the effect of doping by Ru on the photocatalytic activity of SrTiO₃ based photocatalyst using DFT calculations. They found that the intra-band gap states introduced by Ru dopant promote faster charge carriers recombination.

Studies show that the introduced in-gap states can be avoided by codoping strategies. For example, Kato and Kudo revealed in experimental studies that codoping of Ta or Sb and Cr into the pure SrTiO₃ is a successful way for improving the photocatalytic efficiency of H₂ evolution. They found that, codoping Ta⁵⁺ or Sb⁵⁺ to Sr sites and Cr³⁺ in the Ti sites, contribute to the charge compensation establishing [60;61]. Besides, Miyauchi et al. [62] and Wang et al. [63] showed that (La, N) codoped SrTiO₃ exhibits good efficiency towards H₂ production under visible light due to the decrease in structure defects after doping. They

explained that by that codoping of La^{3+} ions in Sr^{2+} sites and N^{3-} in O^{2-} sites maintains the charge compensation and minimizes the O vacancies generation. Mandarin et al., synthesized Gd^{3+} co-doped N- TiO_2 via the sol-gel method [64]. The 2 wt% Gd^{3+} and N co-doped TiO_2 exhibited the highest photocatalytic activity toward hydrogen production in an aqueous solution containing methanol as a sacrificial reagent, which assigned to the efficient charge separation and increased visible light absorption. Lee et al. reported that Cr or Fe-doped $\text{La}_2\text{Ti}_2\text{O}_7$ is capable of producing H_2 from an aqueous methanol solution under visible light [65]. Codoping with Ir and either Sr, Ba, or La into NaMO_3 ($\text{M} = \text{Nb}$ and Ta) makes the host material active for visible-light-driven H_2 or O_2 evolution in the presence of sacrificial reagents, and the activity is strongly dependent on the concentration and type of codopant(s) employed [66]. As well as, it has been demonstrated in a theoretical investigation by Wei et al. [67] that codoping of either nonmetal (H, F, Cl, Br, I) or metal (V, Nb, Ta, Sc, Y, La) is a successful way to passivate the N-induced in-gap states. Their study aims to exploring the codoping synergistic effects for higher energy conversion efficiency.

4. Bibliographic study of SrTiO_3

4.1. Description of the ideal perovskite structure

The name “perovskite” originally refers to a type of minerals with chemical formula CaTiO_3 ; this mineral was first described in 1830 by the geologist Gustav Rose who named it in honor of a great Russian mineralogist, Count Lev Aleksevich von Perovski. In general, any crystals with the same structure as CaTiO_3 are categorized into the perovskite structure. Ideal perovskites have the general formula ABX_3 ; where A is an alkaline earth or a rare earth, B is a transition metal and X is generally oxygen, fluorine or a halogen. The anion X can also be found as an H^- hydride.

The ideal perovskite is simple cubic and belongs to the $\text{Pm}\bar{3}\text{m}$ space group. It has a pattern of one molecule per mesh ($Z = 1$). The crystallographic pattern of perovskite ABX_3 contains 5 atoms (**Fig. 1.9.**).

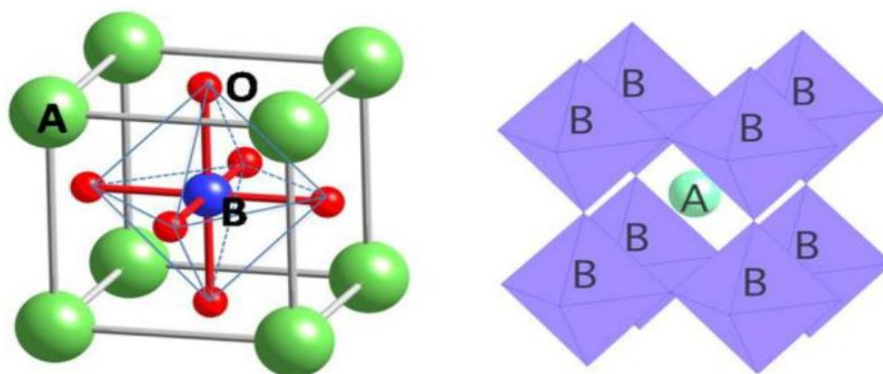


Fig. 1.9. Structural model of an ideal perovskite.

Depending on the choice of origin, there are two ways to describe the structure. In the first, A is at the origin, in position 1a (0, 0, 0), B is in the center of the cube, in position 1b ($1/2$, $1/2$, $1/2$) and the X atoms are found in the middle of each face, in the 3c (0, $1/2$, $1/2$) position (**Fig. 1.10 (a)**). In the second way, the origin is moved by a vector ($1/2$, $1/2$, $1/2$), which causes A to occupy position 1b ($1/2$, $1/2$, $1/2$), B position 1a (0, 0, 0) and the X atoms are in the middle of each stop, in position 3c (0, $1/2$, $1/2$) (**Fig. 1.10 (b)**).

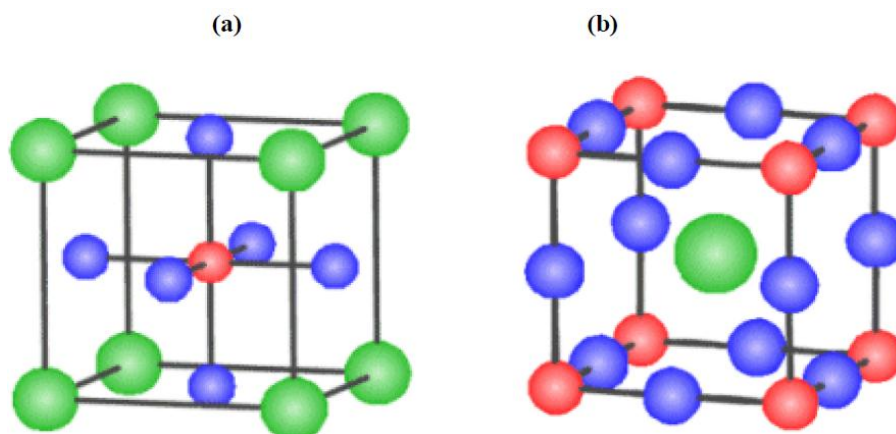


Fig. 1.10. Elementary mesh of the perovskite ABX_3 structure: **(a)** A cation is at the origin and **(b)** B cation is at the origin.

The cation A, generally quite large and not very charged (mono or divalent), has a coordination of 12 in this crystal lattice. The cation B of coordination 6 is a smaller cation (di, tri or quadrivalent). The ionocovalent framework is formed by BX_6 octahedra sharing their vertices in the three crystallographic directions. The association of octahedra forms cavities in which the A anions are located, as shown in **Fig. 1.11**.

Specifically, a given cation B is separated from its six near neighbors by a distance of only $\frac{a}{2}$ where a is the parameter of the cube. This bond is much closer than that connecting each atom A to its twelve neighbours X ($d_{A-X} = \frac{a\sqrt{2}}{2}$).

There are generally two types of perovskites depending on the occupation of sites A and B:

- Simple perovskites whose A and B sites are respectively occupied by a single type of cation (BaLiF₃, CaLiF₃, SrLiF₃, KMgF₃, BaTiO₃, KNbO₃, CaTiO₃, SrTiO₃, ...)
- Complex perovskites in which one/or both A or B sites is/are occupied by different types of cations (PbMg_{1/3}Nb_{2/3}O₃, PbSc_{1/2}Ta_{1/2}O₃, Na_{1/2}Bi_{1/2}TiO₃, ...)

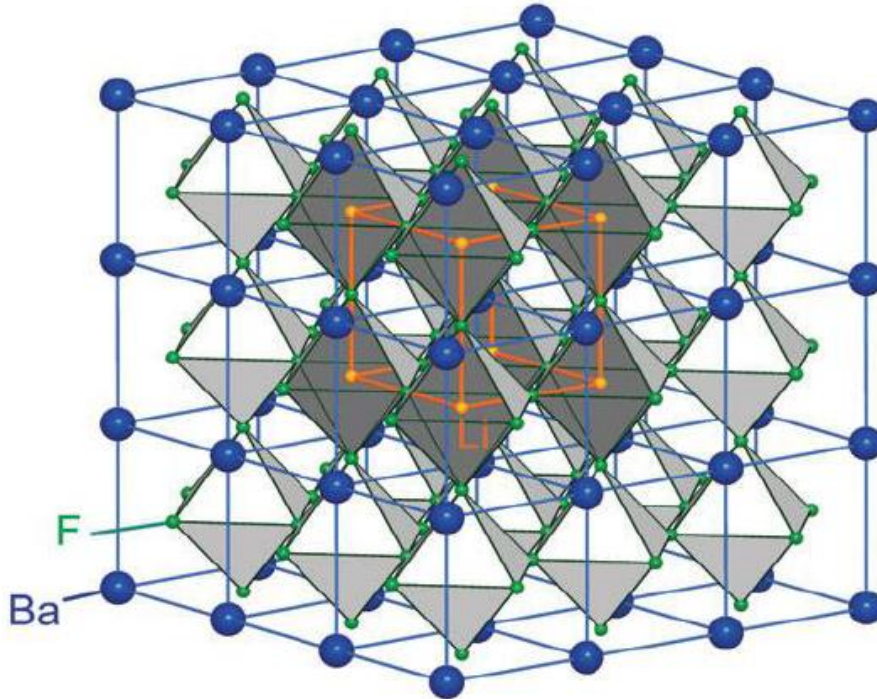


Fig. 1.11. Arrangement of octahedra in the mesh of the ideal perovskite BaLiF₃. [Figure adapted from ref \[68\].](#)

4.2. Stability conditions of the perovskite structures

For an ideal perovskite structure, the ions are tangent to each other and the BX_6 octahedra are then perfectly aligned and form an undeformed three-dimensional network of cubic symmetry. The stability of this ideal structure depends on two factors:

- The volume ratio of the polyhedron of cation A (V_A) to that of cation B (V_B) is exactly 5. This $\frac{V_A}{V_B}$ ratio is a useful quantity which makes it possible to characterize the degree of distortion of the perovskite structure. The smaller it is, the greater the structural distortion.
- The tolerance factor which is equal to 1 and any deviation from this equality implies a deformation of the structure

As an example [69], at room temperature the structure of $SrTiO_3$ is close to the ideal structure described above: $a=3.905 \text{ \AA}$, $V_A= 49.623 \text{ \AA}^3$, $V_B=9.925 \text{ \AA}^3$, $t = 1.002$, $\frac{V_A}{V_B} = 4.9998$.

4.3. Goldschmidt factor

Goldschmidt has defined a quantitative geometric factor, called tolerance factor t or Goldschmidt factor [70], which quantifies the deviation from the ideal structure when $t \neq 1$.

$$t = \frac{(R_X + R_A)}{\sqrt{2}(R_X + R_B)} \quad (1.2)$$

Thus each distortion of the cubic structure implies a deviation of t from the ideal value. We can therefore distinguish several situations depending on the value of the tolerance factor [71], as shown in **Table 1.1**.

Table 1.1

Evolution of crystal structures as a function of the value of the tolerance factor.

Ilmenite	0.75<t<1.06 perovskite			Hexagonal
	0.75<t<0.96 Orthorhombic distortion	0.96<t<0.99 Rhombohedral distortion	0.99<t<1.06 Cubic	

Note that the stability limits of the perovskite phase are defined for t between 0.75 and 1.06.

For ABF_3 -type fluoro perovskites, the Goldschmit factor can be determined from the ionic radii of the atoms which form the structure of these compounds.

$$t = \frac{(R_{F^-} + R_{A^+})}{\sqrt{2}(R_{F^-} + R_{B^{+2}})} \quad (1.3)$$

Fluorides of the cubic perovskite type exist only for: $0.88 < t \leq 1$.

Indeed, if the tolerance factor t is between 0.76 and 0.88, the distortion is orthorhombic and if $t > 1$, the structure is hexagonal.

From an ideal structure, we define derived structures obtained by removing one or more symmetry elements from the space group $Pm\bar{3}m$. Thus derived structures can be obtained by:

- Rotation or tilt of the octahedra due to the size of cation A, either too large or too small for the location;
- Displacement of the cations B from the center of the octahedral;
- Distortion of octahedra due to Jahn-Teller effects [72];
- Increase in covalency of A-X and / or B-X bonds;

4.4. Cubic perovskite $SrTiO_3$

At room temperature, $SrTiO_3$ crystallizes in the ABO_3 cubic perovskite structure (space group $Pm\bar{3}m$) with a lattice parameter of $3.905\text{\AA}$ [73]. The electronic configurations of its constituent elements are shown in the **table 1.2**.

Table 1.2

The electronic configurations of constituent elements of $SrTiO_3$

constituent element	Sr	Ti	O
electronic configuration	[Kr] $5s^2$	[Ar] $4s^2 3d^2$	[He] $2s^2 2p^4$

The $SrTiO_3$ perovskite undergoes a phase transition at 105K and becomes tetragonal ($a = b \neq c$) where the Ti-O octahedra that make up its structure rotate in an alternating pattern; this is called an “antiferrodistortive” transition. The melting point of $SrTiO_3$ is at 2350K. In cubic $SrTiO_3$, the Sr ion is surrounded by twelve oxygen ions belonging to four TiO_6 octahedra. The smaller Ti ion is surrounded by six oxygen ions. Within the TiO_6 octahedra, while a hybridization of the O-2p states with Ti-3d states leads to a pronounced covalent bonding

[74], Sr and O ions exhibit ionic bonding character. For the (100) SrTiO₃ surface, there are two distinct types of atomic alternating planes, one is formed by a SrO plane and the other by a TiO₂ plane [75]. SrTiO₃ is insulating with a gap of approximately 3.15 eV [56]. Its permittivity is high ($\epsilon = 277$). The surfaces of SrTiO₃ are flat and are chemically and mechanically stable.

Because of these structural and insulating properties, which can also be modulated by doping or by the use of multilayers, SrTiO₃ can meet many applications: substrate for the epitaxy of superconductors, electrode for water photocatalysis [76], buffer layer [77], gate dielectric, insulator for dynamic random access memories (DRAM) [78 ;79]. For microelectronics applications, SrTiO₃ should be an attractive material, provided it retains its properties when it is exploited in thin layers. In particular, the high permittivity measured on single crystals could make it possible to reduce the equivalent emitting thicknesses of the gate oxides or to increase the surface density of storage of DRAM devices [80].

5. conclusion

With this chapter, photocatalytic water splitting reaction on semiconductor particles and its main steps have been presented, recent strategies in modification and development of semiconductors for photocatalytic H₂ production has been systematically discussed. Structural properties, electronic properties, domain of application and other properties of SrTiO₃ were briefly mentioned. The next chapters concerning our results of this thesis will focus on introducing foreign elements as promising ways to make SrTiO₃ more effective photocatalyst for water splitting and hydrogen production.

Chapter 2

Density functional theory

Abstract

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Ab initio methods (or first principles methods) in physics are computational methods based on the first principles of quantum mechanics. Its use has increased rapidly in recent years due to the continuous developments of their techniques, the rapid increase of the computing power, and improvements in the numerical methods as well as in the software implementations [81]. One of the most interesting characteristics of these methods is that they are more accessible to new researchers without extensive knowledge of programming and numerical methods. There are many first-principles approaches for determining the ground state and excited states of many-atom systems. Among them, the approach based on the density functional theory (DFT) offers an exact background for the many-body problem but can be solved only approximately and the resulting equation is one electron-like [82]. DFT is based only on fundamental laws and constants and not on empirical input. In this chapter, we explained the foundations of Density Functional Theory. The electron density is the main variable in DFT, since the energy is expressed as a functional (function with a function as variable) of the density. Initially, the Schrödinger Equation and the general many-body problem are presented. Approximations to the many problems, as the Born-Oppenheimer, Hartree and Hartree-Fock approximations are also investigated. Subsequently, the theoretical backbone of DFT, the Hohenberg-Kohn theorems and the Kohn Sham equations are reviewed.

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1. Introduction

The Schrödinger equation is a linear partial differential equation that governs the wave function of a quantum-mechanical system. It was established in its primitive form in 1926 by Erwin Schrödinger and was generalized by Paul Dirac just three years later. Paul Dirac [83] has emphasized on the difficulty of solving the equations of quantum mechanics and desirability of developing practical methods of applying quantum mechanics to explain complex systems. During the same period, Thomas [84] and Fermi [85] proposed a tractable scheme for solving the many-electron problem, in which the electron density $n(\mathbf{r})$ is regarded as central variable rather than the wave function, and the total energy of a system is written as a functional $E^{\text{TF}}[n(\mathbf{r})]$. This Thomas-Fermi model is viewed as the predecessor to modern DFT [86]. However, its accuracy is limited by the errors due to the inaccurate representation of kinetic energy, exchange energy, and the complete neglect of electron correlation. In the following several decades, physicists made great efforts on solving Schrödinger-type equations with local effective potentials and improving numerical methods [87,88,89,90,91], which have been decisive in carrying out density functional calculations. Until 1965, Kohn and Sham introduced the famous Kohn-Sham equation, suggesting an alternative way to implement the DFT [92]. Within the framework of Kohn-Sham DFT, the complex many-body problem of interacting electrons is reduced to a tractable problem of non-interacting electrons moving in an effective potential. DFT is that powerful “approximate practical methods, which can lead to an explanation of the main features of complex atomic systems without too much computation”.

2. The Schrödinger Equation

Quantum mechanics gives a logically consistent theory of matter on the microscopic level. It can be considered as the basic theory for many areas of science and technology including solid state physics, atomic physics, particle physics, nuclear physics, chemistry, molecular biology, laser devices and so on.

The starting point for any discussion of quantum mechanics is based on the Schrödinger equation [93]. The Schrödinger equation is a differential equation which describes how the wave function Ψ represents a quantum particle's motion under the influence of an external potential $V(\mathbf{r})$. The external potential might be the Coulomb electrostatic potential due to the nuclei of the atoms.

The time independent Schrödinger equation for a quantum particle moving in a three dimensional potential energy field $V(r)$ is given by

$$i\hbar \frac{\partial \Psi(r)}{\partial t} = H\Psi(r) \quad (2.1)$$

where H is the Hamiltonian operator, which is the sum of a kinetic energy operator and the potential energy of the system. For a single particle of mass m which is moving through space, the Hamiltonian is given by

$$H = \frac{-\hbar^2}{2m} \nabla^2 + V(r) \quad (2.2)$$

Here, $\hbar$ is the reduced planck constant. A fundamental postulate of quantum mechanics states that the possible results of a measurement of an observable represented by the operator Q are its eigenvalues q_i only [94, 95,96]. The eigenvalue equation is given by

$$Q\Psi_i = q_i\Psi_i \quad (2.3)$$

where Q is an operator and q_i is a number. This is an eigenvalue problem. A solution Ψ of such an equation is called an eigenfunction corresponding to an eigenvalue q_i of the operator Q .

For the time independent Schrödinger equation, the eigenvalue of the Hamiltonian operator is the energy of the system,

$$H\Psi = E\Psi \quad (2.4)$$

3. The many-body problem in a solid

Solid material is a collection of heavy nucleus and light electron particle. If there are N nuclei with each one having Z electrons then we have to deal with $N+ZN$ particles called many body problems. Then we need quantum, many-body problem to study these materials.

Hence, we must solve the many-electron the time independent Schrodinger equation:

$$H\Psi(r_1, \sigma_1, r_2, \sigma_2, \dots, R_1, R_2, \dots) = E\Psi(r_1, \sigma_1, r_2, \sigma_2, \dots, R_1, R_2, \dots) \quad (2.5)$$

Where Ψ is the many-body wavefunction, dependent on the positions and spin of the electrons, r_i, σ_i and the positions of the nuclei, R_i . In principle the wavefunction also depends on the spins of the nuclei, but this will be neglected. The reason is that we can treat the nuclei

in a solid as classical particles within the Born-Oppenheimer approximation (discussed in the next section). The Hamiltonian H of the system of electrons and nuclei is:

$$\begin{aligned}
 H(R, r) &= T_e(r) + V_{ee}(r) + V_{en}(R, r) + T_n(r) + V_{nn}(r) \\
 &= -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + \sum_{i, I} \frac{Z_I e^2}{|r_i - R_I|} - \sum_I \frac{\hbar^2}{2m_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|}
 \end{aligned} \tag{2.6}$$

Where the subscript e and n indicate the electron and nucleus, m_e and m_I are the mass of electron and nucleus. Different electrons and nuclei are denoted by lower case i, j and upper case subscripts I, J respectively. Z_I is the charge of nuclei.

4. Born-Oppenheimer approximation

The many-body problem cannot be solved analytically for any system more complicated than the dihydrogen cation (H_2^+) and thus approximations have to be made. A first one is the Born Oppenheimer (BO) approximation, considering the electrons to move in the field of fixed nuclei. The justification of the BO approximation is the fact that the nuclei are much heavier than the electrons, the ratio of their masses being ~ 1800 for the lightest element, H. The direct consequence of BO is the decomposition of the many-body wavefunction into an electronic wavefunction ψ and a nuclear wavefunction χ :

$$\Psi(r_1, \sigma_1, r_2, \sigma_2, \dots, R_1, R_2, \dots) = \psi(r_1, \sigma_1, r_2, \sigma_2, \dots; R_1, R_2, \dots) \cdot \chi(R_1, R_2, \dots) \tag{2.7}$$

The electronic wavefunction depends on the nuclear positions as parameters and not as variables, since the electrons rearrange immediately as the nuclear positions are altered.

In relation to the Pauli Exclusion Principle for fermions, the electronic wavefunction is antisymmetric under the interchange of two electrons. Filling in wavefunction (2.7) into the Schrödinger equation (2.6), the following electronic eigenvalue equation is obtained:

$$H_{BO} \psi(r_1, \sigma_1, r_2, \sigma_2, \dots; R_1, R_2, \dots) = E_e(R_1, R_2, \dots) \psi(r_1, \sigma_1, r_2, \sigma_2, \dots; R_1, R_2, \dots) \tag{2.8}$$

The BO Hamiltonian contains only those terms of the general Hamiltonian (2.6) involving electrons:

$$H_{BO} = T_e + V_{ext} + V_{int} \tag{2.9}$$

In this expression, the electronic Hamiltonian includes three distinct operators: the kinetic energy of the electrons T_e , the fixed external nuclear potential acting on the electrons V_{ext} and

the electronic interactions V_{int} , which can be trivially obtained. This hamiltonian is central to the theory of electronic structure.

The associated energy $E_e(R_1, R_2, \dots)$ only depends on the nuclear coordinates and not on the electronic coordinates. The total energy of the many-body system in the BO approximation is:

$$E_{\text{tot}} = E_e + T_n + E_n \quad (2.10)$$

where the last two terms represent the classical kinetic energy and the classical electrostatic energy.

5. Hartree approximation

The simplest approximation of the wavefunction for the many - electron Schrödinger equation is to assume that electrons act like independent electrons. The wavefunction with N independent electrons is then

$$\Psi(\{r_i\}) = \psi_1(r_1)\psi_2(r_2) \dots \psi_N(r_N) \quad (2.11)$$

Here, $\psi_i(r_i)$ is the wavefunction of the i^{th} electron, where different wavefunctions of electrons are orthonormalized. Henceforth, the $\{R_I\}$ are suppressed in the wavefunction since nuclei are treated as fixed in positions. The set of variables $\{r_i\}$ includes the coordinates of space and spin. The energy of the many-electron system within Hartree approximation can be written as

$$E^H = \langle \Psi(\{r_i\}) | H | \Psi(\{r_i\}) \rangle \quad (2.12)$$

In order to calculate the stationary state with the lowest energy of the system, the method of Lagrange multipliers are utilized. Furthermore, the constraint is that the different wavefunctions of electrons are orthonormalized. Therefore, the variation with respect to any wavefunction and Lagrange multiplier E is satisfied [97,98]

$$\frac{\delta}{\delta \psi_k^*(r)} (E^H - \sum_i^N \sum_j^N E_{i,j}^H (\langle \psi_i(r_i) | \psi_j(r_j) \rangle) - \delta_{i,j}) = 0 \quad (2.13)$$

The single-particle Hartree equation is derived from Eq. 3.12 as

$$\left(-\frac{\nabla^2}{2} + \sum_I^{N'} \frac{Z_I}{|r-R_I|} + \sum_{j \neq i}^N \left\langle \psi_j(r') \left| \frac{1}{|r-r'|} \right| \psi_j(r') \right\rangle \right) \psi_i(r) = \epsilon_i^H \psi_i(r) \quad (2.14)$$

Here, **Eq. 2.14** is a group of dependent single-particle equations. ϵ_i^H is identified as the eigenvalue for this single-electron Hartree equation. If $j = i$ in the above equation, it means

that electrons are allowed to interact with themselves, which results in the self-interaction error.

In summary, from the Hartree approximation, the ground states can be achieved and the many electron equation becomes N single-electron equations. These two features are important to understand the Hartree-Fock approximation and the Kohn-Sham equation.

6. Hartree-Fock approximation

Hartree-Fock method [99,100], treats the many-electron wave function as a product of single particle functions, i.e.

$$\Psi(r_1, r_2, \dots, r_N) = \psi_1(r_1) \dots \psi_N(r_N) \quad (2.15)$$

Each of the functions satisfies a one-electron Schrödinger equation

$$\left[-\frac{1}{2}\nabla^2 + V_{ext} + V_i \right] \psi_i(r) = \varepsilon_i \psi_i(r) \quad (2.16)$$

with a potential term arising from the average field of the other electrons, i.e. the Coulomb potential V which is given by

$$V_i = \sum_{j(\neq i)}^N \int dr' \frac{1}{|r-r'|} \psi_j^*(r') \psi_j(r') \quad (2.17)$$

and an external potential due to the nuclei V_{ext} . Fermi statistics can be incorporated into this picture by replacing the product wave function by a properly determinant function for a fixed number N of electrons. Due to the Pauli Exclusion Principle, the total wave function for the system must be antisymmetric under particle exchange:

$$\Psi(r_1, r_2, \dots, r_i, \dots, r_j, \dots, r_N) = -\Psi(r_1, r_2, \dots, r_j, \dots, r_i, \dots, r_N) \quad (2.18)$$

Where r_i includes coordinates of position. A Slater determinant wavefunction [101] which satisfies antisymmetry is used instead of the simple product form,

$$D = \begin{vmatrix} \psi_1^\sigma(r_1) & \psi_1^\sigma(r_2) & \dots & \psi_1^\sigma(r_N) \\ \psi_2^\sigma(r_1) & \psi_2^\sigma(r_2) & \dots & \psi_2^\sigma(r_N) \\ \dots & \dots & \dots & \dots \\ \psi_N^\sigma(r_1) & \psi_N^\sigma(r_2) & \dots & \psi_N^\sigma(r_N) \end{vmatrix} \quad (2.19)$$

Where, σ indicates the spin. We can rewrite the Schrödinger equation into the Hartree-Fock form [102]:

$$\left[\frac{1}{2}\nabla^2 + V_{ext}(r) + V_{Hartree}(r) + V_x^i(r) \right] \psi_i^\sigma(r) = \varepsilon_i \psi_i^\sigma(r) \quad (2.20)$$

With

$$V_{Hartree}(r) = \sum_j \int dr' \frac{1}{|r-r'|} \Psi_j^{\sigma*}(r') \Psi_j^{\sigma}(r') \quad (2.21)$$

$$V_x^i(r) = - \sum_j \int dr' \frac{1}{|r-r'|} \Psi_j^{\sigma*}(r') \Psi_i^{\sigma}(r) \frac{\Psi_j^{\sigma}(r)}{\Psi_i^{\sigma}(r)} \quad (2.22)$$

$V_{Hartree}(r)$ being the classical Coulomb potential (Hartree potential). Additionally, the Hartree-Fock approximation leads to nonlocal exchange term V_x , which makes the Hartree-Fock equations difficult to solve.

7. Thomas-Fermi approach

Thomas [84] and Fermi [85] are taking a different approach, which is a scheme based on the electronic density of the system, $n(r)$:

$$n(r) = N \int dr_2 \dots \int dr_N \Psi(r, r_2, \dots, r_N) \Psi^*(r, r_2, \dots, r_N) \quad (2.23)$$

The Thomas-Fermi method assumed that the motions of the electrons are uncorrelated, the electron-electron interaction energy only comes from the electrostatic energy and that the corresponding kinetic energy can be written into an explicit functional of the density, describing the free electrons in an homogeneous gas with density equal to the local density at any given point.

$$E_{TF}[n] = C \int dr n(r)^{5/3} + \int dr V_{ext}(r) n(r) + \frac{1}{2} \int dr \int dr' \frac{n(r) n(r')}{|r-r'|} \quad (2.24)$$

The first term is the local approximation to the kinetic energy with $C = 3/10 (3\pi^2)^{2/3} = 2.871$ in atomic units. The second and third terms are the external energy and the classical electrostatic Hartree energy respectively. The density and energy of the ground state can be obtained by the method of Lagrange multipliers, to minimize the above functional $E_{TF}[n]$ for all possible $n(r)$ subject to the constraint of total constant number of electrons:

$$N = \int dr n(r) \quad (2.25)$$

leads to the following stationary condition,

$$\delta\{E_{TF}(n) - \mu \int dr n(r)\} = 0 \quad (2.26)$$

The Lagrange multiplier μ is the Fermi energy. Finally, we got the Thomas-Fermi equations

$$\frac{5}{3} n(r)^{2/3} + V_{ext}(r) + \int \frac{n(r')}{|r-r'|} - \mu = 0 \quad (2.27)$$

that can be solved directly to obtain the density of the ground state.

Thomas-Fermi theory suffers from many deficiencies; probably the most serious defect is that it does not predict bonding between atoms, so that solids cannot form in this theory. The main source of error comes from the crude approximation of the kinetic energy, which represents a substantial portion of the total energy of the system. Another shortcoming is the over simplified description of the electron-electron interactions. It is treated classically and thus neglects the exchange interaction which was lately extended and formulated by Dirac [87]. In next Section, we will introduce the density functional formalism, which is developed based on the Thomas-Fermi model for the electronic structure of materials.

8. The fundamentals of Density Functional Formalism

In Density Functional Theory (DFT) the electron density $n(r)$ is the principal quantity. The aim of DFT is to reformulate the quantum mechanical theory in terms of the density instead of the wavefunction. As such, the historical predecessor of DFT is the Thomas-Fermi approach (1927-1928).

A functional is a function with another function as a variable, denoted $F[f]$. For instance, in DFT, the energy is written as a functional of the density, $E[n]$. The functional derivative is defined as:

$$\frac{\delta}{\delta f(x)} F[f] = \lim_{\epsilon \rightarrow 0} \frac{F[f(x) + \epsilon \delta(x-x')] - F[f(x)]}{\epsilon} \quad (2.28)$$

Important properties of functional derivation include:

$$\frac{\delta}{\delta f(x)} \left(\int F[f] dx \right) = \frac{\delta F[f]}{\delta f(x)} \quad (2.29)$$

$$\frac{\delta}{\delta f(x)} \left(\int F[f] f(x) dx \right) = \frac{\delta F[f]}{\delta f(x)} f(x) + F[f(x)] \quad (2.30)$$

$$\frac{\delta}{\delta f(x)} \left(\frac{1}{2} \int \int g(x, x') f(x) f(x') dx dx' \right) = \int g(x, x') f(x') dx' \quad (2.31)$$

In view of the extensive study of the Thomas-Fermi scheme and its well-known deficiencies, we discuss the further developments and improvements of the density functional formalism in this section. Two basic theorems of the density functional formalism were first derived by Hohenberg and Kohn [103]. These remarkably powerful theorems formally established the electron density as the central quantity describing electron interactions in many-body systems. As an exact theory of many-body systems, they can be applied to any

system of interacting particles in an external potential, $V_{ext}(r)$. The two theorems are now stated as follows:

- **Theorem 1.** For any system of interacting particles under the influence of an external potential $V_{ext}(r)$, the external potential $V_{ext}(r)$ is a unique functional of the electron density $n(r)$.
- **Theorem 2.** The exact ground state energy can be obtained variationally for any particular $V_{ext}(r)$, the density $n(r)$ that minimizes the total energy is the exact ground state density $n_0(r)$.

According to these two theorems, the total energy functional can be viewed as a functional of $n(r)$ and written in the following form,

$$E_{HK}[n] = T[n] + E_{int}[n] + \int dr V_{ext}(r)n(r) + E_{nn} \quad (2.32)$$

The functional includes all internal energies $E_{int}[n]$, kinetic energy $T[n]$, the energy of external potential and interaction energy of nuclei E_{nn} . Although the Hohenberg-Kohn theorems are extremely powerful, they do not offer a way of computing the ground-state density of a system in practice.

9. The Kohn-Sham equations

About one year after the seminal DFT paper by Hohenberg and Kohn, Kohn and Sham developed a simple method for carrying-out DFT calculations, that retains the exact nature of DFT [92]. They assume that the ground state density of interacting system is equal to that of certain non-interacting system. This enables us to use the independent-particle Kohn-Sham equation (KS equation) to describe the non-interacting system, which is exactly soluble by incorporating all the difficult many body terms into an exchange-correlation functional. Therefore, we can obtain the ground state density and energy of the interacting system by solving the KS equations, with the accuracy limited only by the approximations in the exchange-correlation functional.

The functional of the real system is:

$$E[n] = T[n] + E_{in}[n] + E_{ext}[n] \quad (2.33)$$

We can rewrite $E_{int}[n]$ as:

$$\begin{aligned} E_{int} &= \frac{1}{2} \int \int dr dr' \frac{n(r)n(r')}{|r-r'|} + E'_{XC} \quad (2.34) \\ &= E_H + E'_{XC} \end{aligned}$$

where the first term is the Hartree energy, the classical Coulomb interaction energy in the electron gas, while E'_{XC} is the correction due to quantum mechanical exchange and correlation (XC). Functional derivation to n , using Equations (2.29) and (2.31) yields:

$$\frac{\delta E[n]}{\delta n} = \frac{\delta T}{\delta n} + V_H(r) + \frac{\delta E'_{XC}}{\delta n} + V_{ext}(r) = \mu \quad (2.35)$$

In this expression

$$V_H(r) = \int \frac{n(r')}{|r-r'|} \quad (2.36)$$

is the Hartree potential and μ is the chemical potential. The functional of the auxiliary system of non-interacting electrons contains an effective potential $V_{KS}(r)$ replacing the interaction. The functional reads:

$$E[n] = T_0[n] + \int V_{KS}(r)n(r)dr \quad (2.37)$$

Functional derivation using Equation (2.29) leads to:

$$\frac{\delta E[n]}{\delta n} = \frac{\delta T_0}{\delta n} + V_{KS}(r) = \mu \quad (2.38)$$

From the equality the chemical potential in Equations (2.35) and (2.38), the effective KS potential can be specified:

$$V_{KS}(r) = \frac{\delta T}{\delta n} - \frac{\delta T_0}{\delta n} + \frac{\delta E'_{XC}}{\delta n} + V_H(r) + V_{ext}(r) \quad (2.39)$$

Here the first three terms can be combined to:

$$\frac{\delta T}{\delta n} - \frac{\delta T_0}{\delta n} + \frac{\delta E'_{XC}}{\delta n} = \frac{\delta E_{XC}}{\delta n} = V_{XC} \quad (2.40)$$

an XC-type potential. As such, the KS potential is:

$$V_{KS}(r) = V_{XC} + V_H(r) + V_{ext}(r) \quad (2.41)$$

The corresponding Hamiltonian of the non-interacting system is:

$$\hat{H} = \sum_{i=1}^N -\left(\frac{1}{2}\nabla_i^2 + V_{KS}(r_i)\right) = \sum_{i=1}^N \hat{h}_{KS}(i) \quad (2.42)$$

The solution of the Schrödinger equation is - since there are no interactions - a Slater determinant:

$$\Psi = |\psi_1, \psi_2, \dots, \psi_N| \quad (2.43)$$

leading to the KS equations:

$$\hat{h}_{KS}(i)\psi_i(r) = \varepsilon_i\psi_i(r) \quad (2.44)$$

Where $\psi_i(r)$ are the KS orbitals and ε_i are the KS eigenvalues. The ground state density follows from the KS orbitals through:

$$n_0(r) = \sum_i |\psi_i(r)|^2 \quad (2.45)$$

The challenge in the KS approach is to find suitable approximations for the XC functional:

$$E_{XC}[n] = T[n] - T_0[n] + E_{int}[n] - E_H[n] \quad (2.46)$$

This will be the subject of the next chapter, in which several functionals will be discussed.

In the Hartree energy $E_H[n]$, the electron in the KS orbital under study is included in $n(r)$. Consequently, as the XC energy is approximated, the self-interaction does not fully cancel in the KS approach. The generalization of the KS approach to allow for spin-polarization is straightforward. KS equations for both spin components can be established.

We will now derive an expression for the total electronic energy in the KS method. The total energy functional reads, using **Eq (2.46)**:

$$E[n] = T[n] + E_{int}[n] + E_{ext}[n] \quad (2.47)$$

$$= T_0[n] + E_H[n] + E_{XC}[n] + E_{ext}[n]$$

We can rewrite $T_0[n]$, making use of the KS equations:

$$T_0[n] = \sum_{i=1}^N \varepsilon_i - \int V_{KS}(r)n(r)dr \quad (2.48)$$

and fill in $V_{KS}(r)$ as given in Equation (2.41) to obtain:

$$T_0[n] = \sum_{i=1}^N \varepsilon_i - \int V_{KS}(r)n(r)dr \quad (2.49)$$

$$= \sum_{i=1}^N \varepsilon_i - \int (V_{XC}(r) + V_H(r) + V_{ext}(r))n(r)dr$$

$$= \sum_{i=1}^N \varepsilon_i - \int V_{XC}(r)n(r)dr - 2E_H[n] - V_{ext}[n]$$

Combining this with **Eq. (2.47)** produces:

$$E[n] = \sum_{i=1}^N \varepsilon_i - E_H[n] + E_{XC}[n] - \int V_{XC}(r)n(r)dr \quad (2.50)$$

It is thus found that the total electronic energy is not simply a summation of the KS eigenvalues ε_i . The functional $E_{XC}[n]$ can be written as:

$$E_{XC}[n] = \int \varepsilon_{XC}(n(r))n(r)dr \quad (2.51)$$

From Equation (2.31) for functional derivation it follows that:

$$V_{XC}[n] = \frac{\delta E_{XC}[n]}{\delta n(r)} = \varepsilon_{XC}(n(r)) + \frac{\delta \varepsilon_{XC}[n]}{\delta n(r)} n(r) \quad (2.52)$$

Therefore, the total energy reads:

$$E[n] = \sum_{i=1}^N \varepsilon_i - E_H[n] - \int \frac{\delta \varepsilon_{XC}[n]}{\delta n(r)} n(r)dr \quad (2.53)$$

Contrary to the HF method, the total energy in the KS approach is not necessarily an upper bound of the true total energy. The reason is that the KS equations have not been derived from the variational principle.

The KS equations can be solved self-consistently. This is shown schematically in **Fig. 2.1**. The iteration starts with an initial (trial) value for the electron density $n(r)$. Given an XC functional, the KS potential $V_{KS}(r)$ follows from the initial density. Now the KS equations can be solved, yielding the KS orbitals $\psi_i(r)$. They lead to a new electron density $n(r)$ and a total energy. The density is fed as input to the iteration and this is repeated until self-consistency is reached. In practice, this self-consistency is assessed in terms of the convergence of the total energy. If subsequent values of the total energy differ less than the convergence criterion that has been selected, the total energy, forces, stresses etc. can be output.

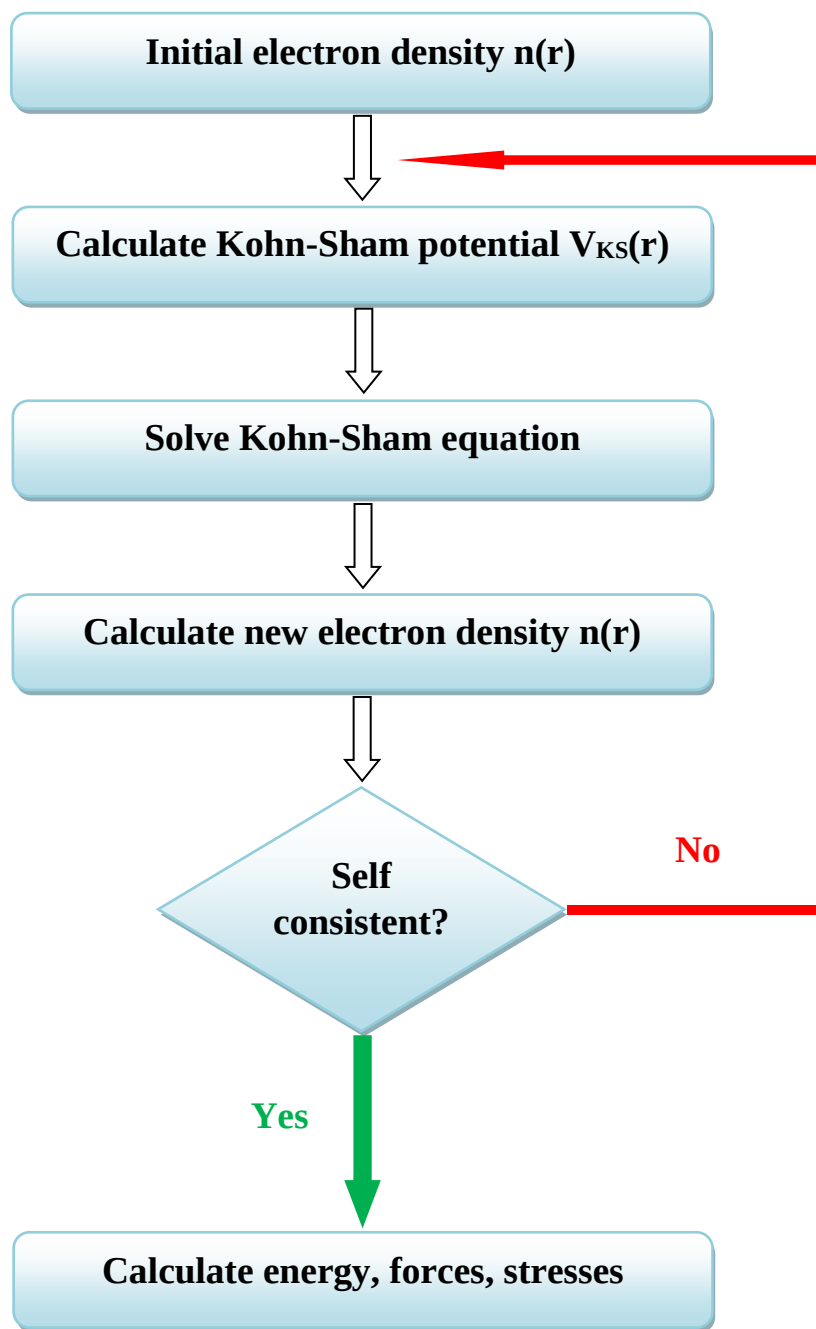


Fig. 2.1. Scheme of the self-consistent solution of the Kohn-Sham equations.

Chapter 3

Methodology

Abstract

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In this chapter we explained how the exchange correlation potential can be treated through various approximations (LDA, GGA and GGA+U), then we submitted the modified becke-johnson potential (mBJ). Also, we presented the fundamental concepts of the linearized /augmented plane wave plus local orbitals (L/APW+lo). We showed also the different versions of (L/APW+lo) and their main developing steps in terms of linearization, full potential, local orbitals and mixed basis sets. Finally we presented the wien2k code.

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1. Introduction

Once the DFT equations are defined in terms of the functional, there are several techniques to solve them. A natural basis for calculating the one-electron wave functions in periodic solids are plane waves (PWs) corresponding to Bloch functions labeled by the k vector of the first Brillouin zone (BZ). PWs are, however, a very inefficient basis set for describing the rapidly varying wave functions close to the nuclei. In order to overcome this difficulty one can either eliminate these oscillations, due to the presence of the core electrons, as done in pseudo potential calculations or one can augment the PW basis set.

One example of the latter approach has led to the linearized /augmented plane wave plus local orbitals (L/APW+lo) method that is now established to be one of the most accurate schemes and thus will be the focus of the present chapter.

2. Exchange and correlation functionals

The main challenge for practical use of the Kohn-Sham equations is to find a good approximation for the exchange-correlation functional. Numerous approximations have been proposed. J. P. Perdew and K. Schmidt have suggested an informative way for categorising the existing various E_{xc} functionals, known as "Jacob's ladder" (**Fig. 3.1**) [104]. Most commonly used exchange-correlation functionals will be briefly discussed in the following part, some of which have been employed in this thesis.

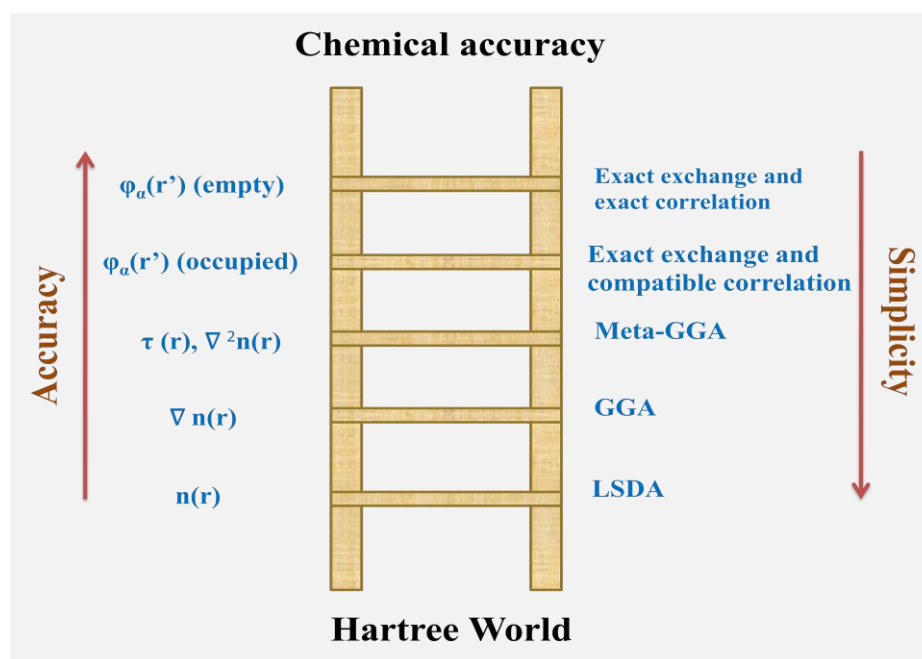


Fig. 3.1. The schematic illustration of "Jacob's ladder" of exchange correlation functional in DFT proposed by J.P. Perdew [104]. Here $n(r)$, $\nabla n(r)$, $\tau(r)$ and $\nabla^2 n(r)$ are referred to the electron density, the gradient of the density, the kinetic energy density and the second derivative of the density.

2.1. The Local Density Approximation (LDA)

The most widely used form of E_{xc} is the so-called Local Density Approximation (LDA). That is, the exchange and correlation energy of homogeneous electron gas. In this approximation, the exchange-correlation energy at each point of the real space, E_{xc} , is assumed to be equal to that energy of a uniform electron gas with the same electronic density.

$$E_{xc}^{LDA}[n] = \int \epsilon_{xc}^{hom}[n]n(r)dr \quad (3.1)$$

Where $\epsilon_{xc}^{hom}[n]$ is the exchange-correlation energy per electron in a homogeneous electron gas of density $n(r)$. The $\epsilon_{xc}(n)$ is known exactly in the high-density limit, and can be accurately computed at any density. This equation is, by construction, exact for the homogeneous electron gas and we can expect it to work well for systems where the density has small spatial variations, or where the electron-electron interaction is well-screened.

From the non-interacting homogeneous electron gas, the exchange energy is explicitly known as an analytic term:

$$\epsilon_x^{LDA}[n] = \frac{-3}{4\pi} (3\pi^2 n)^{1/3} \quad (3.2)$$

The explicit expression of the correlation part $\epsilon_x^{LDA}[n]$ is achieved from accurate quantum Monte-Carlo simulations of the homogeneous electron gas at selected densities [105]. This formalism can be naturally generalized to spin-polarized system, known as Local Spin Density Approximation (LSDA). For a partially polarized homogeneous electron gas, the exchange correlation energy per electron depends on both the total mean electron density $n = n_{\uparrow} + n_{\downarrow}$ and the spin polarization $\sigma = n_{\uparrow} - n_{\downarrow}$. By interpolating between the unpolarized and the fully polarized case, we obtain the exchange-correlation energy for LSDA:

$$E_{xc}^{LSDA}[n, \sigma] = \int \epsilon_{xc}^{hom}(n(r), \sigma(r))n(r)dr \quad (3.3)$$

Despite its simplicity, the LDA works quite well in many systems, no matter they are quasi homogeneous or not. It is because LDA fulfils the sum rule on exchange-correlation hole, which gives rise to error compensation on computing the exchange-correlation energy. Typically, LDA overestimates exchange energy E_x and underestimates correlation energy E_c . LDA has many drawback, we list a few of them:

- The LDA tends to overestimate cohesive energies, resulting in over binding.
- The electrons are not localised enough in space.
- The long-range effects (e.g. image effects, van der Waals bonds) are completely missing, due to the extremely local nature of the LDA. Therefore, the potential that an electron feels when approaching an atom or a surface is badly described by the LDA. The hydrogen bond is also poorly reproduced in many chemical reactions.

2.2. The Generalized Gradient Approximation (GGA)

As expected, any real electron system is non-homogeneous with electron density varying in space. Reasonably, the gradients of the density should be considered into the approximations to describe such variations. However, it was realized that there is no need to include the gradient expansion order by order. Instead, the density and its gradient, is good enough to construct the new functionals, which are currently known as generalized gradient approximations (GGA) [106]:

$$E_{XC}^{GGA}[n, \sigma] = E_{XC}^{LSDA}[n, \sigma] + \int \epsilon_{xc}^{GGA}(n(r), \sigma(r)) n(r) dr \quad (3.4)$$

In many cases, GGA can largely improve LDA results with accuracy, e.g. GGA describes XC effects in atoms and molecules much better than LDA. It also has its own drawbacks:

- GGA often overcorrects LDA. Bond lengths are estimated 0-2% larger than experimental values and cohesive energy is resulted in 10-20% smaller.
- GGA cannot describe long-range effects, such as Van der Waals, which is the same as LDA.
- GGA underestimates the band gap energies.

2.3. DFT+U

The standard approximations in DFT calculations normally give poor answers on the “strongly correlated” systems, in which the potential energy dominates over the kinetic energy and often involve transition element or rare earth atoms. A common way of modifying DFT calculations is the addition of an on-site Coulomb repulsion (“Hubbard U”) as done in the “DFT + U” scheme [107,108]. The on-site Coulomb interactions are particularly strong for localized d and f electrons, but can be also important for p localized orbitals. The strength of the on-site interactions are usually described by parameters U (on site Coulomb) and J (on site

exchange), and practically, by an effective $U_{\text{eff}} = U - J$ parameter, while the rest of valence electrons are treated at the level of “standard” approximate DFT functionals. Within DFT+U the total energy of a system can be written as follows:

$$E_{\text{DFT}+U} = E_{\text{DFT}} + \sum_{\alpha} \frac{U_{\text{eff}}}{2} \text{Tr}(\rho^{\alpha} - \rho^{\alpha} \rho^{\alpha}) \quad (3.5)$$

Where ρ^{α} is the atomic orbital occupation matrix. The DFT+U can be understood as adding a penalty functional to the DFT total energy expression that forces the on-site occupancy matrix in the direction to either fully occupied or fully unoccupied levels.

2.4. The modified Becke –Johnson

The modified Becke-Johnson potential by Tran and Blaha (TB-mBJ, mBJ) was developed specifically to give correct predictions of the band gap [109]. It formally belongs to the meta-GGA family of functionals, i.e., it uses τ in addition to ρ . It is modeled after the Becke-Johnson (BJ) potential [110]

$$V_X^{\text{BJ}}(r) = V_X^{\text{Slater}}(r) + \frac{1}{\pi} \sqrt{\frac{5}{12}} \sqrt{\frac{2\tau(r)}{\rho(r)}} \quad (3.6)$$

The BJ potential is trying to mimic the optimized effective potential, i.e., a local potential whose corresponding orbitals minimize the total energy of the Slater determinant of those orbitals [111,112]. The V_X^{Slater} is the Slater potential which was proposed to model the Coulomb potential created by an exchange hole [91]. The TB-mBJ potential is a simple modification of the BJ potential

$$V_X^{\text{TB-mBJ}}(r) = cV_X^{\text{BR}}(r) + (3c - 2) \frac{1}{\pi} \sqrt{\frac{5}{6}} \sqrt{\frac{\tau(r)}{\rho(r)}} \quad (3.7)$$

where the additional parameter c is introduced and the exact Slater potential V_X^{Slater} replaced by the approximate Becke-Rousel exchange potential [113] which was shown to produce nearly identical results for atoms [110]. The Becke-Rousel exchange potential

$$V_X^{\text{BR}}(r) = -\frac{1}{b(r)} \left(1 - e^{-x(r)} - \frac{1}{2} x(r) e^{-x(r)} \right) \quad (3.8)$$

is an approximation to the Slater potential using only local and semi-local density information (the density, gradient and laplacian of the density and the kinetic energy density) [113] where b is defined as

$$b^3 = \frac{x^3 e^{-x}}{8\pi\rho} \quad (3.9)$$

and x satisfies the following nonlinear equation

$$\frac{x e^{-2x/3}}{x-2} = 4\pi^{\frac{2}{3}} \frac{\rho^{5/3}}{\nabla^2 \rho - 2D} \quad (3.10)$$

Where

$$D = \tau - \frac{1}{4} \frac{(\nabla \rho)^2}{\rho} \quad (3.11)$$

The parameter c from the TB-mBJ potential is defined as follows

$$C = A + B \left(\frac{1}{V_{cell}} \int_{cell} \frac{\nabla \rho(r')}{\rho(r')} d^3 r' \right)^e \quad (3.12)$$

where A , B , and e are empirical parameters obtained by minimization of the mean absolute relative error for the band gap of a fixed list of solids. There are three sets of parameters available. The first one comes from the original manuscript by Tran and Blaha [109] with values of $A = -0.012$, $B = 1.023$ and $e = 0.5$ (TB-mBJ orig.), however it was later argued that the TB-mBJ band gaps obtained with those values are still somewhat underestimated. Koller et al. [114] devised a new parameterization, using an improved (more balanced) set of materials for the parameters optimization and ended with improved parameter values (TB-mBJ imp.) $A = 0.488$, $B = 0.5$ and $e = 1$. They also used a subset of the materials with band gap below 7 eV to construct a third parameterization optimized specifically for small band gapsemiconductors, with values $A = 0.267$, $B = 0.656$ and $e = 1$ (TB-mBJ semi.).

An important note on the TB-mBJ is that it is in fact only an exchange potential, not a functional (i.e., there is no energy functional E_x such that $V_x^{TB-mBJ} = \frac{\delta E_x}{\delta \rho}$), and it uses the LDA for correlation potential and both exchange and correlation energy. Due to this reasons the energy calculated with the TB-mBJ does not have any physical meaning, since it is just a LDA energy on top of the charge density calculated with TB-mBJ exchange and LDA correlation potential and hence the TB-mBJ is not suitable for methods making use of the total energy (such as the structural relaxation based on the minimization of total energy).

The TB-mBJ can give KS band gaps comparable to much more computationally expansive quasi-particle band gaps from GW approaches and in excellent agreement with experimental photoemission data, it was argued that for some materials the good band gap comes at the cost of worse overall electron structure with respect to the GGA [115]. While

majority of the report are optimistic when it comes to the ability of TB-mBJ to predict correct band gaps, and some reports find the TB-mBJ satisfactory even for the calculation of optical properties [116, 117,118] some other works suggest that TB-mBJ provides worse results for optics. When compared to the more advanced GW-based approaches, Kresse et al. [119] found that while the TB-mBJ yields similar one-electron energies as the self-consistent GW approach, the bands are too narrow, leading to a "compressed" optical spectrum with too small excitation energies at higher energies.

3. Full Potential Linearized / Augmented Plane Wave Plus Local Orbitals - FP-L/APW+LO

3.1.The augmented plane wave method (APW)

In 1937 Slater [90,120] introduced augmented plane waves (APW) as basis functions for solving the one-electron equations, which now correspond to the Kohn–Sham equations within DFT. In the APW scheme the unit cell is partitioned into two types of regions: (i) spheres centered around all constituent atomic sites r_α with a radius R_α , and (ii) the remaining interstitial region, abbreviated as (I) (see **Fig. 3.1**). In this case the wave functions are expanded into PWs each of which is augmented by atomic solutions in the form of partial waves, i.e. a radial function times spherical harmonics. In particular, radial solutions of Schrödinger's equation are employed inside non overlapping atom centered spheres and plane waves in the remaining interstitial zone.

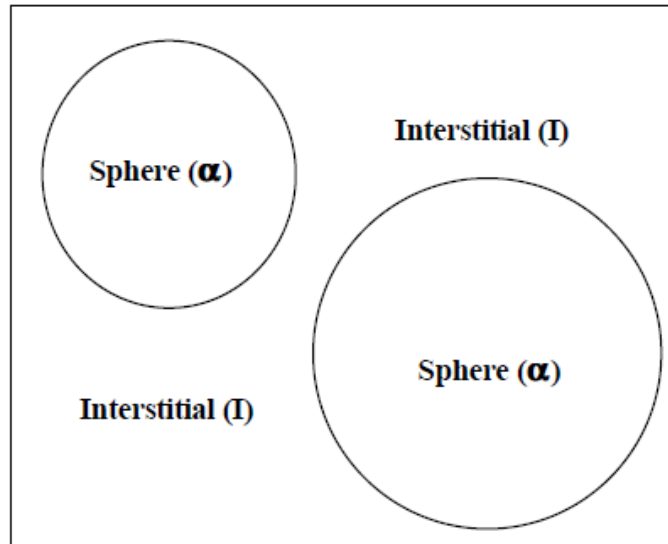


Fig. 3.2. Adaptation of the basis set by dividing the unit cell into atomic spheres and interstitial regions.

The introduction of such a basis set is due to the fact that close to the nuclei the potential

and wave functions are very similar to those in an atom, while between the atoms then are smoother. The APWs consist of:

$$\varphi(\vec{r}) = \begin{cases} \sum_{lm} a_{lm}^\alpha u_{lm}^\alpha(r, \varepsilon) Y_{lm}(\vec{r}), & r < R_\alpha \\ \Omega^{-1/2} \sum_G C_G \exp(i(\vec{k} + \vec{G})\vec{r}), & r \in I \end{cases} \quad (3.13)$$

In the above relations φ is the wave function, Ω is the unit cell volume, $\vec{r}$ is the position inside sphere α with the polar coordinates $\vec{r}$, $\vec{k}$ is a wave vector in the irreducible Brillouin zone (IBZ) and u_{lm} is the numerical solution to the radial Schrödinger equation at the energy ε . The KS orbitals $\Psi_i(\vec{r})$ are expressed as a linear combination of APWs $\varphi(\vec{r})$.

Inside the MT sphere a KS orbital can only be accurately described if ε in the APW basis functions is equal to the eigen-energy, ε_i . Therefore, a different energy-dependent set of APW basis functions must be found for each eigen-energy. C_G and a_{lm} are expansion coefficients; E_l is a parameter (set equal to the band energy) and V the spherical component of the potential in the sphere.

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l \right] r u_{lm}(r) = 0 \quad (3.14)$$

The use of these functions has been motivated by Slater by noting that plane waves are the solutions of the Schrödinger's equation in a constant potential and radial functions are solutions in a spherical potential. This approximation to the potential is called "muffintin" (MT).

Since the continuity on the spheres boundaries needs to be guaranteed on the dual representation defined in **Eq. (3.13)**, constraint must be imposed. In the APW method this is done by defining the u_{lm} in terms of C_G in the spherical harmonic expansion of the plane waves.

$$u_{lm} = \frac{4\pi i^l}{\Omega^{\frac{1}{2}} u_l(r)} \sum_G C_G J_l(|k + g|) Y_{lm}^*(\vec{k} + \vec{G}) \quad (3.15)$$

The coefficient of each lm is matched at the sphere boundary and the origin is taken at the centre of the sphere (R is the sphere radius). The u_{lm} are determined by the plane wave coefficients (C_G) and the energy parameters E_l , which are the variational coefficients in APW method. The functions labeled G are the augmented plane waves (APWs) and consist of single plane waves in the interstitial zone, which are matched to the radial functions in the spheres.

A more flexible and accurate band structure calculational scheme is the LAPW method where the basis functions and their derivatives are made continuous by matching to a radial function at fixed E_l plus its derivative with respect to E_l .

3.2. The linearized augmented plane wave method (LAPW)

Several improvements to solve the energy dependence of the basis set were tried but the first really successful one was the linearization scheme introduced by Andersen [121] leading to the linearized augmented plane wave method. In LAPW the energy dependence of each radial wave function inside the atomic sphere is linearized by taking a linear combination of a solution u at a fixed linearization energy and its energy derivative $\dot{u}$ computed at the same energy.

$$\varphi(\vec{r}) = \begin{cases} \sum_{lm} [a_{lm}^\alpha u_{lm}^\alpha(r) + b_{lm}^\alpha \dot{u}(r)] Y_{lm}(\vec{r}), & r < R_\alpha \\ \Omega^{-1/2} \sum_G C_G \exp(i(\vec{k} + \vec{G})\vec{r}), & r \in I \end{cases} \quad (3.16)$$

where the b_{lm} are coefficients for the energy derivative analogous to the a_{lm} . The basis functions inside the spheres are linear combinations of a radial functions $u_l(r)Y_{lm}(r)$ and their energy derivatives ($u_l(r)Y_{lm}(r)$ and $\dot{u}_l(r)Y_{lm}(r)$ are the augmenting functions). The u_l are defined as in the APW method (Eq. 3.14) and the energy derivative, $\dot{u}_l(r)Y_{lm}(r)$ satisfies the following equation:

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l \right] r \dot{u}_{lm}(r) = r u_{lm}(r) \quad (3.17)$$

The LAPWs provide a sufficiently flexible basis to properly describe eigen functions with eigen energies near the linearization energy, which can be kept fixed. This scheme allows us to obtain all eigen energies with a single diagonalization in contrast to APW.

The LAPWs are plane waves in the interstitial zone of the unit cell which match the numerical radial functions inside the spheres with the requirement that the basis functions and their derivatives are continuous at the boundary. In this method no shape approximations are made and consequently such a procedure is often called "full-potential LAPW" (FP-LAPW). The much older muffin-tin approximation corresponds to retain only the $l = 0$ and $m = 0$ component in Eq. (3.17). A spherical average inside the spheres and the volume average in the interstitial region are thus taken.

Inside atomic sphere a linear combination of radial functions times spherical harmonics, $Y_{lm}(r)$, is used. The linear combination of $u_l(r)$ and $\dot{u}_l(r)$ constitutes the so called

"linearization" of the radial function. $u_l(r)$ and $\dot{u}_l(r)$ are obtained by numerical integration of the radial Schrödinger equation on a radial mesh inside the sphere.

The LAPWs have more variational freedom inside the spheres than APWs. This greater flexibility is due to the presence of two radial functions instead of one; non-spherical potentials inside spheres can be now treated with no difficulty. There is however, a price to be paid for the additional flexibility of the LAPWs: the basis functions must have continuous derivatives and consequently higher plane wave cut-offs are required to achieve a given level of convergence. Further, the asymptote problem ($u_{lm}(R)$ appears in the denominator of expression (Eq 3.15) and if zero leads to a decoupling between plane waves and radial functions. In the vicinity of the asymptote the secular determinant is strongly varying) found in the APW method is now overcome by the presence of the non-zero $u_{lm}(R)$ value.

The solutions of the KS equations are expanded in this combined basis according to the linear variation method:

$$\Psi_k = \sum_n c_n \varphi_{kn} \quad (3.18)$$

and the coefficients c_n are determined by the Rayleigh-Ritz variational principle. The convergence of this basis set is controlled by a cut-off parameter $R_{mt} \cdot K_{max}$, where R_{mt} is the smallest atomic sphere radius in the unit cell and K_{max} is the magnitude of the largest K_n vector in (eq. 3.18)

3.3. The augmented plane wave plus local orbitals method (APW+lo)

An alternative approach was proposed by Sjöstedt et al. [122], namely the APW+lo (local orbitals) method. Here the augmentation is similar to the original APW scheme but each radial wave function is computed at fixed linearization energy to avoid the non-linear eigenvalue problem that complicated the APW method. Thus only the condition of continuity can be required and the basis functions may contain a kink at the sphere boundary.

$$\varphi(\vec{r}) = \begin{cases} [a_{lm}^{\alpha, lo} u_{lm}^{\alpha}(r) + b_{lm}^{\alpha, lo} \dot{u}(r)] Y_{lm}(\vec{r}), & r < R_{\alpha} \\ 0, & r \in I \end{cases} \quad (3.19)$$

The local orbitals are evaluated at the same fixed energy as the corresponding APWs. The two coefficients are determined by the normalization and the condition that the local orbital has zero value at the sphere boundary. In this version, $\dot{u}$ is independent of the PWs, since it is only included for a few local orbitals and not associated with every plane wave.

Recently it was demonstrated that this new scheme can reach the same accuracy as LAPW but converges faster in terms of number of PWs [123]. The highest efficiency was found for a mixed basis set in which the “physically important” l -quantum numbers are treated by APW+lo but the higher l by LAPW. It was shown in [123] that quantities such as the total energy, forces converge significantly faster with respect to the number of basis functions than with the pure LAPW procedure but reach the same values. In LAPW the force changes sign and thus the atom would move in the wrong direction for a too small basis set, whereas in the APW+lo scheme the force converges smoothly and much faster. For large systems the matrix size N can be about halved and thus the computational cost can be an order of magnitude less, since the diagonalization scales with N^3 .

The new scheme combines the best features of all APW-based methods available. The LAPW converges somewhat more slowly than the APW method as has already been pointed out by Koelling and Arbman[124], since the constraint of having differentiable basis functions makes LAPWs less optimally suited to describe the orbitals inside the sphere.

This justifies going back to APW but the energy-independent basis introduced in LAPW is crucial for avoiding the nonlinear eigenvalue problem and thus is kept, too. The local orbitals provide the necessary flexibility [125].

4. The full potential calculation

The muffin tin approximation was frequently used in the 1970s and works reasonable well in highly coordinated (metallic) systems such as face centered cubic (fcc) metals. However, for covalently bonded solids, open or layered structures, Muffin tin approximation is a poor approximation and leads to serious discrepancies with experiment.

In all these cases a treatment without any shape approximation is essential. Both, the potential and charge density, are expanded into lattice harmonics (inside each atomic sphere) and as a Fourier series (in the interstitial region).

$$V(\vec{r}) = \begin{cases} \sum_{lm} V_{lm} Y_{lm}(\vec{r}) & \text{inside sphere,} \\ \sum_k V \exp(i\vec{K}\vec{r}) & \text{outside sphere.} \end{cases} \quad (3.20)$$

Thus their form is completely general so that such a scheme is termed full-potential calculation. The choice of sphere radii is not very critical in full potential calculations in contrast to muffin tin approximation, in which one would obtain different radii as optimum choice depending on whether one looks at the potential (maximum between two adjacent atoms) or the charge density (minimum between two adjacent atoms). Therefore in muffin tin

approximation one must make a compromise but in full-potential calculations one can efficiently handle this problem.

5. The Wien2K code

The WIEN2k package is a computer program written in Fortran that performs quantum mechanical calculations on periodic solids. It was originally developed by Peter Blaha and Karl Heinz Schwarz from the Institute of Materials Chemistry of the Vienna University of Technology. The first public release of the code was done in 1990. Then, the next releases were WIEN93, WIEN97, and WIEN2k. It basically uses the full potential (linearized) augmented plane-wave and local-orbitals [FP-(L) APW+lo] basis set to solve the Kohn–Sham equations of density functional theory.

This package allows to study most of the electronic structure properties of a crystalline solid: electron density, density of states (DOS), various types of spectra, magnetism (ferromagnetic, antiferromagnetic and non-magnetic configurations), non-collinear magnetism, band structure, Fermi surface, in different exchange-correlation potentials including the local density approximation (LDA), various generalized gradient approximation (GGA) (Perdew-Wang [126] or Perdew-Burke-Ernzerh of [127], Wu-Cohen [128]), meta-GGA [129,130] and the LDA+U method [108] in various flavors for the double counting terms, as well as the so called Tran-Blaha modified Becke-Johnson potential [109], and hybrid functional [131]. The structure of the Wien2k program with its main calculation steps are shown in the **Fig. 3.3.** below.

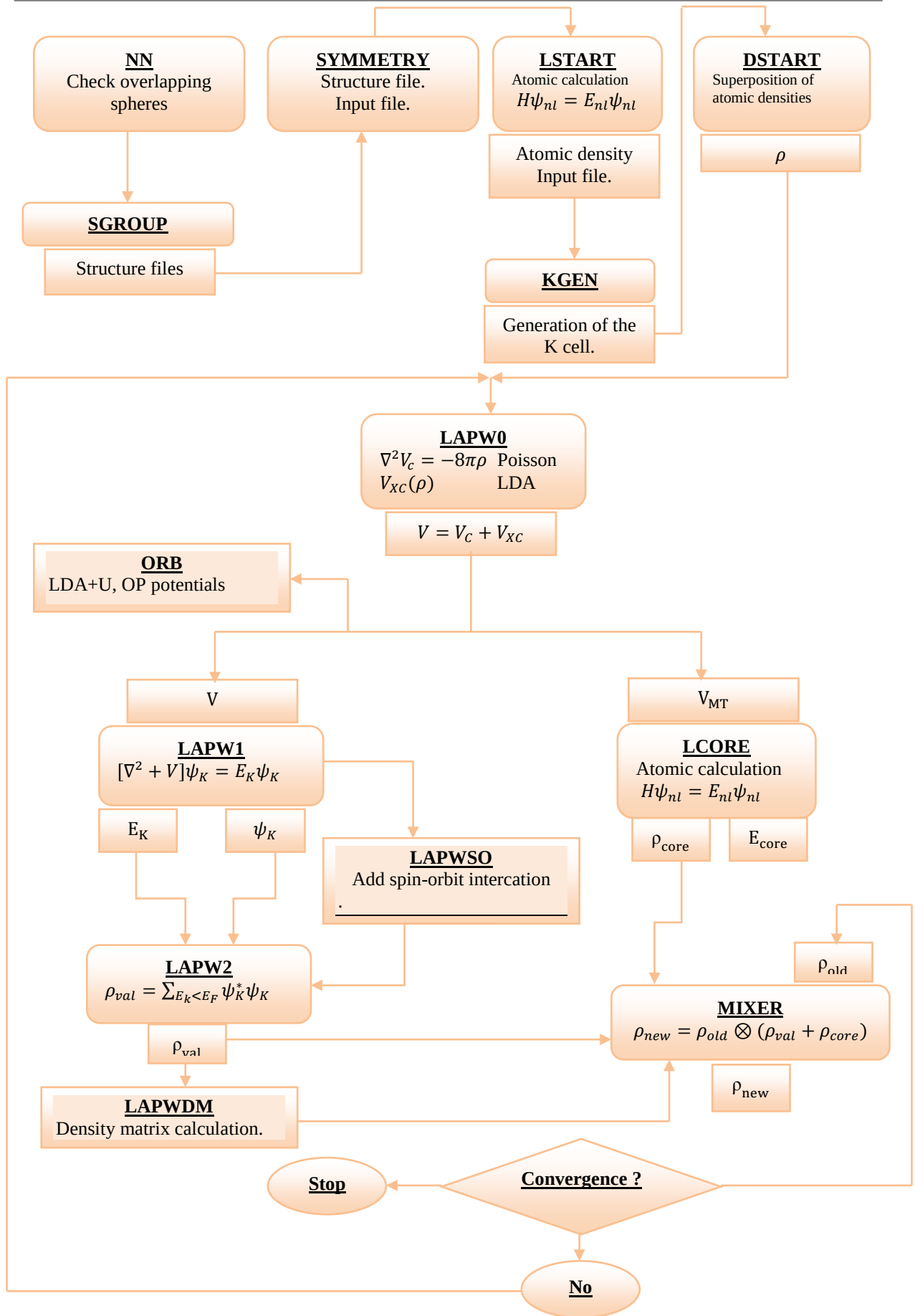


Fig. 3.3. The structure of the Wien2k program with its main calculation steps

Part II

Investigation of monodoping and codoping effect on the electronic, optical and photocatalytic properties of strontium titanate for visible-light driven hydrogen production from water.

Chapter 4

DFT study of Mn, S, Se, and Te monodoped SrTiO₃ for visible light-driven photocatalytic hydrogen production

Abstract

Band-gap narrowing is an interesting step for harvesting solar light with SrTiO₃ for efficient photocatalytic hydrogen production. The goal of this chapter is to investigate the effect of manganese and chalcogenides (sulfur, selenium and tellurium) atoms doping on the stability, electronic, optical, and photocatalytic properties of strontium titanate (SrTiO₃) bulk through DFT calculations. Defect formation energies, band structures, density of states, electronic density distributions, and optical absorption, for undoped, Mn doped, S doped, Se doped and Te doped SrTiO₃, are thoroughly studied using DFT in its GGA approximation. Band alignments are calculated with the purpose of ensuring the thermodynamic validity of the studied compounds for water splitting reaction. The abilities of systems, towards the photocatalytic hydrogen production from water splitting are discussed in the basis of obtained results.

1. Introduction

Since the pioneering work, of Honda and Fujishima [12], significant progress has been marked in the field of photocatalytic water splitting for solar hydrogen production, and various photocatalytic water-splitting systems have been developed. For example, SrTiO₃ crystal has received a great attention, due to its chemical stability, low cost and safety. This compound although does not respond to the visible light due to its wide band gap, many studies indicate its ability to work in the visible field; this prompted researchers to search the adequate ways to shifting its absorption into the visible light region, and by consequent boosting its photocatalytic performance. Among the used methods, doping has been considered as typical, due to its simplicity, effectiveness and low cost. In fact, introducing foreign elements into the host SrTiO₃ can alter its electronic band structures to lower energy gaps through three distinct ways: (i) Lowering the conduction band (CB) level through mixing Ti 3d states and states of dopants. (ii) Raising the valence band (VB) level through O 2p states and dopants states mixing, and/or (iii) inducing new energy levels of the dopants between the VB and CB. For example, Zhou et al.[132] investigated the effect of Mn doping on the electronic structure and visible light absorption of SrTiO₃. They found a conduction band edge lowering of about 0.4 eV owing to the hybridization between Mn 3d and Ti 3d states; this leads to an improvement in the visible light absorption ability for the doped system compared to the pure one. Besides, an experimental study shows that S doping into SrTiO₃ shifts its absorption spectrum into the visible light region and increases its photocatalytic efficiency [133]. The reason of this improvement has been revealed theoretically by mean of density functional theory, as it indicated that the 3p states of sulfur mix well with the 2p states of oxygen and rise the top of valence band to higher energy levels, which leads to band gap decreasing [134]. Besides, the investigation of Ag⁺ ions doped SrTiO₃ indicated that inside the band gap, appear some isolated miniband formed from Ag 4d states, resulting in the visible light absorption [135]. Finally, The study of C, N, Mo and W doping effects on the SrTiO₃ reveals an improvement in the visible light response of material due to the apparition of mid-gap states; however, its photocatalytic efficiency was low [136].

2. Calculation methods

Our calculations have been carried out by Wien2K software package, where the physical properties are obtained based on density functional theory. It adopts the full-potential (linearized) augmented plane-wave ((L)APW) plus local orbitals (lo) method [137]. The

calculations of structures optimization, stability, electronic properties and optical properties were carried out using GGA (Generalized Gradient Approximations) with PBE (Perdew, Burke and Ernzerhof) parametrization.

The calculation method that we adopted is based on partitioning the unit-cell into two regions (**Fig.4.1 (a)**) where different basis sets are used. The interstitial region, where a plane wave expansion is used:

$$\varphi_{k_n} = \frac{1}{\sqrt{\omega}} e^{ik_n \cdot r} \quad (4.1)$$

Where $k_n = k + K_n$; k is the wave vector in the first Brillouin zone and K_n are the reciprocal lattice vectors.

And the region of atomic spheres where a linear combination of radial functions times spherical Harmonics $Y_{lm}(r)$ is adopted:

$$\varphi_{k_n} = \sum_{lm} [A_{lm,k_n} u_l(r, E_l) + B_{lm,k_n} \dot{u}_l(r, E_l)] Y_{lm}(\hat{r}) \quad (4.2)$$

where $u_l(r, E_l)$ expressess the (at the origin) regular solution of the radial Schrödinger equation for energy E_l and the spherical part of the potential in the considered sphere; $\dot{u}_l(r, E_l)$ constitute the energy derivative of u_l evaluated at the same energy E_l . The coefficients A_{lm} and B_{lm} are functions of k_n .

The cutoff parameter which controlled the convergence of this basis set is chose to be $R_{mt}K_{max} = 7$, Where R_{mt} is radius of smallest atomic sphere in the unit cell and K_{max} is the magnitude of the largest K vector in equation. The radius of muffin-tin spheres (RMT) values used for Sr, Ti, O, S, Se, Te, and Mn atoms were respectively, 1.70 a.u., 1.85 a.u., 1.63 a.u., 1.58a.u., 1.80 a.u., 1.85 a.u. and 1.89 a.u.

The calculations were carried out with an energy convergence criterion of 10^{-4} Ry, and by a [7x7 x7] grid, corresponding to 800 k-points in the irreducible Brillouin zone.

In the calculations, 2x2x2 supercells of pure cubic SrTiO₃ are constructed; In order to study the properties of strontium titanate and making attempts to improve its photocatalytic properties, we introduced one foreign atom (Mn, S, Se or Te) into the host compound modelled by a 2x2x2 suppercell of cubic SrTiO₃. In our calculations, we take into consideration that Mn prefers to replace Ti than Sr in SrTiO₃ [132;138], and takes the form of Mn⁴⁺ in Ti site [139], and that introducing S, Se and Te in O sites helps to maintain charge balance in the studied systems. The calculations were repeated with changing the positions of foreign atoms until the most stable structure was obtained (**See Fig. 4.1. (b) to (f)**).

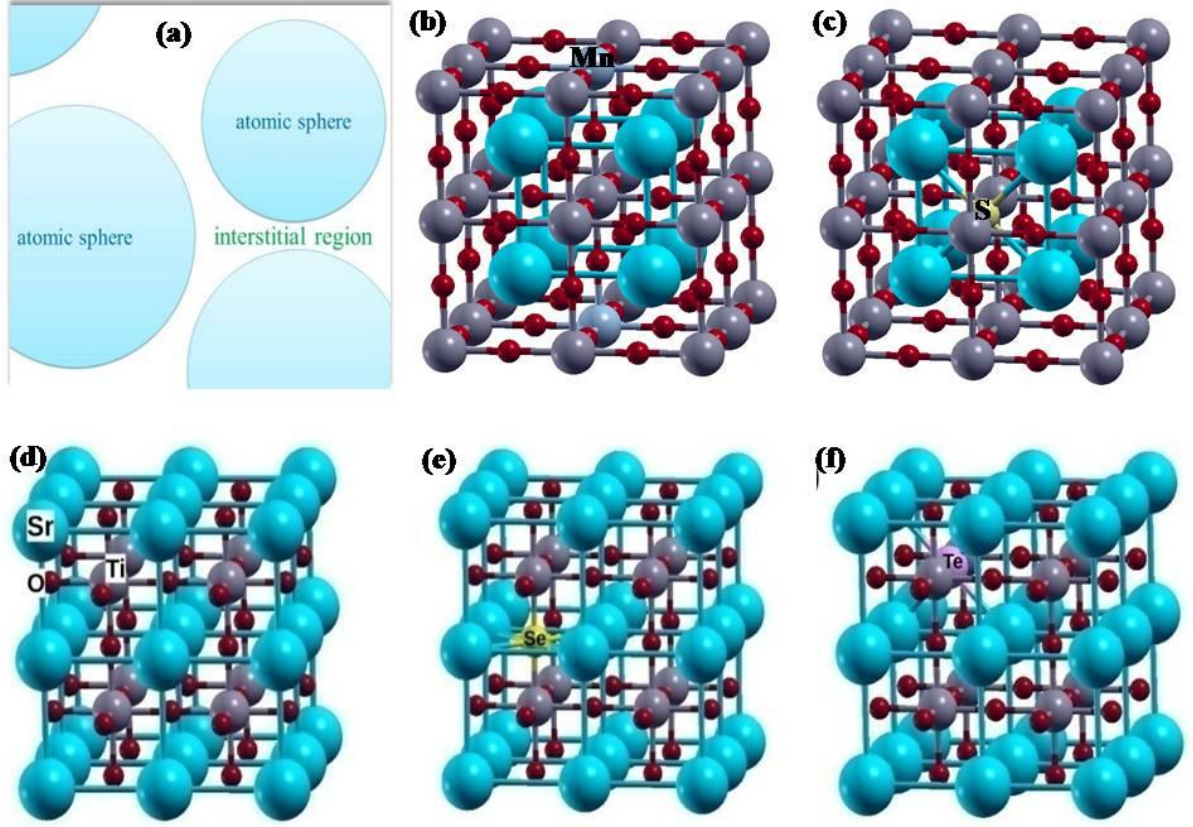


Fig. 4.1. (a) Partitioning of the unit cell adopted in the calculations method; the optimized 2 x 2 x 2 supercell of: (b) Mn doped, (c) S doped, (d) pure, (e) Se doped and (f) Te doped SrTiO₃, respectively.

For optical properties, the calculations adopt the random-phase approximation (RPA), with a Drude-like shape for the intra-band contribution [140]. These properties are obtained through solving the following complex dielectric function:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad (4.3)$$

In which $\varepsilon_1(\omega)$ expresses the real part calculated following the Kramers-kronig transformation:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} p \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (4.4)$$

And $\varepsilon_2(\omega)$ designates the imaginary part calculated using summation over the empty states

$$\varepsilon_2(\omega) = \left(\frac{4\pi e^2}{\omega^2 m^2} \right) \sum_{i,j} \int \langle i | M | j \rangle^2 f_i (1 - f_j) * \delta(E_f - E_i - \omega) d^3k \quad (4.5)$$

p refers to the principal value of the integral, e indicates the elementary charge, m is standing to the electron's mass, M express the dipole matrix element, i and j designate respectively, the

initial and final states, f_i is the Fermi-Dirac Distribution Function for the i -th state and E_i constitute the energy of an electron in the i -th state with a wave number k .

Knowing $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$, the absorption coefficient $\alpha(\omega)$, can be obtained by the formula [141]:

$$\alpha(\omega) = \sqrt{2}\omega \sqrt{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)} \quad (4.6)$$

3. Structural parameters and stability

At room temperature, strontium titanate, SrTiO₃, crystallizes in a cubic system, with space group $Pm\bar{3}m$ [142]. As presented in **Fig. 4.2**, the Ti cation is 6-fold coordinated with six oxygen anions, forming tilt octahedra. The Sr cations are located in the central position among these octahedral. Besides, **Fig. 4.3. (a), (b) and (c)** present respectively, the unit cell with Sr in the origin, the unit cell with Ti in the origin and the energy vs. volume curve for cubic SrTiO₃. The optimized lattice constant is $a = 3.941 \text{ \AA}$, in agreement with experimental data ($a = 3.905 \text{ \AA}$) [73], and previous GGA calculations [143,144]. The calculated Ti-O and Sr-O bond lengths are respectively, $2.065 \text{ \AA}$ and $2.920 \text{ \AA}$.

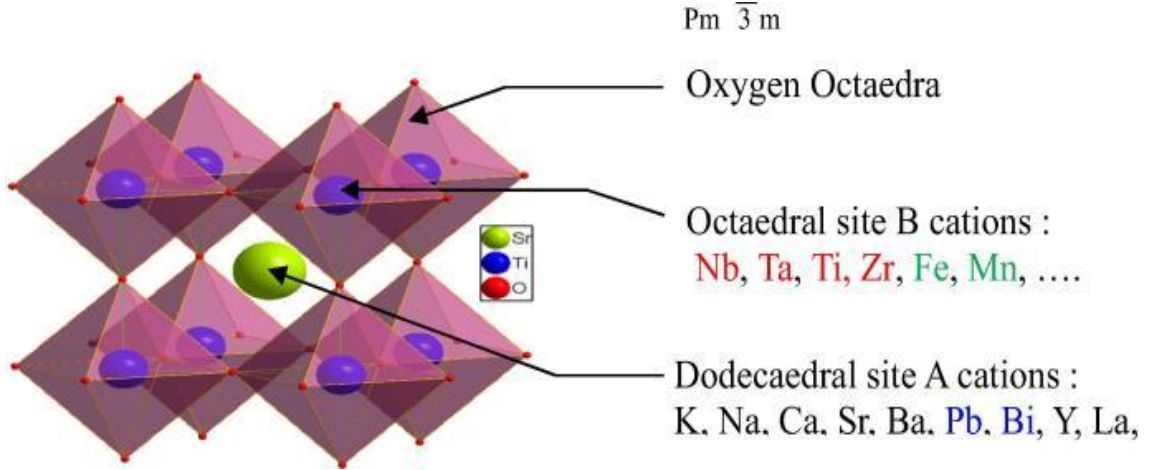


Fig. 4.2. Octahedral and dodecahedral environment in cubic perovskite SrTiO₃ [145]

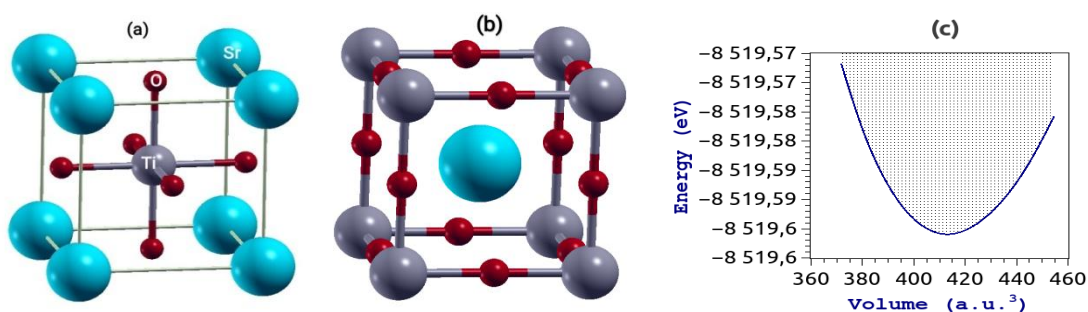


Fig. 4.3. The optimized unit cell ((a) Sr in the origin (b) Ti in the origin) and the volume vs. energy plot (c) for cubic SrTiO₃.

The introduction of doping elements (Mn, S, Se and Te) into the pure SrTiO₃ leads to some variations in the bond lengths as shown in **table 4.1.**, which can be explained by the volume and electronegativity differences between introduced and replaced atoms and the variation of interatomic interactions induced by atoms changing.

Table 4.1.

Bond lengths in pure and monodoped SrTiO₃ structures (in unit of Å)

Systems Bonds	Pure SrTiO ₃	Mn doped SrTiO ₃	S doped SrTiO ₃	Se doped SrTiO ₃	Te doped SrTiO ₃
Ti-O	1.971	1.964	1.995	2.004	2.026
Mn-O	-	1.964	-	-	-
Ti-S	-	-	1.995	-	-
Ti-Se	-	-	-	2.004	-
Ti-Te	-	-	-	-	2.026
Sr-O	2.787	2.778	2.821	2.834	2.865
Sr-S	-	-	2.821	-	-
Sr-Se	-	-	-	2.834	-
Sr-Te	-	-	-	-	2.865

To determine the proper growth conditions of created Mn doped, S doped, Se doped and Te doped SrTiO₃ compounds we calculated their defect formation energies respectively by the following formulas:

$$E_f(\text{Mn doped SrTiO}_3) = E_{\text{Mn doped SrTiO}_3} - E_{\text{undoped SrTiO}_3} + \mu_{\text{Ti}} - \mu_{\text{Mn}} \quad (4.7a)$$

$$E_f(\text{S doped SrTiO}_3) = E_{\text{S doped SrTiO}_3} - E_{\text{undoped SrTiO}_3} + \mu_{\text{O}} - \mu_{\text{S}} \quad (4.7b)$$

$$E_f(\text{Se doped SrTiO}_3) = E_{\text{Se doped SrTiO}_3} - E_{\text{undoped SrTiO}_3} + \mu_{\text{O}} - \mu_{\text{Se}} \quad (4.7c)$$

$$E_f(\text{Te doped SrTiO}_3) = E_{\text{Te doped SrTiO}_3} - E_{\text{undoped SrTiO}_3} + \mu_{\text{O}} - \mu_{\text{Te}} \quad (4.7d)$$

Where, $E_{\text{Mn doped SrTiO}_3}$, $E_{\text{S doped SrTiO}_3}$, $E_{\text{Se doped SrTiO}_3}$, $E_{\text{Te doped SrTiO}_3}$ and $E_{\text{undoped SrTiO}_3}$ represent the calculated total energy for respectively, Mn doped SrTiO₃, S doped SrTiO₃, Se doped SrTiO₃, Te doped SrTiO₃ and undoped SrTiO₃ supercells. μ_{Ti} , μ_{Mn} , μ_{O} , μ_{S} , μ_{Se} and μ_{Te} indicate the chemical potential of respectively, titanium, manganese, oxygen, sulfur, selenium and tellurium calculated from their most stable solids. μ_{Ti} from bulk alpha-titanium [146], μ_{Mn} from alpha manganese [147], μ_{S} from sulfur-6 [148], μ_{Se} from bulk trigonal selenium [149], μ_{Te} from rhombohedral form of tellurium [150]. μ_{O} is equal to half the energy of an oxygen molecule confined inside a cubical box of 15x15x15 Å³ (**Fig. 4.4.**).

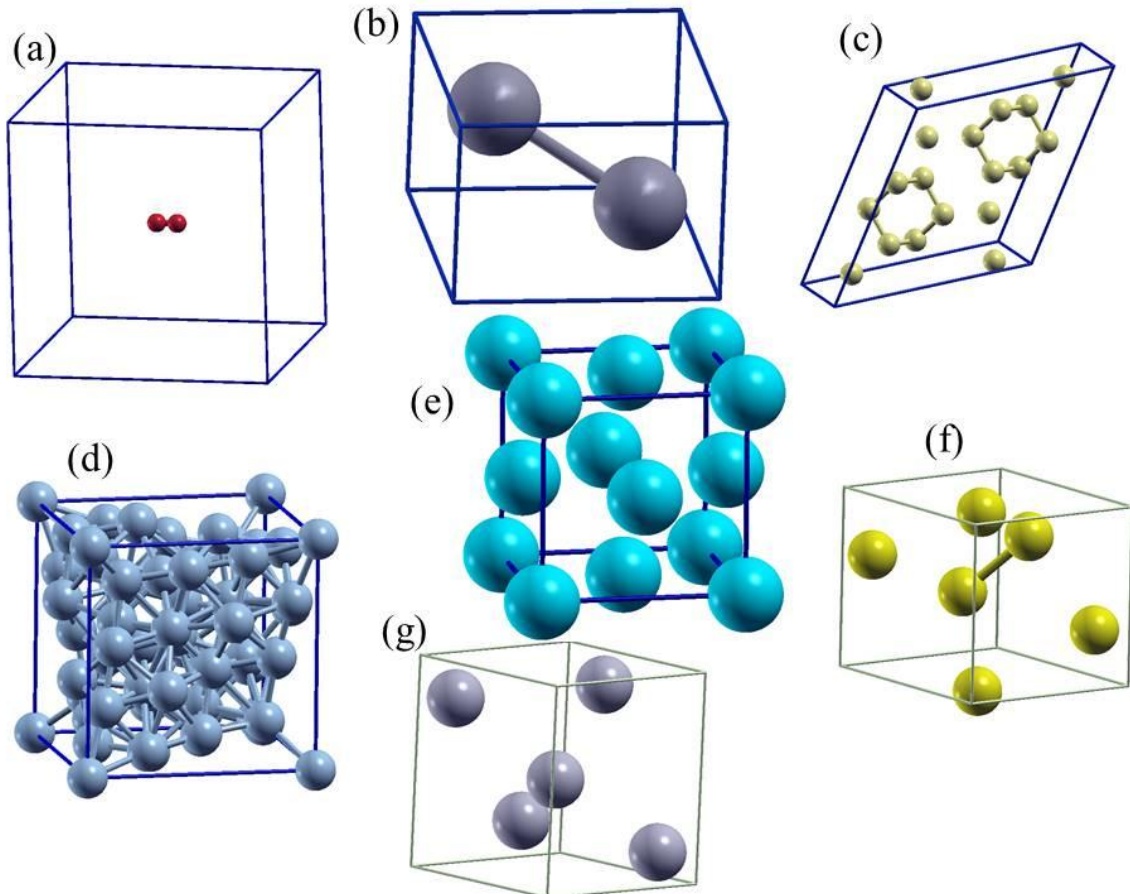


Fig. 4.4. The utilized structures for chemical potentials calculations **(a)** molecule of O₂ confined at the center of a 15x15x15 Å³ cubic box **(b)** maille of alpha-titanium **(c)** maille of sulfur-6 **(d)** maille of alpha manganese **(e)** maille ccp, structure of strontium **(f)** maille of Trigonal selenium **(g)** maille of rhombohedral form of tellurium.

It is well known that the defect formation energy is a parameter which depends on the growth conditions. Therefore, we have examined the Ti-rich and the O-rich conditions.

In the equilibrium condition between the reservoir of Sr, Ti, O and SrTiO₃, μ_O , μ_{Sr} , and μ_{Ti} satisfy the relation:

$$\mu_{Sr} + \mu_{Ti} + 3\mu_O = \mu_{SrTiO_3(bulk)} \quad (4.8)$$

In a Ti-rich condition, μ_{Ti} is obtained from its corresponding stable bulk, while μ_O is obtained from **Eq (4.8)**. In an O-rich condition, μ_O is the half of one O₂ molecule energy as described above, while μ_{Ti} is obtained from **Eq (4.8)**. The μ_{Sr} is calculated from the energy of the Sr atom in the bulk crystal (Cubic closest packed, ccp, structure) [151]. The results are presented in **table 4.2**. It is noted that the doping is energetically more favorable as the defect formation energy value becomes smaller.

Table 4.2.

Defect formation energies of Mn doped, S doped, Se doped and Te doped SrTiO₃ (in unit of eV).

	Mn doped SrTiO ₃	S doped SrTiO ₃	Se doped SrTiO ₃	Te doped SrTiO ₃
E _f (Ti-rich)	1.97	-2.69	4.30	9.62
E _f (O-rich)	-30.58	8.18	14.38	19.68

From **table 4.2**, it can be seen that S-doped, Se doped and Te doped SrTiO₃ prefer to grow under Ti-rich condition while Mn-doped SrTiO₃, prefers to form in an O-rich environment. Besides, **table 4.2** shows that the formation energies are positive for doping with Se and Te in both conditions, with some preference for The Ti-rich condition, which means that making these compounds in experiment requires energy from the surroundings. The similar thing occurs in the case of doping with S in the O-rich condition and in the case of doping with Mn under Ti-rich condition. Moreover, it appears that for creating S doped SrTiO₃ under Ti-rich condition and Mn doped SrTiO₃ under O-rich condition, the reaction is exergonic because of E_f is negative.

4. Electronic properties

Since the electronic properties provide useful information to understand the nature of the optical properties, we have calculated band structures (**Fig. 4.5.**), density of states (DOS) (**Fig. 4.6.**) and the electronic density distribution (**Fig. 4.7.**) for undoped, Mn doped, S doped, Se doped and Te doped SrTiO₃.

4.1. Band structures

Fig. 4.5. (a) shows that the band gap of undoped SrTiO₃ is direct at the Γ point, which is in line with the reported results [152]. Besides, the obtained band gap value is 1.800eV, in concordance with the previous reported value of 1.73 eV [132], but underestimated compared to the experimental result (3.15eV) [153] due to the well known drawback of Generalized Gradient Approximation implementation [154].

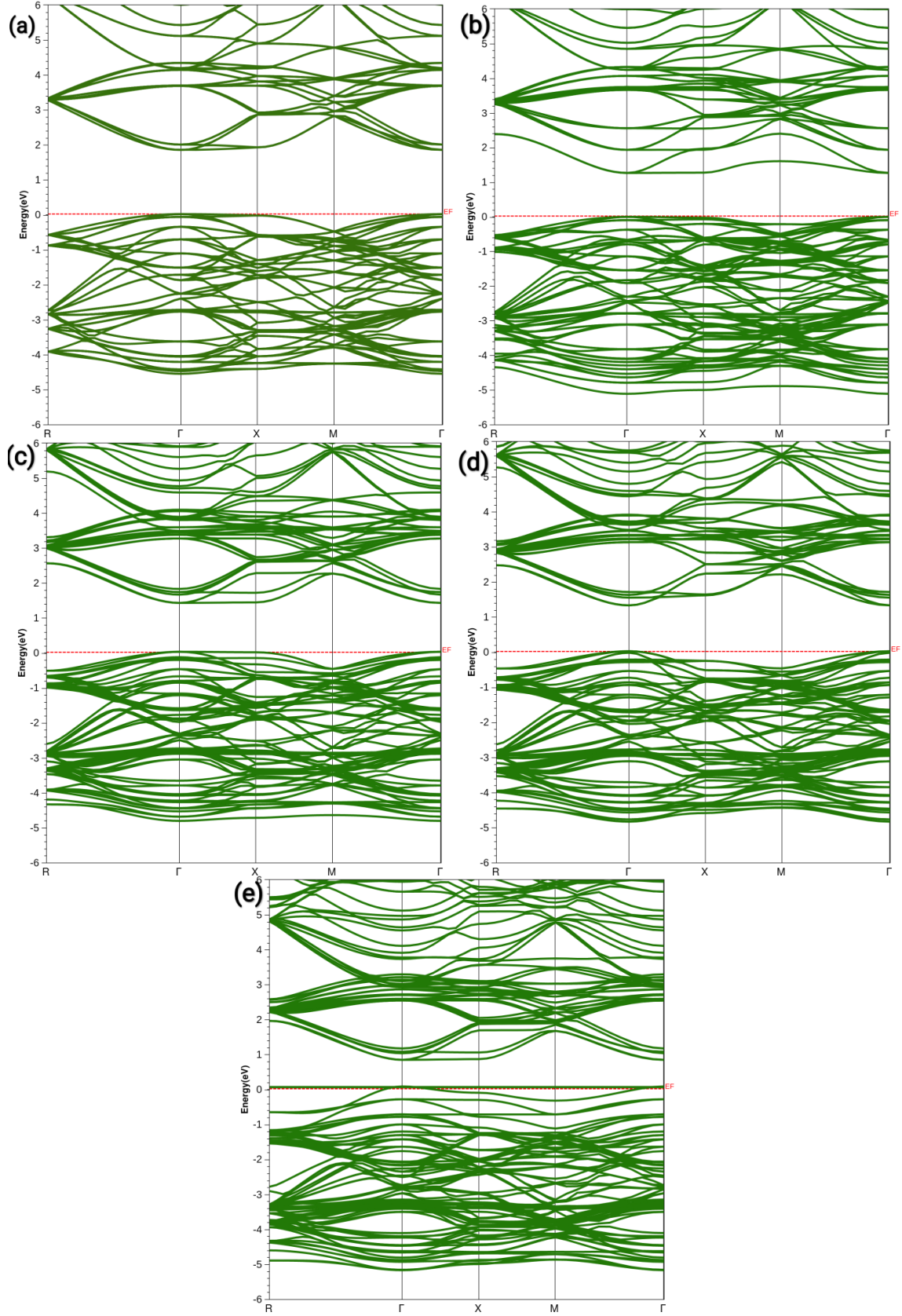


Fig. 4.5. Calculated band structures of (a) Undoped, (b) Mn doped (c) S doped (d) Se doped and (e) Te doped SrTiO₃.

The introduction of Mn, S, Se or Te into the host SrTiO₃ leads to significant band gap reducing, predicting a significant optical absorption shifting towards greater wavelengths. The introduction of Te atom into the SrTiO₃ material shows further band gap narrowing compared to Mn, S and Se insertion, which indicates a good improvement in the visible light absorption. This may improve the photocatalytic efficiency of SrTiO₃ significantly. Besides, **Fig. 4.5. (b), (c), (d) and (e)** show that all the doped structures have a direct band gap at the Γ point, which is beneficial for optical transitions; however it facilitates the recombination of electrons and holes as a hindering factor to photocatalytic performance of materials.

The calculated band gap energies for all systems are presented in the **table 4.3.**,

Table 4.3.

Calculated band gap energy for undoped, Mn doped, S doped, Se doped and Te doped SrTiO₃.

System	Undoped SrTiO ₃	Mn doped SrTiO ₃	S doped SrTiO ₃	Se doped SrTiO ₃	Te doped SrTiO ₃
Calculated E _g (eV)	1.80	1.25	1.39	1.28	0.76
E _g with scissors operator included (eV)	3.15	2.60	2.74	2.63	2.11

4.2. Density of states

Fig. 4.6. shows that the VB of undoped SrTiO₃ is dominated by 2p states of oxygen, whereas its CB is contributed largely by Ti 3d states. After S, Se or Te monodoping, the p states of Sulfur, selenium or tellurium reinforce the contribution of 2p states of oxygen in the VB, leading to VB level up warding. For Mn doping the 3d states of manganese hybridize with 3d states of titanium leading to CB down warding. All these types of doping leads to a significant band gap narrowing in different degrees. The stronger effect of Te compared to other dopants is more obvious in the more narrowing of band gap energy.

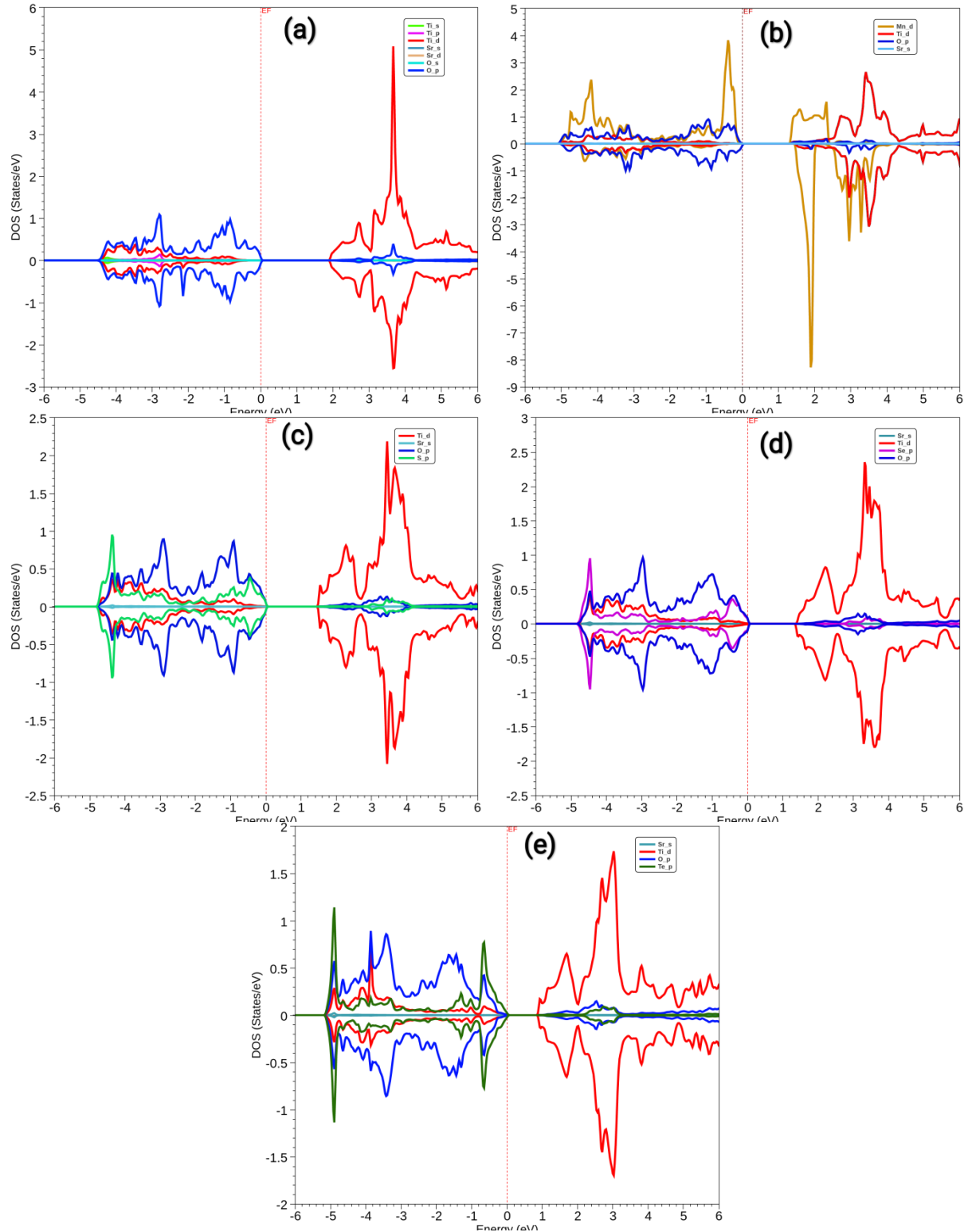


Fig. 4.6. Density of states of (a) Undoped, (b) Mn doped (c) S doped (d) Se doped and (e) Te doped SrTiO₃.

For all cases, no isolated state in mid-gap is appeared; which can be explained by that Mn takes the form of Mn⁴⁺ in Ti site in Mn doped SrTiO₃, and that the number of valence electrons in the S doped, Se doped and Te doped SrTiO₃ crystals remains the same after

replacing an O with a S, Se and Te, respectively, due to the resemblance of valence shells of these atoms; this helps to reduce the recombination effect between the electrons and holes; Therefore, the photo-catalytic efficiency of these doped systems is boosted.

4.3. Charge density distribution

Fig. 4.7. Shows the bonding properties in undoped and monodoped compounds. It appears that in undoped SrTiO₃, Sr-O bond is ionic, while Ti-O is covalent which is in line with previous results [155]. After doping with Mn, S, Se and Te, the ionic character of Sr-O bond decreases while the covalency strength of Ti-O bond increases. Besides, the Sr-S bond in S doped SrTiO₃, the Sr-Se bond in Se doped SrTiO₃ and Sr-Te bond in Te doped SrTiO₃ are covalent, and the covalency strength of Mn-O bond is higher than that of Ti-O bond in Mn doped SrTiO₃. This can be explained by the difference of electronegativity between dopants atoms and host atoms, and may be the origin of observed band gap narrowing in monodoped systems.

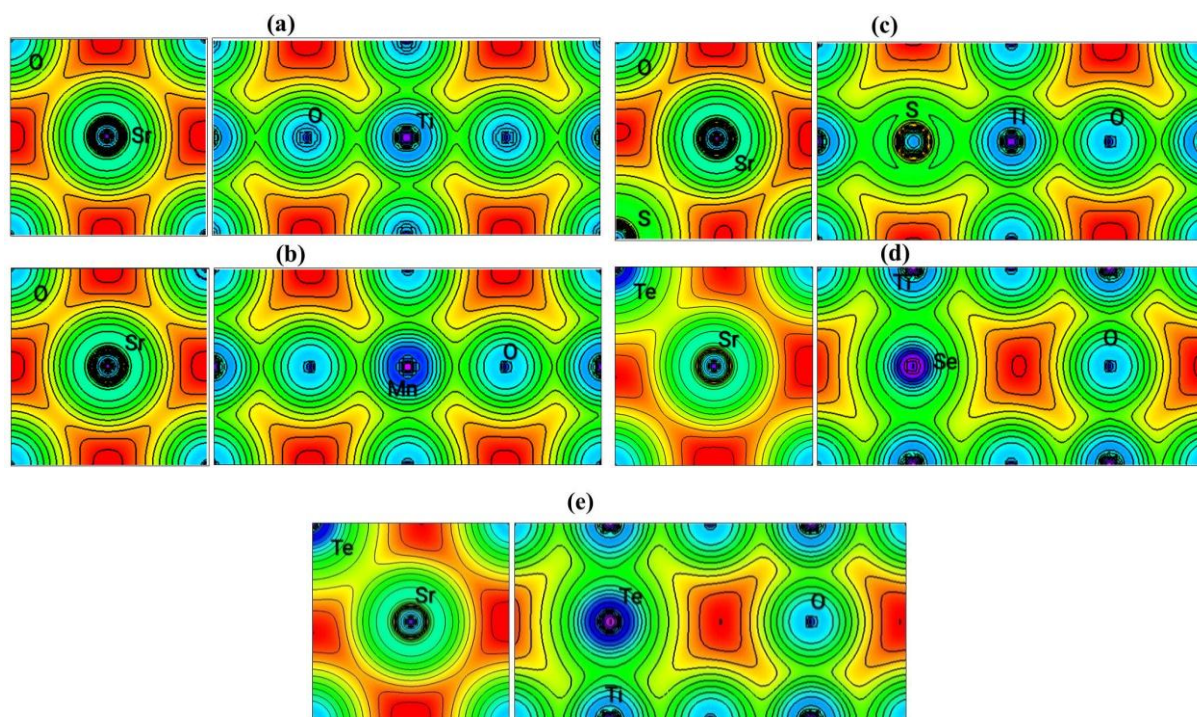


Fig. 4.7. Electronic density distributions of (a) Undoped, (b) Mn doped (c) S doped (d) Se doped and (e) Te doped SrTiO₃.

5. Optical properties

Because of the underestimated band gap of undoped SrTiO₃, we introduced a scissors operator of 1.35 eV (band gap difference between experimental and calculated values) to obtain accurate optical properties in the visible region.

Fig. 4.8. present, the imaginary part $\epsilon_2(\omega)$ of the dielectric function $\epsilon(\omega)$ calculated for undoped, Mn doped, S doped, Se doped and Te doped SrTiO₃, as a function of the incident photon energy.

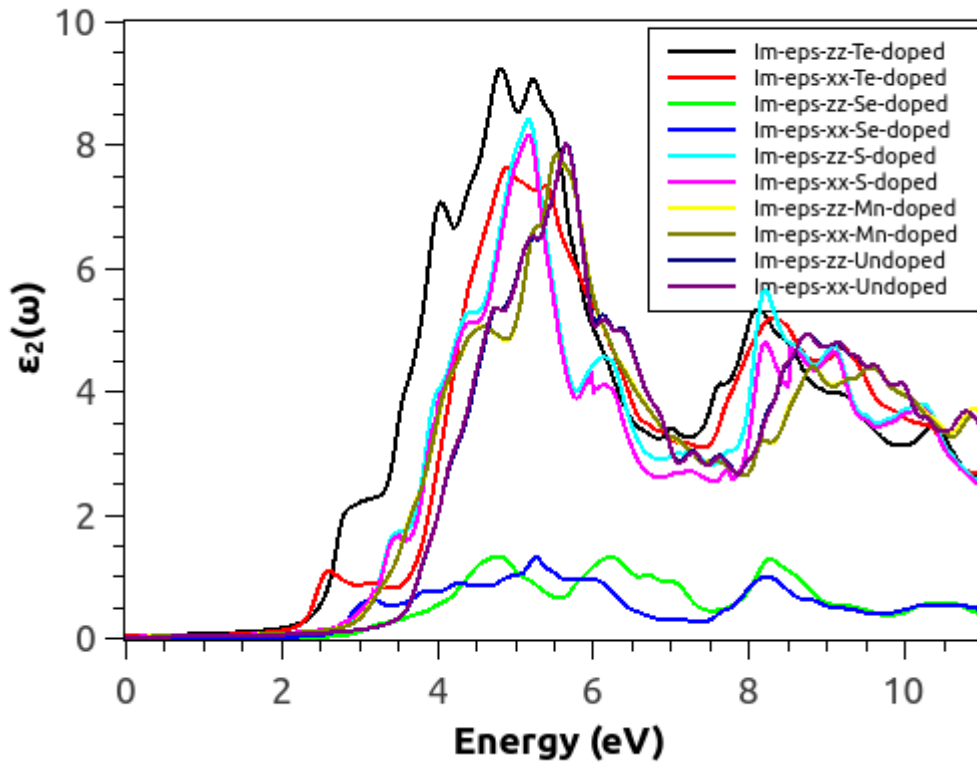


Fig. 4.8. The imaginary part of the dielectric function of undoped, Mn doped, S doped, Se doped and Te doped SrTiO₃.

Our calculated results for $\epsilon_2(\omega)$ show that the threshold energy of SrTiO₃ shifts to lower energies after monodoping with Mn, S, Se and Te and the more shifting occurs after doping with Te; this can be explained by the band gap narrowing caused by these types of doping. Besides, the curves of monodoped systems show apparition of some peaks in the visible light region, indicating the possibility of interband transitions from valence to conduction band states, which indicates an expansion to the visible light region for the response of SrTiO₃. This may leads to a photocatlytic yield improving.

Fig. 4.9. (a) and (b) display the UV-vis absorption spectra of undoped, Mn doped, S doped, Se doped and Te doped SrTiO₃ systems, as a function of energy and wave length in both directions of electric field. It is clearly seen that the absorption of undoped compound is isotropic and its edge lies in the UV domain due to its wide band gap. In comparison, in the case of Mn, S and Se monodoping, the curves of absorption in both polarizations are slightly decaled but extended into the visible region due to narraowed band gap of about 2.60 eV, 2.74 eV and 2.63 eV, respectively, which correspond to the absorption edges of 477 nm , 453 nm and 472 nm, respectively; these results are consistent with the large red-shifts in UV-vis spectra reported by Le et al. [156] for S-doped SrTiO₃ and by Wu et al. [157] for Mn-doped SrTiO₃. For Te doped SrTiO₃, we remark that the absorption has been shifted significantly in both directions of electric field, from the ultraviolet into higher wave length ($\lambda=588$ nm) in the visible light region, which is due to the significant narrowing of band gap ($E_g=2.11$ eV) induced by tellurium insertion effect. This means that the absorption of SrTiO₃ was extensively ameliorated by Te doping, and the created compound will be a promising photocatalyst under visible light irradiation.

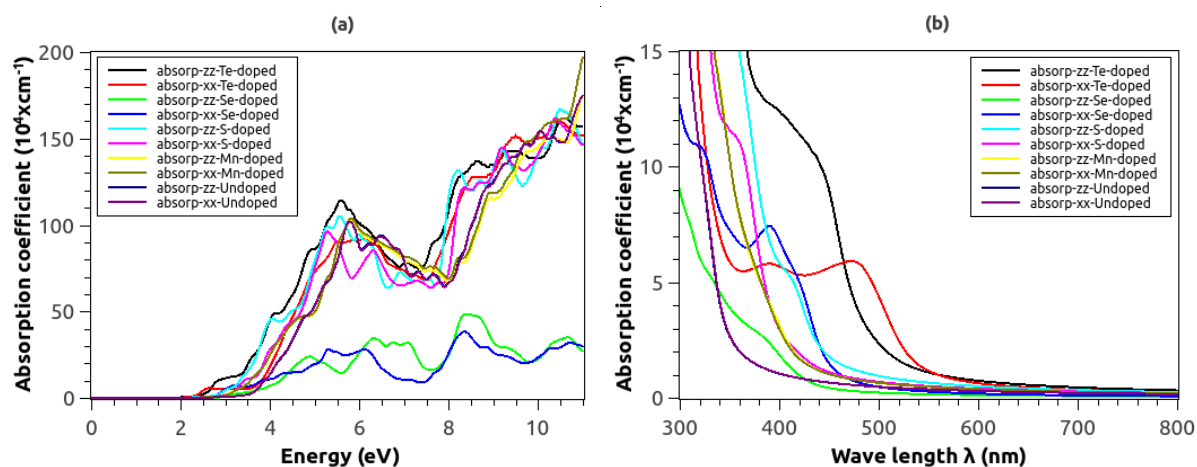
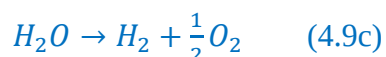
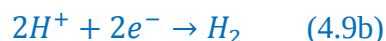


Fig. 4.9. The Absorption coefficient in terms of energy **(a)**, and wave length **(b)**, for undoped, Mn doped, S doped, Se doped and Te doped SrTiO₃.

6. Photocatalytic properties

In photocatalytic water splitting process a heterogeneous semiconductor material is used as photocatalyst. Under illumination, the photons absorbed into the semiconductor (suspended in water) can excite electrons in the valence band (VB) into the conduction band (CB) leaving excited holes in the VB. The photogenerated electron-hole pairs then migrate to the surface of the photo-catalyst, and initiate the oxydo-reduction reactions with adsorbed water molecules

in the active sites. This leads to obtain the dihydrogen H₂ and di-oxygen O₂, simultaneously, according to the following equations:



Equations (15a) and (15b) express the half equation for oxidation and reduction, respectively. The equation (15c) gives the overall equation for water splitting.

For the photogenerated electron—hole pairs to be used for water splitting reaction, the CBM potential should be more negative than the reduction potential of H⁺/H₂ (0 eV vs. normal hydrogen electrode NHE), and the VBM potential should be more positive than the oxidation potential of O₂/H₂O (1.23 eV vs. normal hydrogen electrode NHE) as it is illustrated in **Fig.4.10**. Therefore, the photocatalyst must be a semiconductor with band gap energy more than 1.23 eV, and its CBM and VBM must sandwich the water redox levels, to be used for water splitting.

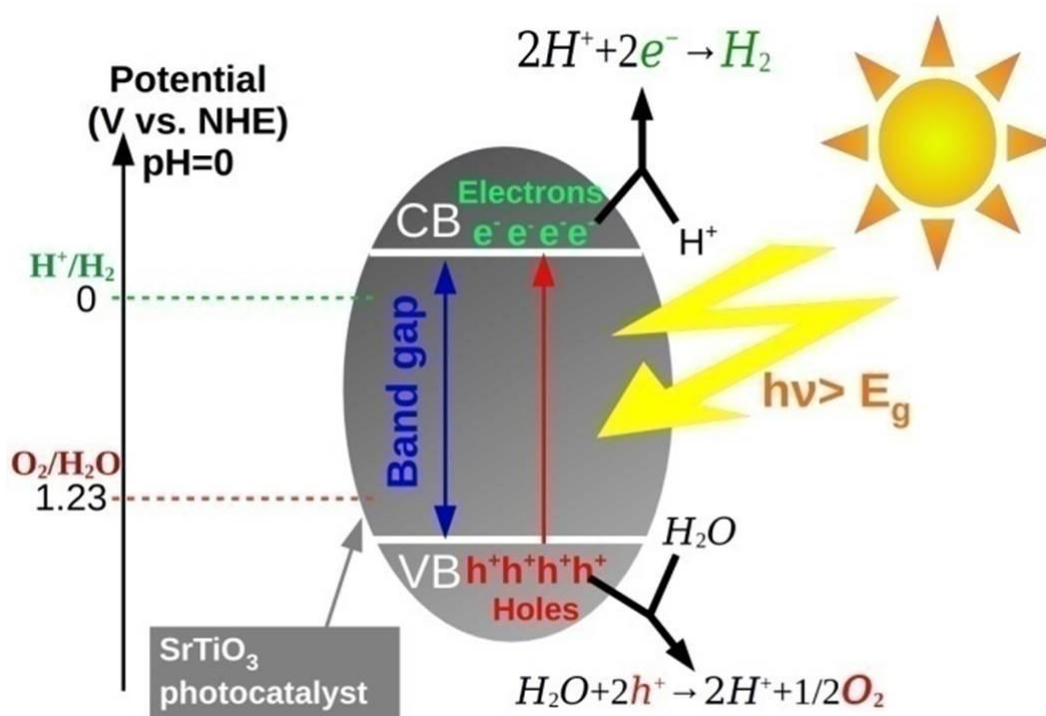


Fig. 4.10. Schematic for photocatalytic water splitting process.

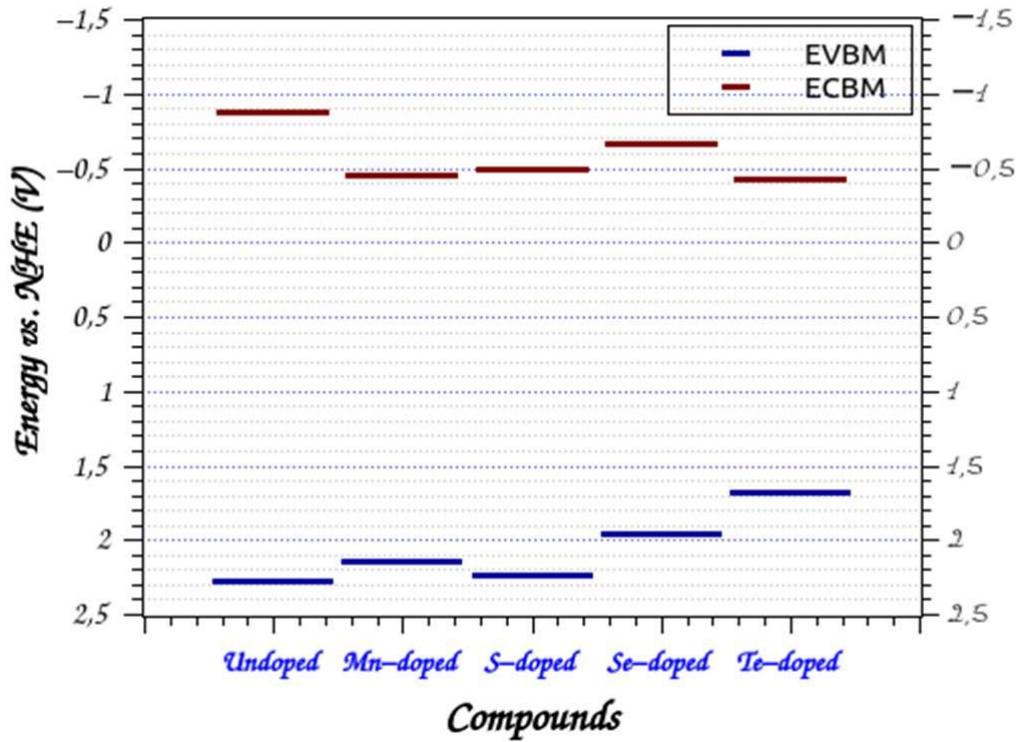


Fig. 4.11. The band alignment of the undoped, Mn doped, S doped, Se doped and Te doped SrTiO₃.

To verify that the above conditions are met, we calculated the CBM and VBM potentials for all undoped, Se doped and Te doped SrTiO₃ using the formulas [158]:

$$E_{CBM} = -\frac{1}{2}E_g + \chi + E_0 \quad (4.10a)$$

$$E_{VBM} = E_g + E_{CBM} \quad (4.10b)$$

Where $E_0 = -4.5$ eV is the energy level of the normal hydrogen electrode (NHE) below the zero vacuum energy level, E_g is the band gap energy, χ is the absolute electronegativity of system calculated by the formulas:

$$\chi_{SrTiO_3} = (\chi_{Sr}\chi_{Ti}\chi_O^3)^{\frac{1}{5}} \quad (4.11a)$$

$$\chi_{SrTiO_{3-x}M_x} = (\chi_{Sr}\chi_{Ti}\chi_O^{3-x}\chi_M^x)^{\frac{1}{5}} \quad (4.11b)$$

Where χ_{SrTiO_3} the absolute electronegativity of pure SrTiO₃, $\chi_{SrTiO_{3-x}M_x}$ the absolute electronegativity of M-doped SrTiO₃ system (M= Se, Te and x=0.125 for one M atom

substitutes for one O atom), χ_{Sr} , χ_{Ti} , χ_{O} and χ_{M} are of Sr, Ti, O and M elements, respectively. According to the study of Bartolotti [159]: $\chi_{\text{Sr}}=1.75$, $\chi_{\text{Ti}}=3.05$, $\chi_{\text{O}}=8.92$, $\chi_{\text{Se}}=5.91$ and $\chi_{\text{Te}}=5.35$. For Mn doped and S doped SrTiO₃, the CBMs and VBMs were obtained from the PDOS plots considering the relative shifts as compared to those of undoped SrTiO₃.

The obtained CBM and VBM positions vs. NHE at pH=0 for all systems are summarized in **table 4.4.**, and their corresponding alignments are plotted in **Fig. 4.11.**

Table 4.4.

Calculated CBM and VBM potentials vs. NHE, for undoped, Mn doped, S doped, Se doped and Te doped SrTiO₃.

System	Undoped SrTiO ₃	Mn-doped SrTiO ₃	S-doped SrTiO ₃	Se-doped SrTiO ₃	Te-doped SrTiO ₃
E _{CBM} potential (eV)	-0.88	-0.46	-0.50	-0.67	-0.43
E _{VBM} potential (eV)	2.27	2.14	2.24	1.96	1.68

It is demonstrated that the CBM and VBM for the Undoped SrTiO₃ straddle the water redox potentials, which means that water can be split into H₂ and O₂ by pure SrTiO₃. Besides the calculated CBM potential of pure SrTiO₃ is 0.88 eV, which is in line with the experimental result of Xu et al. [160]. **Fig. 4.11.** also shows that the CBM is significantly shifted in the downward direction due to doping with Se and S, and further shifted in the same direction due to doping with Mn and Te. This means that photo-reduction ability is improved. Besides, the VBM is slightly shifted upward by S and Mn doping and further shifted upward by Se and Te doping, leading to photo-oxidation capacity improvement. Moreover, the CBM positions of all doped systems are above the hydrogen reduction level and their VBM positions are below the water oxidation level. Consequently, water can be decomposed into H₂ and O₂ for all doped systems. Besides, the absence of isolated states in the forbidden band, and the good absorptive ability in the visible region for these systems, make them a part of promising materials for H₂ production by photocatalytic water splitting. This positive effect of selenium and tellurium on the optical and photocatalytic properties of SrTiO₃ is similar to the effect revealed experimentally in Se-doped TiO₂ [161;162], Te-doped TiO₂ [163] and S-doped SrTiO₃ [156]. The comparison between these doped systems indicates that Te-doped SrTiO₃

has the more suitable band gap energy, absorptive ability and band edges levels for producing hydrogen from photo-catalytic water splitting.

7. Conclusion

In summary, compared to the undoped SrTiO₃, the Mn, S, Se and Te doping can reduce the width of band gap significantly. The increase of covalency strength of Ti-O bond and the decrease of ionicity strength of Sr-O bond through doping Mn in the Ti site or doping S, Se and Te atoms in O site may be the origin of observed band gap narrowing. All the Mn, S, Se and Te doping enhance the absorption of SrTiO₃ in the visible light region. But the Te doping enhanced more effectively the optical absorption in the visible light region and strengthen the red-shift, which is likely due to the higher covalency strength of Ti-Te bond in Te-doped SrTiO₃ compared to the covalency strength of Mn-O in Mn-doped SrTiO₃, Ti-S in S-doped SrTiO₃ and Ti-Se in Se-doped SrTiO₃. The narrowed band gaps are free from any isolated states, which expected to help in inhibiting the faster recombination of photogenerated carriers and consequently improve the photocatalytic performance. The potentials of the CBMs and VBMs satisfy the thermodynamic requirements to trigger the water splitting reaction. Hence we suggest that the doping of Mn, S, Se and Te (particularly Te) into the SrTiO₃ material is one of the better choices to improve the yield for photosplitting of water under visible light.

Chapter 5

Improving the photocatlytic performance of SrTiO₃ under visible light, by S/Mn-, Se/Mn- and Te/Mn-codoping.

Abstract

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Taking the same route of the previous chapter, in this chapter, we turned to the study of the modified SrTiO₃ photocatlyst with codoping strategy. Specifically, we illuminated the advantages of codoping in improving the photocatlytic performance of SrTiO₃.

We studied the influence of S/Mn-, Se/Mn- and Te/Mn-codoping on the stability of SrTiO₃ and its electronic, optical and photocatlytic properties. We found that these types of codoping lead to easy feasible systems due to the synergistic effect of codopants. In addition, we found that codoping with (sulfur, selenium or tellurium) and manganese can alter the electronic structure and the absorption properties of SrTiO₃ to a large extent, which may increase its photocatalytic performance in the visible light range. In particular, Te/Mn codoping is expected to improve greatly the visible light photocatalytic activity of SrTiO₃.

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1. Introduction

The ionic monodoping can shift the optical absorption spectrum of SrTiO₃ to longer wave length, which enhances its visible light response; however, in some cases, this can induce isolated mid-gap states, particularly when the dopant has different valence from the host [164], these mid-gap states may act as electron-hole pair recombination centers and minimize the photoconversion efficiency. For example, in an experimental and theoretical study, Bae et al. [165] showed that doping noble metals (Ru, Rh, Ir, Pt, Pd) in the perfect SrTiO₃ introduces new energy levels between the VBM and CBM. This improves the photon harvesting ability, but does not guarantee an improvement in photocatalytic H₂ generation, because these mid-gap levels act as trapping centres, which promote the unfavourable effect of recombination. Also, chen et al. [59] studied the effect of doping by Ru on the photocatalytic activity of SrTiO₃ based photocatalyst using DFT calculations. They found that the mid-gap states introduced by Ru dopant promote faster charge carriers recombination. Liu et al. studied the effect of C, N, Mo and W doping on the electronic and optical properties of SrTiO₃, they found that N- and C - monodoping on the O site and Mo- and W - monodoping on the Ti and Sr site, enhances the photocatalytic ability by introducing mid-gap states, but can restrain the charge carrier mobility leading in reducing the photo conversion efficiency, and they explain the appearance of mid-gap states by the excess electrons introduced by dopants [136].

Additionally to the creation of isolated states in the band gap, the mono-doping may also has other limitations, such as the limited solubility of dopant, and the association of doping with spontaneous formation of compensating defects [166]. Therefore, to overcome the monodoping limitation, codoping is regarded as an efficient way. For example, Yu et al. [167] Experimentally found that the coexistence of Ag and F in SrTiO₃ could effectively suppress the recombination of photo-generated electron/hole pairs for efficiently improving the photocatalytic activity. Besides, Yu et al. [168] found that the codoping of Cr and N into SrTiO₃ showed a higher photocatalytic activity for H₂ production. This is attributed to that the charge balance was maintained by codoping of N and Cr into SrTiO₃ without forming vacancies, which is beneficial for eliminating the recombination of photogenerated electron-hole pairs, thus enhancing the photocatalytic activity. Moreover, Liu et al. [] reported that codoping with (N–N, N–P and P–P) was predicted to be promising for visible-light photocatalysis of SrTiO₃, due to the synergistic effect of dopants which eliminates the acceptors states emerging above the Fermi level and decreases the band gap significantly.

Besides, Kato and Kudo [60;61] revealed that codoping of Sb or Ta and Cr into SrTiO₃, exhibits a quite high activity in H₂ generation. This can be ascribed to that the charge balance was kept by codoping of Sb⁵⁺ or Ta⁵⁺ and Cr³⁺ in Ti⁴⁺ sites of SrTiO₃.

Consequently, the present chapter is concerned with the investigation of the effect of S/Mn-, Se/Mn- and Te/Mn-codoping on the enhancement of photocatalytic water splitting property of SrTiO₃ in the visible light range.

2. Computational methods

Spin-polarized DFT calculations have been carried out using WIEN2k package. The exchange-correlation interaction was treated in the level of the GGA-Perdew-Burke-Ernzerhof (GGA-PBE) approximation. The parameter of $R_{\text{mt}}K_{\text{max}}$ is chosen to be seven (K_{max} is the maximum of the reciprocal lattice vector used in the plane wave expansion and R_{mt} is the smallest muffin-tin radius in the unit cell). The separation energy between the core and valence states is -7.0 Ry. The energy convergence criterion and charge convergence criterion of the SCF calculations were set to 0.0001 Ry and 0.001 eV, respectively. For k -space integration, a grid of $7 \times 7 \times 7$ k points in the first Brillouin zone is used. The muffin-tin sphere radii (R_{mt}) of Sr, Ti, O, Mn, and S atoms are set to be 1.70, 1.85, 1.63, 1.85, and 1.58 a.u., respectively. The optimized lattice parameter of pure SrTiO₃ is founded to be 3.942 Å, which seems reasonably in line with the previous reported results [143,153].

All calculation models are constructed with $2 \times 2 \times 2$ supercell of SrTiO₃, which contains 8 Sr atoms, 8 Ti atoms, and 24 O atoms. The monodoped system is modeled by replacing either one of the Ti or O atoms by Mn or S, respectively from supercell, and in the case of codoping, we simultaneously introduce both Mn and S into SrTiO₃. In our calculations, we only consider Ti-site doping for Mn because the Mn tends to enter the Ti-site in SrTiO₃ [132,138], in which Mn exists in the form of Mn⁴⁺ ion [139], and O-site doping for X=S, Se, Te, to maintain charge balance in the S, Se, and Te doped SrTiO₃ ($\text{O}^{2-} \equiv \text{X}^{2-}$) and in the codoped SrTiO₃ ($\text{Ti}^{4+} + \text{O}^{2-} \equiv \text{Mn}^{4+} + \text{X}^{2-}$).

3. Structure optimization

In the SrTiO₃ unit cell there are three dissimilar positions of oxygen; therefore, to evaluate the feasibility of doped SrTiO₃ structures, we have made all the doping configurations of the S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO₃ supercells

and compared the total free energies for each type codoping. The most energetically favorable configurations for these codoped systems are shown in **Fig. 5.1**.

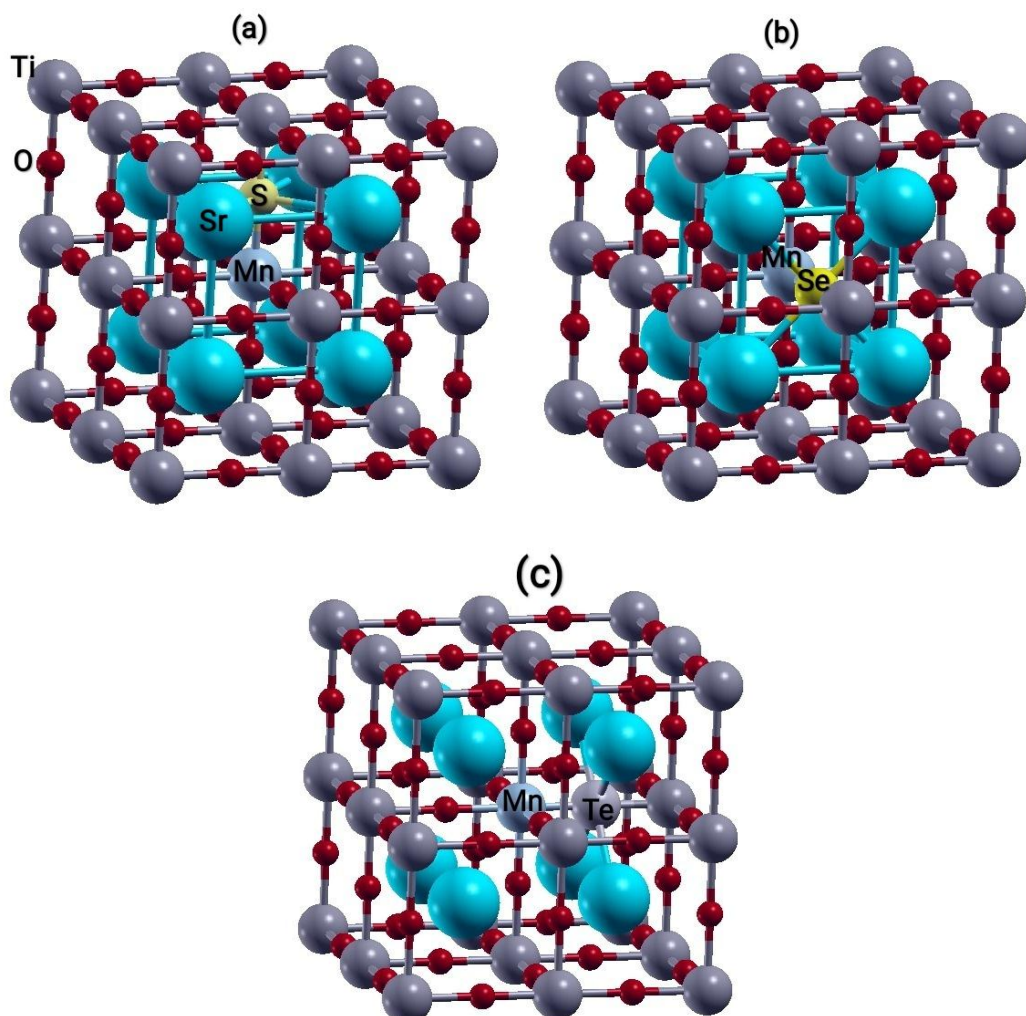


Fig. 5.1. The 2 x 2 x 2 supercell of: **(a)** S/Mn-codoped **(b)** Se/Mn-codoped and **(c)** Te/Mn-codoped SrTiO₃, respectively.

After that the volume variations with cell parameters have been carried out for the stable systems and the corresponding optimized lattice constants are summarized in **Table 5.1**.

Table 5.1.

Calculated lattice constant for undoped, S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO₃.

System	Undoped SrTiO ₃	S/Mn-codoped SrTiO ₃	Se/Mn-codoped SrTiO ₃	Te/Mn-codoped SrTiO ₃

Lattice constant (Å)	3.941	3.971	3.979	4.222
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According to the obtained results, the calculated lattice constant for the pure system is in good agreement with experimental [73] and theoretical [134] results. Besides, the lattice constant increases progressively from undoped SrTiO₃ to S/Mn-codoped SrTiO₃, to Se/Mn-codoped SrTiO₃ to Te/Mn-codoped SrTiO₃, due to the progressive increase of the ionic radius [169] of chalcogenide atoms, from O to S to Se to Te, respectively.

$$r_{O^{2-}} = 1.35\text{\AA} < r_{S^{2-}} = 1.84\text{\AA} < r_{Se^{2-}} = 1.98\text{\AA} < r_{Te^{2-}} = 2.21\text{\AA}$$

To evaluate the relative stability of the studied systems, their defect formation energies were calculated, using the following formula:

$$E_f = E_{\text{codoped}} + \mu_O + \mu_{Ti} - E_{\text{undoped}} - \mu_X - \mu_{Mn} \quad (5.1)$$

Where;

- E_{codoped} is the total energy of the codoped SrTiO₃ supercell,
- E_{undoped} is the total energy of SrTiO₃ without doping,
- μ_O , μ_{Ti} , μ_X (X=S, Se, Te) and μ_{Mn} are the chemical potentials of respectively, O, Ti, S, Se, Te and Mn elements, obtained by SCF calculations *where*:
 - μ_O is the energy of one O atom obtained from the total energy of an O₂ molecule ($\mu_O = 1/2 E_{O_2}$) confined at the center of a 15x15x15 Å³ cubic box.
 - Each of μ_{Ti} , μ_X (X=S, Se, Te) and μ_{Mn} , corresponds to the energy of an atom in the respective bulk crystal.

As it has been explained in the previous chapter, we calculate the formation energies for all codoped systems under Ti-rich and O-rich conditions. The calculated results are listed in **Table 5.2.**

Table 5.2.

Defect formation energies for different codoped SrTiO₃ structures (in unit of eV)

	S/Mn-codoped	Se/Mn-codoped	Te/Mn-codoped
E_f (Ti-rich)	-1.75	7.25	12.61
E_f (O-rich)	-23.34	-12.93	-4.52

From **table 5.2**, it can be seen that all compounds are easy feasible in experiment under O-rich condition of growth due to the negative values of defect formation energies. Besides, for the same reason, it is easy to perform S/Mn-codoped SrTiO₃ in experiment under Ti-rich environment. By contrast, the defect formation energy is positive for Se/Mn-codoped SrTiO₃ and Te/Mn-codoped SrTiO₃ under Ti-rich condition, which means that the formation of these materials is difficult in experiment and requires useful energy from the surroundings.

4. Electronic structures

The calculated band structures of S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO₃ are illustrated in **Fig. 5.2**. The fermi energy is set to 0 eV on the axis of ordinates.

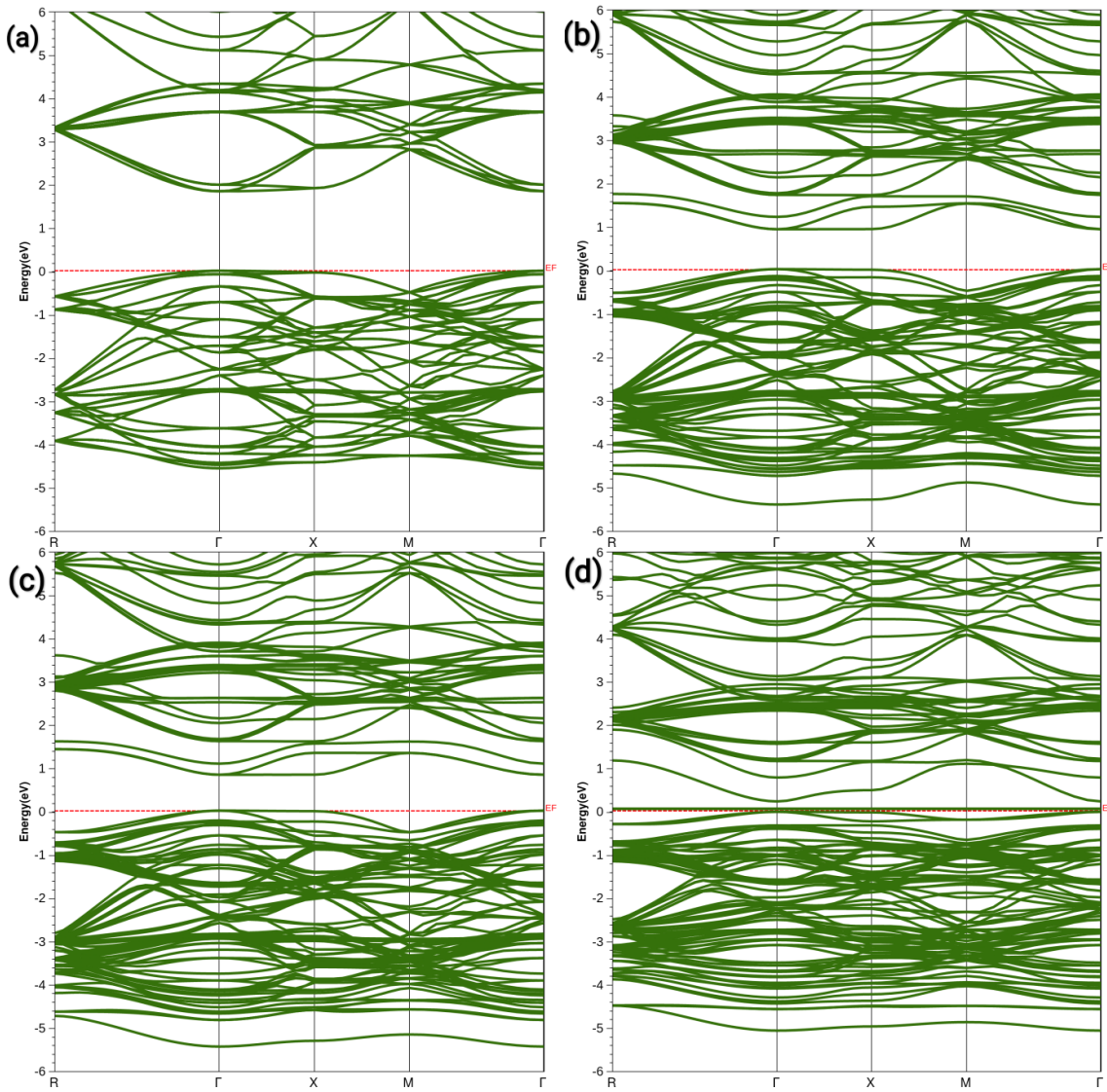


Fig. 5. 2. Band structures of (a) undoped, (b) S/Mn-codoped, (c) Se/Mn-codoped and (d) Te/Mn-codoped SrTiO₃.

For all systems, both valence band maximum (VBM) and conduction band minimum (CBM) occur at Γ point, which is in concordance with previous theoretical calculations for undoped SrTiO₃ [152]. The band gap values for the different systems are summarized in **table 5.3**.

Table 5.3.

Calculated band gap, E_g , for undoped, S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO₃.

System	undoped	S/Mn-codoped	Se/Mn-codoped	Te/Mn-codoped
E_g (eV)	1.800	0.898	0.789	0.109
E_g with scissors operator included (eV)	3.150	2.248	2.194	1.459

The band gap value of undoped SrTiO₃ is in good agreement with previous theoretical results using the same method [152,132]. However, based on the available literature all these results are largely underestimated. This is explained by the well-known problem of GGA-PBE method within DFT [170]. Besides, the band gap energy decreases progressively from the undoped system, to the codoped with S/Mn, to the codoped with Se/Mn, to the codoped with Te/Mn, which indicates that the visible light absorption ability will be progressively improved in this order.

To further examination of doping effect on the electronic properties, we calculate the partial density of states (PDOS) near the Fermi levels and the distribution of electronic density in some planes of the undoped, S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO₃ as shown in **Fig. 5.3.** and **Fig. 5.4.**, respectively.

For undoped SrTiO₃, The PDOS is shown in **Fig. 5.3. (a)**, our results are similar to the previous theoretical results [152,143]; illustrating that the valence band maximum (VBM) is essentially O 2p orbital in character while the conduction band minimum (CBM) is mainly contributed by Ti 3d orbital. Besides, the analysis of contours of valence electrons charge density around the Sr, Ti and O atoms in **Fig. 5.4. (a) and (a')** shows that the Ti-O bond is covalent, while, Sr-O bond is ionic.

For S/Mn-codoped SrTiO₃, as shown in **Fig. 5.3. (b)** the VBM is composed of O 2p states mixed with S 3p and Mn 3d states, which illuminates the covalent character of S-Mn and O-Mn bonds. Besides, the Mn 3d states appeared in the bottom of conduction band and

constituted a continuum with CBM, which contributes to the significant narrowing of band gap. This will promote the visible light absorption and photocatalytic performance of SrTiO₃. The significant band gap reducing can be ascribed on one hand to emergence of Mn 3d states on the CBM, and on the other hand to the increase of covalency strength of S-Mn and O-Mn bonds compared to that of O-Ti bonds in the undoped system and the decrease of the ionicity of S-Sr bonds compared to that of O-Sr bonds in undoped SrTiO₃, Which is due to the smaller difference of electro-negativities between S and Mn and between S and Sr in codoped system compared to that between O and Ti and between O and Sr, respectively, in the pure system.

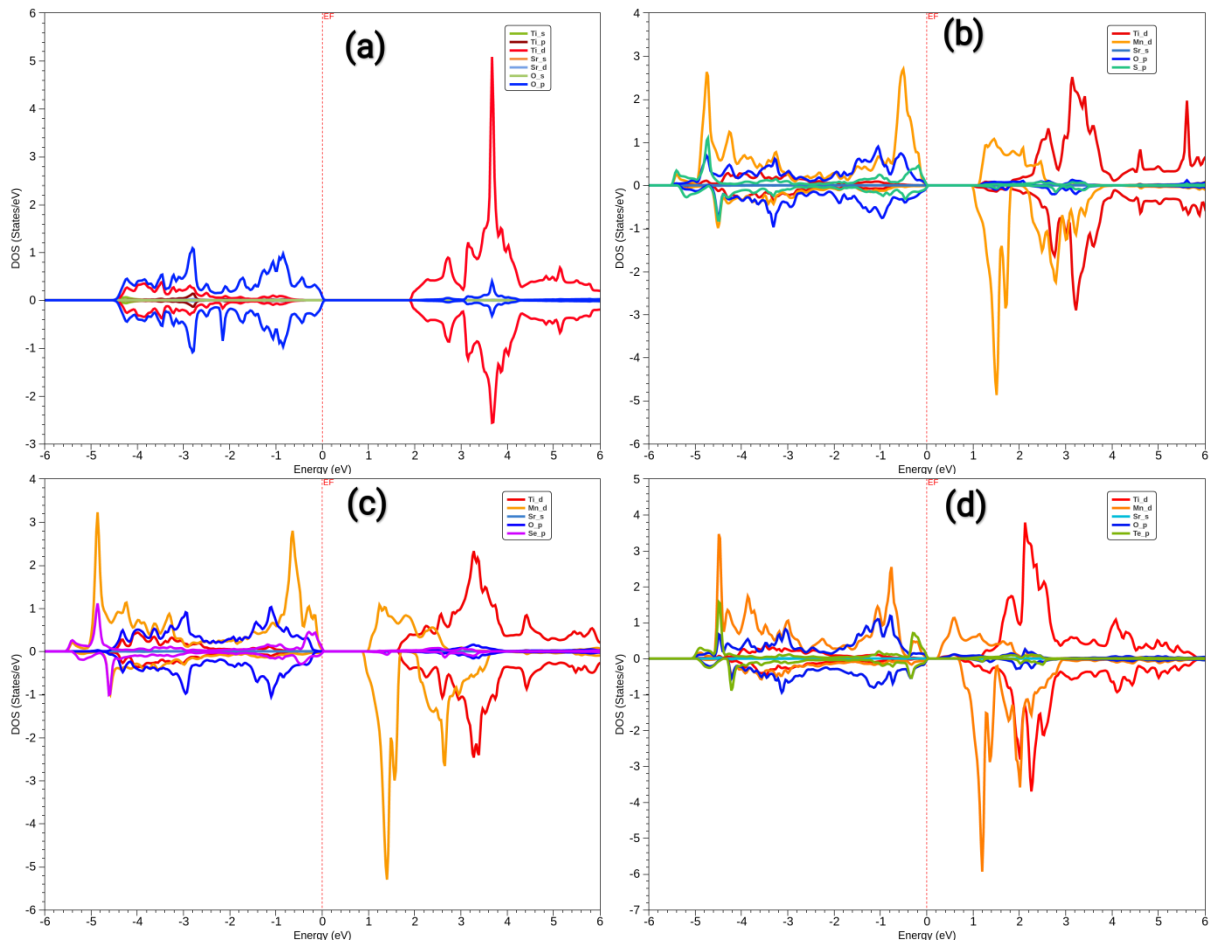


Fig. 5.3. PDOS of (a) undoped, (b) S/Mn-codoped, (c) Se/Mn-codoped, (d) Te/Mn-codoped SrTiO₃

In the Se/Mn-codoped SrTiO₃ case, as illustrated in **Fig. 5.3 (c)**, the VBM is composed of O 2p states and Se 4p states hybridized with Mn 3d states, indicating the covalent character of Mn-Se and Mn-O bonds. The CBM is mainly dominated by Ti 3d states. Besides, the band gap is narrowed by nearly 0.96eV. Hence, a decrease of electronic transition energy between

VBM and CBM could be occurred, leading to a red-shift in optical absorption edge. The observed band gap narrowing can be explained from **Fig. 5.4.** by that the covalency strength of Se-Ti and Se-Mn bonds in Se/Mn-codoped SrTiO₃ is higher compared to that of O-Ti bonds in undoped SrTiO₃, and that the ionicity strength of Se-Sr and O-Sr bonds in Se/Mn-codoped SrTiO₃ is lower than that of O-Sr bonds in undoped SrTiO₃, and this is probably due to the lower electronegativity of Se compared to that of O.

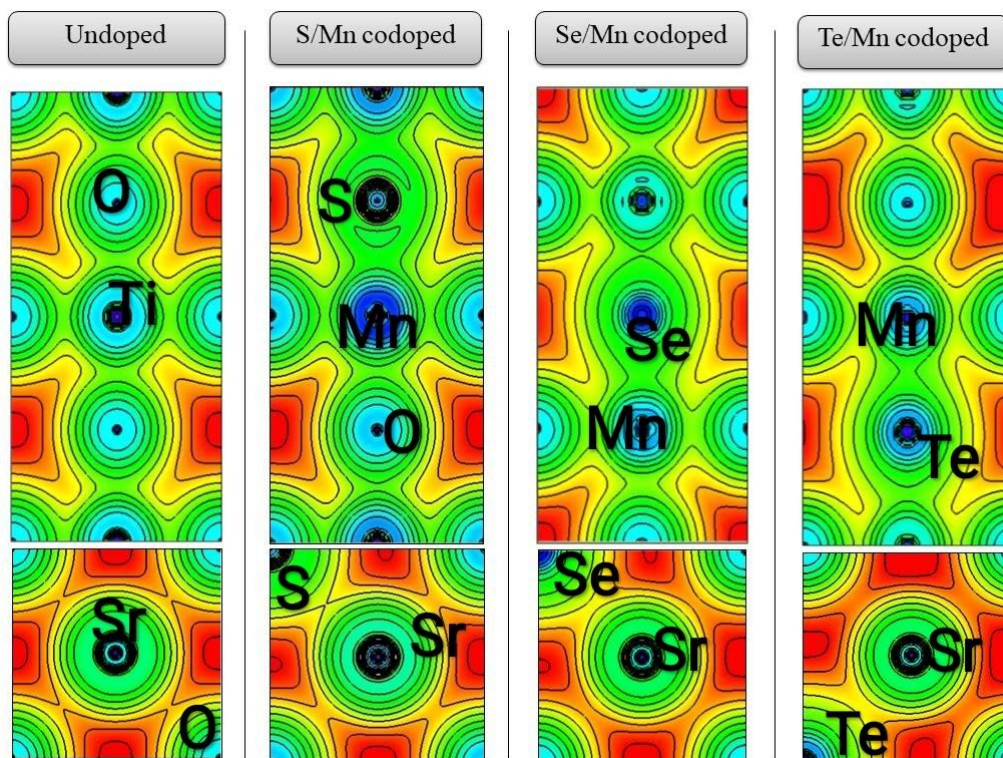


Fig. 5.4. Electronic density distributions of undoped, S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO₃.

In the Te/Mn-codoped SrTiO₃ case, the PDOS of **Fig. 5.3. (d)** shows that the VBM is composed of O 2p states and Te 5p states hybridized with Mn 3d states, illustrating the covalent property of Mn-O and Mn-Te bonds, which is in agreement with the corresponding charge density distribution in **Fig. 5.4.** In the CBM, the Mn 3d states mix with some O 2p and Ti 3d states and constitute a continuum with the bottom of conduction band; this lowers the CBM significantly and leads to band gap narrowing, without promoting the recombination effect. In all codoped systems, the absence of isolated states in the forbidden band can be explained by that the manganese ion adopt the Mn⁴⁺ form in these cases [139], and that the S,

Se and Te atoms have the same valence shell like that of O atom, which maintains the charge balance in the crystals.

5. Optical properties

Fig. 5.5. (a) and (b) present respectively, the real, $\epsilon_1(\omega)$, and imaginary, $\epsilon_2(\omega)$, parts of the dielectric function $\epsilon(\omega)$ calculated for undoped, S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO₃ as a function of the incident photon energy.

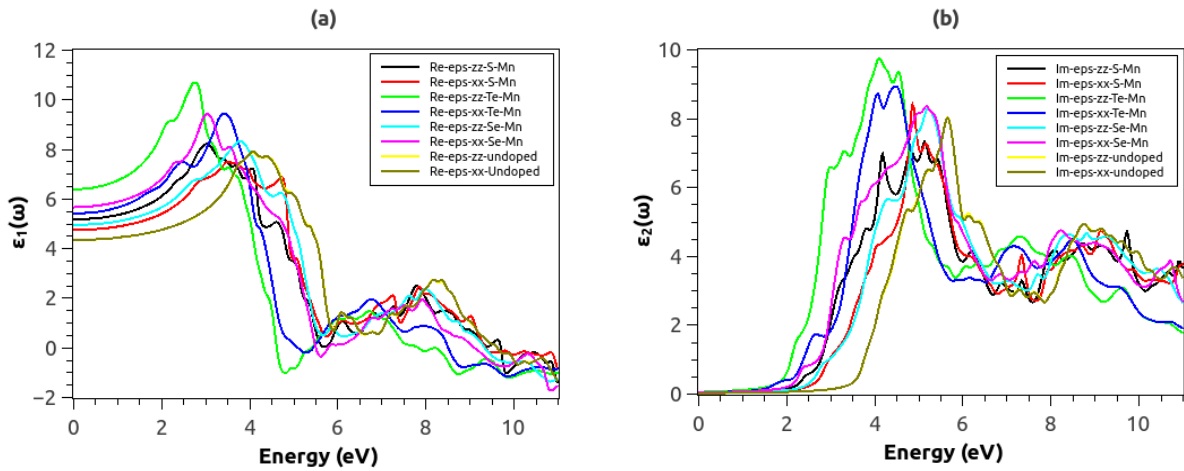


Fig. 5.5. The (a) real and (b) imaginary parts of the dielectric function of undoped, S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO₃.

The value of the static refractive index along the xx-axis (parallel polarization of electric field), $n_{xx}(0) = \sqrt{Re\epsilon_{xx}(0)}$, and along the zz-axis (perpendicular polarization of electric field), $n_{zz}(0) = \sqrt{Re\epsilon_{zz}(0)}$ for all compounds deduced from **fig. 5.5. (a) and (b)** are presented in **table 5.4.**,

Table 5.4.

Static refractive index obtained from $\epsilon_1(\omega)$ curve for undoped, S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO₃ in both directions of electric field.

System	Undoped SrTiO ₃		S/Mn-codoped SrTiO ₃		Se/Mn-codoped SrTiO ₃		Se/Mn-codoped SrTiO ₃	
	xx-axis	zz-axis	xx-axis	xx-axis	xx-axis	zz-axis	xx-axis	zz-axis
The static refractive index $n(0)$	2.09	2.09	2.18	2.28	2.38	2.23	2.33	2.53

Our calculated results for $\epsilon_2(\omega)$ (**Fig. 5.5. (b)**) show that the threshold energy of SrTiO₃ shifts to lower energies after codoping with S/Mn and Se/Mn and shifts more after codoping with Te/Mn for both polarizations; this can be explained by the band gap narrowing caused by these three types of codoping. Besides, the curves of all codoped systems show apparition of some peaks in the visible light region in both xx and zz directions, indicating the possibility of interband transitions from valence to conduction band states, which indicates an expansion of response of SrTiO₃ to the visible light region. This may improve the photocatlytic performance.

Fig. 5.6. (a) shows the obtained optical conductivity in terms of energy for the investigated three systems. The optical conductivity can be utilized to investigate the propagation and dissipation of electromagnetic wave in matter. Although the curves of codoping structures mimic the curves of undoped system, one can remark that the presence of S/Mn or Se/Mn or Te/Mn, shifts the optical conductivity of SrTiO₃ towards lower energy and lower value of optical conductivity. This can be explained by that the interaction with radiation changes due to the redistribution of charges caused by introduced dopants.

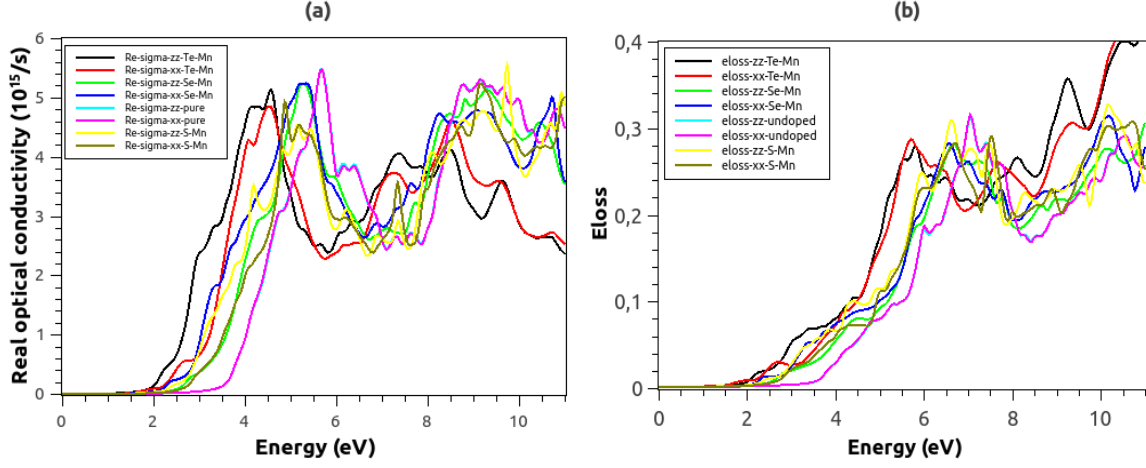


Fig. 5.6. The (a) Optical conductivity and (b) Electron energy loss spectrum of undoped, S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO₃.

Fig. 5.6. (b) displays the energy loss function with the change of energy. This physical quantity is very useful to characterize the loss in the energy during an electron fast traversing through a medium [171]. We remark in the curves that the energy loss for all systems is weak for lower energy regime and increases with energy increasing; it displays two coincide sharp peaks (for both directions xx and zz) for energy of 7.03 eV for undoped SrTiO₃. These peaks shift to lower energies of 5.72eV , 6.54 eV and 5.70 eV and becomes less intense after codoping with respectively, S/Mn, Se/Mn and Te/Mn atoms. Below 10 eV energy, the displayed peaks are attributed to π electrons, while these of high energy correspond to $\pi+\sigma$ plasmons. The single peaks are indicating the unique collective excitations while multiple peaks are indicating several collective excitations [172].

Fig. 5.7. (a) and (b) show the critical dispersion relationships of all systems, i.e. the refractive index ($n(\omega)$) and extinction coefficient ($k(\omega)$) spectra , in both directions. In fact, $n(\omega)$ indicates to the phase velocity of electromagnetic wave in a medium and relates to the refraction of an incident light by a material, while $k(\omega)$ relates to the amount of absorption of a photon when propagates in the material. Both $n(\omega)$ and $k(\omega)$ depend on the wavelength [173]. Since $n(\omega)$ and $k(\omega)$ parameters are derived from the calculated real and imaginary parts of the dielectric function, their behavior is closely related to the dielectric function. The shown values of static refractive index, $n(0)$ in **fig. 5.7. (a)** are close to the results of **table 5.4.**, satisfying the condition $n(0) = \sqrt{Re\epsilon(0)}$ which reflects the rationality of our calculations. From the **fig. 5.7. (b)** and **fig. 5.8. (a)** which displays the absorption spectra, we can observe that $k(\omega)$ depends on the spectrum of absorbed energy. Both the $k(\omega)$ and the

absorption spectrum $\alpha(\omega)$ remain in concordance for undoped and codoped systems. This means that when $k(\omega)$ shows an increasing tendency the absorption also indicates an identical tendency and vice versa. This resemblance can be explained by that the extinction coefficient $k(\omega)$ and the absorption coefficient $\alpha(\omega)$ are interrelated by the formula [174],

$$K(\omega) = \frac{\alpha(\omega)\lambda}{4\pi} \quad (5.2)$$

Where λ indicates to the wave length of incident photon.

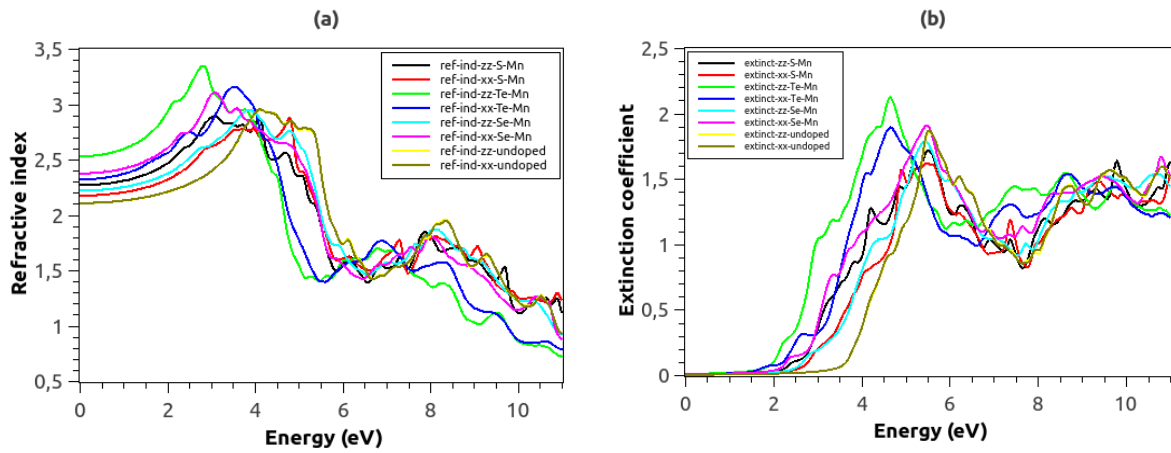


Fig. 5.7. The (a) refractive index and (b) Extinction coefficient of undoped, Se/Mn codoped and Te/Mn codoped SrTiO₃.

Fig. 5.8. (a) depicts the variation of reflectivity of pure and codoped SrTiO₃ in both directions of electric field. It appears for undoped SrTiO₃ that the curves of reflectivity for both polarizations coincide, which means that the light is unpolarized by this material. Besides, the curves of reflectivity of pure SrTiO₃ exhibit a peak of 36.24% at the energy of 5.48 eV. In low energy range, the reflectivity of S/Mn codoped SrTiO₃ is higher than that of pure system with the reflectivity in perpendicular polarization is higher than that in parallel polarization. About the energy of 5.25 eV the reflectivity of S/Mn codoped system becomes lower than that of pure SrTiO₃. For Se/Mn-codoped SrTiO₃, we observe that the reflectivity in parallel polarization is slightly high than that in the perpendicular polarization, and both present respectively, a peak of 37.91% and another of 34.46%, at respectively, the energy of 5.48 eV and 5.43 eV. For Te/Mn-codoped SrTiO₃, we observe that the reflectivity in parallel polarization is lower than that in the perpendicular polarization, and present respectively, a peak of 36.38% and of 40.80%, at respectively, the energy of 4.64 eV and 4.67 eV.

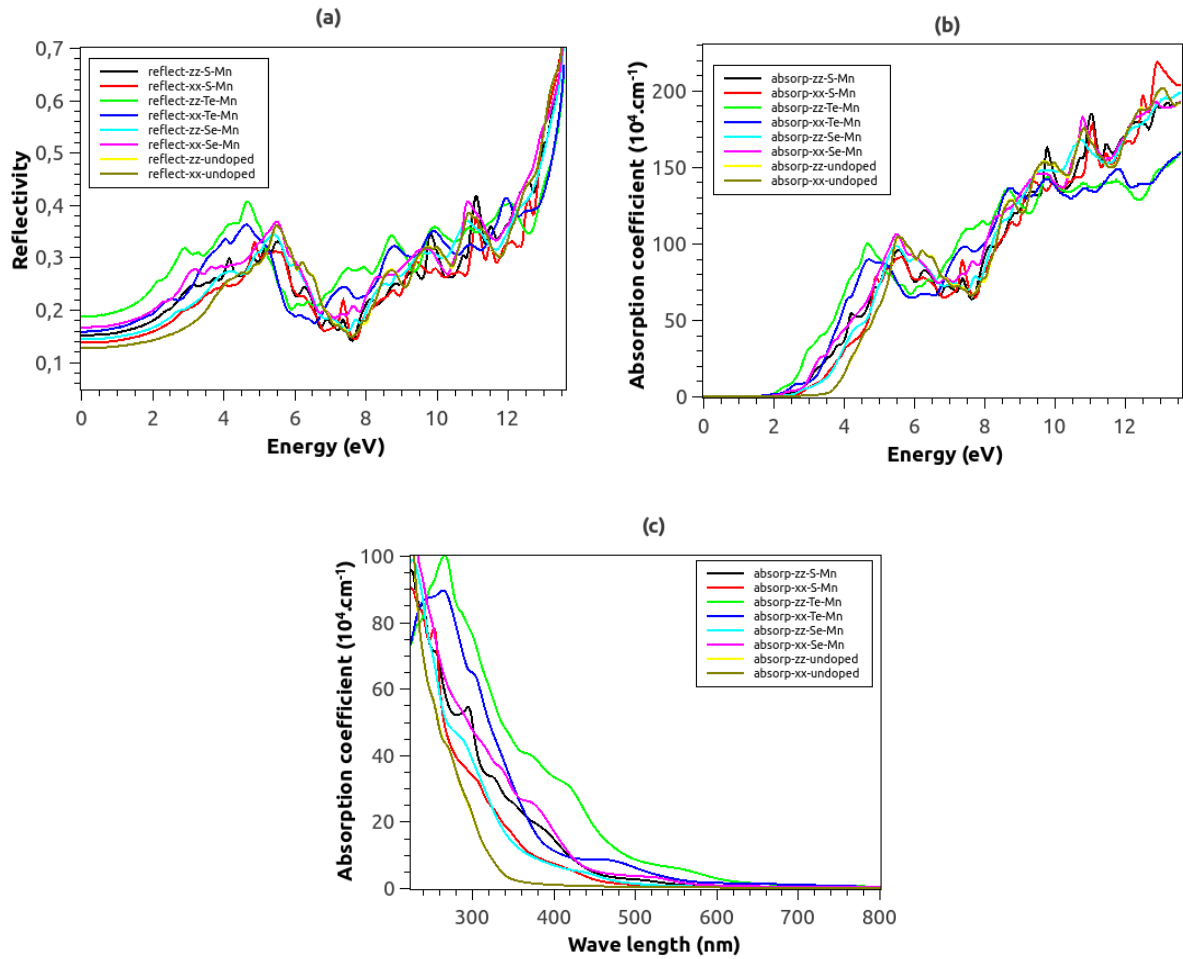


Fig. 5.8. The (a) reflectivity and (b) Absorption coefficient of undoped, S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO₃.

Also, we remark that in both directions of electric field, the reflectivity of Te/Mn-codoped SrTiO₃ is higher than those of S/Mn-codoped SrTiO₃ and Se/Mn-codoped SrTiO₃ which are slightly higher than that of undoped SrTiO₃. Also we remark that all systems exhibit lower reflectivity when exposed to visible light. This suggests that these compounds possess attractive characteristics as transparent semiconductors [175] and may be as good photocatalysts.

Fig. 5.8. (b) and (c) displayed the UV-vis absorption spectra of undoped, S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO₃ systems, as a function of energy and wave length in both directions of electric field. The curves show that the spectra of pure SrTiO₃ in both directions of electric field are confused. Besides, it is clearly seen that SrTiO₃ responds only to UV light due to its large band gap. For S/Mn-codoped and Se/Mn-codoped SrTiO₃, the curves of absorption in both polarizations are slightly shifted into the visible light region due

to their narrowed band gaps of about 2.25 eV and 2.19 eV, respectively; these correspond to the absorption edges of 552 nm and 567 nm, respectively. After codoping SrTiO₃ with Te/Mn, the observed absorption edge lies in the IR domain with energy of 1.46 eV, corresponding to the wave length of 851 nm. Thus, the absorption has been shifted from the ultraviolet into the IR domain via visible light domain, which is due to the significant narrowing of band gap by the synergistic effect of tellurium and manganese. This means that the absorption of SrTiO₃ was extensively ameliorated by Te/Mn-codoping, and the created compound will be a promising photocatalyst under visible light irradiation.

6. Photocatalytic properties

Like in the previous chapter, to check the availability of codoped systems for photocatalytic water splitting, we calculated their CBMs and VBMs potentials using the formulas [158]:

$$E_{CBM} = -\frac{1}{2}E_g + \chi + E_0 \quad (5.3a)$$

$$E_{VBM} = +\frac{1}{2}E_g + \chi + E_0 \quad (5.3b)$$

Where $E_0 = -4.5$ eV for normal hydrogen electrode (NHE) designates the scale factor relating between the absolute vacuum scale and the reference electrode redox level, E_g denotes the band gap energy, χ indicates the absolute electronegativity of system calculated by the formulas:

$$\chi_{SrTiO_3} = (\chi_{Sr}\chi_{Ti}\chi_O^3)^{\frac{1}{5}} \quad (\text{pure SrTiO}_3) \quad (5.4a);$$

$$\chi_{SrTi_{1-x}Mn_xO_{3-y}Se_y} = (\chi_{Sr}\chi_{Ti}^{1-x}\chi_{Mn}^x\chi_O^{3-y}\chi_{Se}^y)^{\frac{1}{5}} \quad (\text{Se/Mn codoped SrTiO}_3) \quad (5.4b);$$

$$\chi_{SrTi_{1-x}Mn_xO_{3-y}Te_y} = (\chi_{Sr}\chi_{Ti}^{1-x}\chi_{Mn}^x\chi_O^{3-y}\chi_{Te}^y)^{\frac{1}{5}} \quad (\text{Te/Mn codoped SrTiO}_3) \quad (5.4c).$$

For S/Mn-codoped SrTiO₃, the CBM and VBM were obtained from the PDOS plots considering the relative shifts as compared to those of undoped SrTiO₃.

The absolute electronegativities [159] of different elements are presented in **table 5.5**

Table 5.5.

The absolute electronegativities of different constituent elements of studied systems.

Chemical element	Sr	Ti	O	Mn	Se	Te

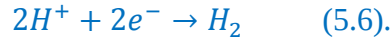
χ	1.75	3.05	8.92	4.33	5.91	5.35
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The calculated CBM and VBM potentials of pure, S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO₃ are displayed in **Fig. 5.9**. We remark that the VBM potential increases for all systems, while their CBM potentials decrease, which means that both photo-reduction ability and photo-oxidation ability are ameliorated for all these photocatalysts. So the S/Mn-, Se/Mn- and Te/Mn-codopings, are beneficial for improving the photocatalytic performance of SrTiO₃ under visible light illumination.

Besides, we remark in the figure that the VB holes (h^+_{VB}) in S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO₃ systems lay below the redox potential of O₂/H₂O; therefore, h^+_{VB} may react with H₂O to produce the oxygen gas, following the formula:



Besides, the reduction potential of the CB electrons (e^-_{CB}) for all these systems lay above the redox potential of H⁺/H₂, which means that the e^-_{CB} may react with H⁺ to form H₂ gas, following the formula:



It appears that the reduction of H⁺ and the oxidation process of H₂O occurred simultaneously which prevent the accumulation of holes in the valence band and thus reduce the undesirable e^-_{CB} - h^+_{VB} recombination phenomenon. Comparing these results with each other and with other previous results which aim to improve the photocatalytic performance of SrTiO₃ through doping, we can conclude that the band gap achieved by Te/Mn-codoping is an ideal result. Consequently, this system can be considered as promising for photocatalytic hydrogen production from water under visible light.

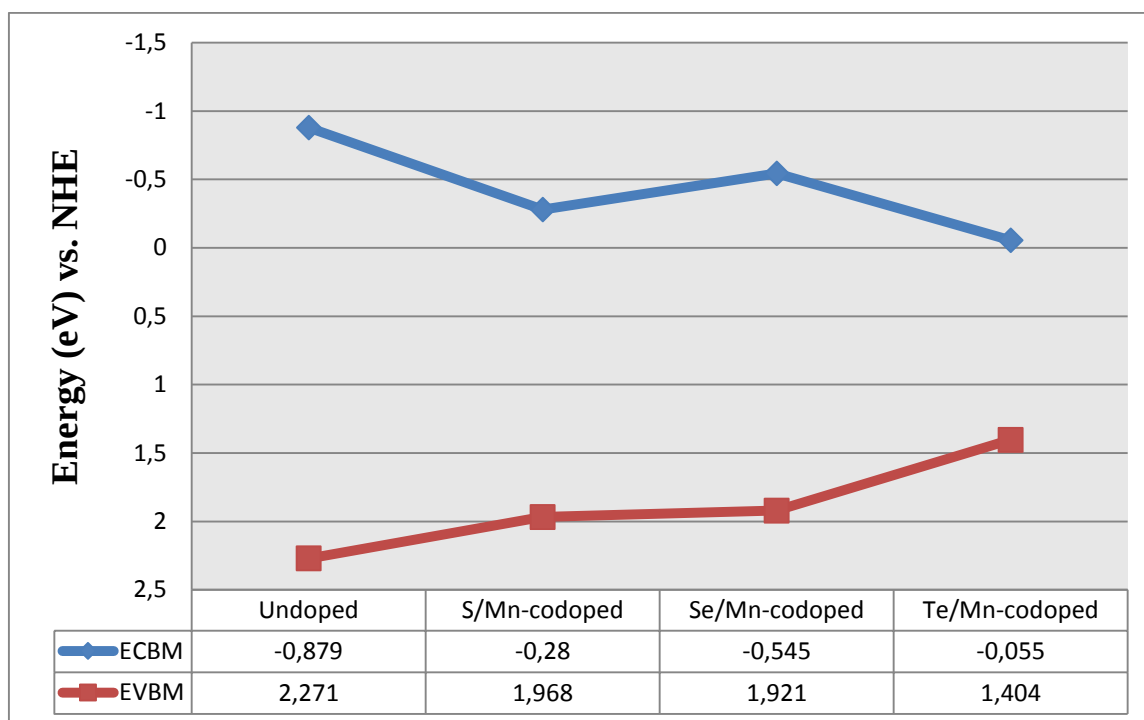


Fig. 5.9. The band alignment of the undoped, S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO₃.

7. Conclusion

We used DFT calculations to evaluate the stability, electronic, optical and photocatalytic properties of pure, S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO₃. We discussed the stability of all doping cases based on the computed formation energies, and explored the band structures, density of states and electronic density distributions of pure and doped systems. Besides, we analysed the optical and photocatalytic performance for all systems based on their absorption spectra, variations of imaginary part of dielectric function and band alignments. Our findings show that the narrowing of band gap, absorption spectrum shifting into the visible light region and the photocatalytic performance of SrTiO₃ is further improved in the case of Te/Mn-codoping.

Conclusions and perspectives

Abstract

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This last chapter is concerned with the conclusions and perspectives consisting of conclusions drawn from obtained results and perspectives for further work in the field of photocatalytic water splitting and hydrogen production.

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1. Conclusions

Photocatalytic hydrogen production from water under solar light irradiation is an attractive and appealing technology to generate green and renewable hydrogen fuel to reduce CO₂ emission and air pollution. Amongst semiconductor photocatalysts, strontium titanate (SrTiO₃) is particularly note worthy for its unique properties; however, its use for photocatalytic hydrogen generation is restricted due to its wide band gap; as it can only activated by ultraviolet (UV) light which represents 2-5% of sunlight. Consequently, it is imperative to investigate the photocatalytic production of H₂ using SrTiO₃, particularly, the modification of the optoelectronic properties of SrTiO₃ in order to improve its photoconversion efficiency in visible light region.

The electronic, optical and photocatalytic properties of SrTiO₃ can be improved through several approaches, among them, the doping of SrTiO₃ with foreign elements. Previous studies described in the Literature review have demonstrated the feasibility of using several chemical elements ions as potential dopants for UV or visible light induced photocatalysis. Subsequently, the monodopants, Mn, S, Se and Te, and codopants Mn/S, Mn/Se and Mn/Te codopants were chosen in this research to reduce the band gap; extending light absorption in the visible light range and diminishing the rate of charge recombination thus maximizing this process for better product yield.

This present work, placed within the field of photocatalytic production of hydrogen, represents the first theoretical study of these monodoped and codoped SrTiO₃ systems for photocatalytic H₂ production, with the aim of optimizing the performance under visible light irradiation. The summary of our results which concerned the defect formation energy calculation and presented in **Fig. 6.1.**, shows that the monodoped systems are not stable enough to growth under both O-rich and Ti-rich environment, except S-doped SrTiO₃ is stable under Ti-rich condition and Mn doped SrTiO₃ is stable under O-rich condition. By contrast, codoped systems show a simplicity to fabricate compared to monodoped compounds; we found that all codoped systems are easy feasible (negative defect formation energies) under O-rich condition and S/Mn-codoped SrTiO₃ is easy feasible under Ti-rich condition also; this can be explained by the synergistic effect of codopants which lead to the formation of charge compensated systems and facilitates the formation of Ti-vacancies and O-vacancies. Besides, these noticeable results obtained by codoping strategy, indicate to the utility of codoping in the synthesis of a promising photocatalytic materials for the hydrogen production.

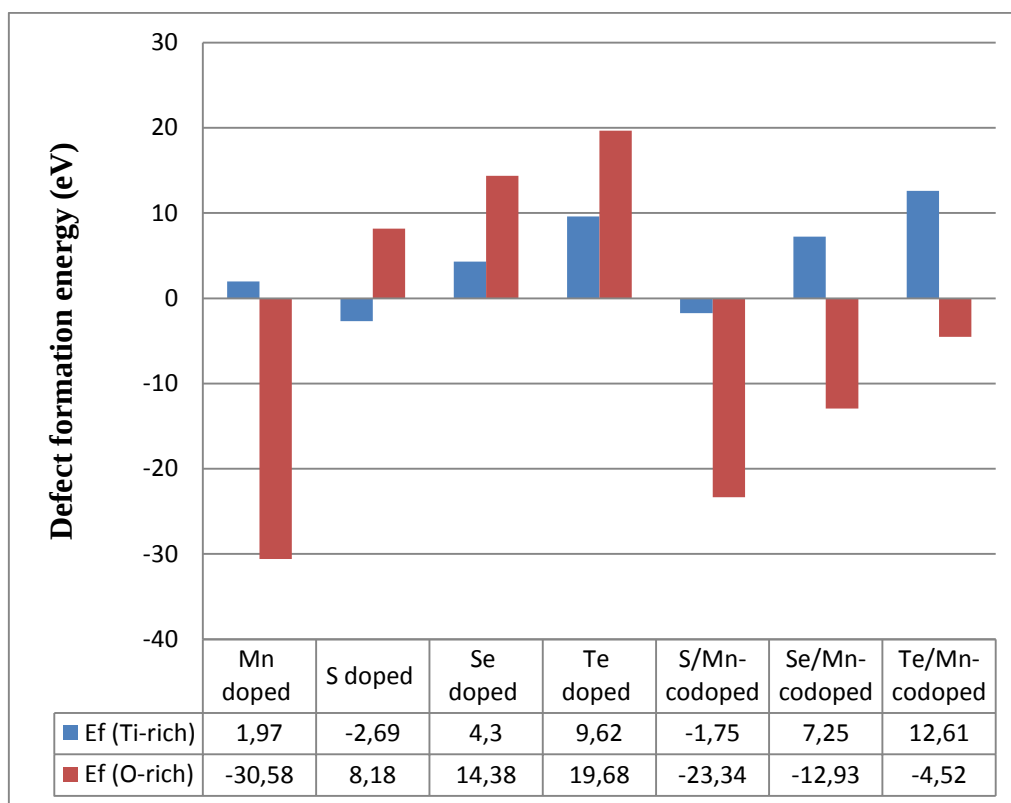


Fig. 6.1. Summary of defect formation energies of all studied monodoped and codoped SrTiO_3 systems (in unit of eV).

In other hand, All the studied Mn-monodoped, S-monodoped, Se-monodoped, Te-monodoped, S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO_3 systems exhibit in varying degree, narrow band gaps, visible light response and suitable band edges. Notably, Te doping into the crystal of SrTiO_3 presents the best results in monodoped systems. Moreover, codoping Te and Mn ions into SrTiO_3 in codoped systems results in an adequate band alignment and optimal electronic and optical properties; this can lead to an optimal solar hydrogen production from water using this material.

For the band gap narrowing resulted from monodoping and codoping the summary of our results is displayed in the **Fig. 6.2**.

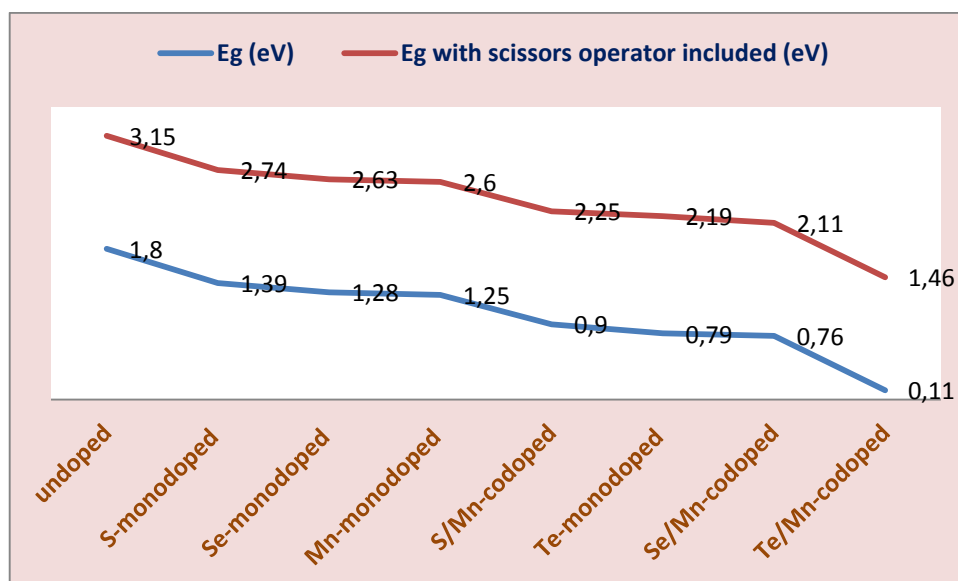


Fig. 6.2. Summary of band gap energies of all studied monodoped and codoped SrTiO_3 systems (in unit of eV).

One can observe that the single doping with Mn reduces the band gap of SrTiO_3 due to the contribution of Mn 3d states in both CB and VB, and that associating chalcogenide atoms (S, Se or Te) with Mn atoms into the SrTiO_3 exhibits a band gap reduction which is inversely proportional to the atomic number of utilized chalcogenide atom (See **Fig. 6.3.**). This result may be due to the progressive increase of energy of p states in the range of O, S, Se and Te atoms ($E_{(\text{Te } 5p)} > E_{(\text{Se } 4p)} > E_{(\text{S } 3p)}$), which increases the potential of VBM potential and decreases that of CBM.

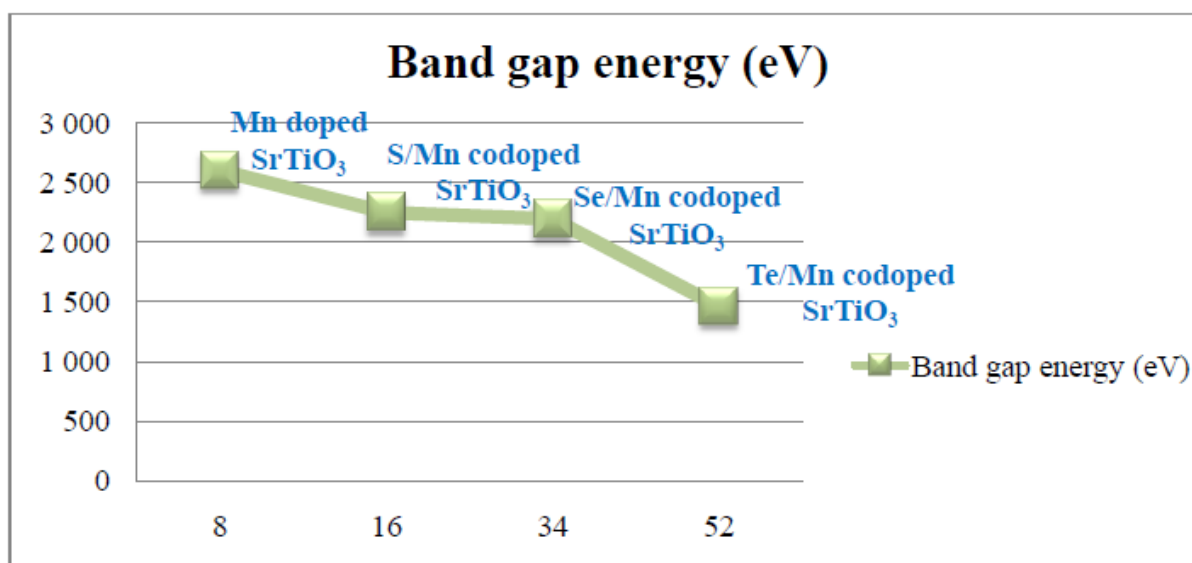


Fig. 6.3. Variation of band gap for SrTiO_3 through codoping with Mn in the Ti-site and chalcogenides (S, Se or Te) in O-site.

The decrease in the band gap of SrTiO_3 after doping leads to the observed red-shift and probably to an enhancement of photocatalytic performance. The corresponding absorption edges are summarized in **Table 6.1** and displayed in the **Fig. 6.4**.

Table 6.1

The absorption edges for calculated band gap of undoped, Mn-doped, S-doped, Se-doped, Te-doped, S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO_3 .

System	undoped	S-doped	Se-doped	Mn-doped	S/Mn-codoped	Te-doped	Se/Mn-codoped	Te/Mn-codoped
Absorption edge (nm)	393,97	452,92	471,86	477,31	551,56	566,67	588,15	850

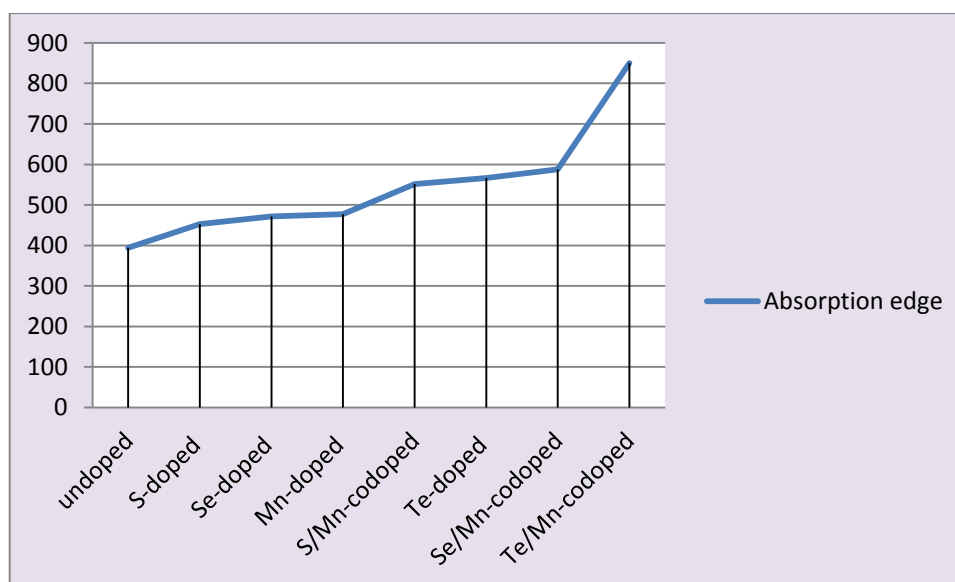


Fig. 6.4. The absorption edges for calculated band gap of undoped, Mn-doped, S-doped, Se-doped, Te-doped, S/Mn-codoped, Se/Mn-codoped and Te/Mn-codoped SrTiO_3

2. Perspectives

SrTiO_3 -based photocatalysts is among the most investigated wide band gap semiconductors. The method of introducing foreign elements in SrTiO_3 photocatalyst is largely utilized to induce visible light absorption and subsequently to enable photocatalytic activity. Nonetheless, very limited knowledge is available on the adverse effect of dopants on the photophysical properties of the compounds (e.g., if the benefit derived from dopant-induced visible light activity is outweighed by a loss of UV light activity). This should be

properly studied in the future. It requires specifying the dopants which induce visible light absorption, with preserving the others important properties of SrTiO_3 . On another hand, imagination and designing complex perovskites with appropriate elements at A and B sites through computational tools based on DFT are highly effective to create desired photocatalysts systems.

Besides, suppression of the recombination of the photogenerated electron/hole pairs is the key to all photocatalytic processes and is essential for charge survival. The promising ways to decrease the rate of charge recombination in SrTiO_3 include: i) heterojunction creation, which pushes the electrons and holes in opposite directions; ii) Z-scheme photocatalysis which involves a two-step photoexcitation and also prevents the recombination process and promotes charge separation as do heterojunctions; and iii) co-catalyst incorporation, which extracts electrons from the CB level of the photocatalyst. In addition, the reaction kinetics and molecular mechanisms must be considered carefully when further developing SrTiO_3 -based photocatalytic systems. Last but not least, SrTiO_3 has not yet been applied as commercial photocatalyst. Thus, in future, the researchers must give much interest to obtain more efficient SrTiO_3 to scale-up the laboratory studies and designing a robust and efficient photocatalytic system as a major future challenge.

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