

COMPARATIVE STUDY OF HYDROGEN EVOLUTION OVER PEROVSKITES AND
OTHER OXIDES

by

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There are no secret to success.
It is the result of preparation, hard work, and learning from failure.

Colin Powell

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ABSTRACT

COMPARATIVE STUDY OF HYDROGEN EVOLUTION OVER PEROVSKITES AND OTHER OXIDES

This study aims to compare the hydrogen evolution efficiency of photocatalysts based on titanate, tantalate, and niobium perovskite as well as some other oxides in 20% aqueous solution of various sacrificial agent. The solid-state reaction (SSR) method was used to prepare perovskites while nanopowder TiO_2 , Ta_2O_5 and Nb_2O_5 were used directly as purchased. 1 wt.% Pt cocatalyst was loaded on the samples by the incipient-to-wetness impregnation method; 0.2 wt.% Au, 1 wt.% Cu and 0.2 wt.% Au-0.8 wt.% Cu cocatalysts were also tested by loading them over TiO_2 via deposition precipitation with urea (DPU) and sequential-DPU (S-DPU) methods. The hydrogen production rate on Pt/SrTiO_3 under UV-VIS irradiation was much higher in D(+)-glucose monohydrate (GLU) ($136.2 \mu\text{mol/h.g}_{\text{cat}}$), methanol (MeOH) ($107.2 \mu\text{mol/h.g}_{\text{cat}}$), and ethylene glycol (EG) ($112.5 \mu\text{mol/h.g}_{\text{cat}}$) solutions but it decreased after a maximum. However, the hydrogen generation rate in formic acid (FA) ($54.8 \mu\text{mol/h.g}_{\text{cat}}$) and glycerol (GLY) ($14.6 \mu\text{mol/h.g}_{\text{cat}}$) solutions were more stable. Pt/TiO_2 was also tested in GLY solution, and the hydrogen production rate was found as $1146 \mu\text{mol/h.g}_{\text{cat}}$ indicating a better potential than SrTiO_3 . 0.2 wt.% Au/ TiO_2 catalyst also produced $1085.1 \mu\text{mol/h.g}_{\text{cat}}$ hydrogen even though Au loading is five times lower than Pt; furthermore, this catalyst also resulted in $201.4 \mu\text{mol/h.g}_{\text{cat}}$ hydrogen, which is still significant and much higher than Pt under visible light irradiation. The distribution and size of shiny spherical gold particles around 40-50 nm size on TiO_2 was observed by the scanning electron microscope (SEM) while the band gap energies were determined around 2.97 eV, which is quite close to TiO_2 , using UV-VIS spectroscopy by Kubelka-Munk method. X-ray diffraction (XRD) showed that mainly anatase phase exists in nanopowder TiO_2 while SrTiO_3 was mainly in the cubic crystal phase.

ÖZET

PEROVSKİT VE DİĞER OKSİTLERİN ÜZERİNDE HİDROJEN OLUŞUMUNUN KARŞILAŞTIRMALI ÇALIŞMASI

Bu çalışma, titanat, tantalat ve niyobyum perovskitlerini ve bazı diğer oksitleri temel alan fotokatalizörlerin çeşitli ayırıcı maddelerin %20 sulu çözeltisinde hidrojen üretim verimliliklerini karşılaştırmayı amaçlamaktadır. Perovskitleri hazırlamak için katı hal sentezi kullanılırken, nano formdaki TiO_2 , Ta_2O_5 , Nb_2O_5 satın alınıp direkt olarak kullanılmıştır. Ağırlıkça %1 Pt eş katalizörü örneklerin üzerine tam ıslak emdirme yöntemi ile eklenip, ağırlıkça %0.2 Au, %1 Cu ve %0.2 Au-%0.8 Cu eş katalizörleri ise TiO_2 üzerine tortu çökertme ve sıralı tortu çökertme yöntemleriyle eklenerek test edilmiştir. Ultraviyole-görünür ışık altında Pt/ SrTiO_3 'e ait hidrojen üretim D(+) glikoz monohidrat ($136.2 \mu\text{mol/h.g}_{\text{cat}}$), metanol ($107.2 \mu\text{mol/h.g}_{\text{cat}}$), etilen glikol ($112.5 \mu\text{mol/h.g}_{\text{cat}}$) çözeltilerinde oldukça yüksek iken, maksimum değerlerden sonra azalmıştır. Ancak formik asit ve gliserin çözeltilerindeki hidrojen üretim oranları daha stabildir. Ayrıca Pt/ TiO_2 , gliserin çözeltisinde test edilmiş ve $1146 \mu\text{mol/h.g}_{\text{cat}}$ hidrojen üretimi ile SrTiO_3 'den daha yüksek potansiyele sahip olduğunu göstermiştir. Ağırlıkça % 0.2 Au/ TiO_2 katalizörü, Au yükleme miktarı Pt'den beş katı kadar az olmasına rağmen $1085.1 \mu\text{mol/h.g}_{\text{cat}}$ hidrojen üretmiştir ve görünür ışık altında bile hidrojen üretimi, $201.4 \mu\text{mol/h.g}_{\text{cat}}$ ile ciddi sayılabilecek düzeyde ve Pt'den oldukça yüksek olmuştur. 40-50 nm civarında ki parlak ve küresel altın nano parçacıklarının TiO_2 üzerindeki dağılımı ve boyutu SEM ile incelenirken band aralık enerjileri Kubelka-Munk method yardımıyla UV-VIS spektroskopisinde yaklaşık olarak 2.97 eV bulunmuştur ki bu değer TiO_2 'nin band aralık değerine oldukça yakındır. XRD sonuçları, nano form TiO_2 için anatase fazının varlığını ve SrTiO_3 için kübik kristal fazın varlığını göstermiştir.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	iv
ABSTRACT.....	v
ÖZET	vi
TABLE OF CONTENTS.....	vii
LIST OF FIGURES	ix
LIST OF TABLES	xiii
LIST OF ACRONYMS/ABBREVIATIONS	xiv
LIST OF SYMBOLS	xvi
1. INTRODUCTION	1
2. LITERATURE SURVEY	5
2.1. Fundamentals of Photocatalytic Water Splitting.....	5
2.2. Photocatalysts used in Water Splitting Processes	10
2.3. Perovskite Photocatalysts.....	14
2.3.1. Titanate-Based Perovskites	17
2.3.2. Tantalate-Based Perovskites.....	20
2.3.3. Niobium-Based Perovskites	23
2.3.4. Other Perovskites.....	25
2.4. Preparation Methods of Catalysts	26
2.5. Sacrificial Reagents used in Photocatalytic Water Splitting Processes	30
2.6. The Effect of Dopants and Cocatalysts	33
3. EXPERIMENTAL WORK.....	43
3.1. Equipment and Chemicals.....	43
3.2. Catalyst Preparation	45
3.3. Catalyst Characterization	47

3.4. Experimental Set-up and Hydrogen Evolution Analysis	48
4. RESULTS AND DISCUSSION	50
4.1. Preliminary Experiments.....	50
4.2. The Effect of Catalyst Materials	52
4.3. The Effect of Sacrificial Reagents	54
4.4. The Effect of Cocatalyst and Irradiation.....	58
4.5. Characterization	60
5. CONCLUSION AND RECOMMENDATIONS	64
5.1. Conclusion.....	64
5.2. Recommendations	65
REFERENCES	66

LIST OF FIGURES

Figure 2.1. The photocatalytic water splitting reactions basis.....	6
Figure 2.2. Theoretically maximum solar-to-hydrogen (STH) efficiency and the photocurrent density of photoelectrodes to the band gap	8
Figure 2.3. The band gaps and band edge positions of commonly used semiconductors with respect to the vacuum level and the normal hydrogen electrode (NHE) at pH=0.....	9
Figure 2.4. Schematic illustrations of photocatalysts types: single material photocatalyst (a)-(b), heterojunction photocatalyst (c), and Z-scheme photocatalyst	11
Figure 2.5. Schema of type I, II, and III heterojunction photocatalysts (a) and Schema of partial contact and core-shell photocatalysts (b)	13
Figure 2.6. (a) Average hydrogen generation rates of commonly used perovskites depended on B-sites, and (b) depended on A-sites (solid depictions for ultraviolet (UV); dashed depictions for visible light)	15
Figure 2.7. General crystal structure of BaTiO ₃ perovskite (a), and Na ₂ Ta ₂ O ₆ double perovskite (b) (oxygen: red, A-site cation: green and purple, BO ₆ octahedra: grey and blue)	16
Figure 2.8. The simple titanate perovskites, their bandgaps and band edges against the redox potential of water splitting	18
Figure 2.9. The elements supplying visible light activity for the titanate-based perovskites	18

Figure 2.10. Crystal pattern for (a) LiTaO_3 , (b) NaTaO_3 and (c) KTaO_3	21
Figure 2.11. The monoclinic phase of NaTaO_3 for Ta–O–Ta bond angle (red:O, green: Na, and grey: Ta atoms)	22
Figure 2.12. A general structural illustration of alkali niobium-based perovskites.....	24
Figure 2.13. Frequently used perovskites preparation methods in terms of hydrogen production rates	27
Figure 2.14. Frequently used perovskites preparation methods in terms of surface area ...	28
Figure 2.15. Frequently used perovskites preparation methods in terms of band gap	28
Figure 2.16. Frequently used perovskites preparation methods in terms of crystal structure (A: amorphous, C: cubic, H: hexagonal, M: monoclinic, O: octahedral, Or: orthorhombic, P: polyhedron, R: rhombohedral, T: tetragonal)	29
Figure 2.17. The decomposition path way of glycerol on TiO_2 in a photocatalytic process	33
Figure 2.18. A schematic illustration of doped (a) and cocatalyst added (b) SrTiO_3 structure.....	34
Figure 2.19. The dopants enhance the hydrogen generation performance on TiO_2	36
Figure 2.20. Tuning band gap of widely used perovskites by various dopant elements	37
Figure 2.21. The illustration of localized surface plasmon resonance.....	41

Figure 3.1. The SSR method and cocatalyst loading steps.	46
Figure 3.2. The outside (a) and inside (b) of the photoreactor.	48
Figure 3.3. The overall experimental set-up.	49
Figure 4.1. Burned and stuck NaTiO_3 and $\text{Ca}_{0.01}\text{Na}_{0.49}\text{Ti}_{0.5}\text{O}_{1.255}$ samples in the crucible.	52
Figure 4.2. The hydrogen generation performance of 1 wt.% Pt loaded samples: Pt/SrTiO_3 , Pt/BaTiO_3 , Pt/KNbO_3 , $\text{Pt/Ta}_2\text{O}_5$ and $\text{Pt/Nb}_2\text{O}_5$ for 10 hours under UV-VIS light irradiation.	53
Figure 4.3. The effects of the sacrificial reagents on the hydrogen evolution performance of Pt/SrTiO_3 during 10 hours under UV-VIS light (MeOH: methanol, D.W.: distilled water, MIX: $\text{Na}_2\text{S}+\text{Na}_2\text{SO}_3$, EG: ethylene glycol, TEA: triethylamine, FA: formic acid, GLU: D(+)-glucose monohydrate, GLY: glycerol, and max. evolution rates were given with bold).	54
Figure 4.4. The hydrogen production performance of Pt/SrTiO_3 under UV-VIS light for 72 h stability test (the maximum H_2 production was given with bold).	56
Figure 4.5. The photocatalytic hydrogen generation performances of $\text{Pt/SrTi}_{0.9}\text{Cr}_{0.1}\text{O}_{3.1}$ both in FA and GLY (20 wt.%) solutions under UV-VIS light irradiation (the maximum rates were given by bold).	57
Figure 4.6. The hydrogen generation performance of Pt/TiO_2 under UV-VIS irradiation with GLY (20 wt.%) aqueous solution for 10 hours (the maximum rate was given by bold).	58

Figure 4.7. The effect of cocatalyst and irradiation on 0.2 wt.% Au/TiO ₂ , 1 wt.% Cu/TiO ₂ , and 0.2 wt.% Au-0.8 wt.% Cu/TiO ₂ under UV-VIS and VIS irradiation in GLY aqueous solution (the maximum rates were represented with bold).	59
Figure 4.8. SEM images of 0.2 wt.% Au/TiO ₂ in the range of 500 nm (a) and 2 μ m (b). .	61
Figure 4.9. $(F(R)h\nu)^2$ versus $h\nu$ for 0.2 wt.% Au/TiO ₂ , 1 wt.% Cu/TiO ₂ and 0.2wt.% Au-0.8 wt.% Cu/TiO ₂	62
Figure 4.10. XRD results of 1 wt.% Pt/TiO ₂ and 1 wt.% SrTiO ₃ photocatalysts.	63

LIST OF TABLES

Table 1.1. Percentage share of energy sources for the future	3
Table 3.1. Equipment used in the experiments.....	43
Table 3.2. Chemicals used in the experiments.....	44
Table 4.1. Variables and levels of Taguchi experimental design.	50
Table 4.2. Combinations of Taguchi experimental design	51
Table 4.3. The band gap energy of prepared photocatalysts.	62

LIST OF ACRONYMS/ABBREVIATIONS

CB	Conduction band
DPU	Deposition Precipitation with Urea
D.W.	Distillated Water
EG	Ethylene Glycol
ES	Electro-Spinning
FA	Formic Acid
GC	Gas Chromatography
GLU	D(+)-glucose monohydrate
GLY	Glycerol
HER	Hydrogen Evolution Reaction
HT	Hydrothermal
IE	Ion-Exchange
K	Molar Absorption Coefficient
LSPR	Localized Surface Plasmon Resonance
MeOH	Methanol
MIX	$\text{Na}_2\text{S}+\text{Na}_2\text{SO}_3$
MFC	Mass Flow Controller
NHE	Normal Hydrogen Electrode
OER	Oxygen Evolution Reaction
PC	Polymerized-Complex

PEC	Photoelectrochemical
PTP	Pechini-Type Process
PWS	Photocatalytic Water Splitting
QY	Quantum Yield
R	Diffuse Reflectance
S	Scattering Factor
S-DPU	Sequential Deposition Precipitation with Urea
SEM	Scanning Electron Microscope
SG	Sol-gel
SSR	Solid-State Reaction
STH	Solar-to-Hydrogen-Energy
TEA	Triethylamine
UV	Ultraviolet
UV-VIS	Ultraviolet-Visible
VB	Valence band
VIS	Visible
TWh	Tetrawatt hours
XRD	X-Ray Diffraction

LIST OF SYMBOLS

ΔG	Gibbs Free Energy
e^-	Electron
E_g	Band Gap Energy, eV
h	Planck's constant, eV.s
h^+	Holes
P	Power, mW/cm ²
$rate$	Rate of Generated Hydrogen ($\mu\text{mol/h.g}_{\text{cat}}$)
ϑ	Frequency, 1/s

1. INTRODUCTION

Currently, the energy requirement for 7.7 billion people in the world is about 25,000 terawatt hours (TWh), and this is expected to grow up by another 10,000 TWh in next 30 years. This continuously rising demand creates new challenges like global warming and climate change due to the emission of greenhouse gases (Coyne and Li, 2018), and causes worldwide increase in researches for the alternative and sustainable energy production processes from the renewable natural resources such as solar, wind, geothermal and tidal wave (Desai, 2019; Kalyanasundaram, 2010).

The solar light is the largest renewable energy resource and is the origin of the power sources like wind, sea-wave, hydraulic power, biomass, and fossil fuels. The total amount of solar energy irradiated on the earth per hour is almost equivalent to the total amount of energy consumed by human per year. Thus, the development of innovative technologies for solar energy conversion and storage is vital to solve the energy scarcity problem of the World (Miseki and Sayama, 2018; Morton, 2006). Moreover, the solar energy can be also used to produce hydrogen from water, and further contribute to a sustainable society; the abundance of sunlight and water are great assets to support the generation of hydrogen, which may be used in vehicles, spacecraft propulsion, aircrafts, other electric devices and chemical industry (Tada and Naya, 2018; Basher and Ali, 2019).

Hydrogen is an excellent and clean energy carrier and may be generated from water, hydrocarbons, and other organic matters (Saadetnejad and Yildirim, 2018). Currently, hydrogen is produced from oil (18%), natural gas (48%), coal (11%) and water electrolysis (4%) (Gupta and Rao, 2017). The catalytic reforming of methane (CH_4) and other hydrocarbons are the major source of hydrogen production but it has severe disadvantages (Tao *et al.*, 2017; Tao *et al.*, 2010). The major disadvantages of these processes include the poor yield, high cost and severe pollution to the environment. On the other hand, the production of hydrogen from water using sunlight is potentially inexpensive, pollution-free and it can be done using technologies like photocatalytic water splitting (PWS) (Saadetnejad and Yildirim, 2018; Gupta and Rao, 2017).

Water can be split into hydrogen and oxygen using various methods including photo-electrochemical (PEC) (Bu and Ao, 2017), photocatalytic (Maeda and Domen, 2010), radiolysis (Cecal *et al.*, 2003), photo-biological (Akkerman, 2002) methods and thermal decomposition (Lede, 1983). In PEC water splitting, solar energy is converted into chemical energy as hydrogen via dipped semiconductors in a water-based electrolyte (United States Department of Energy, 2020). In the case of PWS, powdered semiconductors either in suspensions in water or some other solvent is illuminated and then redox reactions occur to generate hydrogen and oxygen via electron excitation from the valence band to the conductance band (Idriss, 2020; Gratzel, 1983).

The radiolysis (chemo-nuclear water splitting) exploits nuclear radiation or kinetic energy of fission products for exciting and splitting the water molecules into hydrogen and oxygen. However, the requirement of containment of the reactive material makes the radiolysis an unpractical way in current reactors (Naterer *et al.*, 2013). Photo-biological processes benefit from microorganisms to conduct the water splitting reaction by the generation of oxygen and hydrogen using sunlight. Low hydrogen and oxygen production rate are the main drawbacks of this process due to easily inhibition of the hydrogen evolution reaction (HER) by oxygen and it is unsafe due to the probability of having the explosive mixture of oxygen and hydrogen gaseous.

In the thermal decomposition pathway, the hydrogen is released from the different resources molecules such as coal, natural gas, and biomass. Moreover, hydrogen can be generated from feedstock like water through heat produced in closed-chemical cycles. High production cost and handicaps for environment standout as the basic disadvantage of thermal decomposition processes (United States Department of Energy, 2020). Consequently, among these processes, the photocatalytic water splitting can be considered as the best one as an efficient, green and inexpensive process with the ease of operation.

Table 1.1. Percentage share of energy sources for the future. (Balat and Kırtay, 2010).

Source of Energy	1998	2025	2050
Fossil fuels	88	62	29
Nuclear energy	10	2	2
Hydrogen from solar energy	-	7	31
Electricity from solar energy	-	11	16
Heat from solar energy	-	18	22
Energy from solar energy	2	25	35
Hydrogen	-	11	34

As for the future expectation of energy sources, it demonstrates that hydrogen energy generated from solar energy can replace today's commercial energy production alternatives. As shown in Table 1.1, the shares of hydrogen, both from solar energy and other methods are expected to grow to 18% in 2025 and 65% in 2050. Even the 31% share of hydrogen from solar energy is a highly promising alternative by itself compared to the other energy sources (Balat and Kırtay, 2010). Thus, the hydrogen from solar energy by photocatalytic water splitting with the help of its inexpensive and ease operation condition can be good candidate to contribute to the fulfillment of the energy demand of future.

Various Ti-based catalysts such as TiO_2 , SrTiO_3 , NaTiO_3 , KTiO_3 (Yoshida *et al.*, 2014), LaTiO_3 (Lu *et al.*, 2017), BaTiO_3 (Xie *et al.*, 2019), BiTiO_3 , (Wang and Wang, 2012), CaTiO_3 (Yang *et al.*, 2018), FeTiO_3 (Seo *et al.*, 2017), MgTiO_3 (Li *et al.*, 2012), MnTiO_3 , (Zhu *et al.*, 2015) have been used for this purpose in PWS applications. Similarly Ta-based catalysts like Ta_2O_5 , NaTaO_3 (Sfirloaga *et al.*, 2015), KTaO_3 (Chen *et al.*, 2007), LaTaO_3 (Wu *et al.*, 2010), BiTaO_3 (Chen *et al.*, 2008), LiTaO_3 (Gonzalez *et al.*, 2003) as well as the Nb-based alternatives like Nb_2O_5 , NaNbO_3 , KNbO_3 (Goh *et al.*, 2003), BiNbO_3 , (Chen *et al.*, 2010), KNbO_3 , AgNbO_3 (Ye *et al.*, 2009), LiNbO_3 (Yui and Liu, 2007), LaNbO_3 (Wei *et al.*, 2009) have been also utilized. However, TiO_2 (especially its nano forms) and SrTiO_3 have been widely investigated due to their thermal and chemical stability, super hydrophilicity, low toxicity, and natural geologic abundance. In addition to water splitting to yield H_2 , these catalysts have been also used in many solar energy related field such as wastewater treatment, photodegradation of pollutants and hazardous

materials, artificial photosynthesis (Wu and Overburg, 2015; Gao *et al.*, 2015; Tan *et al.*, 2019).

However, the poor absorption under visible light, fast recombination of electron–hole and the slow transfer kinetics of the charge carriers to the media highly reduce the photocatalytic activities of TiO₂-based catalysts. Therefore, researchers have been tried to cope with these problems with various solutions like the use of cocatalyst for reducing the recombination of electron–hole pair, doping to improve the optical absorption properties of semiconductor, and the construction of heterogeneous junctions (Suligoj *et al.*, 2018; Tan *et al.*, 2019). Additionally, various sacrificial reagents such as methanol (MeOH), lactic acid, isopropanol, oxalic acid, sodium sulfide (Na₂S), sodium sulfite (Na₂SO₃), ethylene glycol (EG), glycerol (GLY), triethylamine (TEA), formic acid (FA), glucose or as directly waste water can be used for improving these ineffectual conditions (Marotta *et al.*, 2014; Ortiz *et al.*, 2019; Tahir and Fajrina, 2019). Nevertheless, the performance of photocatalytic water splitting is not yet sufficiently high for commercialization.

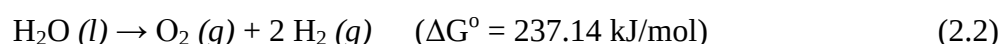
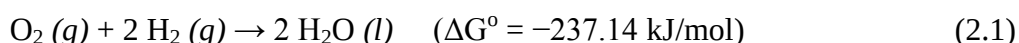
The aim of this thesis is to investigate and compare various perovskite photocatalysts compositions that are suitable for photocatalytic water splitting reaction to produce hydrogen. At the same time, different sacrificial reagents were also tested to improve the efficiency of PWS. For this, the photocatalysts such as TiO₂, Ta₂O₅, Nb₂O₅ were used directly while ATiO₃, ATaO₃, and ANbO₃ (A represent various elements) were also prepared by solid-state reaction, under several temperature, A/B ratios, dopants were prepared and tested under various conditions such as various sacrificial reagents-aqueous mixtures, cocatalyst, and lighting conditions.

Following chapters respectively contain the literature survey to comprehend the present status of photochemical water splitting (Chapter 2), experimental methods and procedures used in this work (Chapter 3), and the presentation and discussion of the results obtained under the light of previous works (Chapter 4); finally, the conclusions are summarized with some recommendations for future work (Chapter 5).

2. LITERATURE SURVEY

2.1. Fundamentals of Photocatalytic Water Splitting

Water and sunlight are the most plentiful, pure, sustainable and natural resources of energy on the face of the earth. Conversion of them to hydrogen has been defined as an ideal way toward the solution of environmental problems related to the use of fossil fuels (Ahmad *et al.*, 2015). Hydrogen production via water splitting, with TiO_2 as the photocatalyst in a photoelectrochemical cell, was first reported by Fujishima and Honda in 1972 (Fujishima and Honda, 1972). Water splitting for the generating of hydrogen and oxygen on a semiconductor catalyst is a promising method to turn sunlight into pure and renewable energy forms. However, this process needs considerably high energy to proceed. Gibbs free energy (ΔG) of the water decomposition is equal to 237.2 kJ/mol at 293 K and it is positive; thus, the water splitting process has not a self-generated reaction and this creates a problem in terms of thermodynamics (Phoon *et al.*, 2019; Navarro *et al.*, 2009).



The required energy identified by the Nernst equation is equal to 1.23 eV for water splitting into hydrogen and oxygen. Because of this, semiconductors should absorb at least 1.23 eV energy from the photon, in theory, to stimulate the reaction (Kment *et al.*, 2017). The energy at the range between 1.6-1.8 eV is required to be able to split water naturally owing to possible energy losses (Choudhary *et al.*, 2012; Ahmad *et al.*, 2015). For this reason, to conduct the water splitting process naturally, the semiconductors having band gap energy in the range of 1.6-2.2 eV have the potential of being the favorable catalysts.

The basis of photocatalytic water splitting reactions is given in Figure 2.1 (Ahmad *et al.*, 2015). Basically, the photocatalytic water splitting reaction works according to the

following mechanism: a semiconducting material absorbs light, and its electrons from the valence band (VB) are excited and promoted to the conduction band (CB) creating holes in the valence band (VB) and generating hole/electron pair (h^+/e^-). By the action of this pair (h^+/e^-), the water molecule will be oxidized and reduced to oxygen and hydrogen, respectively (Suarez-Quezada *et al.*, 2019).

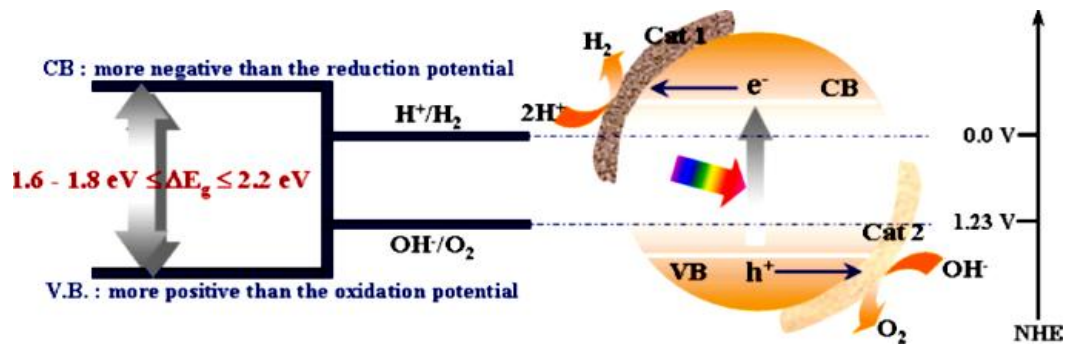
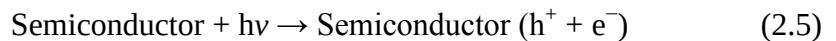
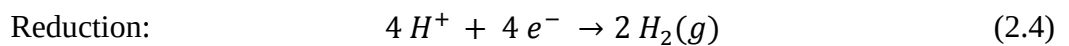
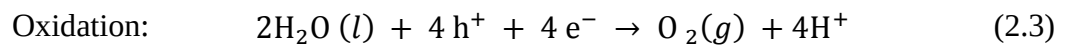


Figure 2.1. The photocatalytic water splitting reactions basis (Ahmad *et al.*, 2015).

In this process, the oxidative (oxygen evolution reaction – OER) and reductive (hydrogen evolution reaction – HER) reactions (redox reactions) take place concurrently (2.1 and 2.2) with the utilization of solar light; the semiconductor absorbs the light; generate free electron (e^-) and a hole (h^+) as in (2.3) to initiate the reactions (Nguyen *et al.*, 2003). This artificial way to promote the water splitting reaction is assisted by semiconductor materials and catalysts (photocatalysts) (Phoon *et al.*, 2019).



The efficiency of the system can be described by solar-to-hydrogen energy conversion energy (STH). As it can be seen in the Equation 2.6, STH formulation consists of division of output energy of hydrogen evolved by energy of incident solar light. Here P

is equal to energy density of incident sunlight while the area represents the area irradiated by the sunlight (Ipek and Uner, 2019; Yuan *et al.*, 2016).

$$STH = \left[\frac{rate \left(\frac{\text{mmol H}_2}{s} \right) \times 237\,000 \frac{\text{J}}{\text{mol}}}{P \left(\frac{\text{mW}}{\text{cm}^2} \right) \times Area \text{ (cm}^2\text{)}} \right] \quad (2.6)$$

In addition to this, the hydrogen generation rate (rate), and quantum yield (QY) are also important to qualify of the efficiency of the hydrogen production (Yuan *et al.*, 2016).

$$rate = \left[\frac{n \text{ (mole of H}_2 \text{ or O}_2\text{)}}{t \text{ (time)} \times m \text{ (catalyst)}} \right]_{\text{catalyst based}} \quad (2.7)$$

$$QY \text{ (\%)} = \left[\frac{\text{number of reacted electrons}}{\text{number of absorbed electrons}} * 100 \right] \quad (2.8)$$

The suitable light absorption range, the effective charge separation, migration and transfer to the electrolyte for redox reactions should be provided by the materials used for photocatalysts or photoelectrodes so that the higher water splitting efficiency can be obtained. Hence, these are the points that should be taken into consideration for choosing desired semiconductors with high water splitting performance as well.

The first requirement is to have a material with suitable light absorption range. The maximum STH efficiency is defined theoretically in Figure 2.2 via the band gap of semiconductors. To get high a STH efficiency, the semiconductor should absorb the sunlight with a small band gap but in wide spectra range. If semiconductors are categorized according to band gap size, the ones having large band gap like WO₃, ZnO, SnO₂, Ta₂O₅, BaTiO₃, SrTiO₃, TiO₂, and so on, can be considered as suitable for the ultraviolet (UV) region of the solar light. On the other hand, the semiconductors with intermediate band gap such as BiVO₄, BiFeO₃, Fe₂O₃ can absorb visible region of the solar light; however, they have poor charge carrier rates. As for the optimum band gap semiconductors like GaAs, CdTe, Si, CdSe, CuO, Cu₂O, the corrosion is a serious problem (Mishra *et al.*, 2003; Berardi *et al.*, 2014; Yoon *et al.*, 2000).

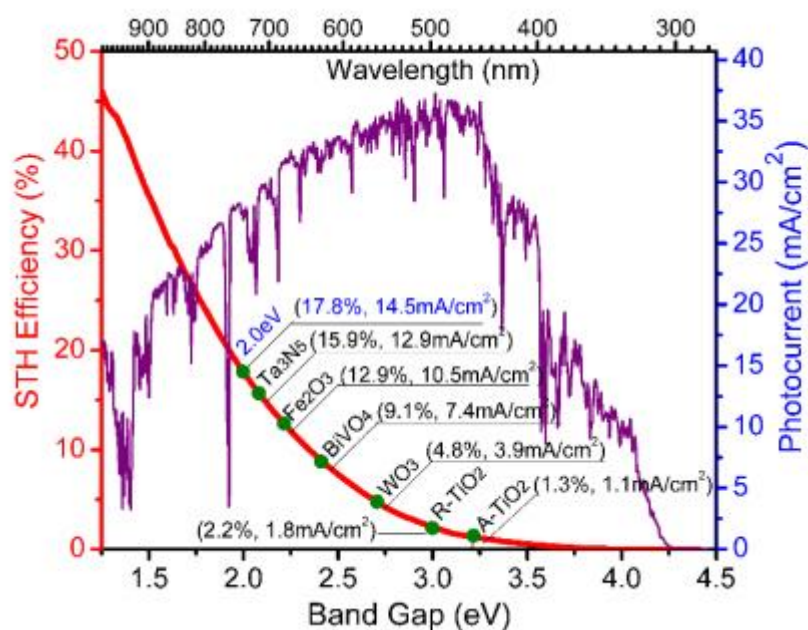


Figure 2.2. Theoretically maximum solar-to-hydrogen (STH) efficiency and the photocurrent density of photoelectrodes to the band gap (Wu and Li, 2015).

As the second point, the effective charge separation has a significant role in solar water splitting; a major loss of STH efficiency may occur in the event of the charge recombination. Moreover, if the redox potentials of the semiconductor are between the redox potentials of water splitting, the semiconductor oxidizes or reduces itself due to decomposition that the holes or the electrons (Schoonen and Xu, 2000; Hisatomi *et al.*, 2014).

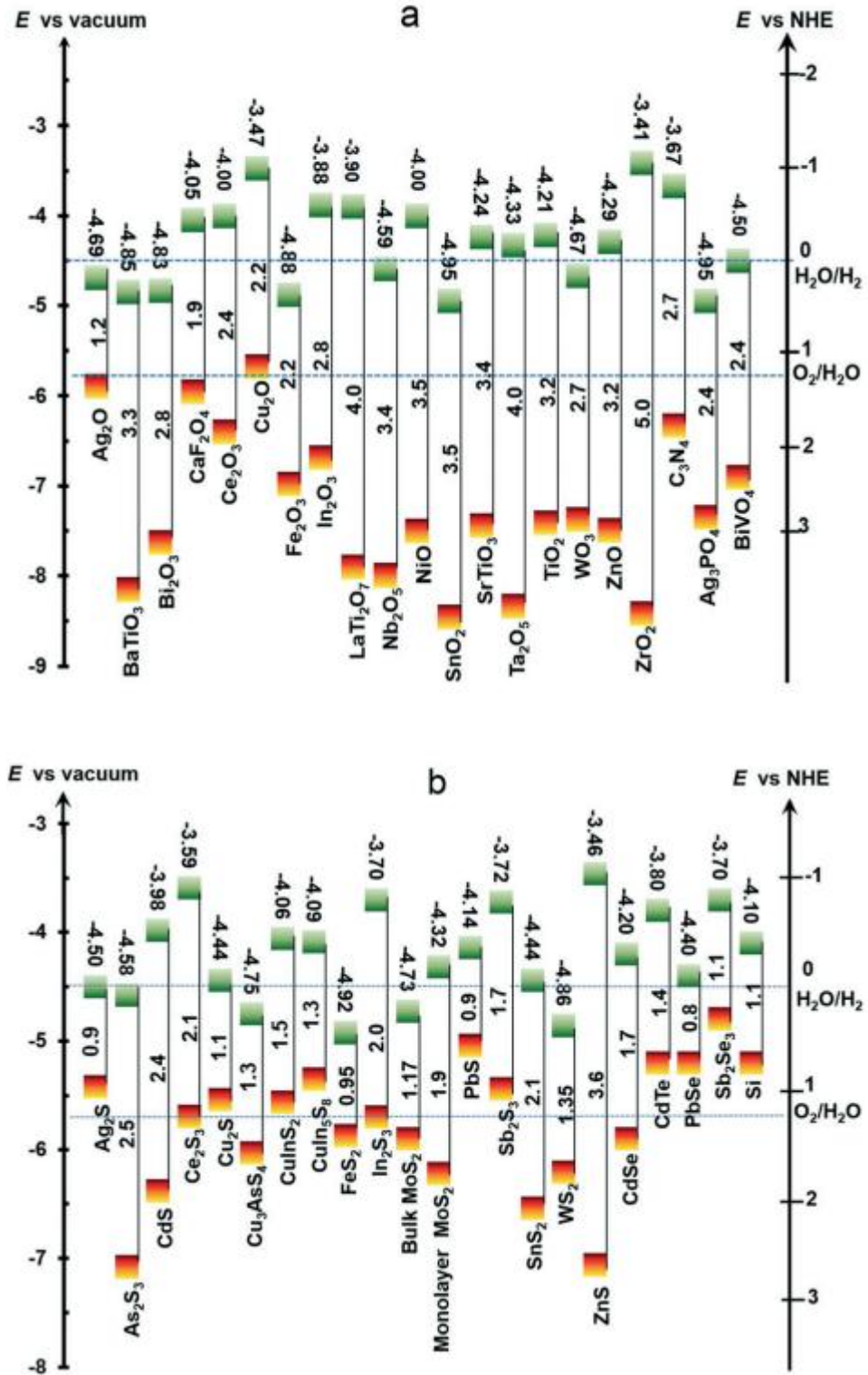


Figure 2.3. The band gaps and band edge positions of commonly used semiconductors with respect to the vacuum level and the normal hydrogen electrode (NHE) at pH=0 ((a)

Chen *et al.*, 2012; (b) Chen and Wang, 2012).

In Figure 2.3, the CB and VB edges of the semiconductors at pH=0 are represented by the green-top squares and the red-yellow-bottom squares respectively. The numbers at the top are the exact conduction band level while the number between the squares presents the band gap. The two dashed lines show the water redox reaction potentials. (Wu and Li, 2015; Schoonen and Xu, 2000).

SrTiO₃ can be a fair example to understand process easily. The CB and VB squares of SrTiO₃ are out of the redox potential of water. Thus, thermodynamically, SrTiO₃ tends to do the reduction and oxidation of water rather than the reduction or oxidation itself. Ag₂S, on the other hand has narrower band gap as can be seen easily in Figure 2.3; it has a reduction and oxidation potential values lower than the water splitting redox potential. Therefore, Ag₂S decomposes itself instead of the water during the redox reaction.

As for the last point, high charge mobility and long charge carrier diffusion length should be taking into account. The charge recombination is responsible for a major loss of the solar energy conversion efficiency. High charge mobility and long charge carrier diffusion length are demanded to ensure a low charge recombination rate.

Alongside these points, strong catalytic activity to reduce the over potential, good stability in the electrolyte in terms of chemical, electrochemical, and photoelectrochemical properties as well as the sustainability and low cost to supply green processes are the other important issues for desired semiconductor materials (Wu and Li, 2015).

2.2. Photocatalysts used in Water Splitting Processes

To efficiently convert solar energy by a photocatalyst, the photocatalyst should possess suitable band gap first to provide both effectual light absorption and suitable CB and VB levels for water-splitting redox reactions. Second, the catalysts should be suitable for the separation and transfer of photogenerated charges, (Li and Li, 2017). In photocatalysis, the charge separation and recombination are reversible processes. The recombination of photoexcited charges takes place at a very fast timescale (ps–μs). Therefore, during the water splitting process, the redox reactions on the surface of the catalyst have to be conducted within the lifetimes of photoexcited charges (Hisatomi *et al.*,

2014). Powerful separation and effective transfer of photogenerated charges are essential for PWS. Third, the surface active sites should capture the electrons and holes quickly; since the surface reaction usually occurs at the larger timescale (μs – s), it is vital boost them in the construction of an efficient photocatalyst system (Li and Li, 2017).

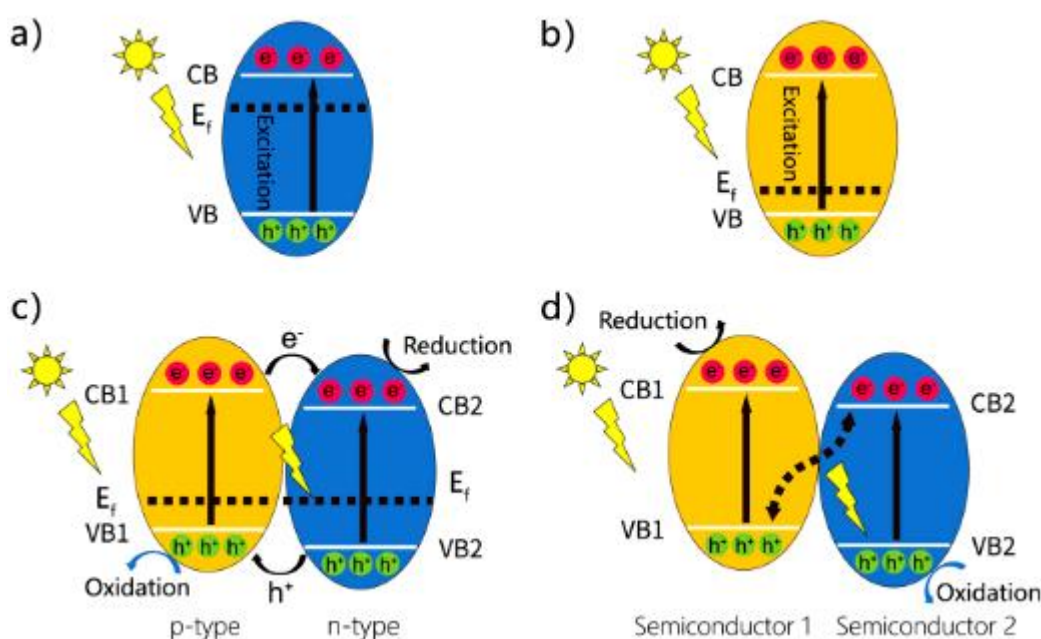


Figure 2.4. Schematic illustrations of photocatalysts types: single material photocatalyst (a)-(b), heterojunction photocatalyst (c), and Z-scheme photocatalyst (d) (Djurisic *et al.*, 2020).

Several photocatalysts have been demonstrated to be active under ultraviolet (UV) or visible (VIS) light irradiation for photocatalytic water splitting. On the basis of the junction type, photocatalysts can be classified into two main groups: one is the single material photocatalysts and the other is semiconductor-heterojunction photocatalysts (binary or more junction including Z-scheme systems) (Pawar and Lee, 2015). Basic illustrations of single material photocatalyst, semiconductor-heterojunction photocatalyst and Z-scheme photocatalyst are given in Figure 2.4.

Single material photocatalysts, like n-type and p-type semiconductors, have been used in various applications such as hydrogen production and CO_2 reduction. Even if this

type photocatalysts are one of the first studied catalysts among the other photocatalysts, they require further improvement to reach higher efficiencies because they suffer from many difficulties like concurrently suitable energy band lines, reaching narrow bandgap, and low recombination losses in a single material. Nonetheless, these difficulties can be resolved with the help of some strategies. These are arrangement and utilization of native defect, the addition of dopants to adjust the optical and electronic properties, the control and design of morphology, surface area, and crystal structure and the use of sensitizers like organic dyes or metal complexes to improve the light absorption (Kumar and Rao, 2017; Vyas *et al.*, 2016; Dhakshinamoorthy *et al.*, 2016; Djuricic *et al.*, 2020).

As for heterojunction photocatalysts, they can be composed in metal–semiconductor or semiconductor–semiconductor and classified as type I, type II, and type III according to energy band alignments, as depicted in Figure 2.5. On the other hand, as related to the material morphology of them, heterojunction photocatalysts can be also categorized like partial contact photocatalysts or core-shell photocatalysts. At the interface, the band gap alignment is an essential in the efficient heterojunction photocatalyst design (Behera *et al.*, 2019) because, when two materials contact each other, the band edge alignment is affected considerably by interface characteristics such as the defects and surface dipoles. In addition to this, the particle size, the arrangements of these particles and facet dependence highly dominate the band alignment and band bending (Uddin *et al.*, 2017). Especially, facet supplies the charge transport between different contacting surfaces and improves photocatalytic activity (Huang and Madasu, 2019).

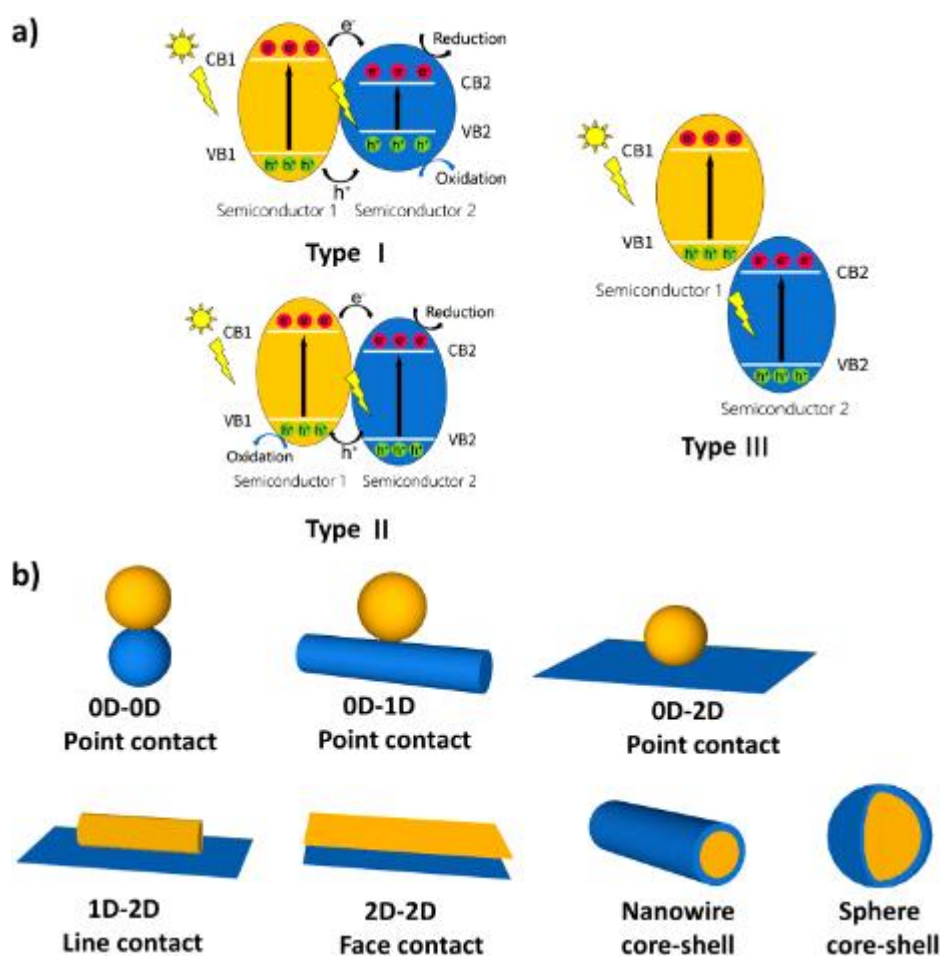


Figure 2.5. Schema of type I, II, and III heterojunction photocatalysts (a) and Schema of partial contact and core-shell photocatalysts (b) (Djurisic *et al.*, 2020).

When two semiconductor photocatalysts contact partially, this connection type can be named, on basis of the morphology, as point contact for one of them having nanoparticles structure, line contact for nanowire/ribbon/sheet type photocatalysts, and face contact for both of two dimensional photocatalysts (Low *et al.*, 2017). Several common heterojunction photocatalysts can be counted, like $\text{Ag}_2\text{O}/\text{Bi}_5\text{O}_7\text{I}$ (Chen *et al.*, 2018), CdS/MoS_2 (Han *et al.*, 2017), $\text{CeO}_2\text{—AgI}$ (Li *et al.*, 2019), $p\text{-CaFe}_2\text{O}_4/n\text{-ZnFe}_2\text{O}_4$ (Behera *et al.*, 2019), $\text{NiO}/g\text{-C}_3\text{N}_4$ (Liu *et al.*, 2018), $g\text{-C}_3\text{N}_4/\text{ZnIn}_2\text{S}_4$ (Lin *et al.*, 2018), $g\text{-C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$ (Wang *et al.*, 2017), $\text{In}_2\text{S}_3/\text{CdIn}_2\text{S}_4$ nanotubes (Wang *et al.*, 2017), amorphous $\text{ZnS}/g\text{-C}_3\text{N}_4$ (Hao *et al.*, 2018), $\text{ZnIn}_2\text{S}_4\text{—In}_2\text{O}_3$ (Wang *et al.*, 2018), $g\text{-C}_3\text{N}_4/\text{phosphorene}$ (Ran *et al.*, 2018).

Heterojunctions generally are better than single material photocatalysts in terms of the performance issues but this is not enough to improve the light absorption and charge carrier separation. Thus, researchers benefit from Z-scheme heterojunctions and plasmonic photocatalysts. The mechanism of a Z-scheme photocatalyst, as depicted in Figure 2.4 works on the basis of the creation of a wider energy level rather a heterojunction photocatalysts, of which one catalyst's oxidation value to another's reduction value (Jiang *et al.*, 2018). By this way, a Z-scheme photocatalyst can provide a theoretical maximum solar energy conversion efficiency up to 40% for water splitting processes. This is ~10% higher than single photocatalysts efficiency (Wang *et al.*, 2018).

The Z-scheme photocatalysts are divided into three types. First are the liquid Z-scheme systems; a reversible redox mediator in solution is commonly used for this type. Second is the solid-state Z-scheme catalysts, which are preferred more because of some difficulties of the liquid Z-scheme system such as low pH tolerance, light harvesting issues, and backward reactions. The solid-state Z-scheme photocatalysts have metal or carbon based conductors, and these conductors in the system act like electron mediators (Jiang *et al.*, 2018). Finally, in a direct Z-scheme heterojunction, the main goal is to build a wider difference between lower VB minimum position (oxidation) and higher CB minimum position (reduction) energy levels. In this way, developed redox ability can be supplied for the system (Xu *et al.*, 2018).

2.3. Perovskite Photocatalysts

The perovskites are the metal oxides that are symbolized in the basic formula of ABX_3 . In this formula, the large and small cation is represented by A and B in turn, while X is an anion and commonly identified with oxygen or sometimes halogens. Due to the easier side of the B-site classification, the perovskites are generally categorized with the help of B-sites elements in perovskites structure (Can and Yıldırım, 2019; Kanhere and Chen, 2014). Commonly used perovskites based on B-sites and A-sites are presented respectively in Figure 2.6.a and Figure 2.6.b according to their average hydrogen generation performance and frequency (with the bubble size) in the literature (Can and Yıldırım, 2019).

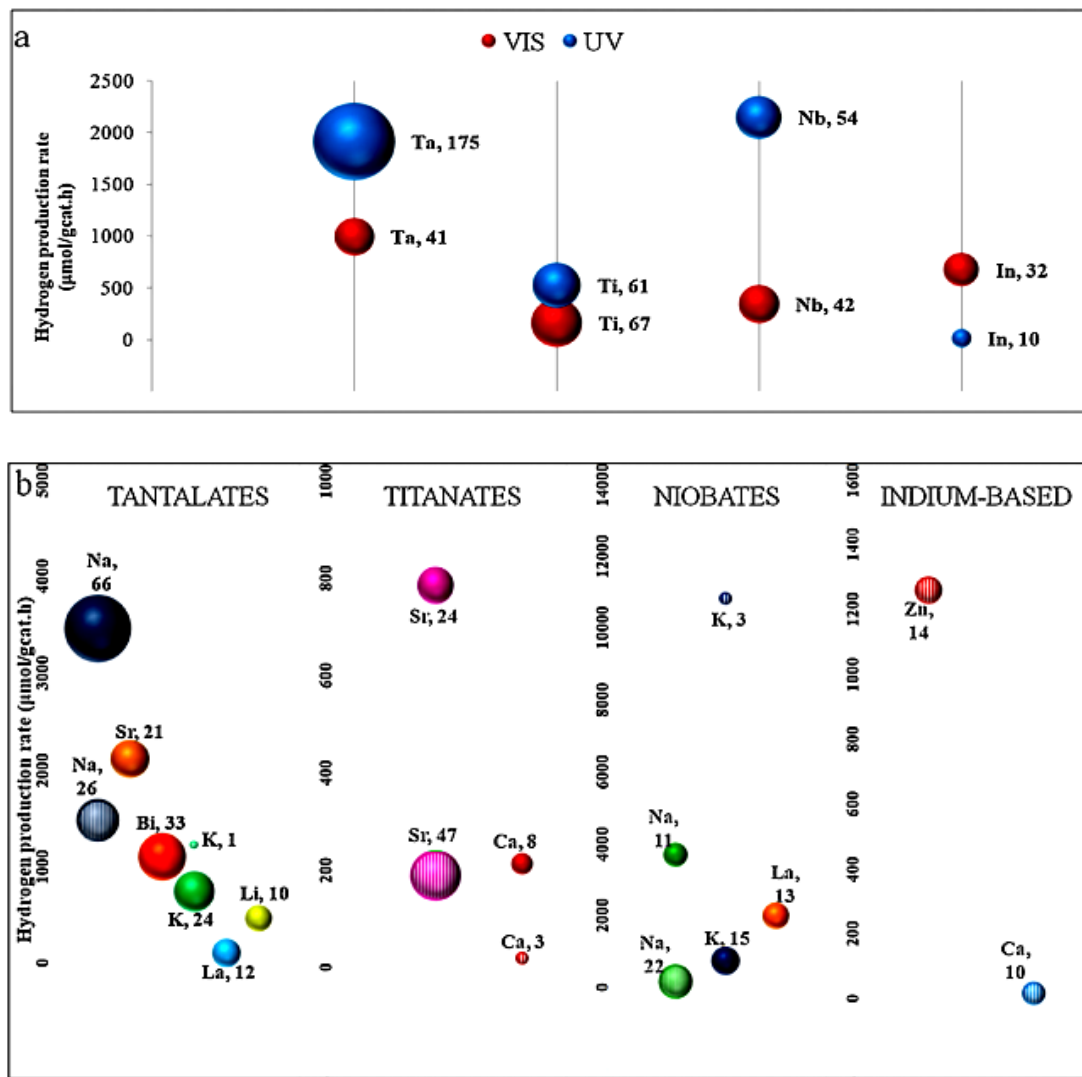


Figure 2.6. (a) Average hydrogen generation rates of commonly used perovskites depended on B-sites, and (b) depended on A-sites (solid depictions for ultraviolet (UV); dashed depictions for visible light) (Can and Yildirim, 2019).

The perovskite are used in many applications due to their numerous properties depending on the structure like the piezoelectric features of BaTiO_3 , PbZrO_3 , PbTiO_3 (Damjanovic, 2001; Bhalla *et. al.*, 2000), the multiferroic behavior of BiFeO_3 thin films, and great performance of SrTiO_3 on photocatalysis, (Kanhere and Chen, 2014). As it can be seen in Figure 2.7, the crystal structure of the perovskite consists of corner junction of BO_6 octahedra and 12 oxygen connected A cations, stayed in between the eight BO_6 octahedra. In fact that, a cubic lattice is expected to owe to the perfect structure of the octahedral connection, but the tilting of the octahedra occurs through the A and B-site

cations, the ionic radii and electronegativity properties; thus, tilting of the octahedra results in structures with lower symmetry. In addition to this, the oxygen or any other anion is strongly bonded by B-site cations whereas the interactions between the oxygen and A-site cations are comparatively weaker. In order to achieve the different perovskite crystal geometries, these interactions can be changed based on the type of the cations locating the lattice sites (Kanhere and Chen, 2014). For instance, different angles of tilting in the form of the octahedra can be brought about different crystal fields, so different crystal fields give rise to different electronic and optical features. The band structure, electron and hole transfer, dielectric properties and photoluminescence can be affected by the angles of tilting (Zhang *et al*, 2006; Li *et al*, 2006).

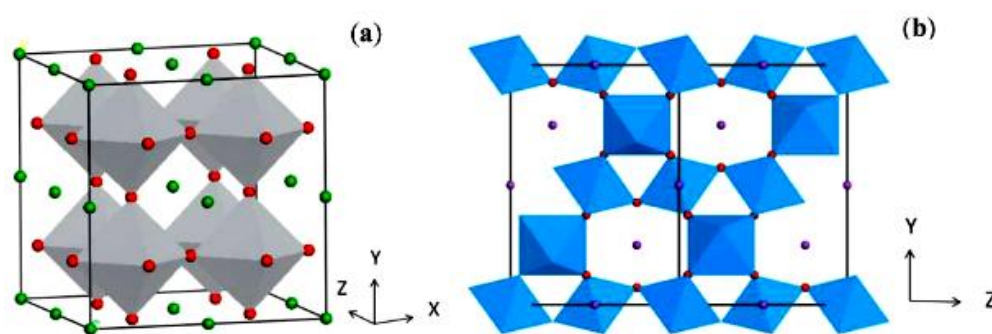


Figure 2.7. General crystal structure of BaTiO₃ perovskite (a), and Na₂Ta₂O₆ double perovskite (b) (oxygen: red, A-site cation: green and purple, BO₆ octahedra: grey and blue) (Kanhere and Chen, 2014).

For several reasons, perovskites may give important performance advantages compared to the binary oxides as photocatalysts. The first reason is that, the favorable band edge potentials allowing various photoinduced reactions could be provided by perovskites. Example for the comparison of perovskites and the binary oxides, adequately cathodic CB energies for the hydrogen generation can be supplied from various perovskites. Secondly, a wider range by designing and shifting the band structure is provided by means of A- and B- site cations in the lattice. Thirdly, various researches have demonstrated that the combination of the effects like piezoelectricity or ferroelectricity and the photocatalysis

can be used for the improvement of photocatalytic activity (Shi and Guo, 2012; Kanhere and Chen, 2014).

As the result, by this time, numerous perovskite materials have been investigated in the field of photocatalysis, and their applications in both UV and VIS light was tried to be improved. Especially, promising photocatalysts in visible light-driven systems can be counted as titanates, tantalates, niobates, ferrites and vanadates (Kanhere and Chen, 2014). Furthermore, as shown in Figure 2.6, titanate, tantalate and niobium-based perovskites stand out from the other perovskites and, if A and B sites are brought together, it can be easily seen that the most common five perovskites are NaTaOs, SrTiOs, BiTaOs, NaNbOs and KTaOs in the database constructed by Can and Yildirim.

2.3.1. Titanate-Based Perovskites

For a long time, the titanate perovskites in the general structure of $ATiO_3$ as metal-oxide materials have been studied for photocatalytic applications. Here, A represents metal compounds of the perovskites. Even if titanates have photoactive characteristics, several titanates do not have sufficient photocatalytic performance owing to their bandgap or band edges; for example, their bandgap or band edges may not fit with the criteria for PWS (Adnan *et al.*, 2018). The most of titanates like $SrTiO_3$, $BaTiO_3$, and $MnTiO_3$ possess the bandgap values above 3 eV (Schoonen and Xu, 2000), which is suitable for UV irradiation. The bandgaps and band edges of the simple titanate perovskite with respect to the redox potential of water splitting are given in Figure 2.8.

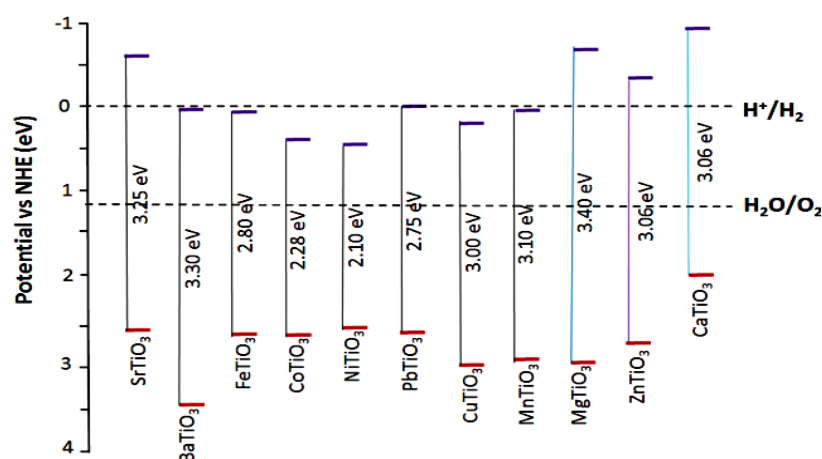


Figure 2.8. The simple titanate perovskites, their bandgaps and band edges against the redox potential of water splitting (Adnan *et al.*, 2018).

Whereas there is a common idea about titanates because of favorable photostability and corrosion prevention qualifications in aqueous solutions, powdery TiO₂ photocatalyst cannot decompose water absent the help of cocatalysts in ATiO₃ structure (A = Sr, Ba, Ca, Mn, Co, Fe, Pb, Cd, Ni) (Shi and Guo, 2012).

1 H hydrogen 1.008	2 He helium 4.003
3 Li lithium 6.941	4 Be beryllium 9.012
11 Na sodium 22.99	12 Mg magnesium 24.31
19 K potassium 39.10	20 Ca calcium 40.08
37 Rb rubidium 85.47	38 Sr strontium 87.62
55 Cs cesium 132.9	56 Ba barium 137.3
87 Fr francium 223	88 Ra radium 226

21 Sc scandium 44.96	22 Ti titanium 47.87	23 V vanadium 50.94	24 Cr chromium 52.00	25 Mn manganese 54.94	26 Fe iron 55.85	27 Co cobalt 58.93	28 Ni nickel 58.69	29 Cu copper 63.55	30 Zn zinc 65.41
39 Y yttrium 88.91	40 Zr zirconium 91.22	41 Nb niobium 92.91	42 Mo molybdenum 95.94	43 Tc technetium 98	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4
71 Lu lutetium 175.0	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6
101 Lr lawrencium 262	102 Rf rutherfordium 261	103 Db dubnium 262	104 Sg seaborgium 266	105 Bh bohrium 264	106 Hs hassium 277	107 Mt meitnerium 268	108 Ds darmstadtium 281	109 Rg roentgenium 272	110 Cn copernicium 285

5 B boron 10.81	6 C carbon 12.01	7 N nitrogen 14.01	8 O oxygen 16.00	9 F fluorine 18.99	10 Ne neon 20.18
13 Al aluminum 26.98	14 Si silicon 28.09	15 P phosphorus 30.97	16 S sulfur 32.07	17 Cl chlorine 35.45	18 Ar argon 39.95
31 Ga gallium 69.72	32 Ge germanium 72.64	33 As arsenic 74.92	34 Se selenium 78.96	35 Br bromine 79.90	36 Kr krypton 83.80
49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium 209	85 At astatine 210	86 Rn radon 222
113 Uut ununtrium 284	114 Fl flerovium 289	115 Uup ununpentium 288	116 Lv livermorium 292	117 Uus ununseptium 293	118 Uuo ununoctium 294

Figure 2.9. The elements supplying visible light activity for the titanate-based perovskites (Kanhare and Chen, 2014).

Apart from the other titanate-based perovskites, the most commonly studied titanate perovskite is SrTiO_3 (Sanwald *et al.*, 2018). Even though SrTiO_3 with simple cubic structure ($\text{Pm}\bar{3}\text{m}$, $a = 3.9 \text{ \AA}$) and a quite large indirect band gap of 3.25 eV promises to be able to work only under UV conditions, its band edges surpass the redox potential of the water splitting reactions (Van Benthem *et al.*, 2001). The stoichiometric water splitting under UV lumination by means of a co-catalyst such as Rh or NiOx, SrTiO_3 can be observed and these studies have been conducting widely for improvement of the performance under visible light conditions (Townsend *et al.*, 2012). Dopants applications such as Mn, Ru, Rh, and Ir metals on the Ti site had outstanding attention early years because the band gap of these dopants causes mid-gap levels, so visible light absorption can be possible on doped perovskites with these dopants. Mn and Ru metals doping for O_2 evolution, and Ru, Rh, and Ir metals doping for H_2 evolution, were reported to be suitable in literature (Konta *et al.*, 2004; Chen *et al.*, 2012).

Rh doping as in SrTiO_3 was also studied on BaTiO_3 . According to a reported study, quantum yield of 0.5% under 420 nm was observed. Moreover, BaTiO_3 , as a HER catalyst, has also been utilized to split water in the Z scheme with Pt/ WO_3 (Maeda, 2014).

Calcium titanate or namely CaTiO_3 is one of the most widely used perovskite minerals and has a band gap of 3.6 eV. The investigations on Cu doping in CaTiO_3 under visible light have been commonly reported for photocatalytic water decomposition (Zhang *et al.*, 2010). Cu doping supports both absorptions of visible light and increase of hydrogen production performance in UV conditions with the assistance of NiOx co-catalyst. Furthermore, Co-doped CaTiO_3 , with narrow the band gap, works with Ag and La under visible light (Zhang *et al.*, 2012). These studies about doped systems with high photocatalytic activity, should take the host materials into consideration first, because the host materials have an inevitable role in creating efficient photocatalysts; in addition to this, the features effected from doping (like $e^- - h^+$ recombination, effective mass of electron/hole, and decreased crystallinity) are also important.

As for NiTiO_3 and CoTiO_3 , they have narrower band gaps (2.10 eV and 2.28 eV in turn) compared to other titanates; however, their CB is lower than the water oxidation potential making them favorable for PEC water splitting. NiTiO_3 and CoTiO_3 demonstrate photocatalytic activity in terms of OER and HER in alkaline solutions in the absent any co-catalysts; however, the current was too low to generate H_2 (Qu *et al.*, 2013; Qu *et al.*,

2012). NiTiO_3 has also been employed for other photocatalytic applications, such as the degradation of nitrobenzene under VIS light.

FeTiO_3 and PbTiO_3 , with similar band gaps of approximately 2.8 eV, have also been investigated due to their fascinating charge separation and photocatalytic performance (Truong *et al.*, 2012; Zhang *et al.*, 2015). Both materials are reported to have ferroelectric behavior, which promotes electron-hole separation at the interface of two materials (Li *et al.*, 2017). However, few researchers have examined these materials for photoelectrochemical (PEC) water splitting (Adnan *et al.*, 2018).

MnTiO_3 and CdTiO_3 perovskites with F-doping and nanofiber structure can also enhance photocatalytic activity in term of degradation of pollutants and charge separation under visible light (Kanhere and Chen, 2014).

2.3.2. Tantalate-Based Perovskites

Alkali tantalates with a common formula of ATaO_3 (as A: Ag, K, Li, and Na) are studied in connection to various favorable features like electrochemical reduction, photocatalytic performance, the unique superconductivity, and electromagnetic characteristics (Yiguo *et al.*, 2015). In addition to these, they are also taken a lot of interest because alkaline tantalates can carry on effective overall water splitting reactions during UV conditions due to the eligibility of their VB and CB potential values to conduct water splitting process (Kato *et al.*, 2003; Yamakata *et al.*, 2003; Kato and Kudo, 2001). As in Figure 2.10, while A-site of tantalate perovskites, occupying by twelve O^{2-} , is generally connected by comparatively bigger cations such as K, Li, and Na, The B-site (Ta) consists of smaller cations having six coordinations (Yiguo *et al.*, 2015). The bond angles for LiTaO_3 , NaTaO_3 and KTaO_3 tantalate-based perovskites in the form of Ta–O–Ta coordination can be given are 143° , 163° and 180° respectively (Kato and Kudo, 2003).

The investigation of the interaction between crystallinity and the delocalization of energy in alkali tantalate-based perovskites has shown that the movements of excitation energy can be speeded up and the band gap reduced in the event that the Ta–O–Ta bond angle come near to 180° (Wiegel *et al.*, 1994). Therefore, the excited delocalization energy raises in the order of LiTaO_3 , NaTaO_3 and KTaO_3 and this show that KTaO_3 can be

assumed to have better photocatalytic activity than other tantalates. (Kanhare and Chen, 2014).

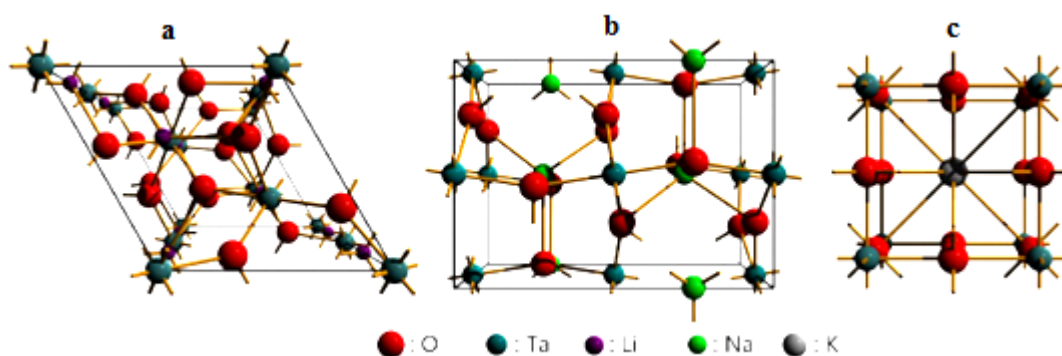


Figure 2.10. Crystal pattern for (a) LiTaO_3 , (b) NaTaO_3 and (c) KTaO_3 (Yiguo *et al.*, 2015).

Preparation methods used for alkali tantalates have a huge impact on the structural properties as morphology, size, and composition. The common methods used for this are the solid state reaction (SSR), hydrothermal (HT), sol-gel (SG), solvothermal and molten salt; SSR is the most widely utilized method among them. In this method, the composition of alkali tantalate salts and tantalum pentaoxide is mixed at high temperatures (Yiguo *et al.*, 2015).

As for sol-gel method, it has a great effect on not only structure but also photocatalytic activity. Because, when NaTaO_3 nanoparticles are prepared with sol-gel method, density states close the band edges as well as monoclinic phase with indirect band gap and nearly 180° bond angle of Ta–O–Ta can be observed as shown in Figure 2.11. When SSR and SG methods are compared in terms of activity of NaTaO_3 , it was found that there are the orthorhombic phase, direct band gap, and bond angle of 163° in the connection of Ta–O in NaTaO_3 with SSR method; however, in SG method, there are monoclinic phase, the larger surface area resulting in improved properties in the electronic and crystalline structure. Thereby, NaTaO_3 prepared by SG method has comparatively enhanced photocatalytic activity than that prepared by SSR method (Hu and Teng, 2007).

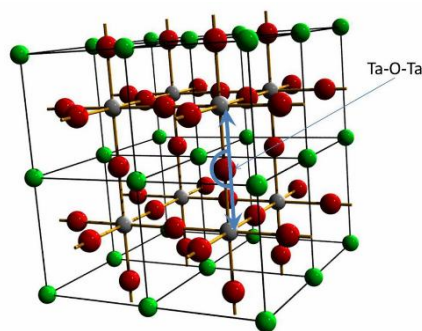


Figure 2.11. The monoclinic phase of NaTaO_3 for Ta–O–Ta bond angle (red:O, green: Na, and grey: Ta atoms) (Yiguo *et al.*, 2015).

Alongside SG method, the molten-salt method is also applied to synthesize NaTaO_3 and KTaO_3 photocatalysts. Even though NaTaO_3 and KTaO_3 photocatalysts synthesized by SG method have single high crystalline nanocubes around 100 nm, both SG and SSR methods limit the activity for alkali tantalates by leading lower surface areas. On the other hand, more ordered nanocrystals nucleation including well-defined particles, morphologies, crystallinity and high surface areas can be obtained by hydrothermal synthesis approach (Su *et al.*, 2008). Nano-sized Ta_2O_5 and NaTaO_3 , KTaO_3 and RbTaO_3 cubes prepared by HT method can be given as an example for this (Gompel *et al.*, 2014). It was reported that pH highly influenced the preparation of nanoparticles; the incremental pH values result in different morphologies such as agglomeration in acidic medium, sticks basic ambient, and cube shapes in neutral media (Koll *et al.*, 2013).

In addition to synthesis strategies for improvement of the photocatalytic activity on tantalate-based perovskites, the effects of doping with different elements have been also studied mostly for the enhancement of visible region activity of the photocatalyst. Studies conducted on NaTaO_3 demonstrated that doping and co-doping of certain elements such as Bi, La-Co, La-Cr, La-Ir, La-Fe showed significant photocatalytic activity for hydrogen generation under visible light condition (Kanhare *et al.*, 2011; Kanhare *et al.*, 2012; Yi and Ye, 2007; Yi and Ye, 2009; Yang *et al.*, 2010; Iwase *et al.*, 2009). Zhao *et al.* reported that co-doped NaTaO_3 with La-N was useful to work in visible range because both anion and cation doping were available through co-doping (Zhao *et al.*, 2011). Additionally, Han *et al.* computationally studied the anionic (N, F, P, Cl, S) doping and determined some useful anions like N and P in visible light conditions (Han *et al.*, 2009).

AgTaO₃ has a smaller band gap value of 3.4 eV than other alkali tantalates. When AgTaO₃ is doped with 30% Nb and loaded with NiO cocatalyst, it can work in visible region (Ni *et al.*, 2013). As for the co-doping effect, the co-doping of N-H results in a suitable band gap of 2.9 eV on AgTaO₃ for visible light conditions. The co-doping of N-H and N-F in AgTaO₃ can supply charge balance and enhanced carrier mobility (Li *et al.*, 2013).

Even if the photocatalytic activity of tantalate-based perovskites (ATaO₃, A: Li, Na, K) can be enhanced from ten to a hundred by excessive addition of alkali, and as a bare alkali tantalate photocatalyst, LiTaO₃ can demonstrate the higher activity than NaTaO₃ and KTaO₃ possible due to its higher conduction band states than the others. The same argument seems to be valid for SrTa₂O₆, BaTa₂O₆, and CaTa₂O₆ tantalate-based photocatalysts as well (Kato and Kudo, 1999).

Even though KTaO₃ with the band gap of 3.6 eV have been usually used under UV condition for water splitting, there are also few the investigations reporting the improvements of visible light performance of KTaO₃ photocatalysts (Kanhare and Chen, 2014).

2.3.3. Niobium-Based Perovskites

Alkali niobium-based perovskites with a common structure of ANbO₃ (as A: Ag, Cu, K, Li, and Na) are taken a lot of attention, because niobium oxides can be defined as a sophisticated material leading to outstanding features on material groups that they are added. Niobium oxides can demonstrate efficient performance in a lot of technological devices as transparent conductive oxides, photochromic tools, electrolytic capacitors in solid form, and so on (Nico *et al.*, 2016). Like titanate and tantalate based photocatalysts, niobium-based photocatalysts can perform under UV irradiation with high photocatalytic activity (Kanhare and Chen, 2014).

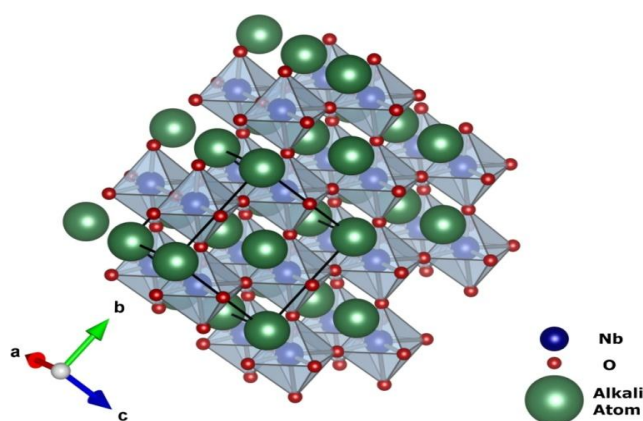


Figure 2.12. A general structural illustration of alkali niobium-based perovskites (Momma and Izumi, 2011).

The band gap of the perovskites can be put down by changing A-site alkali metals with silver (Ag); AgNbO_3 can reach a band gap of nearly 2.7 eV. The photocatalytic activity of AgNbO_3 is also affected highly the form of the particle. Studies have reported that polyhedron-shaped particles are preferable in order to generate O_2 (Li *et al.*, 2009). The doping can also help to enhance the photocatalytic performance; La doping, for instance, was reported to improve the photocatalytic performance for degradation of gaseous 2-propenol (Li *et al.*, 2009).

CuNbO_3 is a p-type semiconductor and has a monoclinic crystalline structure with a band gap of 2.0 eV. In the event of utilizing as a photocathode, studies reported that it can reach 5% impact to turn photon into electron (Joshi *et al.*, 2011).

KNbO_3 and NaNbO_3 can perform in the UV conditions due to their band gap values, which are respectively 3.14 eV and 3.08 eV. To be able to work in visible light conditions, certain alterations should be applied on the band structure to conduct favorable photocatalytic reactions (Liu *et al.*, 2007). Doping and co-doping are most commonly applied solutions. N-doped NaNbO_3 and KNbO_3 can be shown as an example for this; whereas N-doped NaNbO_3 degraded 2-propanol under visible light, N-doped KNbO_3 was used for investigations of both water splitting and organic pollutant decontamination (Shi *et al.*, 2009; Wang *et al.*, 2013). When comes to co-doping effect, co-doping of La and Bi in NaNbO_3 resulted in good photocatalytic activity under visible light (Liu *et al.*, 2011).

Lithium niobate, LiNbO_3 , have been attracted more interest than other niobium-based perovskites because of familiar prominence as a transparent semiconductor owing a band gap of around 3.7 eV. In addition, it is also taken attention due to piezoelectric properties and nonlinear-electrical-optic coefficients (Nico *et al.*, 2016). Since LiNbO_3 has a wide band gap of 3.7 eV, it is needed a proper doping for visible light. Thus, researchers have been mostly studied on doped LiNbO_3 to keep up the performance of lanthanides showing optical activity via proper doping applications (Graca *et al.*, 2007; Nico *et al.*, 2011).

2.3.4. Other Perovskites

Alongside perovskite photocatalysts given above, the other perovskites with iron, vanadium, cobalt, bismuth, antimony, and nickel in B-site have been are also used for photocatalytic applications. Most of them, for instance iron-based perovskites, can be active under the visible light, and they have been utilized for pollutants decomposition. LaFeO_3 having a band gap of 2.1 eV has shown excellent performance not only for pollutant degradation but also for hydrogen production under visible light radiation (Passier *et al.*, 2001). The doping has been improved the photocatalytic efficiency further; it was observed that BiFeO_3 doped with Ca enhances the catalytic activity for Congo Red dye decomposition (Kovendhan *et al.*, 2011). Hydrogen production performance from ethanol aqueous mixture has also conducted on PrFeO_3 and it was resulted in a total H_2 yield of $2847 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ under 200 W tungsten lamp (Terao, 1963).

As a vanadium-based perovskite, AgVO_3 also has two photocatalytically active types as $\alpha\text{-AgVO}_3$ and $\beta\text{-AgVO}_3$ with different crystal structures (Konta *et al.*, 2003). Due to band gap energy value, $\beta\text{-AgVO}_3$ (E_g 2.3 eV) performs more efficiently in photocatalytic reactions than $\alpha\text{-AgVO}_3$ (E_g 2.5 eV). However, the conduction band potential of AgVO_3 is not enough to generate hydrogen, so AgVO_3 is commonly preferred for the decomposition of volatile contaminant and production of oxygen. $\beta\text{-AgVO}_3$ nanowires and composition of AgBr-AgVO_3 for Rhodamine B pollutant, and Ag-loaded AgVO_3 for bisphenol have shown favorable performance for the degradation processes (Xu *et al.*, 2012; Sang *et al.*, 2013; Ju *et al.*, 2013). In addition to this, cobalt-based perovskites such as LaCoO_3 are also used in the photocatalytic degradation field; The oxygen deficient LaCoO_3 was

reported to be active for the degradation of methyl orange under visible irradiation with a band gap of 2.7 eV (Sun *et al.*, 2010).

Bismuth as B-site element was also used to form perovskites like AgBiO_3 , NaBiO_3 , KBiO_3 , and LiBiO_3 active in degradation of organic contaminations (Takei *et al.*, 2011). NaBiO_3 (E_g 2.53 eV) gave good photocatalytic activity in the decomposition of phenol and methylene blue, and it was showed better photocatalytic performance than TiO_2 photocatalyst when it was doped with N. (Takei *et al.*, 2011; Kako *et al.*, 2006). Besides, the composition of two NaBiO_3 and BiOCl has also shown higher electron-hole separation (Chang *et al.*, 2011).

AgSbO_3 can also work in visible region. Researches demonstrated that it can not only generate for oxygen owing to sacrificial reagents but also degrade a lot of organic pollutants such as methane blue or Rhodamine B. (Singh *et al.*, 2009). Likewise, AgSbO_3 and LaNiO_3 , together, can also decompose methane blue under visible light radiation (Tang *et al.*, 2011). When Cu doping applied in LaNiO_3 , its hydrogen generation performance could be enhanced (Li *et al.*, 2010).

Recently, LaCrO_3 in solid solution form, $\text{Gd}_2\text{Ti}_2\text{O}_7/\text{GdCrO}_3$ and $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$ photocatalyst have been studied to generate hydrogen (Shi *et al.*, 2010). Especially, GdCrO_3 is a promising one, because it can work under the visible light due to its band gap value of 2.5 eV (Parida *et al.*, 2011; Kato *et al.*, 2003).

2.4. Preparation Methods of Catalysts

The preparation method is another undeniable fact behind of the photocatalytic activity of perovskites. Even if there are a lot of different conventional or new methods such as solid-state reaction (SSR), sol-gel (SG), hydrothermal synthesis (HT), polymerized-complex (PC), electro-spinning (ES), ion-exchange (IE), Pechini-type process (PTP), co-precipitation, and flux-type process, the most common methods are the SSR, SG, HT, or PC due to their easiness in implementation and suitable features to improve the photocatalytic activity.

In the study conducted by Can and Yildirim, the works in the literature works classified in terms of perovskites preparation methods; the generally used methods for perovskite preparation in both UV and VIS light conditions against the average hydrogen production was presented in Figure 2.14 demonstrates (Can and Yildirim, 2019). Among them, the solid state reaction (SSR) method is the most widely used perovskite preparation method so that the results obtained with the other methods are generally compared with the SSR method like in this study prepared by Can and Yildirim. As it can be seen from Figure 2.13, the SSR methods provided higher hydrogen production rate as well as the HT method in UV condition, but same is not true for the visible light performance; the SSR resulted in lower performance under visible light conditions. The SSR method is also reported to lead to smaller surface area (Figure 2.14). On the other hand, the band gap of the resulting co-catalyst is also depending on the preparation method as is shown in Figure 2.15; the SSR seems to produce as the larger band gap values.

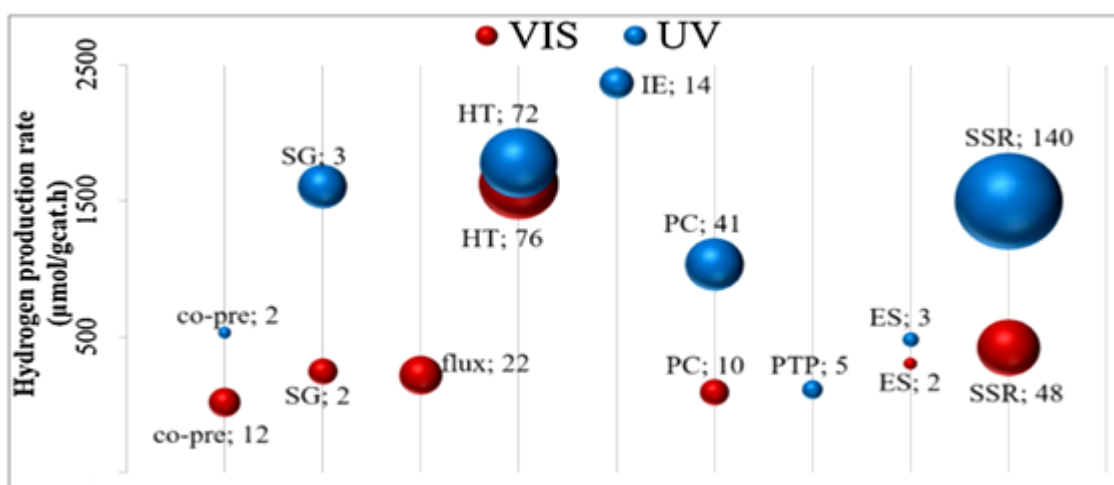


Figure 2.13. Frequently used perovskites preparation methods in terms of hydrogen production rates (Can and Yildirim, 2019).

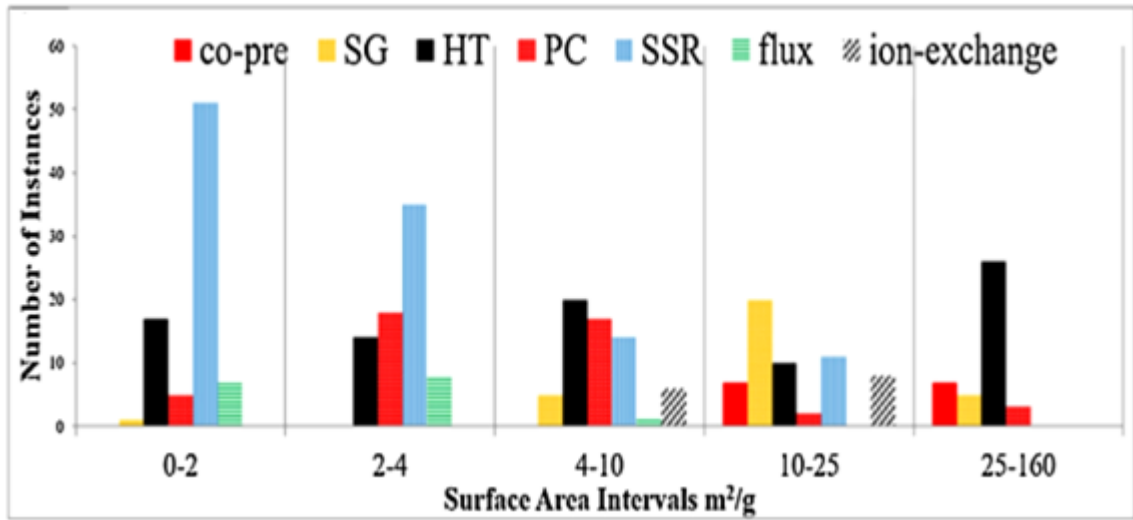


Figure 2.14. Frequently used perovskites preparation methods in terms of surface area (Can and Yıldırım, 2019).

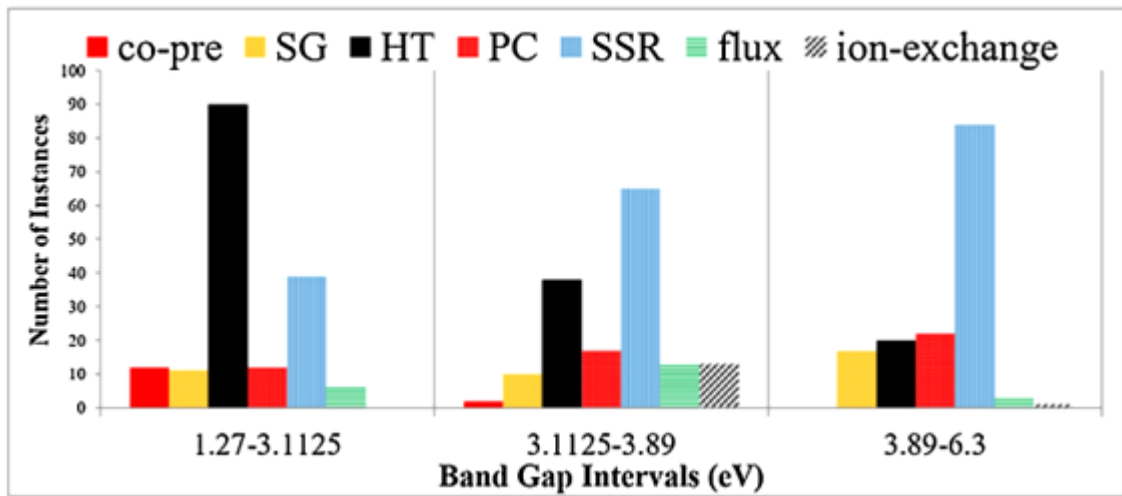


Figure 2.15. Frequently used perovskites preparation methods in terms of band gap (Can and Yıldırım, 2019).

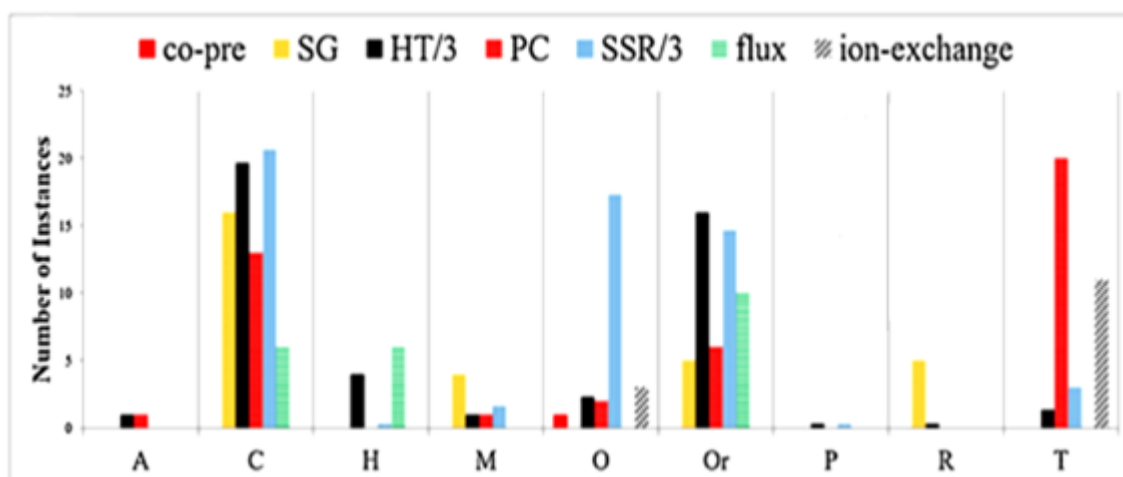


Figure 2.16. Frequently used perovskites preparation methods in terms of crystal structure (A: amorphous, C: cubic, H: hexagonal, M: monoclinic, O: octahedral, Or: orthorhombic, P: polyhedron, R: rhombohedral, T: tetragonal) (Can and Yıldırım, 2019).

Lastly, the crystal structures for the SSR method have orthorhombic, cubic and octahedral crystalline shapes (as in Figure 2.16). The structural effect of the method was explained by the study of Can and Yıldırım that the hydrogen generation rate observed in 13 articles having octahedral structure is $866.5 \mu\text{mol gcat}^{-1} \text{h}^{-1}$ but for the production rate of orthorhombic and cubic forms obtained from 38 articles is $1079 \mu\text{mol gcat}^{-1} \text{h}^{-1}$. Another study shows that the hydrogen evolution rate of cubic SrTiO_3 synthesized via the PC method is $3.2 \mu\text{mol g}^{-1} \text{h}^{-1}$ and certainly three times higher than the hydrogen evolution rate of cubic SrTiO_3 synthesized via the SSR method. Researchers observed that smaller and more uniform particle size were obtained with the PC method compared to those obtained with the SSR methods (Liu *et al.*, 2008).

The HT method has a remarkable hydrogen generation rate compared to the SSR method. For an instance, the NaNbO_3 prepared with the HT method has provided two times higher hydrogen product rate rather than NaNbO_3 synthesized with the SSR method while the PC method has given six times greater hydrogen production rate (Li *et al.*, 2008). Besides, while the rectangular and cubic shapes were resulted from the HT method, the samples with the spherical shape can be obtained by the SSR. Another effect of the HT method pointed out by the researchers was the behavior of the edges of the HT catalyst as

an active site. It was observed that the activity of KTaO_3 prepared by the SG method in UV conditions was two times higher than that of the HT method (Hu *et al.*, 2013).

As for the methods like polymerized-complex (PC) and the sol-gel (SG), the research conducted by Jeong *et al.* can be given an example. It was shown that as a catalyst of the PC method, $\text{NiO/Sr}_3\text{Ti}_2\text{O}_7$ produced more hydrogen than that of the SSR in UV irradiated ambient. According to the report, the basic reasons for this high hydrogen evolution rates is due to the higher surface area, purity and longevity of the PC method catalysts (Jeong *et al.*, 2006). In terms of crystallinity, the study of Hu and Teng gave a favorable example of orthorhombic and cubic NaTaO_3 catalysts synthesized by the SSR and the SG in turn. The catalyst prepared by the SG method having 23 times higher hydrogen production performance was stand out more than that of the SSR. Thus, the researchers believed that higher surface area, smaller particle size, and as a result of lower calcinations temperatures of the SG method; high crystallinity led improved photocatalytic activity of NaTaO_3 catalyst (Hu and Teng, 2007).

2.5. Sacrificial Reagents used in Photocatalytic Water Splitting Processes

Sacrificial reagents (electron donors) have a significant role in photocatalytic hydrogen generation because water splitting process requires an uphill reaction to evolve hydrogen energy, and the sacrificial reagents can provoke the process by reacting with the photoexcited holes in the VB and preventing the recombination of the photo-excited electron-hole pairs (Liu *et al.*, 2018; Kumaravel *et al.*, 2019). There is a lot of sacrificial reagents used for photocatalytic hydrogen production such as methanol (MeOH), sodium sulfite (Na_2S), sodium sulfide (Na_2SO_3) or mixture of sodium sulfite and sodium sulfide, ethylene glycol (EG), triethylene amine (TEA), formic acid (FA), glucose, glycerol (GLY) and so on. In addition to this, certain sacrificial reagents can work better on the different photocatalyst due to their chemical properties. For instance, while methanol as a form of the alcohol can work well on oxide perovskites, triethanolamine as an organic reagent can work better on carbon-based photocatalysts. Sodium sulfide/sodium sulfite as an inorganic sacrificial reagent works also in concert with sulfide photocatalysts rather than the other type of photocatalysts (Kumaravel *et al.*, 2019).

MeOH is generally preferred for oxide perovskite catalysts. Yuan et al. studied on nano TiO₂ (P25) photocatalyst in existence of 10 vol % aqueous methanol solution under UV light (Yuan *et al.*, 2016). They showed that methanol as an agent in the medium could generate hydrogen of 42 $\mu\text{mol g}^{-1} \text{h}^{-1}$. In another study, Shen et al. reported that whereas pure TiO₂ demonstrated a hydrogen evolution rate of $\sim 20 \mu\text{mol g}^{-1} \text{h}^{-1}$ in visible light conditions, black TiO₂ gave hydrogen rate of 130.5 $\mu\text{mol g}^{-1} \text{h}^{-1}$ in same condition (Shen *et al.*, 2017). Kumaravel et al. conducted an investigation on the effect of different sacrificial agents (Kumaravel *et al.*, 2019). They proved the alcohol form of sacrificial reagents efficiency on the oxide perovskites. It was reported that TiO₂ (P25) exhibited higher performance with hydrogen evolution rate of $\sim 75 \mu\text{mol g}^{-1} \text{h}^{-1}$ than that of inorganic sacrificial agents Na₂SO₃ (40.8 $\mu\text{mol g}^{-1} \text{h}^{-1}$).

However, the sodium sulfite (Na₂S) and the sodium sulfide (Na₂SO₃) or both mixtures can work well with sulfide photocatalysts. In another experiment of Kumaravel et al., the performance of CdS sulfide-based photocatalyst was tested with variety sacrificial agents (Kumaravel *et al.*, 2019). They demonstrated that Na₂S/CdS, and Na₂SO₃/CdS combinations with hydrogen production rate of 181.2 $\mu\text{mol g}^{-1} \text{h}^{-1}$ and 154.8 $\mu\text{mol g}^{-1} \text{h}^{-1}$ respectively could give higher performance rather than alcohol and organic reagents. Moreover, the photocatalytic H₂ generation on oxide form of photocatalysts in Na₂S and Na₂SO₃ aqueous solution under UV and visible light irradiations were investigated by Gomathisankar et al. The maximum hydrogen evolution rate of 933 $\mu\text{mol g}^{-1} \text{h}^{-1}$ was reached on B/CuO/ZnO nanocomposite under the UV irradiation (Gomathisankar *et al.*, 2013). This study is also reported that inorganic reagents can also increase the performance on oxide photocatalyst in the event of suitable composite or the other complex type of oxide photocatalysts.

Ethylene glycol is generally expected to be beneficial for photocatalytic hydrogen production due to its origin comes from the alcohol. Lopez et al. studied on a homemade Pt/TiO₂ (P25) photocatalyst to observe the effect of sacrificial agents such as methanol, ethanol, ethylene glycol, glycerol (Lopez *et al.*, 2015). As a result of their studies, they found that Pt/TiO₂ with EG could be suitable alternative for hydrogen generation with maximum yield of 1985.80 $\mu\text{mol g}^{-1} \text{h}^{-1}$ in 7.34 molar aqueous solution of EG. In the other side, Gultom et al. showed that graphene oxide as an inexpensive cocatalyst in Zn(O,S)/GO nanocomposite with EG aqueous mixture performed the worst

one among the others, because the catalyst material had sulfide and this is undesired for improvement with alcohol originated sacrificial reagents, so it proved also the conformity of catalyst and sacrificial agent types (Gultom *et al.*, 2019).

Triethylene amine is another important reagent used in the photocatalytic processes. Cao *et al.* tested photo-reduction of CuSO_4 in TEA aqueous solution (5 % v/v) to obtain both Cu_2O or Cu nanoparticles and hydrogen (Cao *et al.*, 2020). They found that this photocatalytic system in visible light conditions had low hydrogen production efficiency but the hydrogen production could sustain hydrogen generation for longer times.

Wang *et al.* compared formic acid, methanol and methylamine sacrificial agents in hydrogen production on $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ photocatalyst (Wang *et al.*, 2017). The composition of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and formic acid gave the highest hydrogen rate of $845 \mu\text{mol g}^{-1} \text{h}^{-1}$. They reported that this high rate was due to the lower oxidative power and permittivity of formic acid as the ability of electron donors to provide electron is addressed by oxidation potential.

Glucose is an organic sacrificial agent that also has importance in photosynthetic processes; hence, the photocatalytic effect of glucose cannot be underestimated. Bellardita *et al.* conducted an experiment on Pt/TiO₂ P25 with glucose (Bellardita *et al.*, 2016). They reported that Pt/TiO₂ P25 could perform during 7 hours with the hydrogen production rate of $440 \mu\text{mol g}^{-1}$.

Glycerol may take a huge role in the photocatalytic hydrogen production, because it is the main byproduct of the biodiesel production; an enormous amount of glycerol is expected to be produced each year during the biodiesel synthesis. Its storage is also problem for manufacturers due to the environmental concerns. Because of this, the usage of glycerol as a waste material in the field of other chemical industries especially in photocatalysis takes significant attention by the researchers. Slamet *et al.* tested Cu(5%)-N-TiO₂ photocatalyst with glycerol as a sacrificial reagent (Slamet *et al.*, 2015). They found that Cu(5%)-N-TiO₂ photocatalyst with 50% v/v glycerol solution could give the best hydrogen evolution rate of $\sim 800 \mu\text{mol g}^{-1} \text{h}^{-1}$ among the other volume and loading alternatives. Alongside this study, Slamet *et al.* worked on Pt(1%)-N-TiO₂ nanotube to produce hydrogen by means of glycerol sacrificial reagents (Slamet *et al.*, 2013). They observed that Pt(1%)-N-TiO₂ nanotube in 10% volume of glycerol aqueous solution can

generate the hydrogen to rate of $3017 \mu\text{mol g}^{-1} \text{h}^{-1}$. In addition to the cocatalyst and doping effect on the catalyst, this outstanding result can be also explained with the suitability of both catalyst and sacrificial agent types. The decomposition path way of glycerol on TiO_2 photocatalyst is given as in Figure 2.17.

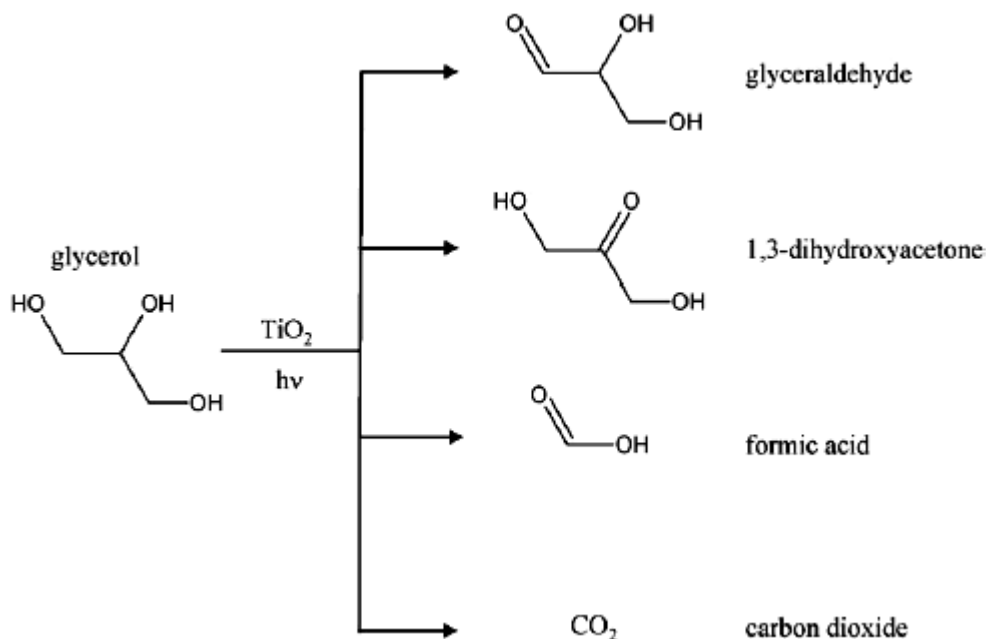


Figure 2.17. The decomposition path way of glycerol on TiO_2 in a photocatalytic process (Augugliaro *et al.*, 2010).

2.6. The Effect of Dopants and Cocatalysts

As depicted in Figure 2.18.a, when any elements those are different than the original elements in structure, are inserted in the structure of the catalyst materials in place of an anion or cation part, it is defined as doping or dopant effect (Adnan *et al.*, 2018). Doping modification results in alteration of the band structure and change of the band gap value due to addition of new element forbidden band level. The cations of materials can be just changed with a dopant having a correlative radius and charge features. Doping of Cr^{3+} and Ta^{5+} ions on cation part and of F^- on anion part in SrTiO_3 lattice structure is a good example for this; since Ti^{4+} has a radius of 0.0605 nm, it can be replaced with an ion

having radius around 0.060 nm like Cr^{3+} (0.0615 nm) and Ta^{5+} (0.064 nm) ions. Besides, O^{2-} with 0.140 nm can be replaced with F^- because of having a radius (0.133 nm) near to O^{2-} (Kang *et al.*, 2014).

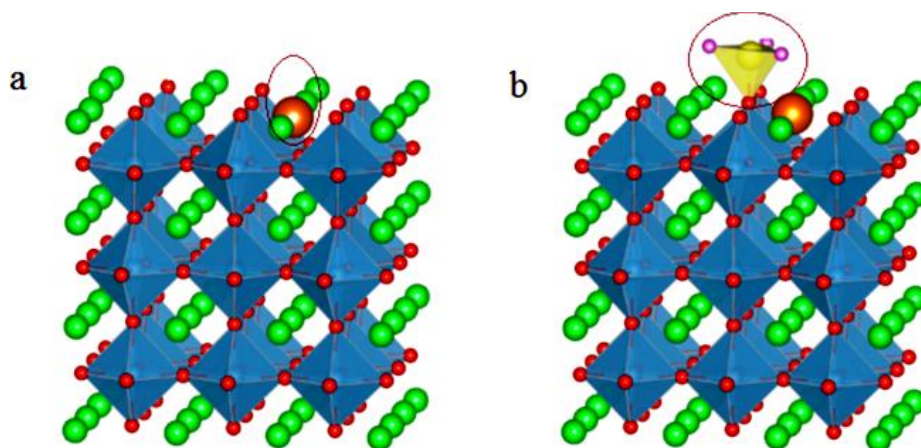


Figure 2.18. A schematic illustration of doped (a) and cocatalyst added (b) SrTiO_3 structure (Comes *et al.*, 2014).

The doping modifications can be categorized according to the number of dopant like single, double and tri-element doping. In single-element doping at cation sites depicted with A and B in perovskite structures, single sites are changed with just one type of element as in Figure 2.18.a, but generally this changing happens at B-sites, while in single-element doping at anion side, which is presented with X in structure, just replaces with oxygen atom of the perovskites, thus the acceptor levels of photocatalysts below the CB can be obtained by means of anion doping. For an example, while oxygen as the single-element dopant in the structure of SrTiO_3 is changed with nitrogen ions, the photocatalytic activity of doped SrTiO_3 in visible light condition increases (Yan *et al.*, 2009). Rh^{4+} ion doping on B site of SrTiO_3 brings about higher acceptor level than the CB of non-doped SrTiO_3 (Shen *et al.*, 2013). Zn-doped BaTiO_3 is another example of A site doping; the CB of BaTiO_3 gets more negative according to the reduction potential of H^+/H_2 due to going up the CB of doped BaTiO_3 (Gao *et al.*, 2011; Fasasi *et al.*, 2008). In another investigation, as a single-element Al-doped perovskite $\text{La}_2\text{AlTaO}_7$ has reached lower CB under UV light

irradiation than the pristine form, and it generated hydrogen even in the absence of a cocatalyst (Yin *et al.*, 2003).

The double-element doping includes the insertion of two type elements on B-site or more than one of A, B and X. It has observed in a study that Cr^{3+} and Ta^{5+} double-element doping on cation part of SrTiO_3 resulted in hydrogen production rate of $211.4 \mu\text{mol g}^{-1} \text{h}^{-1}$ under visible light (Kang and Park, 2011). However, when Cr was doped as single-element in the structure of SrTiO_3 , it could increase the rate of hydrogen evolution just to $97.7 \mu\text{mol h}^{-1}$ (Sun *et al.*, 2015). As in Cr and Ta double-element doped SrTiO_3 , Cr (at A-site) and Sb (at B site) double doping in SrTiO_3 also demonstrated better activity under visible irradiation than that of single-element doped or undoped catalysts (Luo and Maggard, 2006).

In another study, La and Cr double doped CaTiO_3 could work in visible light, because co-doping modification with La and Cr led to observe red shift in the band gap of CaTiO_3 (Wang *et al.*, 2018; Lu *et al.*, 2017). When it comes to niobium-based perovskites, double-doped Bi_2NbO_7 with La (A-site) and Al (B-site) has proved increased photocatalytic activity in UV condition via electronic structure change and optical absorption (Li *et al.*, 2009). Along similar lines, the study carrying about co-doped perovskites performance demonstrated that double-doped LaNbO_3 with H and In was one of the best among the other samples, double-doping supplied lower band gap and larger surface area (Wei *et al.*, 2009).

hydrogen 1 H 1.008	Most widely studied dopants Widely studied dopants Less studied dopants																helium 2 He 4.003				
lithium 3 Li 6.94	beryllium 4 Be 9.01															boron 5 B 10.81	carbon 6 C 12.01	nitrogen 7 N 14.01	oxygen 8 O 16.00	fluorine 9 F 18.99	neon 10 Ne 20.18
sodium 11 Na 22.99	magnesium 12 Mg 24.31															aluminium 13 Al 26.98	silicon 14 Si 28.09	phosphorus 15 P 30.97	sulphur 16 S 32.06	chlorine 17 Cl 35.45	argon 18 Ar 39.95
potassium 19 K 39.10	calcium 20 Ca 40.08	scandium 21 Sc 44.96	titanium 22 Ti 47.88	vanadium 23 V 50.94	chromium 24 Cr 52.00	manganese 25 Mn 54.94	iron 26 Fe 55.85	cobalt 27 Co 58.93	nickel 28 Ni 58.69	copper 29 Cu 63.55	zinc 30 Zn 65.39	gallium 31 Ga 69.72	germanium 32 Ge 72.64	arsenic 33 As 74.92	selenium 34 Se 78.96	bromine 35 Br 79.90	krypton 36 Kr 83.79				
rubidium 37 Rb 85.47	strontium 38 Sr 87.62	yttrium 39 Y 88.91	zirconium 40 Zr 91.22	niobium 41 Nb 92.91	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.10	rhodium 45 Rh 102.90	palladium 46 Pd 106.40	silver 47 Ag 107.90	cadmium 48 Cd 112.40	indium 49 In 114.80	tin 50 Sn 118.70	antimony 51 Sb 121.80	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.30				
caesium 55 Cs 132.90	barium 56 Ba 137.30	57-71		hafnium 72 Hf 178.50	tantalum 73 Ta 180.90	tungsten 74 W 183.90	rhenium 75 Re 186.20	osmium 76 Os 190.20	iridium 77 Ir 192.20	platinum 78 Pt 195.10	gold 79 Au 197.00	mercury 80 Hg 200.50	thallium 81 Tl 204.38	lead 82 Pb 207.20	bismuth 83 Bi 209.00	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]			
francium 87 Fr [223]	radium 88 Ra [226]	89-103		rutherfordium 104 Rf [261]	dundubium 105 Db [268]	seaborgium 106 Sg [271]	bohrium 107 Bh [270]	hassium 108 Hs [277]	meitnerium 109 Mt [276]	darmstadtium 110 Ds [281]	roentgenium 111 Rg [280]	copernicium 112 Cn [285]	nihonium 113 Nh [284]	flerovium 114 Fl [289]	moscovium 115 Mc [288]	livermorium 116 Lv [293]	tennessine 117 Ts [294]	oganeson 118 Og [294]			
		lanthanum 57 La 138.90	cerium 58 Ce 140.10	praseodymium 59 Pr 140.90	neodymium 60 Nd 144.20	promethium 61 Pm [145]	samarium 62 Sm 150.40	europtium 63 Eu 152.00	gadolinium 64 Gd 157.20	terbium 65 Tb 158.90	dysprosium 66 Dy 162.50	holmium 67 Ho 164.90	erbium 68 Er 167.20	thulium 69 Tm 168.90	ytterbium 70 Yb 173.00	lutetium 71 Lu 175.00					
		actinium 89 Ac [227]	thorium 90 Th 232.00	protactinium 91 Pa 231.00	uranium 92 U 238.00	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]	lawrencium 103 Lr [262]					

Figure 2.19. The dopants enhance the hydrogen generation performance on TiO_2 (Kumaravel *et al.*, 2019).

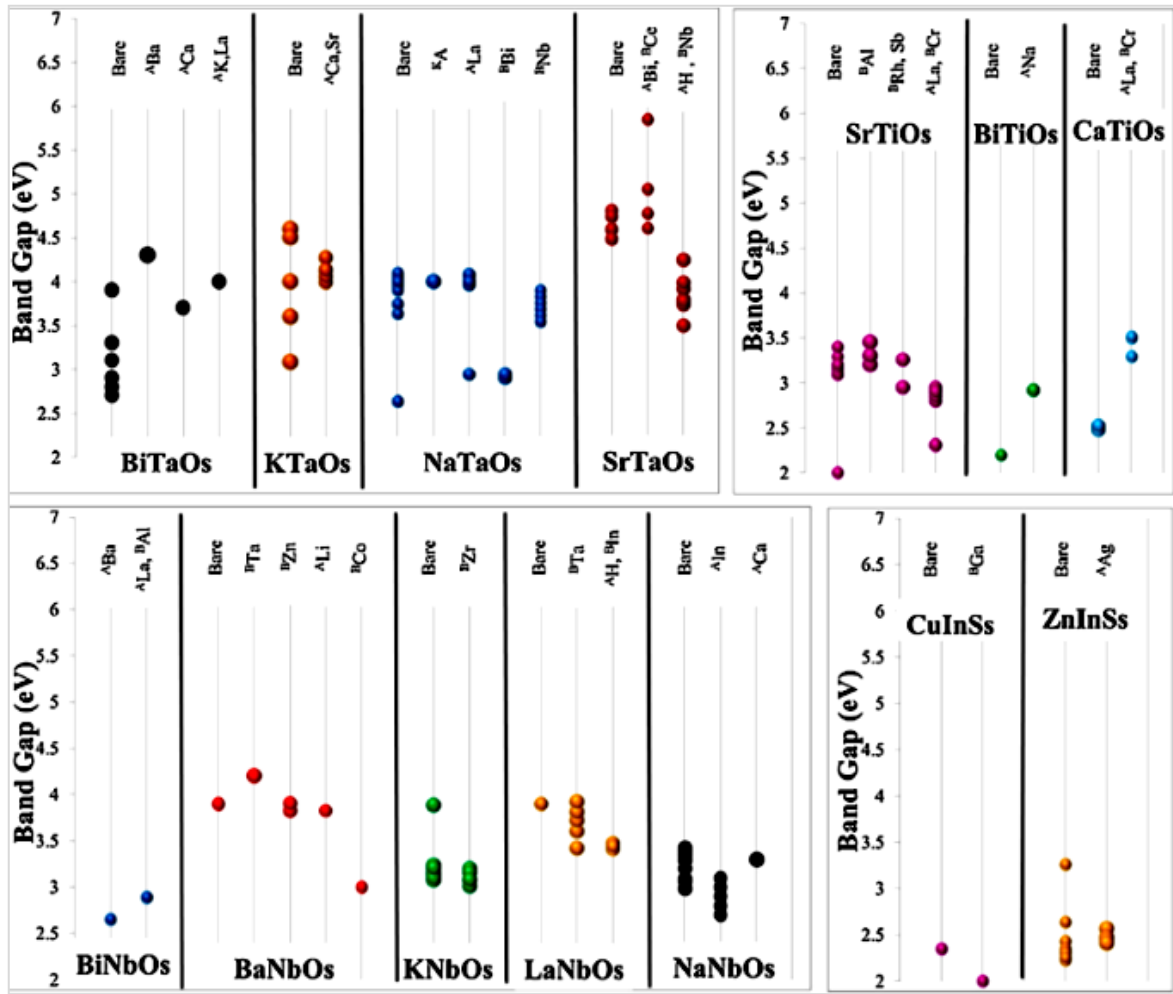


Figure 2.20. Tuning band gap of widely used perovskites by various dopant elements (Can and Yildirim, 2019).

In tri-element doping, two of three foreign elements are doped on A- or B-sites and another is doped on X-sites in the perovskite. Researchers have reported that tri-element doping on SrTiO_3 , having Cr^{3+} and Ta^{5+} as cation doping elements and F^- as an anion doping element, leads the rest elements in original structure to change their the charge in order to make a balance in the material (Lu *et al.*, 2017; Kang and Park, 2011). In addition to number of dopant, its amount has also significant role, since the material structure can be destroyed through overmuch addition of the dopants. This amount can be decided via the experiments processing in variety dopant ratios. For instance, the research by Kang and Park showed that tri-element doped SrTiO_3 with Rh, Ta and F could give H_2 yield of $4123.7 \text{ mmol g}^{-1} \text{ h}^{-1}$ and 6.60 % STH quantum efficiency in the event of the optimum

ratios of 0.15 mol %, 0.15 mol % and 6 mol % respectively; however, the increment in amount of F causes recombination in charge carrier and prevent the hydrogen production (Adnan *et al.*, 2018; Kang and Park, 2011).

Besides the bandgap modification of perovskites, loading metal or metal oxide materials as a cocatalyst on the perovskites is another effective way to improve the photocatalytic activity. Unlike the doping method, the cocatalyst application does not alter the structure of the perovskites. In this method, the surface of the catalyst is just loaded with cocatalyst or cocatalysts to create a junction as in Figure 2.18.b and improve its charge separation (Adnan *et al.*, 2018). Excited electrons move to the CB and then a hole comes to the VB, after this step in the photocatalytic process, the recombination results from the electron having potential. The main reason behind of the recombination is low electron mobility due to defects or disablements in the photocatalyst (Ida and Ishihara, 2014). At this point, the electron recombination is tried to hinder via the assistance of cocatalyst, which can be novel metals or metal oxides, because cocatalysts catch up with the excited electrons due to different Fermi levels of each material.

The cocatalysts can be loaded onto the surface of photocatalyst in the form of dispersed nanoparticles to create active points (Maeda and Domen, 2007). The couple of two noble metals or one noble metal and its oxide form result in multi-heterojunction within the surface of the catalyst and can demonstrate higher photocatalytic performance owing to the band edge of the catalyst having co-operative promoters (Adnan *et al.*, 2018). In addition to this, the cocatalysts can be applied on the surface of the perovskites with a few main methods such as impregnation, deposition-precipitation and co-precipitation.

The impregnation method includes two types. One of them is the incipient-to-wetness impregnation method and the other is the wet impregnation. The general idea behind this method is the application of metal precursor solution onto the catalysts or support surfaces. In the incipient-to-wetness impregnation method, the volume of impregnating solution should be matched the pore volume of the catalyst or support, so during the impregnation, the catalyst should be wetted by the exact volume of metallic precursor solution without excess volume, because the concentration of metallic precursor solution determines the metal loaded on the catalyst. The excess volume of the metallic precursor solution is utilized in wet impregnation application. In this approach, the volume of impregnating solution can be overpassed the pore volume of catalyst, because wet

impregnation method is conducted by the adsorption. Thus, this excessive amount apart from the sucked volume of solution by the catalyst will be vaporized during the heating step, after metal ions and the surface of the catalyst interact each other. In addition to the volume of precursor solution, there are also several important points having a huge role in the drying and calcination steps affecting the features of the catalyst like temperature, heating time, and rate (Haukka *et al*, 1999; Prati and Villa, 2011).

The co-precipitation method mixes the alkaline and the aqueous mixture of active metal salts with a catalyst or a support for a certain concentration so that the cocatalyst particles formed precipitate on the surface. In next step of the method, the filtration or centrifuging as well as washing, drying and finally calcinations steps occurs in turn. Several parameters can affect the efficiency of the co-precipitation method such as pH, density of salt, temperature, and vaporization (Deraz, 2018; Haukka *et al*, 1999; Prati and Villa, 2011).

The deposition-precipitation method deposits metals and its oxide, sulfide, hydroxide forms in small particle sizes onto a catalyst or a support. The deposition process occurs in the liquid phase via a chemical reaction. The formation of the metal compound having low solubility in the solvent is created by this chemical reaction. For instance, metal hydroxides precipitation from an aqueous solution is used commonly, and the addition of hydroxyl ions is generally obtained from an alkaline or urea solution. At final step, the metal hydroxide onto a suspended support material is deposited by incrementally decreasing pH value of the metal salt solution used urea. The main benefit of the deposition-precipitation method is that narrow distributions of small size particle can be achieved for high metal loading. Additionally, this method is much more reproducible method from one experiment to another (De Jong, 2009). Lee *et al.* published comprehensive study for describing the excellent effect of deposition-precipitation method on particle size and high loading amount of cocatalyst. They reported that the nickel metal with 50 wt% and a particle size range of 6–8 nm could be loaded on a nonmicroporous carbon nanofiber supports (Van der Lee *et al.*, 2005).

One of the most common used cocatalysts is Pt, which is utilized in titanate, tantalate and niobium-based perovskites to enhance the hydrogen evolution rate (Chen *et al.*, 2010). Whereas the hydrogen generation rises until a certain amount of Pt loading, the photocatalytic activity is decreased through shielding effect when the Pt amount surpasses

this point, and the optimum amount of Pt loading depends on the catalysts (Chen *et al.*, 2014; Kanhere *et al.*, 2012; Wang *et al.*, 2012; Zhang *et al.*, 2013; Wang and Wang, 2012).

A powder form of N-doped SrTiO₃ and TiO₂ composites loaded with 2 wt% Pt was studied in 0.05 molar oxalic acid aqueous solution under visible light conditions by Yan *et al.* (Yan *et al.*, 2009). Pt loaded composite photocatalyst has generated 5100 g_{cat}⁻¹ h⁻¹ hydrogen. According to Yan *et al.*, the heterojunction with a special energy band gap created by this composite and the optimal loading of Pt as a cocatalyst was the reason of this outcome (Kang and Park, 2016). In another work, Pt–Ni₃/CdS photocatalyst has a HER of 48.96 mmol h⁻¹ g⁻¹ and a quantum efficiency of 44.0% under visible light. Here, the reason for the improvement in photocatalytic activity is the synergetic effect of Pt and Ni₃ on the band edge of the photocatalyst (Mao *et al.*, 2018). Bare and Pt loaded NaTaO₃ particles were researched in terms of the effect of Pt as a cocatalyst on the hydrogen evolution rate. The research has shown that Pt nanoparticles has the role as active sites and presence of Pt nanoparticles leads to the enhancement on HER by retarding the $e^- - h^+$ recombination rate (Jana *et al.*, 2014).

Alongside Pt as a cocatalyst, Rh loaded SrTiO₃ in visible light conditions for PWS was reported by Ham *et al.* It is reported that the reverse reaction of hydrogen production could be prevented by loading of Rh (Ham *et al.*, 2016). Another titanate-based perovskite KTiO₃ was loaded with Rh by Yoshida *et al.* The experiments conducted under visible light have shown that Rh loaded KTiO₃ under visible light not only blocked recombination reactions but required different preparation methods for different amount of Rh loading (Yoshida *et al.*, 2014). Apart from the above, Takayama *et al.* investigated a lot of cocatalysts with KCaSrTa₅O₁₅. As a result of their investigation, they reported that Rh as a cocatalyst had a poor efficiency in UV conditions (Takayama *et al.*, 2014).

While Ru with higher visible light activity is preferred to load on the perovskites as a cocatalyst (Li *et al.*, 2014; Takayama *et al.*, 2014; Asai *et al.*, 2014), several studies argued about its weakness on the photocatalytic activity. For instance, Ru was tested together with Ag, Au, Rh, Pt, and NiO as cocatalyst and it observed that Ru had at least photocatalytic activity among them under UV irradiation (Takayama *et al.*, 2014).

As a transition metal oxide, NiO_x and RuO_x are favorable and widely used cocatalysts. Even if they can be used with various perovskite catalysts, it observed that they

could operate specially well with tantalate and niobate-based perovskites (Liu *et al.*, 2008; Chen *et al.*, 2014; Li *et al.*, 2009; Lee *et al.*, 2012; Kato *et al.*, 2002). Because tantalate and niobate-based perovskites have higher CB level than that of NiO_x and RuO_x , the excited electrons in the CB can pass to NiO_x or RuO_x acting as a charge separator on perovskites (Huang *et al.*, 2011; Asai *et al.*, 2014; Ran *et al.*, 2014; Shi and Guo, 2012). NiO_x loaded tantalate-based perovskite was also studied by Li *et al.* It was reported that as a result of NiO loading, a core-shell structure (Ni-NiO) having selectivity for hydrogen and hydroxide ions was obtained (Li *et al.*, 2009). Whereas NiO let for hydrogen ions diffuse, it blocks the diffusion of hydroxide ions. By this way, the recombination of hydrogen and oxygen cannot be possible (Zhou *et al.*, 2009). On the other hand, RuO_2 dispersed on La:NaTaO_3 was studied by Torres-Martinez *et al.* It was observed that La:NaTaO_3 loaded with RuO_2 nanoparticles could improve the activity under UV conditions via its preventive feature of recombination reactions (Torres-Martinez *et al.*, 2010).

In other respects, much more improved photocatalytic activity performance can be taken from the photocatalysts with the implementation of metal nanoparticles having plasmonic effect such as Ag, Al, Au and Cu, and so on. In other words, this effect can be explained like the collective electrons oscillations in the plasmonic nanoparticles or namely can be called localized surface plasmon resonance (LSPR) (as in Figure 2.21), and the photocatalysts having plasmonic effect are called plasmonic photocatalysts.

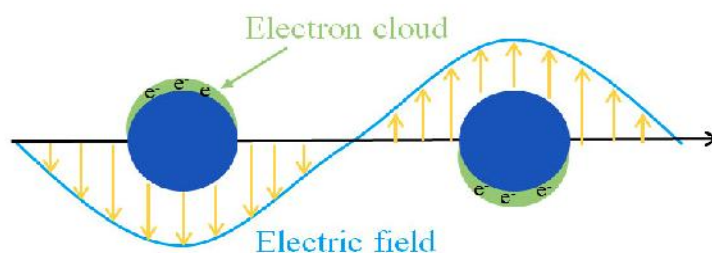


Figure 2.21. The illustration of localized surface plasmon resonance (Xiao *et al.*, 2020).

Due to direct relation between the dielectric function properties of the material and the plasmonic wavelength of the material, plasmonic photocatalysts can be composed for an enhanced photocatalytic activity with the help of the metal oxides in perovskites (Lu *et*

et al., 2017; Choi *et al.*, 2017). As the most common plasmonic nanoparticles, the noble metals Ag and Au nanoparticles due to their strong localized surface plasmonic resonance (LSPR) (Jiang *et al.*, 2019; Ray *et al.*, 2019; Paul *et al.*, 2019), the non-noble metals like bismuth with the advantage of lower cost, and being abundant on the earth, and the non-metallic materials, like MoS₂ are regardable plasmonic nanoparticles (Guo *et al.*, 2018). Shi and Guo conducted a research on Ag loaded KTaO₃ and NaTaO₃. They defined that besides the plasmonic effect of Ag, it could act same like Pt in wider light absorption condition without changing the pattern, particle size and surface area. However, it was also observed that the photocatalytic activity decreased for the excessive loading amount of Ag (Shi and Guo, 2012).

Furthermore, Al and Cu are a proper alternative owing to their plasmonic wavelengths ranging from 150 nm to 600 nm and from 600 nm to 1000 nm, respectively (Jiang *et al.*, 2019; Nie *et al.*, 2018). Apart from the above, the composition of materials like Au(provides plasmonic effect)/CuSe nanosheets(provides plasmonic effect)/Pt(as a cocatalyst) or Au/Ag/Cu₂O core-shell nanorods are the other better alternatives for increasing the photocatalytic performance (Hu *et al.*, 2019; Ma *et al.*, 2019). Ding *et al.* reported that Au-Cu bimetallic CaIn₂S₄ shown increased hydrogen production from Na₂S/Na₂SO₃ solution. The reason behind of this was deduced to the effective charge separation, enhanced light absorption due to LPSR effect of Au-Cu bimetallic cocatalyst (Ding *et al.*, 2018).

3. EXPERIMENTAL WORK

3.1. Equipment and Chemicals

All equipment and chemicals used during the experiments of this thesis are given respectively in Table 3.1 and Table 3.2.

Table 3.1. Equipment used in the experiments.

Name	Source
Gas Chromatograph	Shimadzu GC-2014
Mass Flow Controller	Brooks Instrument 5850
Photo reactor (with Xenon lamp)	Luzchem LZCX-XE
Hot Mirror Assembly (UV filter)	Excelitas Technologies A2-001
UV-VIS Spectrometer	Shimadzu UV-2600
Centrifuge	Nuve NF 400
Oven	GEMO PC109
Ultrasonic Mixer	Alex Machine
Peristaltic Pump	Watson Marlow 120S
pH meter	WTW pH 330i/SET

Table 3.2. Chemicals used in the experiments.

Name	Formula	Molecular Weight (g/mol)	Source
Strontium carbonate	SrCO_3	147.63	Alfa Aesar
Sodium carbonate	Na_2CO_3	105.99	Merck
Calcium carbonate	CaCO_3	100	Merck
Potassium carbonate	K_2CO_3	138.21	Merck
Barium carbonate	BaCO_3	197.34	BDH
Lanthanum (III) oxide	La_2O_3	325.81	Aldrich
Titanium (IV) dioxide (nano powder-P25)	TiO_2	79.87	Aldrich
Titanium (IV) dioxide	TiO_2	79.87	Honeywell
Tantalum (V) oxide	Ta_2O_5	441.89	Alfa Aesar
Niobium (V) oxide	Nb_2O_5	265.81	Alfa Aesar
Chromium (II) chloride	Cr_2O_3	151.99	Alfa Aesar
Copper (II) chloride	CuCl_2	134.45	Aldrich
Gold (III) chloride trihydrate	$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$	393.83	Sigma Aldrich
Tetraammineplatinum (II) nitrate	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	387.21	Sigma Aldrich
Methanol	CH_3OH	32.04	Merck
Sodium sulfide	Na_2S	78.05	Zag Kimya
Sodium sulfite	Na_2SO_3	126.04	Zag Kimya
Ethylene glycol	$\text{C}_2\text{H}_6\text{O}_2$	62.07	Merck
Triethylamine	$\text{C}_6\text{H}_{15}\text{N}$	101.19	Merck
Formic acid	CH_2O_2	46.03	Merck
D(+)-Glucose monohydrate	$\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$	198.17	Merck
Glycerol	$\text{C}_3\text{H}_8\text{O}_3$	92.094	Doga ilac
Urea	$\text{CH}_4\text{N}_2\text{O}$	60.06	Merck
Argon (inert gas for GC)	Ar	39.9	Linde
Nitrogen (inert gas for storage)	N_2	28.014	Linde

3.2. Catalyst Preparation

All prepared perovskites (BaTiO_3 , NaTiO_3 , Ca doped NaTiO_3 , SrTiO_3 , Cr doped SrTiO_3 , NaTaO_3 , La doped NaTaO_3 , and KNbO_3) were synthesized by the SSR method (Saadetnejad and Yıldırım, 2018). A and B-site precursors and dopant materials, which were mixed and milled in a porcelain crucible were: for BaTiO_3 : BaCO_3 and TiO_2 ; for NaTiO_3 : Na_2CO_3 , and TiO_2 ; for Ca doped NaTiO_3 : Na_2CO_3 , CaCO_3 and TiO_2 ; for SrTiO_3 : SrCO_3 and TiO_2 ; for Cr doped SrTiO_3 : SrCO_3 , Cr_2O_3 and TiO_2 ; for NaTaO_3 : Na_2CO_3 and Ta_2O_5 ; for La doped NaTaO_3 : Na_2CO_3 , La_2O_3 and Ta_2O_5 ; for KNbO_3 : K_2CO_3 and Nb_2O_5 .

BaTiO_3 and KNbO_3 were calcined in air at 1273 K for 10 hours and the molar ratio of A-site: B-site was taken as 1:1. Similarly Sr:Ti molar ratio in SrTiO_3 was 1:1 while Cr doped SrTiO_3 had Sr:Ti:Cr molar ratio of 1:0.9:0.1 (calcined in air at 1273 K for 10 hours). Na:Ti molar ratio of 1:1 was used for NaTiO_3 whereas Ca:Na:Ti molar ratio of 0.1:0.49:0.5 was used in Ca doped NaTiO_3 ; they calcined at 1273 K and 1323 K in air for 10 hours respectively. As for doped tantalate-based perovskites, Na:Ta molar ratio of 0.6:0.4 was used NaTaO_3 while the ratio was 0.02:0.98:1 (calcined at 1273 K in air for 10 hours). La doped NaTaO_3 was prepared in two different La:Na:Ta molar ratios as 0.02:0.98:1 and 0.08:0.392:0.6; they both calcined at 1123 K in air for 10 hours. Nanopowder (21 nm) TiO_2 , Ta_2O_5 and Nb_2O_5 were purchased and directly used after adding Pt or Au cocatalysts as given in below.



Figure 3.1. The SSR method and cocatalyst loading steps.

1 wt.% Pt loaded TiO_2 , SrTiO_3 , $\text{SrTi}_{0.9}\text{Cr}_{0.1}\text{O}_{3.1}$, BaTiO_3 , Ta_2O_5 , NaTaO_3 , $\text{La}_{0.02}\text{Na}_{0.98}\text{TaO}_3$, $\text{La}_{0.08}\text{Na}_{0.392}\text{Ta}_{0.6}\text{O}_{1.708}$, $\text{Na}_{0.6}\text{Ta}_{0.4}\text{O}_{1.3}$, Nb_2O_5 , and KNbO_3 were prepared via the incipient-to-wetness impregnation method. The mixtures were dried overnight at 373 K and calcinated at 673 K for 4 hours in air. Alongside Pt cocatalyst, Au, Cu and bimetallic Au-Cu cocatalyst were also applied on the surface of nanopowder TiO_2 . 1 wt.% Cu loaded TiO_2 and 0.2 wt.% Au loaded TiO_2 were prepared through the deposition precipitation with urea (DPU) method. 1.1×10^{-3} M aqueous solution of CuCl_2 (or $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) in distilled water were added into 5 g of TiO_2 and 100 mL distilled water mixture. After stirring CuCl_2 (or $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) solution with TiO_2 in 100 mL distilled water, 0.42 M urea aqueous solution was added into the suspension, and stirred for four hours at 70 °C in order to decompose urea and raise pH to 7-8 interval. Then, the catalyst samples were washed, centrifuged three times, dried overnight at 100 °C and finally calcined at 400 °C for 4 hours in air (Saadetnejad and Yildirim, 2018; Zanella *et al.*, 2002).

The bimetallic 0.2 wt.% Au-0.8 wt.% Cu loaded nanopowder TiO_2 , on the other hand, were prepared using the sequential deposition precipitation with urea (S-DPU) method. First, the copper was deposited on TiO_2 as previously explained DPU procedure above. Then the catalyst sample was centrifuged, dried and calcined at 400 °C for 4 hours in air. After that, all steps were repeated for Au deposition on Cu/ TiO_2 . Both DPU and S-DPU methods were conducted in dark condition to prevent the effect of light on gold and copper particles (Gomez-Cortes *et al.*, 2009; Sandoval *et al.*, 2013).

3.3. Catalyst Characterization

The band-gap of the prepared catalysts was investigated by Shimadzu UV-2600 UV-VIS spectrometer and calculated via Kubelka-Munk method as referred by Escobedo-Morales et al. The reflectance and wavelength data obtained from UV-VIS spectrometer were used to obtain band gap energy of the samples. The molar absorption coefficient (K), and the scattering factor (S) were calculated from the diffuse reflectance (R) of material as in the Equations 3.1 and 3.2, and then Kubelka-Munk function (F(R)) was obtained by means of K and S values as in the Equation 3.3. In next step, $(F(R)h\nu)^2$ versus $h\nu$ was plotted to determine the band gap values of the samples. h is Planck's constant and ν is the frequency (Escobedo-Morales *et al.*, 2019).

$$K = (1 - R)^2 \quad (3.1)$$

$$S = 2R \quad (3.2)$$

$$F(R) = K/S \quad (3.3)$$

Besides UV-VIS spectroscopy, the surface structures, Au and Cu dispersion on the surface of TiO₂ photocatalysts were investigated by the scanning electron microscope (SEM) of Philips XL30 ESEM-FEG at Boğaziçi University Advanced Technologies R&D Laboratory. Finally, the crystal structure of TiO₂ and SrTiO₃ photocatalyst were characterized with Rigaku D/MAX-Ultima+/PC X-Ray diffraction (XRD) equipment at Boğaziçi University Advanced Technologies R&D Laboratory.

3.4. Experimental Set-up and Hydrogen Evolution Analysis

H₂ evolution rates from the distilled water assisted with various sacrificial reagents were conducted in a semi batch photocatalytic reaction system in which argon (Ar) was used as inert-carrier gas with the flow rate of 30 mL/min. The photoreactor and the overall experimental set-up and are given in Figure 3.2 and Figure 3.3 respectively.

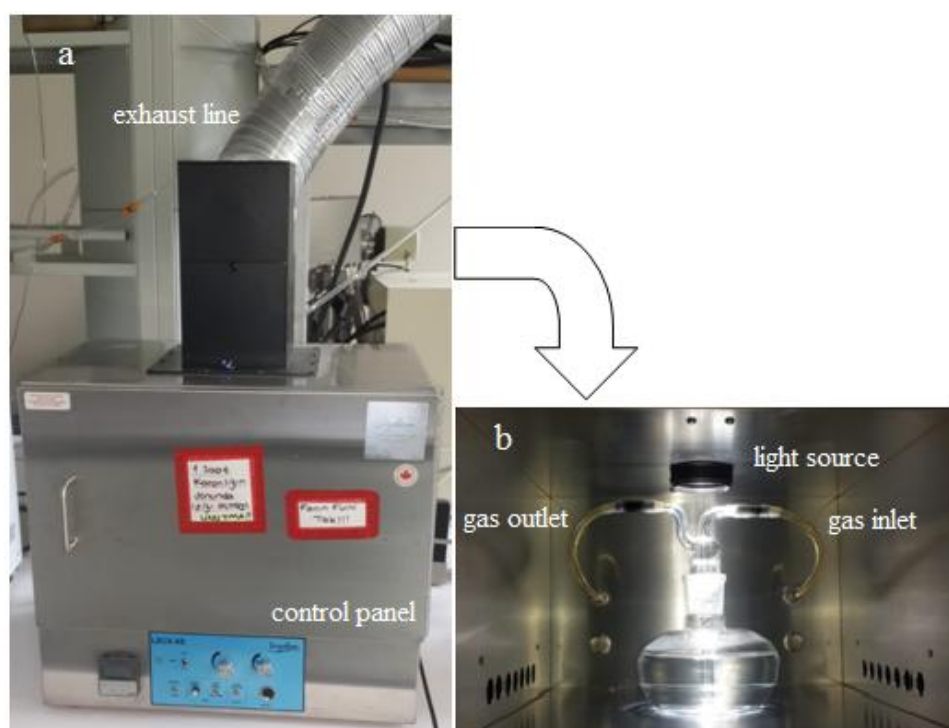


Figure 3.2. The outside (a) and inside (b) of the photoreactor.

2 g_{cat}/L photocatalyst was suspended in 500 mL reaction solution (20 wt.% sacrificial reagent and 80 wt.% distilled water). The photoreactor was irradiated by Luzchem 300 W Xe lamp. The lamp of photoreactor was used with and without the UV filter to observe the effect of the irradiation type. The H₂ production rates were determined by a Shimadzu GC-2014 gas chromatograph. The aqueous glycerol solution was neutral at the beginning of reactions, and the ambient temperature was measured around 313 K during the experiments.

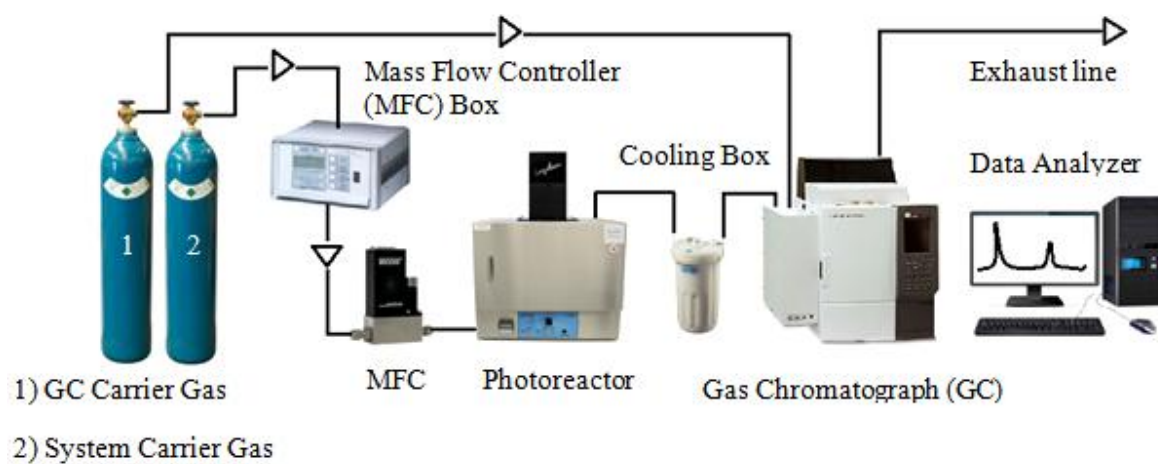


Figure 3.3. The overall experimental set-up.

4. RESULTS AND DISCUSSION

4.1. Preliminary Experiments

The initial objective was to use a Taguchi experimental design with five variables (materials in A and B-sites of perovskites, A/B ratio and SSR temperature) as it was given Table 4.1 and Table 4.2 (Phadke, 1989).

Table 4.1. Variables and levels of Taguchi experimental design.

	Variables				
Levels	A-Site	B-Site	Dopants	A/B (molar ratio)	Temperature (K)
	1	2	3	4	5
1	Na	Ta	La	40/60	1123
2	K	Ta	-	60/40	1223
3	Sr	Ti	Ca	50/50	1323
4	Bi	Nb	Ba	50/50	1423

Table 4.2. Combinations of Taguchi experimental design.

Row-Levels	Column-Variables					
	Expt. No.	A-Site	B-Site	Dopants	A/B (molar ratio)	Temperature (K)
		1	2	3	4	5
1	1	1	1	1	1	1
2	2	1	2	2	2	2
3	3	1	3	3	3	3
4	4	1	4	4	4	4
5	5	2	1	2	3	4
6	6	2	2	1	4	3
7	7	2	3	4	1	2
8	8	2	4	3	2	1
9	9	3	1	3	4	2
10	10	3	2	4	3	1
11	11	3	3	1	2	4
12	12	3	4	2	1	3
13	13	4	1	4	2	3
14	14	4	2	3	1	4
15	15	4	3	2	4	1
16	16	4	4	1	3	2

However, with progress of work, it was observed that the experimental design was not suitable for this work for two reasons. First, some of the samples could not be designed under the same temperature. For example $\text{La}_{0.08}\text{Na}_{0.392}\text{Ta}_{0.6}\text{O}_{1.708}$ and $\text{La}_{0.02}\text{Na}_{0.98}\text{TaO}_3$ at 1123 K, $\text{Na}_{0.6}\text{Ta}_{0.4}\text{O}_{1.3}$ could be synthesized at 1223 K and while NaTaO_3 could be obtained only at 1273 K. Similarly $\text{Ca}_{0.01}\text{Na}_{0.49}\text{Ti}_{0.5}\text{O}_{1.255}$ at 1323 K while NaTiO_3 was stuck on the surface of the porcelain crucibles at 1273 K as in Figure 4.1. Second, most of the formulation tested were found to be inactive despite of significant activities were reported in the literature the tests were performed with 1 wt.% Pt as cocatalyst and 2 g_{cat}/L catalyst in 500 mL solution of MeOH (20 wt.%) under UV-VIS light irradiations.

Considering that the experimental design aims to compare the change of output variables with the changes of inputs, and to find the optimum conditions, it was not possible to proceed further; hence, the remaining experiments were performed by changing the perovskite composition, cocatalyst and other variables in more traditional one at a time manner.



Figure 4.1. Burned and stuck NaTiO_3 and $\text{Ca}_{0.01}\text{Na}_{0.49}\text{Ti}_{0.5}\text{O}_{1.255}$ samples in the crucible.

4.2. The Effect of Catalyst Materials

After the experimental design was abandoned, the most commonly used titanate and niobium-based photocatalysts such as SrTiO_3 , (Liu *et al.*, 2008) BaTiO_3 , (Xie *et al.*, 2019) KNbO_3 (Ding *et al.*, 2008) were synthesized by the SSR method at 1273 K for 10 hours and tested for the water splitting activities. Furthermore, Ta_2O_5 (Thammanoon *et al.*, 2005) and Nb_2O_5 (Chen *et al.*, 2007) were also tested directly to see whether they are active or not; Pt was used as cocatalyst in all these tests.

SrTiO_3 , BaTiO_3 , KNbO_3 , Ta_2O_5 , and Nb_2O_5 catalysts were loaded with Pt cocatalyst and calcined at 673 K for 4 hours. Then, their photocatalytic activities were tested in 500 mL solution of MeOH (20 wt.%) with 2 $\text{g}_{\text{cat}}/\text{L}$ under UV-VIS light irradiation. The hydrogen generation performances of samples are given in Figure 4.2. As it was clearly seen, only SrTiO_3 produced hydrogen under the conditions tested and the maximum hydrogen evolution rate was reached to 107.2 $\mu\text{mol}/\text{h.g}_{\text{cat}}$ during 10 hours.

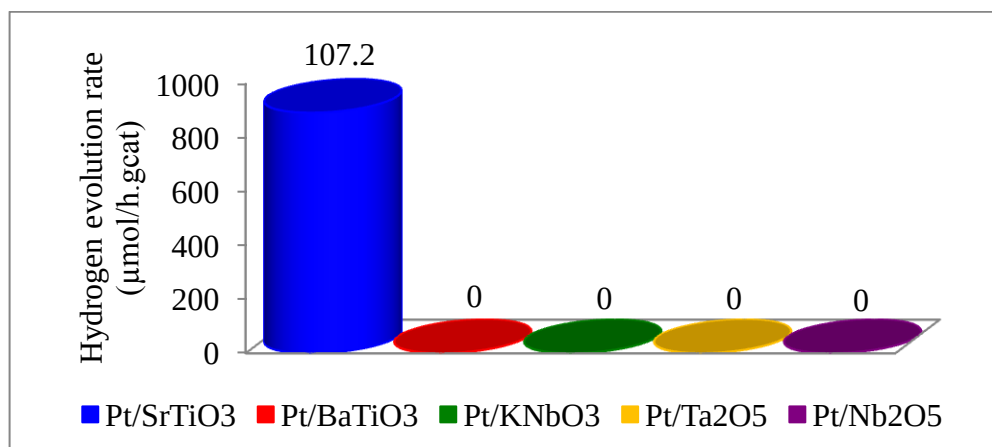


Figure 4.2. The hydrogen generation performance of 1 wt.% Pt loaded samples: Pt/SrTiO₃, Pt/BaTiO₃, Pt/KNbO₃, Pt/Ta₂O₅ and Pt/Nb₂O₅ for 10 hours under UV-VIS light irradiation.

It was known that the structure of perovskite (or any semiconductor) may be changed with doping; this way the light absorption capacity of semiconductor can be improved (for example the material may be more sensitive to visible light) to enhance the hydrogen production activity both under UV and especially VIS light conditions (Wang *et al.*, 2006; Xu *et al.*, 2016; Lacz and Drozd, 2019). Moreover, Cr is considered as a simple and cost-effective dopant with huge potential for this purpose by various investigators (Sun *et al.*, 2015; Xu *et al.*, 2016).

We also tested the performance of 1 mole % Cr doped on SrTiO₃ (SrTi_{0.9}Cr_{0.1}O_{3.1}) and tested with the presence of 1 wt% Pt; however, Cr dopant did not show any benefits in terms of hydrogen production for SrTiO₃ under UV-VIS light and in MeOH aqueous mixture. It was concluded that the poor photocatalytic performance of SrTi_{0.9}Cr_{0.1}O_{3.1} catalyst was resulted from the detrimental effect of Cr⁺⁶ species on the catalysts as in mentioned in the studies of Wang *et al.* (2006) and Xu *et al.* (2016). Also considering the results obtained in preliminary works discussed above as well as the other works undergoing in the laboratory. We decided to continue to work with SrTiO₃ and test the other parameters in the system.

4.3. The Effect of Sacrificial Reagents

The effect of sacrificial reagents was studied only conducted on Pt/SrTiO₃ of 2 g_{cat}/L in 500 mL aqueous mixture of (20 wt.%) sacrificial reagent under UV-VIS light for 10 hours, and the hydrogen generation rates were determined as shown in Figure 4.3.

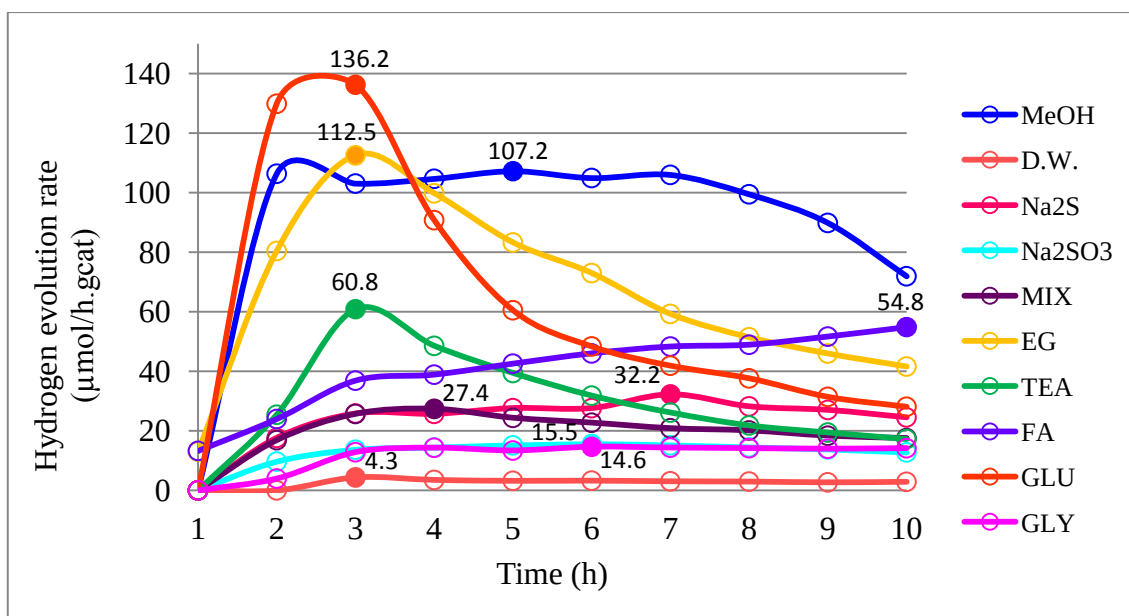


Figure 4.3. The effects of the sacrificial reagents on the hydrogen evolution performance of Pt/SrTiO₃ during 10 hours under UV-VIS light (MeOH: methanol, D.W.: distilled water, MIX: Na₂S+Na₂SO₃, EG: ethylene glycol, TEA: triethylamine, FA: formic acid, GLU: D(+)-glucose monohydrate, GLY: glycerol, and max. evolution rates were given with bold).

Based on their maximum H₂ evolution rates, were found to be GLU (136.2 μmol/h.g_{cat}), EG (112.5 μmol/h.g_{cat}), MeOH (107.2 μmol/h.g_{cat}); however; the performance of first two sharply, and performance of MeOH were gradually decreased with the time; the hydrogen production with TEA, which was already low (60.8 μmol/h.g_{cat}) was also decreased. On the other hand, the performance of Na₂S (32.2 μmol/h.g_{cat}), MIX (27.4 μmol/h.g_{cat}), Na₂SO₃ (15.5 μmol/h.g_{cat}), GLY (14.6 μmol/h.g_{cat}), and D.W. (4.3 μmol/h.g_{cat}) were low but almost constant or decreased slightly with the time. Additionally,

the sacrificial reagents without containing H_2 in their formulations such as Na_2S and Na_2SO_3 have a special benefit due to the higher confidence in the fact that the hydrogen generation was totally from the splitting water (Li *et al.*, 2015) even it is in low rates.

Finally, it can be easily seen that the hydrogen evolution increased continuously when FA, which is also considered as a pollutant, was used as the sacrificial reagent. Although GLY did not performed as well as FA, it should be still considered because, as indicated in Figure 2.17, GLY may decompose and generate FA hence, GLY should be also considered as an attractive potential. The other reason to consider GLY as sacrificial agent is that it is the main by-product of the biodiesel production (10 % of total yield) (Guo *et al.*, 2018). Thus its storage is also huge problem for manufactures (Md. Rahim *et al.*, 2020; Slamet *et al.*, 2015). Moreover, although there are several products containing GLY derivatives, especially in cosmetic industry (Maurino *et al.*, 2008; Dodekatos *et al.*, 2018), a significant level of surplus is expected if the biodiesel become a significant transportation fuel. Consequently, the use of GLY as sacrificial reagents has a huge potential to reduce its potential surplus in future while producing more valuable products as the result of partial decomposition during the water splitting process. Indeed, GLY has been studied extensively before and its completely decomposition took 10 days through the generation and consumption of various intermediate products (Daskalaki and Kondarides, 2009). Considering these, the stability of GLY was further tested over 2 g_{cat}/L Pt/SrTiO₃ in 500 mL, 20 wt.% aqueous mixture of GLY under UV-VIS light for 72; the hydrogen generation rates were almost constant with the maximum H_2 evolution rate of 21.64 $\mu\text{mol/h.g}_{\text{cat}}$ as illustrated in Figure 4.4.

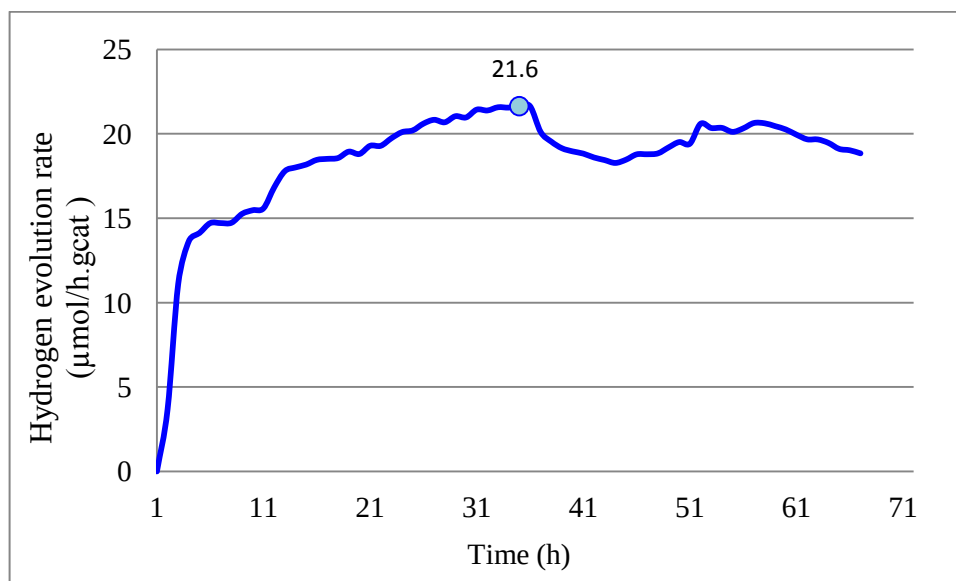


Figure 4.4. The hydrogen production performance of Pt/SrTiO₃ under UV-VIS light for 72 h stability test (the maximum H₂ production was given with bold).

Alongside Pt/SrTiO₃, 2 g_{cat}/L. Pt/SrTi_{0.9}Cr_{0.1}O_{3.1} was also tested in 500 mL 20 wt.% GLY and FA aqueous solutions under UV-VIS light irradiation. This time, the maximum hydrogen evolution rates were obtained with FA and GLY 34.6 μmol/h.g_{cat} and 37.7 μmol/h.g_{cat} respectively as in shown Figure 4.5; Indeed Cr doping in B-site of SrTiO₃ gave better performance in GLY this time as claimed in literature (the performance with FA was lower than pure SrTiO₃); however the initial performance sharply decreased in case of both sacrificial reagent (there was a slight increase after the 9th hour for GLY). Again, this low performance can be explained with Cr⁺⁶ species because these species resulted in consuming of photogenerated electrons at the starting point of the photocatalytic experiment (Wang *et al.*, 2006; Sun *et al.*, 2015).

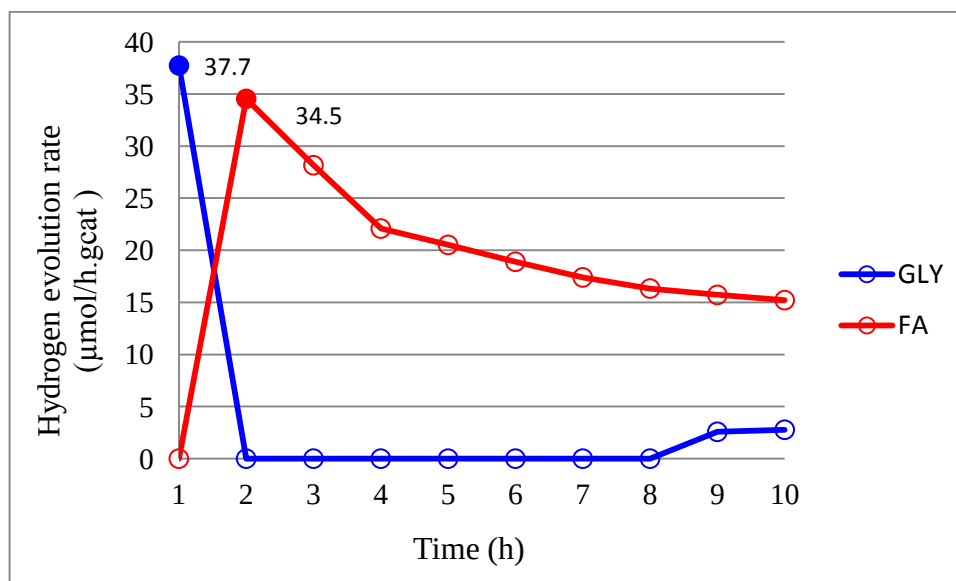


Figure 4.5. The photocatalytic hydrogen generation performances of $\text{Pt/SrTi}_{0.9}\text{Cr}_{0.1}\text{O}_{3.1}$ both in FA and GLY (20 wt.%) solutions under UV-VIS light irradiation (the maximum rates were given by bold).

At the final stage of the experiments on sacrificial reagent effect, Pt/SrTiO_3 was tested also in visible region illumination; however SrTiO_3 with the presence of Pt cocatalyst in GLY solution (20 wt.%) did not generate any hydrogen, probably because SrTiO_3 has large band gap (3.2 eV) and its band gap should be tuned by a cocatalyst working in the VIS light condition such as Au or Cu having LSPR effect (Xue *et al.*, 2017; Ding *et al.*, 2018; Xiao *et al.*, 2020). Additionally we also tested nanopowder TiO_2 because it was reported in several articles that, as a low cost and stable material, the nanopowder TiO_2 is effective to utilize GLY aqueous solutions to split the water and meanwhile reform GLY; (Liu *et al.*, 2008; Dodekatos *et al.*, 2018; Bahruji *et al.*, 2011; Slamet *et al.*, 2013; Slamet *et al.*, 2015). In the line with literature, 2 $\text{g}_{\text{cat}}/\text{L}$ Pt loaded TiO_2 samples were also tested under UV-VIS irradiation in 500 mL GLY solution (20%) for 10 hours, as also found in literature, an average hydrogen evolution of 1146 $\mu\text{mol/h.g}_{\text{cat}}$, which is much higher than any perovskite tested in this work, could be obtained as shown Figure 4.6. Thus, the test of nanopowder TiO_2 with different cocatalysts such as Au and Cu or their bimetallic combinations was decided as the next step of work to check the possibility of obtaining a facile and visible light active cocatalyst as an alternative for Pt.

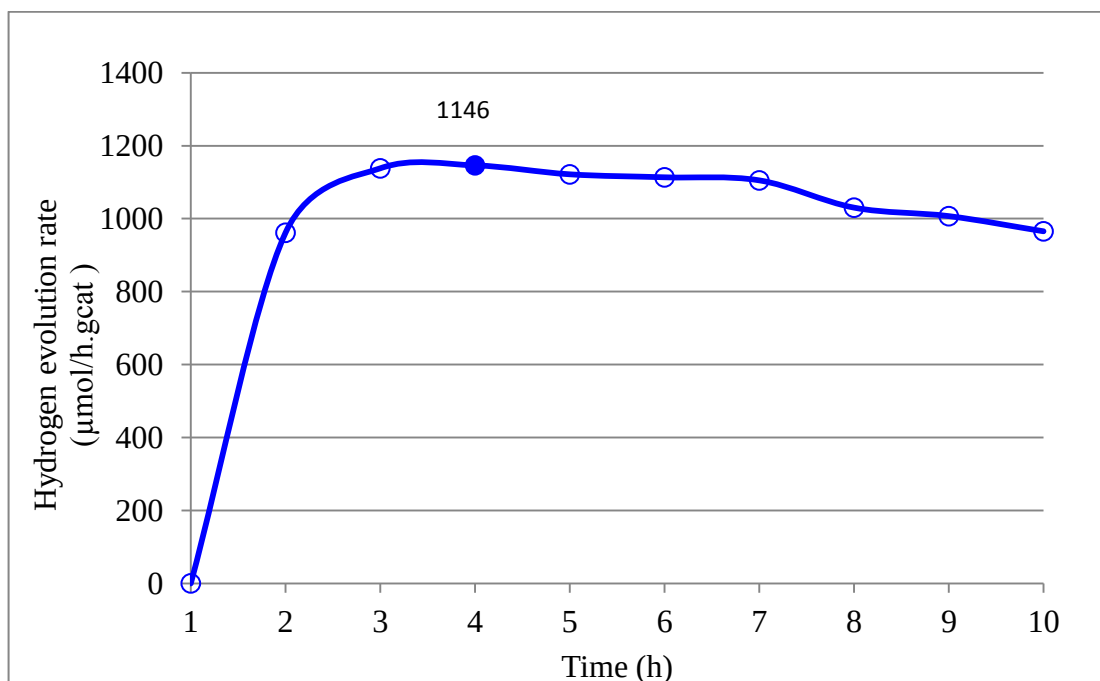


Figure 4.6. The hydrogen generation performance of Pt/TiO₂ under UV-VIS irradiation with GLY (20 wt.%) aqueous solution for 10 hours (the maximum rate was given by bold).

4.4. The Effect of Cocatalyst and Irradiation

In order to utilize prepared photocatalysts in visible light conditions with GLY aqueous solution, the most studied nanopowder TiO₂ was used in the experiments; but this time, the cocatalysts, which have LSPR effect such as Au, Cu was used instead of Pt. For this, 0.2 wt.% Au/TiO₂, 1 wt.% Cu/TiO₂ and bimetallic 0.2 wt.% Au - 0.8 wt.% Cu/TiO₂ were prepared with DPU and S-DPU methods and calcined at 773 K for 4 h. After that, all mono and bimetallic catalyst were tested with 2 g_{cat}/L in 500 mL GLY (20 wt.%) aqueous solutions both under UV-VIS and VIS light irradiation. In addition, 1 wt.% Pt/TiO₂ photocatalyst was also tested under exactly the same condition as a reference. The hydrogen evolution rates of 1 wt.% Pt/TiO₂, 0.2 wt.% Au/TiO₂, 1 wt.% Cu/TiO₂ and bimetallic 0.2 wt.% Au - 0.8 wt.% Cu/TiO₂ photocatalysts are depicted in Figure 4.7.

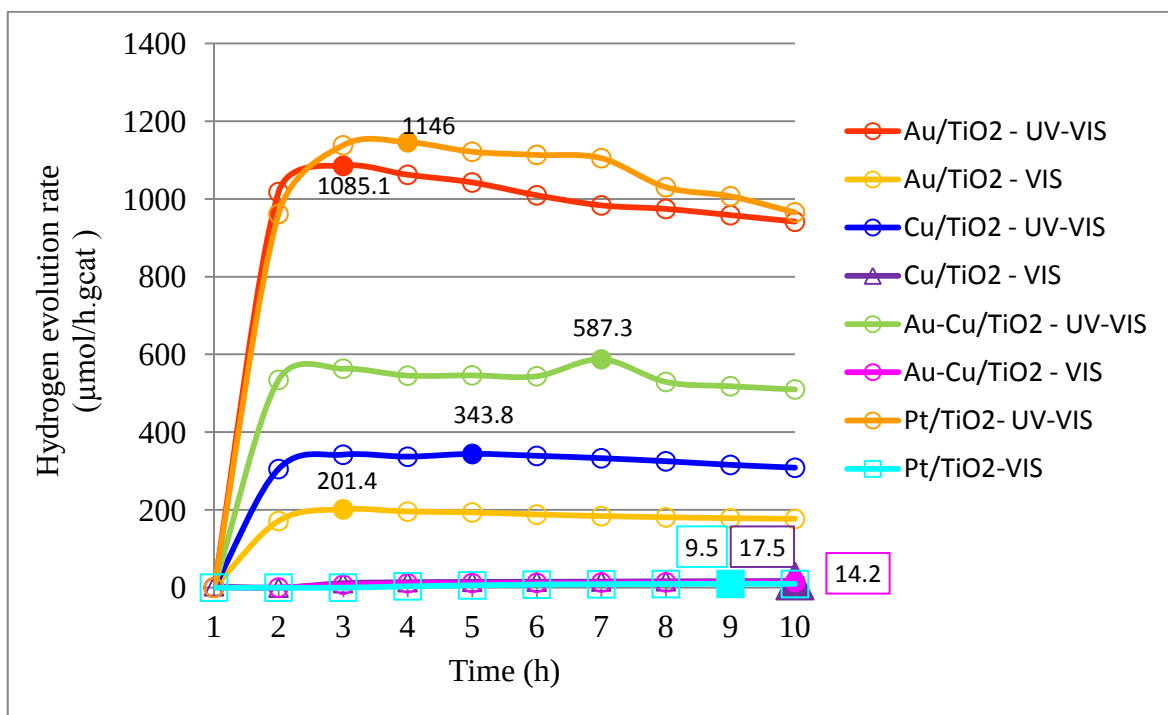


Figure 4.7. The effect of cocatalyst and irradiation on 0.2 wt.% Au/TiO₂, 1 wt.% Cu/TiO₂, and 0.2 wt.% Au-0.8 wt.% Cu/TiO₂ under UV-VIS and VIS irradiation in GLY aqueous solution (the maximum rates were represented with bold).

It can be easily seen from Figure 4.7 that 0.2 wt.% Au/TiO₂ is active as much as 1 wt.% Pt/TiO₂ for H₂ production with the maximum of 1085.1 μmol/h.gcat under UV-VIS irradiation in GLY aqueous mixture. Having almost the same level of H₂ production in two catalysts, even though Au loading is five times lower than Pt, may be attributed to the plasmonic effects of gold nanoparticles on H₂ evolution (Xiao *et al.*, 2020). This may increase the feasibility of using Au considering that Pt is generally more expensive and more sensitive to O₂ and CO (Md. Rahim *et al.*, 2020; Dodekatos *et al.*, 2018). As Figure 4.7 also indicates, Cu/TiO₂ has the lowest level of H₂ production while Au-Cu containing bimetallic catalyst, tested under same ambient condition exhibited a performance between Au/TiO₂ and Cu/TiO₂ with the maximum H₂ production of 587.3 μmol/h.gcat. Since the copper is much cheaper than Au and Pt, it may be considered as a potential catalyst even though the H₂ production rate on this metal is lower in glycerol reforming.

As for the effect of irradiation, while 0.2 wt.% Au/TiO₂ and 1 wt.% Pt/TiO₂ have demonstrated almost the same performance under UV-VIS light conditions in the existence

of GLY aqueous mixture, Pt/TiO₂ have shown the worst performance and Au/TiO₂ have shown the best performance among the other prepared catalysts under VIS light irradiation. It can be explained by effectiveness of plasmonic Au and Cu nanoparticles in neutral conditions under VIS light and their visible light sensitivity with the work function of 5.10 and 4.65 respectively (Kumaravel *et al.*, 2019; Dodekatos *et al.*, 2018). Even if Pt/TiO₂ had the excellent work function values of 5.93 among the others, it could not reach the same hydrogen generation rates under VIS irradiation as Au/TiO₂, Cu/TiO₂ or bimetallic Au-Cu/TiO₂; Pt is more effective cocatalyst under UV-VIS rather than VIS irradiation. Alongside Pt loaded TiO₂ sample, Au/TiO₂, Cu/TiO₂ and bimetallic Au-Cu/TiO₂ could work under VIS light with hydrogen production rate of 201.4 $\mu\text{mol/h.gcat}$, 17.5 $\mu\text{mol/h.gcat}$ and 14.2 $\mu\text{mol/h.gcat}$ respectively. These performances were found to match in work function values, because the higher work function results in the better photocatalytic activity in term of hydrogen generation performance (Kumaravel *et al.*, 2019).

4.5. Characterization

Au/TiO₂, which was the best performed catalysts, was characterized by SEM to investigate distribution and size of gold nanoparticles on TiO₂. In SEM images as depicted in Figure 4.8, the shiny and spherical gold nanoparticles were 40-50 nm size clusters. The gold nanoparticles could be observed as much brighter among the nano TiO₂ particles, because it was much heavier than TiO₂ support. There can be also smaller gold particles on TiO₂ that are not visible in the range of SEM precision. Although there are some agglomerations of gold in only certain areas, the samples generally have well distributed and large number of gold nanoparticles. Furthermore, this well distribution of Au onto TiO₂ was attributed to the effectiveness of DPU method (Zanella *et al.*, 2002).

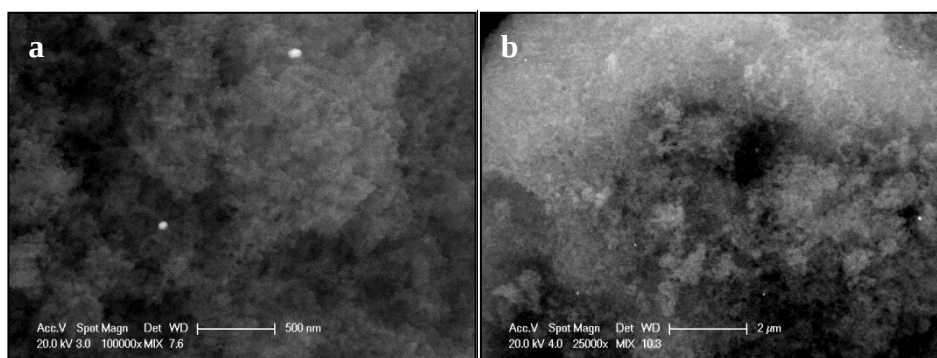


Figure 4.8. SEM images of 0.2 wt.% Au/TiO₂ in the range of 500 nm (a) and 2 μm (b).

The reflectance – wavelength values of each catalyst were measured using UV-VIS spectroscopy by Kubelka-Munk method to calculate direct band-gap energy. $(F(R)h\nu)^2$ versus $h\nu$ was plotted in Figure 4.9 for the band gap illustration of prepared samples such as nanopowder TiO₂, Au/TiO₂, Cu/TiO₂ and Au-Cu/TiO₂. h is Planck's constant and ν is the frequency. Kubelka-Munk function ($F(R)$) was obtained by means of K and S values as in the Equation 3.3.

The band gap energies of the samples were determined by means of the slope of the plots as in Figure 4.9 and demonstrated in Table 4.2. The band gap of samples was about 2.97 eV, which was quite close to TiO₂ indicating that Au, Cu or Au-Cu loading on TiO₂ did not have any effect on the band gap.

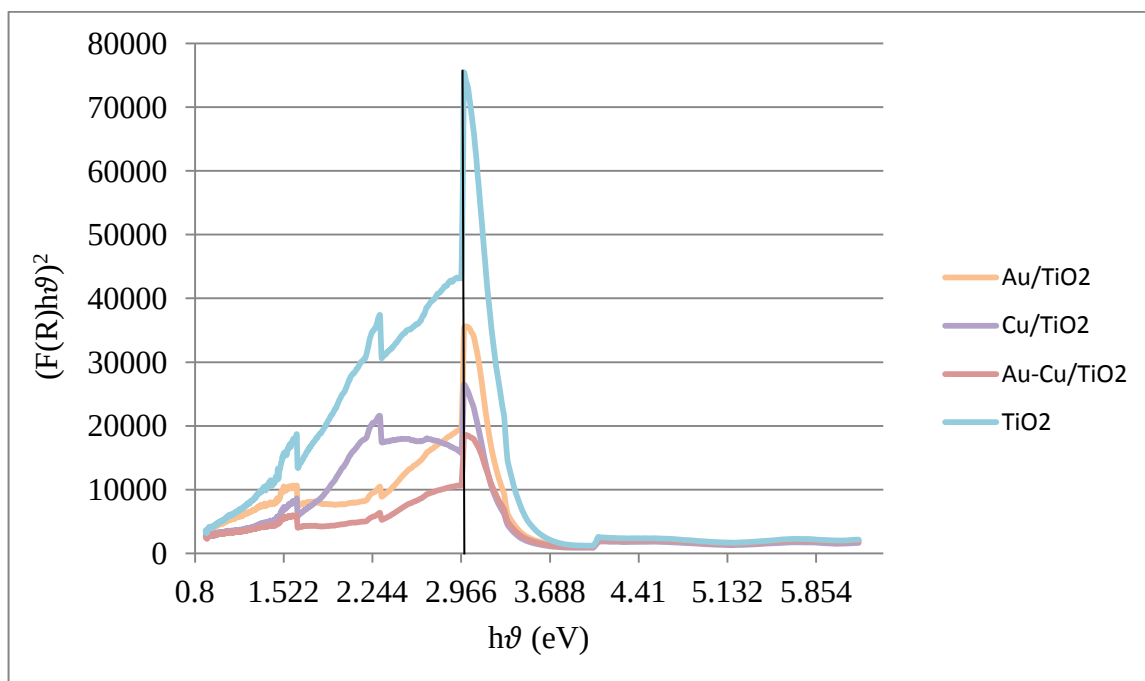


Figure 4.9. $(F(R)h\nu)^2$ versus $h\nu$ for 0.2 wt.% Au/TiO₂, 1 wt.% Cu/TiO₂ and 0.2wt.% Au-0.8 wt.% Cu/TiO₂

Table 4.3. The band gap energy of prepared photocatalysts.

Photocatalyst	Band gap energy (eV)
nanopowder TiO ₂	2.967
0.2 wt.% Au/TiO ₂	2.966
1 wt.% Cu/TiO ₂	2.966
0.2 wt.% Au – 0.8 wt.% Cu/TiO ₂	2.967

The XRD characterization of 1 wt.% Pt/TiO₂ and 1 wt.% SrTiO₃ were also given as in Figure 4.10. The XRD pattern of Pt/TiO₂ showed the existence of anatase phase (101) in the crystalline structure of TiO₂ with the diffraction peaks of 25.401° (PDF#86-1157) (Yang *et al.*, 2020). No peaks related to the rutile phase were observed in the XRD results of Pt/TiO₂. In addition to this, the peaks of Pt at $2\theta = 39.842^\circ$, 46.403° , 67.682° and 81.303° with the planes of 111, 200, 220, and 311 respectively indicated that Pt cocatalyst was successfully loaded onto TiO₂ (PDF#01-087-0646) (Ferreira *et al.*, 2020).

As for 1 wt.% Pt/SrTiO₃, the characteristic diffraction peaks of Pt/SrTiO₃ with 2θ values of 32.539°, 40.08°, 46.601°, 57.902°, and 67.941° corresponding to 110, 111, 200, 211, and 220 planes were appeared in the XRD results of 1 wt.% Pt/SrTiO₃ (JCPDS#73–0661) (Grabowska *et al.*, 2017; Shi *et al.*, 2020). This was attributed the cubic crystal phase of SrTiO₃ and the use of SSR methods for the synthesis of the photocatalyst (Grabowska *et al.*, 2017; Yuan *et al.*, 2016) There was no diffraction peak related to Pt, so it indicated that Pt is highly dispersed onto SrTiO₃.

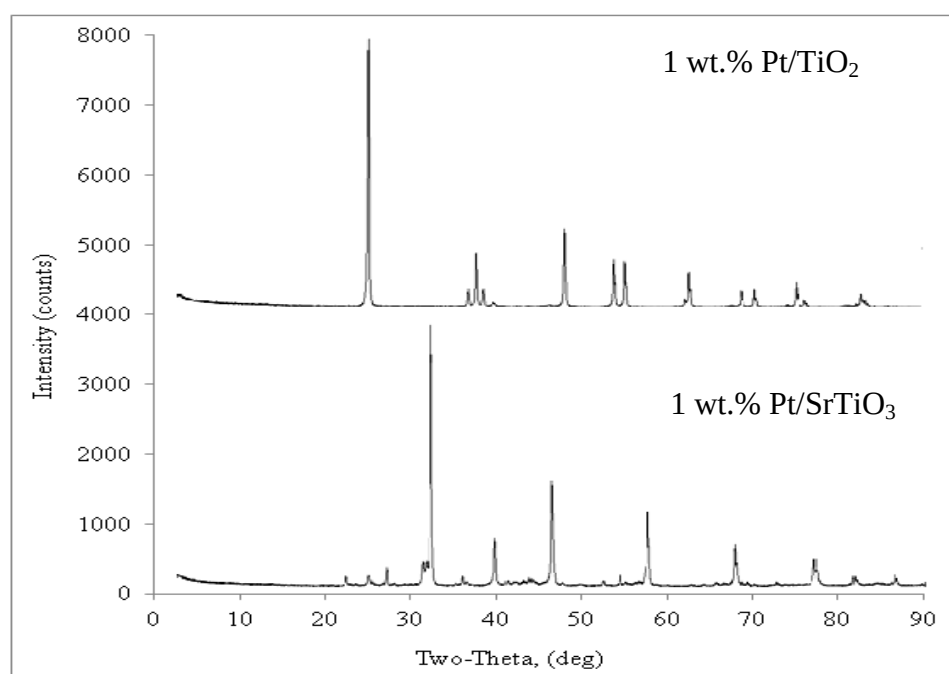


Figure 4.10. XRD results of 1 wt.% Pt/TiO₂ and 1 wt.% SrTiO₃ photocatalysts.

5. CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

A comparative study for the hydrogen evolution performance of titanate, tantalate and niobium-based perovskites was conducted at beginning of this thesis; although the experimental design conducted was not conclusive, the initial results suggested that 1 wt.% Pt/SrTiO₃ Sr:Ti (1:1) was better than the others in 20 wt.% aqueous methanol solution under UV-VIS irradiation. Then, various sacrificial reagents are tested and glycerol was decided for the further investigation; in addition to SrTiO₃, TiO₂ nanoparticles were also tested as the semiconductors while Pt was replaced with Au, Cu and Au-Cu as the plasmonic materials. 1 wt.% Pt loaded to TiO₂ with 20 wt.% aqueous glycerol solution gave the highest hydrogen production rate of 1146 $\mu\text{mol/h.g}_{\text{cat}}$ under UV-VIS irradiation. The 0.2 wt.% Au/TiO₂ gave almost the same performance (1085.1 $\mu\text{mol/h.g}_{\text{cat}}$) under UV-VIS conditions while Cu addition decreased the hydrogen production to 587.3 $\mu\text{mol/h.g}_{\text{cat}}$; 1 wt.% Cu loaded TiO₂ had also a significantly high performance (344.8 $\mu\text{mol/h.g}_{\text{cat}}$) as a cost-effective alternative to Pt or Au. The Au containing catalyst was also quite effective under visible light conditions with the hydrogen production rate of 201.4 $\mu\text{mol/h.g}_{\text{cat}}$ due to the plasmonic effect of gold particles. The other alternatives (Pt, Cu or Au-Cu) were not effective under visible light

The distribution and size of gold nanoparticles on TiO₂ for the best performed catalysts (0.2 wt.% Au/TiO₂) was also investigated, by SEM, and around 40-50 nm size shiny and spherical gold nanoparticles were observed. The band gap energies of the samples were determined about 2.97 eV, which is quite close to TiO₂ indicating that Au, Cu or Au-Cu loading on TiO₂ did not have any effect on band gap. While XRD results for nanopowder 1wt.% Pt/TiO₂ showed the existence of anatase phase, 1 wt.% Pt/SrTiO₃ demonstrated the cubic crystal phase of SrTiO₃.

5.2. Recommendations

The recommendations below can be used to further this study beyond.

- Different synthesis methods such as hydrothermal, polymerized-complex or sol-gel can be used for the catalyst preparation; they can provide better semiconductor properties. The cocatalyst loading can be also improved (for example better distribution over the semiconductor may be obtained) using different loading methods such as photodeposition for Pt and deposition-precipitation with NaOH for Au.
- Solution pH should be controlled during the experiment and some extra injection part should be added into the photoreactor for this. For example, the glycerol can decomposes easier in pH neutral mediums.
- In addition to doping, some additional processes (like reduction) on semiconductor should be implemented. For instance; the black-TiO₂ can be good alternative in terms of visible light driven systems. This material can be also doped with B, N or S elements to enhance more the activity.
- Glycerol, as the main by-product of biodiesel production (10 % of the total yield), may be a significant sacrificial reagent in photocatalytic system to reduce the potential surplus, which may be a serious environmental problem, by producing H₂ or some other valuable chemicals (like dihydroxyacetone, glyceraldehydes and formic acid) using an environmentally friendly process like photocatalytic water splitting.

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