DOI: 10.38061/idunas.658011

IDUNAS	NATURAL & APPLIED SCIENCES JOURNAL	2019 Vol. 2 No. 2 (1-15)

Artificial Photosynthesis with Titania Photocatalysts

Review Article

Hüsnü Arda Yurtsever[1*], Muhsin Çiftçioğlu[2]

[1] *Adana Alparslan Türkeş Science and Technology University, Department of Materials Engineering, Adana, Turkey*
[2] *İzmir Institute of Technology, Department of Chemical Engineering, İzmir, Turkey*

Author E-mails
husnuarda@gmail.com
Tel: +90 322 455 00 00 / 2160
Fax: +90 322 455 00 39
*Correspondence to: H.A. Yurtsever, Adana Alparslan Türkeş Science and Technology University,
Department of Materials Engineering, Adana, Turkey

DOI: 10.38061/idunas.658011

Received: December 11, 2019; Accepted: December 31, 2019

Abstract

Increasing energy demand and global warming due to extensive use of fossil fuels will soon force mankind to use clean and sustainable fuels and artificial photosynthesis is being considered as a promising solution to both problems. Photocatalysis is a light induced process involved in artificial photosynthesis and it will make a great contribution to the solution of environmental problems and generation of renewable energy sources. Titania based photocatalytic materials are one of the widely used materials in artificial photosynthesis research due to their unique chemical and optical properties. Recent research has shown that the activity of titania phases can be improved in the visible light region by several modification techniques. This article aims to present a brief review based on the last 2 decades of global research on the preparation and modification of titania based photocatalysts, their application and importance in artificial photosynthesis and its effect on reducing global warming by the development of a sustainable energy source. This review is mostly based on the PhD thesis of the corresponding author (Yurtsever, 2015).

Keywords: titania, artificial photosynthesis, global warming, sustainable energy

1.INTRODUCTION

Light energy of the sun captured and utilized by plants through photosynthesis processes in which inorganic substances like CO_2 and water are consumed for the synthesis of organic compounds necessary for their survival started and sustains the life processes of animals (Collings and Critchley, 2005). The balance in the plant-animal life processes was disturbed by human activities in the last two hundred years. Anthropogenic CO_2 emissions increased due to the increasing fossil fuel use since the beginning of industrial revolution and the excess CO_2 which cannot be consumed by the plants started to accumulate in the atmosphere.

In 1824, Jean Baptiste Fourier, a French mathematician, discovered that earth's temperature was rising gradually. This discovery which is about the atmosphere's capturing sunlight escaping and sending it back to the earth, led the basic theory of "Global Warming" arise. This theory was named as the "Greenhouse Effect" since 1990s. Scientific research showed that CO_2 emission originating from the fossil fuel usage as the main energy source is the reason for global warming (Collings and Critchley, 2005). Scientists found that earth's global temperature and sea levels raised approximately 0.6_oC and 20 cm, respectively, during 20_{th} century. The average temperature difference reached to 0.6_oC by 2000s. In the year 2100, global CO_2 concentration will reach from the present value of 369 ppmv to 650 ppmv unless the fearless fossil fuel consumption was stopped (Houghton, 2004).

Many governments are trying to take precautions by regulations since the discovery and acceptance of global warming. The most important international agreement to fight with the global warming is the "Kyoto Protocol" which was accepted in 1997. According to this protocol, greenhouse gases emissions would have been reduced beginning from 2005 by 125 countries which accepted this protocol (Collings and Critchley, 2005).

2. ENERGY FROM THE SUN

Energy from fossil fuels (e.g. oil, coal), nuclear energy and renewable energy (e.g. wind, solar and biomass) are possible choices that can be used to satisfy the energy demand of humanity and sustain life on earth. Geopolitical issues about fossil fuels, capital costs of constructing renewable energy producing facilities directed us to use non-sustainable fossil fuels. More than 80% of our energy is provided by fossil fuels at present. Our dependence on fossil fuels to create and sustain the well-being and development of society damages the nature irreversibly.

Use of fossil fuels to sustain the energy production until now caused the aforesaid global warming and pollution problem. Increasing energy demand and global warming due to extensive use of fossil fuels will soon force mankind to use clean and sustainable fuels. Solar energy is one of these sustainable energy resources to meet our present and future energy demand. Being limitless and free makes it a promising choice among these renewable resources. The hourly solar energy flux to the earth is more than the energy that we consume in a year. Our energy need can be provided by harvesting 0.02% of the energy from the sun without using any other energy resources. Solar energy can be converted into electrical energy for the simultaneous production and use or can be converted into heat or chemical energy and stored for the further use (Hammarstrom and Hammes-Schiffer, 2009).

The earth is heated with an energy flux of 1369 W/m_2 after 30% of solar energy is absorbed and scattered in the atmosphere. The reason for the loss of energy is the absorption by gases such as water, ozone, CO_2 and the scattering by clouds and aerosols in the atmosphere. Light with the wavelengths lower than 300 nm is absorbed by ozone, nitrogen and oxygen. Absorption in the infrared region is caused by water and CO_2. Solar radiation spectrum at the top of the atmosphere and at sea level is given in Figure 1. The solar light with a spectrum between 300 nm and 2500 nm reaches to the earth's surface after a portion is absorbed by the atmosphere. Solar radiation consists of three main regions. These are 5% UV (300-400 nm), 40% visible (400-800 nm) and 55% infrared (800-2500 nm) regions.

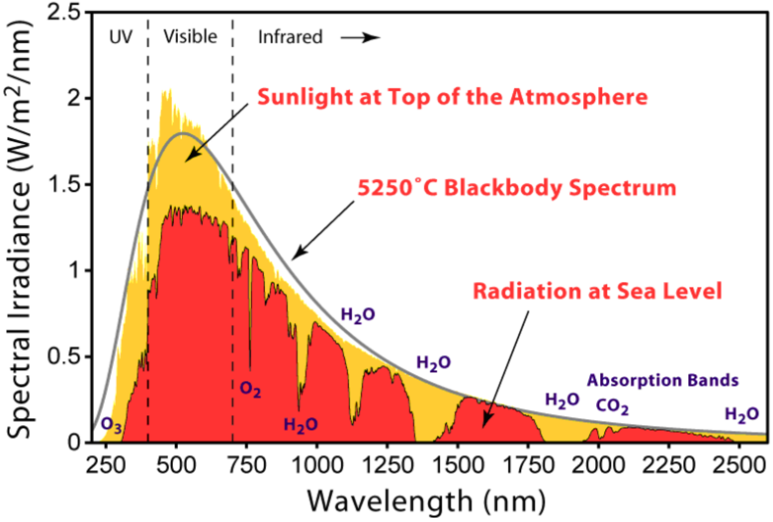


Figure 1. Solar radiation spectrum. (Robert A. Rohde, Global Warming Art project).

3. UTILIZATION OF SOLAR ENERGY VIA PHOTOCATALYSIS

Research on the utilization of solar energy to meet the energy demand gained significant interest in the last years. Among the most solar energy utilization techniques, artificial photosynthesis is promising since renewable and sustainable fuels can be generated while global CO_2 concentration in the atmosphere is reduced. (Cogdell et al., 2010). The properties of the photocatalyst materials have significant effect on the efficiency of the photocatalytic processes and artificial photosynthesis. These materials should be corrosion resistant (Zhu and Zach, 2009), chemically stable and cheap with high and efficient visible light absorption (Silija et al., 2012).

A photocatalyst is a semiconductor which is mostly an oxide of a metal having a specific band gap energy (E_g) between the conduction and valence band. Semiconductor becomes active when it is exposed to light having photons with energies equal to or higher than the band gap energy of that material (Figure 2). An electron (e_-) hops from the conduction band leaving a hole (which can act as a positively charge electron) in the valence band of the semiconductor when the material is excited by photons (Linsebigler et al., 1995).

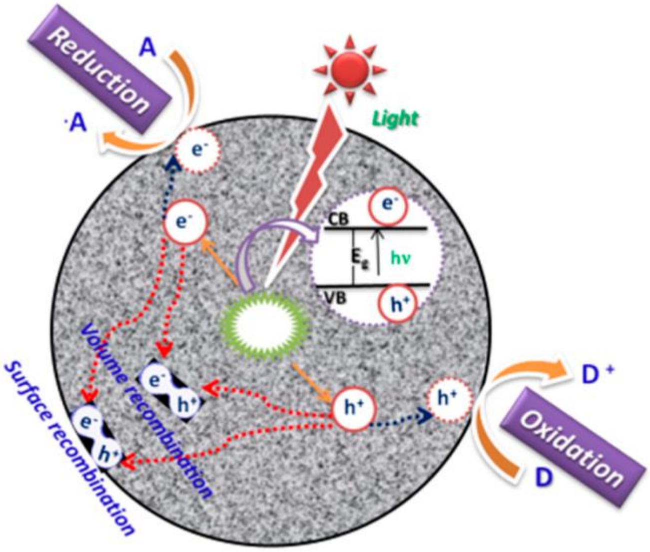


Figure 2. Schematic representation of photocatalysis mechanism (Kumar et al., 2018).

An ideal photocatalyst should have the following characteristics:

- photoactive,
- biologically and chemically inert,
- photostable (i.e., not prone to photocorrosion),
- inexpensive
- non-toxic.

Photocatalytic processes are started and carried on by the electron-hole pairs (e^--h^+) which are generated and separated on the surface of the semiconducting material. Excited electrons and holes can react with electron donors/acceptors adsorbed on the surface which triggers oxidation-reduction reactions or recombine/get trapped in surface states becoming useless from the viewpoint of photocatalysis (Zaleska, 2008). Electron-hole pairs generated in the lattice are separated and captured in suitable parts of the nanostructure to avoid recombination on the surface or in the volume. Holes conduct oxidation reactions and electrons conduct reduction reactions (Linsebigler et al., 1995). Electron transfer is more efficient when the reactants are preadsorbed on the surface of the photocatalyst. The probability and the rate of charge transfer process depend strictly on the band edge position of the semiconducting material and the redox potential of the adsorbed species. The bottom of conduction band of the semiconductor must be at a more negative potential than H^+/H_2 (0 V vs. NHE at pH 0) and the top of the valence band must be at a more positive potential than H_2O/O_2 (1.23 V vs. NHE at pH 0). The minimum electron energy should be 1.23 eV (the corresponding wavelength is around 1000 nm) for water splitting reaction to be thermodynamically possible (Zang, 2011). Some examples of photocatalysts and redox potentials of water splitting and oxidation of organics are given in Figure 3.

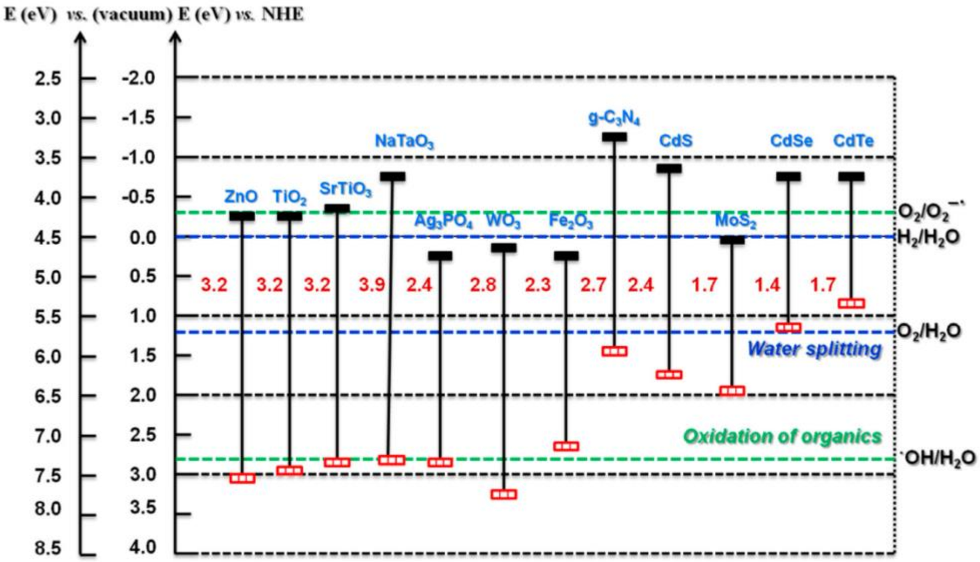


Figure 3. Relationship between band structure of semiconductor and redox potentials of water splitting and oxidation of organics (Kumar et al., 2018).

Nanostructured photocatalytic material preparation techniques were improved and the application area was expanded by the advances in nanotechnology in the last 20 years. Fujishima and Honda conducted the pioneering studies in 1970s to produce renewable energy via artificial photosynthesis and water splitting to produce hydrocarbons and hydrogen (Fusijhima et al., 1972, Inoue et al., 1979). A huge variety of photocatalytic materials to be used in different photocatalytic processes were prepared since Fujishima and Honda. Many oxide, sulfide, nitride based semiconducting materials are used as photocatalysts since they have sufficient band gap energies for photocatalysis. Some examples are TiO_2, WO_3, $SrTiO_3$ α-Fe_2O_3, ZnO, CuO, ZnS, CdS, CdSe, GaN. The band gap energies of these materials are 3.2, 2.8, 3.2, 3.1, 3.2, 1.2, 3.6, 2.4, 1.7, 3.4 eV, respectively (Hoffman et al., 1995). The boundary of UV and visible light regions is around 3.1 eV photon energy which corresponds to the energy of a light with 400 nm wavelength. TiO_2 is the most extensively used photocatalyst due its favorable properties such as biological and chemical inertness, thermal stability, photo/chemical corrosion stability and being cheap. The main applications of TiO_2 based phocatalysts are: photovoltaics, photoinduced superhydrophilicity and in photocatalysis, organic synthesis, degradation of pollutants, nitrogen fixation and artificial photosynthesis including hydrogen production and CO_2 reduction. The diverse applications of TiO_2 make it a favorable and preferred material in the photocatalysis area.

4. NATURAL AND ARTIFICIAL PHOTOSYNTHESIS

In natural photosynthesis plants and cyanobacteria (which are photoautotrophic) synthesize their own building block materials from inorganic compounds such as CO_2, nitrates, sulfates with the help of sunlight energy. Photon energy splits water into oxygen and hydrogen which is then bounded to NADPH (Nicotinamide adenine dinucleotide phosphate). This process, which is called as *Light Reactions*, is conducted at photosynthesis reaction centers embedded in cell wall and includes the electron transfer related to ATP (Adenozine triphosphate) synthesis. In *Dark Reactions*, NADPH, ATP and CO_2 is consumed in Calvin Cycle (Figure 4) to produce carbohydrates (Gan et al., 2019).

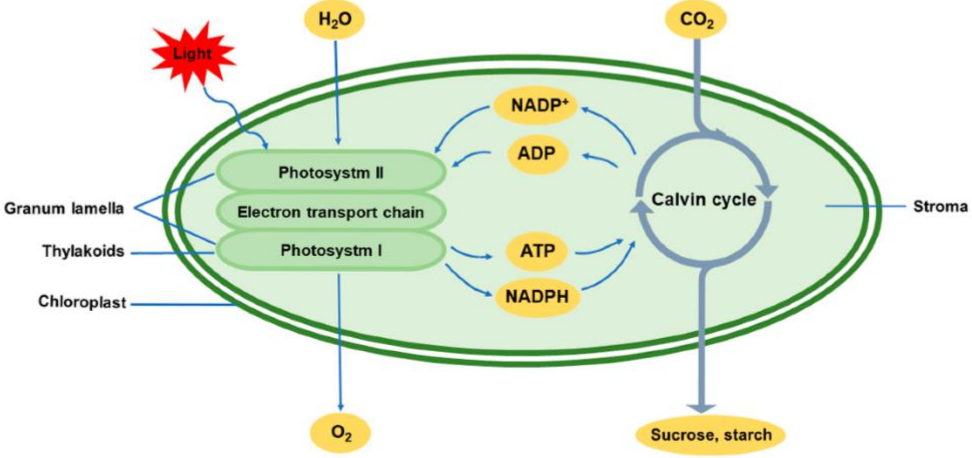


Figure 4. Photosynthesis under normal conditions (Gan et al., 2019).

Biomass, oxygen and also fossil fuels are the products of photosynthesis organized by plants and cyanobacteria. The life on earth is tied to photosynthesis and is a cycle of CO_2. Animals are heterotrophic and need carbohydrates/other organics to survive. They provide the energy for their own life processes by using biomass which is produced by plants. CO_2 is produced when oxygen is consumed. In brief, sunlight captured and utilized by plants is the source of life and related processes on earth.

Solar energy can be utilized by many different ways. Solar cells can transform solar energy into electricity, solar ponds can store the energy from the sun as heat energy and solar energy can be used to generate steam for turbines or transformed into chemical energy via photocatalysis (Hammarstrom and Hammes-Schiffer, 2009). Each method has its own advantages and disadvantages. Artificial photosynthesis is the mimicking of natural photosynthesis and is one of the common photocatalytic processes which convert CO_2 and water into useful chemicals such as methanol, methane, carbon monoxide, other hydrocarbons and hydrogen which can be stored and used as energy source.

CO_2 is a linear molecule (O=C=O) without a dipole moment and is one of the most stable compounds (but not inert) which is mostly produced by oxidation/combustion reactions. CO_2 needs high energy reducing molecules to be converted into hydrocarbons. The Gibbs free energy change of a reaction should be negative in order to be thermodynamically favorable. Most reactions given in Table 1 have positive

Gibbs free energy changes and reaction of CO_2 with H_2O seems thermodynamically unfavorable. High energy input is needed to convert CO_2 into hydrocarbons. Therefore, high temperatures and pressures are needed to activate CO_2. In photocatalysis, CO_2 can be activated by electrons and react with holes at room temperature and atmospheric pressure by the energy input from the sunlight. Reducing molecules such as H_2, H_2O or CH_4 are needed for this purpose among which H_2 seems to be more attractive since the Gibbs free energy changes of the reactions involving H_2 are low or negative. However, it is meaningless to reduce CO_2 with H_2 which has more chemical potential and the system loses its chemical potential by consuming H_2. If H_2 is produced by water splitting without synthetic energy input e.g. solar energy, not the energy from burning fossil fuels, the process would be feasible.

Table 1. Change of Gibbs free energy at 298 K for reactions related to the photocatalytic reduction of CO_2 to various renewable fuels (Zang, 2011).

Reductant	Product	Chemical equation	ΔG^0 (kJ/mol)
H_2	$HCOOH$	$CO_2+H_2 \rightarrow HCOOH$	43
	CH_3OH	$CO_2+3H_2 \rightarrow CH_3OH+H_2O$	4
	CH_4	$CO_2+4H_2 \rightarrow CH_4+2H_2O$	-114
CH_4	CH_3COCH_3	$CO_2+2CH_4 \rightarrow CH_3COCH_3+H_2O$	115
	CH_3COOH	$CO_2+CH_4 \rightarrow CH_3COOH$	71
	$HCHO$	$CO_2+CH_4 \rightarrow 2HCHO$	240
H_2O	$HCOOH$	$CO_2+H_2O \rightarrow HCOOH+1/2O_2$	272
	$HCHO$	$CO_2+H_2O \rightarrow HCHO+O_2$	521
	CH_3OH	$CO_2+2H_2O \rightarrow CH_3OH+3/2O_2$	690
	CH_4	$CO_2+2H_2O \rightarrow CH_4+2O_2$	801
		$H_2O(g) \rightarrow H_2+1/2O_2$	229
		$H_2O(l) \rightarrow H_2+1/2O_2$	237

The reaction of CO_2 with H_2 can be carried out either in gaseous or liquid phases. The form of CO_2 may vary depending on the phase (gas or a dissolved ion in water). Aqueous solutions of NaOH are used mostly in order to increase CO_2 solubility since it is soluble at high pH. CO_2 dissolves in water according to the following equilibrium reactions (Wojtowicz, 2001):

$$CO_2\,(aq) + H_2O \leftrightarrow H_2CO_3 \quad (1)$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad (2)$$

$$HCO_3^- \leftrightarrow H^+ + HCO_3^{2-} \quad (3)$$

Some selected redox potentials involving CO_2 species and hydrocarbons are given in Table 2. Gaseous CO_2 or water dissolved CO_2 (H_2CO_3) can be reduced to CH_3OH, CH_4, $HCOOH$ with anatase TiO_2 whose valence and conduction band potentials are 2.7 and -0.5 V versus NHE, respectively. It is also seen that the reduction of gaseous CO_2 would be easier due to the closeness of the reduction potentials and conduction band potential of anatase TiO_2, however the products of photocatalytic CO_2 reduction with TiO_2 are not restricted to the given ones in Table 2 since the photocatalytic properties of TiO_2 can easily be tuned by several modification methods which may shift the band edge positions or change the reaction mechanism. This table is an illustration of the possible products that may be produced with TiO_2. There are reports of gaseous CO and CH_4 production when CO_2 reduction was carried out in aqueous conditions (Koci et al., 2009 and 2011, Rajalakshmi et al., 2012).

Table 2. Summary of reduction potentials for half-cell reactions at pH 7 in aqueous solution vs. the normal hydrogen electrode (Tahir and Amin, 2013).

Chemical equations	Thermodynamic potential, V vs. NHE
$CO_2 + e^- \rightarrow CO_2^-$	-2.0
$2H^+ + 2e^- \rightarrow H_2$	-0.41
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	-0.61
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	-0.38
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + H_2O$	-0.24
$H_2CO_3 + 2H^+ + 2e^- \rightarrow HCOOH + H_2O$	-0.166
$H_2CO_3 + 6H^+ + 6e^- \rightarrow CH_3OH + 2H_2O$	+0.044
$2CO_3^{2-} + 8H^+ + 6e^- \rightarrow CH_3OH + 2H_2O$	+0.209

The mechanism of photocatalytic reduction of CO_2 consists of water splitting and reduction of CO_2 with species formed in water splitting reactions. Structural and electronic properties of semiconducting photocatalysts determine the important steps in photocatalysis such as the absorption of photons, charge separation/migration and surface adsorption/reactions. Captured holes react with water adsorbed on the surface of the semiconducting material to produce O_2 and H_+. H· radicals are formed by the interaction of H_+ ions with excited electrons. Union of two H_+ ions forms one H_2 molecule. These two steps explain the photocatalytic water splitting mechanism. In the presence of CO_2, electrons interact with CO_2 molecules to form $\cdot CO_-$ radicals (Koci et al., 2009). Newly formed H· and $\cdot CO_-$ radicals react to form CO. Consecutive reactions transform CO to $\cdot CH_3$ radicals. Finally, CH_4 or CH_3OH molecules are formed when $\cdot CH_3$ radicals react with H· or OH· radicals, respectively. These steps along with water splitting steps explain the photocatalytic reduction mechanism of CO_2 into hydrocarbons. The recombination of produced electron hole pairs can cause releasing of heat without chemical work which is not desired in photocatalysis.

5. ARTIFICIAL PHOTOSYNTHESIS WITH TITANIA PHOTOCATALYSTS

Intensive research on artificial photosynthesis (hydrogen production via water splitting and hydrocarbon production by the reduction of CO_2) which may become a key process in the future for sustainable energy needs of humanity and global pollution/warming prevention have been conducted in the last 20 years (Wu et al., 2005, Matejova et al., 2014, Raja et al., 2011, Tan et al., 2012, Uner et al., 2011, Zhang et al., 2009). Fujishima and Honda conducted the pioneering study in 1972 to produce hydrogen on a TiO_2 electrode (Fusijhima and Honda, 1972) and Inoue et al. (Fujishima and Honda who are the leading researchers of photocatalysis of TiO_2 were the co-workers in this study) reported the first photocatalytic reduction of CO_2 in aqueous media via photocatalytic processes by using solar energy in 1979. They used different photocatalysts such as TiO_2, WO_3, ZnO, GaP, CdS and SiC. The products of the reactions were formic acid, methanol, methane and formaldehyde (Inoue et al., 1979). Since then many studies on photoreduction of CO_2 were conducted. Early studies of photocatalytic reduction of CO_2 involved the use of SiC, GaP, $SrTiO_3$, WO_3, $BaTiO_3$, $LiNbO_3$, $CaFe_2O_4$, Cu_2OxH_2O, ZnS, CdS photocatalysts by Inoue et al. (1979), Ogura et al. (1992) and Yoneyama (1997). Intensive research on the photoreduction of CO_2 by using TiO_2 was conducted after this period due to the recognition of its extraordinary properties.

TiO_2 has three stable phases which are anatase, rutile, brookite along with three metastable and five high pressure phases. The lattice structures of anatase, rutile and brookite which are the most frequently used phases, are shown in Figure 5.

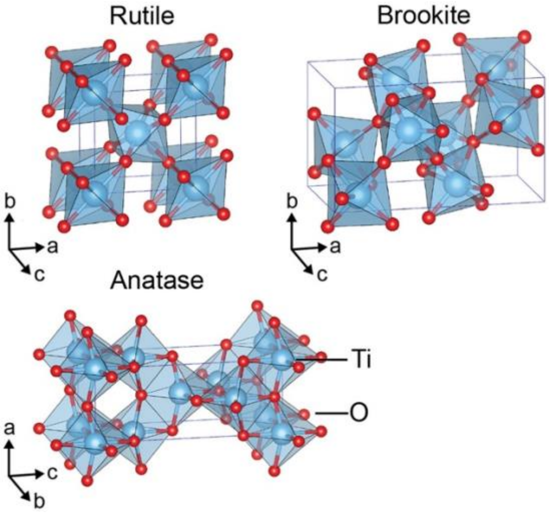


Figure 5. Lattice structures of anatase, rutile and brookite (Haggerty et al., 2017).

TiO_2 can be synthesized by various methods for industrial or laboratory uses. Sulfate and chloride methods are widely used for high production rates; however, alkoxide method is widely used in research for lab-scale applications. These methods are based on the chemical source of the desired product, however chemical vapor deposition, precipitation, hydro/solvothermal, sol-gel, emulsion/micro-emulsion, ultrasound/microwave irradiation, spray pyrolysis, electrochemical synthesis are common methods based on different apparatus used and different chemical and physical principles (Anpo and Kamat, 2010). According to the source, *Alkoxide Method,* according to the principles and apparatus *Sol-Gel* and *Chemical Precipitation Methods* along with a brief information about *Sulfate* and *Chloride Method* are described below.

Sulfate method

In sulfate method, titanium oxysulphate ($TiOSO_4$) which is formed by dissolving titanium minerals in sulfuric acid is treated with a base to form hydrated TiO_2. After heat treatment (calcination) crystalline TiO_2 powders are obtained. Hydrated TiO_2 synthesized by sulfate method has low photocatalytic activity since it has crystal defects which act as centers for recombination of electron-hole pairs, despite the high surface area. The calcined hydrated TiO_2 has also low photocatalytic activity because of the contaminants (sulfate ion or ions from minerals) originating from the method (Gazquez et al., 2014).

Chloride method

This method is also called as vapor method because titanium minerals are reacted with chlorine gas yielding titanium tetrachloride ($TiCl_4$) and oxidized to TiO_2 at 700-1000$_o$C. Crystallization of TiO_2 into anatase or rutile also occurs because of the application of high temperatures. Commercially available Degussa P-25 which is commonly used by researchers is synthesized by using this method. Degussa P-25 has 80 wt.% anatase and 20 wt.% rutile phases and has a very high photocatalytic activity under UV light illumination (Gazquez et al., 2014).

Alkoxide method (Sol-Gel)

Metal alkoxides are mostly used precursors for metal oxide synthesis in laboratory scale since the product of sulfate method has contaminations and chlorine method reaction conditions are hard to control. Metal alkoxide can also be produced in highly pure grade which leads to highly pure metal oxide. TiO_2 can be synthesized from various titanium alkoxides (e.g. titanium ethoxide, titanium propoxide, titanium butoxide). Titanium alkoxide is hydrolysed to form TiO_2 sol/precipitate. TiO_2 sol is then gelated to form polymeric TiO_2. Proper heat treatment of TiO_2 gels leads to highly active TiO_2 with high specific surface areas (Kaneko and Okura, 2002). This method is known as the ***"Sol-gel"*** method in the literature. Sol-gel method has several advantages such as high purity and homogenous product, low temperature synthesis, excellent atomic mixing, precise control of size and surface properties, wide variety of precursors or other chemicals, possibility of different form of products such as films or powders. High amount of solvent usage in this method makes it infeasible for high production rates of TiO_2 (Tseng et al., 2010).

Chemical precipitation

Chemical precipitation is a liquid phase reaction which is used to synthesize insoluble solid particles. Solid particles obtained during precipitation, the precipitate, are formed in the solution due to a reaction or when the solution has been supersaturated by a compound. Titanium precipitates are titanium hydroxide ($Ti(OH)_4$), TiO_2 or titanium oxyhydroxide ($TiO(OH)_3$). Titanium precursor can be alkoxide based or inorganic (e.g. $TiCl_4$). The dissolved precursor solution is mostly precipitated by the use of an alkali solution since Ti^{4+} is soluble in acidic conditions. The precipitates can be crystalline or amorphous particles. After a heat treatment, oxide particles can be obtained. Usually an aqueous or alcohol solution of inorganic salt (sulfate, chloride or nitrate) of desired dopant ion is used to modify TiO_2 and Ti^{4+} is precipitated with dopant ions in an alkali solution (of NH_4OH, NaOH). Unwanted growth of particles is inevitable during calcination. Thus, direct precipitation from a non-aqueous solution may be carried out in order to obtain ultrafine particles.

The commonly known anatase and rutile phases of titania (TiO_2) are the most important and widely used materials in environmental related photocatalytic research and applications. The most important disadvantage of these titania phases is their relatively high band gap energies (in the 3.0-3.2 eV range) which results in absorption of sun light in the ultra-violet (UV) range which represents < 5% of solar radiation spectrum (Nassoko et al., 2012). The reduction and modification of the band gap energies of the titania phases by doping with various elements for more efficient light absorption and the determination of their activities in the photocatalytic degradation of organic molecules and artificial photosynthesis are the main concern of intense research in the last 10-15 years. These dopants comprise heavily nonmetals like C, N, S etc. (Cong et al., 2007, Dong et al., 2011, Park et al., 2006, Rockafellow et al., 2009, Shen et al., 2007, Yang et al., 2010) and transition metals like Cu, Ag, Fe, Co etc. (Akpan and Hameed, 2010, Silija et al., 2012, Baiju et al., 2007, Nie et al., 2009). Research conducted in the last 20 years on the effects of titania phase stability and dye decomposition activities have shown that lanthanide incorporation also reduced the band gap energy, widened absorption into the visible light region and increased the photocatalytic activity of TiO_2 (Choudhury et al., 2013, Li et al., 2004, Obregon et al., 2013, Ranjit et al., 2001, Xiao et al., 2007).

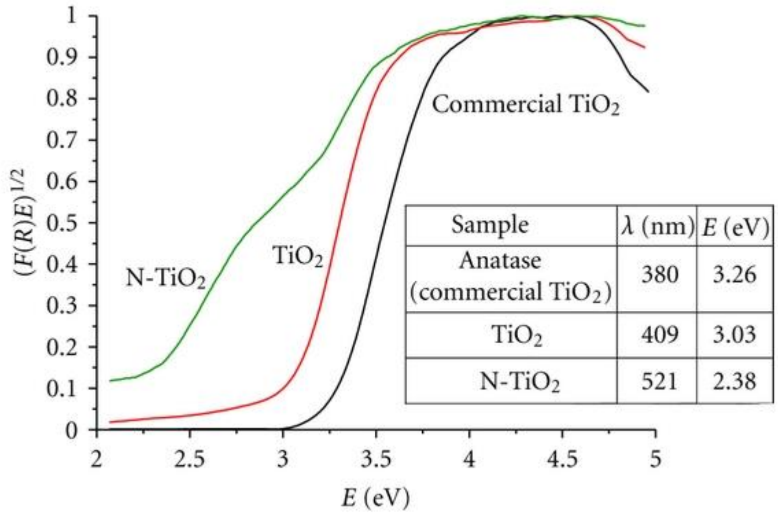
Band gap engineering for improving the photocatalytic activity of TiO_2 can be accomplished by;

- doping TiO_2 with various cations/anions (metal or nonmetal) to introduce sub energy levels between the conduction and valence band (Zaleska, 2008),
- combining with low band gap materials; a coupled semiconductor mechanism in which low band gap semiconductor absorbs the photons of visible light and transfers them to the surface of TiO_2 (Magesh et al., 2009),
- surface modification (Dugandzic et al., 2012),
- using different synthesis routes to modify the crystallite sizes.

Using different synthesis routes such as chemical vapor deposition, precipitation, hydro/solvothermal, sol-gel, emulsion/micro-emulsion, ultrasound/microwave irradiation, spray pyrolysis, electrochemical synthesis methods, as stated previously, may alter the physicochemical, optical and electronic properties by tuning the surface chemistry, pore structure or crystallinity of TiO_2. Phase composition (anatase to rutile weight ratio), crystallite size, band-to-band transitions have significant effect on the band gap energy of semiconductors. Changing the synthesis route may significantly change these properties and thus the band gap energy of TiO_2. Combining TiO_2 with low band gap materials is also another versatile method to improve the optical properties of TiO_2. According to this coupled mechanism, a visible light absorbing material can transfer electrons to the conduction band of TiO_2 and redox reactions are started by these lower energy charge carriers.

Doping TiO_2 with anions/cations is the most preferred one since it is easy to tune the absorption edge by the type or amount of doping ion which leads to the improvement of photocatalytic activity. Interpretations on the contribution of doped ions to the electronic structure of TiO_2 can be done considering the valence band of TiO_2 is at oxygen 2p state and conduction band is at titanium 3d&4s state. Metal doping introduces new energy levels in the band gap of TiO_2 which narrows the band gap and improves the light absorption of TiO_2. Transition metal doping also enables the trapping of electrons which inhibits the electron-hole recombination and improves oxidation-reduction activity of TiO_2. Nonmetal doping improves the light absorption and photocatalytic activity of TiO_2 by three mechanisms. First one is the band gap narrowing by hybridization of oxygen 2p with nonmetal 2p by introducing a new valence band closer to the conduction band. Second one is the introduction of isolated impurity levels in which electrons are excited only by visible light. Electrons in the valence band and impurity level are both excited with UV irradiation, however visible light only excites the electrons in the impurity level. Third one is the creation of holes localized in oxygen vacancies forming $O_{2-.}$ and $OH_{-.}$ radicals which trigger the oxidation reactions (Zaleska, 2008).

Doping can be achieved by various methods e.g. chemical vapor deposition, ion-assisted sputtering, ion implantation and chemical synthesis methods such as sol-gel and chemical precipitation. Mostly used methods are chemical precipitation and sol-gel which were described previously. Transition metals (such as V, Cr, Fe, Co, Ni, Cu) and nonmetals (N, S, C, B, P, I, F) doped TiO_2 photocatalysts were prepared in various research papers presenting the band gap tuning (Bellardita et al., 2011, Magesh et al., 2009, Zaleska, 2008). An example of UV-Vis Diffuse Reflectance spectrum presenting the band gap tuning and red shift of the absorption edge of TiO_2 is given in Figure 6.



Sample	λ (nm)	E (eV)
Anatase (commercial TiO_2)	380	3.26
TiO_2	409	3.03
N-TiO_2	521	2.38

Figure 6. Band gap narrowing of TiO_2 by N doping (Factorovich et al., 2011).

A summary of dopant/composite materials, estimated band gap energies and main products of photocatalytic reduction of CO_2 with TiO_2 based materials reported in research papers from the last 20 years is given in Table 3.

Table 3. A brief summary of the last 20 years of photocatalytic reduction of CO_2 with TiO_2 based materials.

Dopant/ Composite material	Band gap energy (eV)	Main Products	Reference
2.0 wt. % Cu	3.0 eV	MOH	Tseng et al., 2002
Ru/SiO_2	3.04 eV	H, FA, FAL, MN	Sasirekha et al., 2006
RuBpy	NA	MN	Ozcan et al. 2007
Ag	2.74 eV	MN, MOH	Koci et al. 2010
N/nanotube	3.1 eV	FA	Zhao et al. 2012
CeO_2	2.2 eV	MN, CO	Wang et al. 2013
Pt	2.06 eV	MN	Xiong et al. 2015
Au-CdS	2.40 eV	MN	Wei et al. 2015
CPO27-Mg	NA	MN	Wang et al. 2016
NH_2-UiO-66	2.70 eV	CO	Crake et al. 2017
$CuInS_2$	NA	MOH, MN	Xu at al. 2018
Nd	1.83	CO	Yurtsever et al. 2018
AuCu + ZIF-8	NA	MN, CO	Butburee at al. 2019
C_3N_4	2.34	CO, H	Shi et al. 2019

MOH: Methanol, FA: Formic acid, FAL: Formaldehyde, H: Hydrogen, CO: Carbon monoxide, MN: Methane.

6. CONCLUSION

Titania photocatalysts used in artificial photosynthesis will contribute to the development of renewable energy resources in the near future by hydrogen production via water splitting and hydrocarbon production via CO_2 photoreduction. Research conducted in the last 20 years on titania based materials developed towards photocatalytic water splitting and artificial photosynthesis was briefly reviewed in this paper. The superior properties and chemical stability of titania which was the main reason behind its frequent use in the long past history of artificial photosynthesis will continue to make it a popular and preferred material for use in diverse photocatalytic applications in the near future. This review also shows that titania coupled with recently developed novel materials such as metal organic frameworks and 2D nanosheets may present novel and efficient photocatalysts to be used in artificial photosynthesis.

REFERENCES

Akpan, U.G., Hameed, B.H. (2010). The advancements in sol–gel method of doped-TiO2 photocatalysts. *Applied Catalysis A: General*, 375, 1-11.

Anpo, M., Kamat, P.V., (2010). Environmentally benign photocatalysts applications of titanium oxide-based materials. USA: Springer.

Baiju, K.V., Periyat, P., Wunderlich, W., Krishna Pillai, P., Mukundan, P., Warrier, K.G.K. (2007). Enhanced photoactivity of neodymium doped mesoporous titania synthesized through aqueous sol–gel method. *Journal of Sol-Gel Science and Technology*, 43, 283-290.

Bellardita, M., Addamo, M., Di Paola, A., Palmisano, L. (2007). Photocatalytic behaviour of metal-loaded TiO2 aqueous dispersions and films. *Chemical Physics*, 339, 94-103.

Butburee, T., Sun, Z., Centeno, A., Xie, F., Zhao, Z., Wu, D. et al. (2019). Improved CO2 photocatalytic reduction using a novel 3-component heterojunction. *Nano Energy*, 62, 426-433.

Choudhury, B., Borah, B., Choudhury, A. (2013). Ce–Nd codoping effect on the structural and optical properties of TiO2 nanoparticles. *Materials Science and Engineering: B*, 178, 239-247.

Cogdell, R.J., Brotosudarmo, T.H.P., Gardiner, A.T., Sanchez, P.M., Cronin, L. (2010). Artificial photosynthesis – solar fuels: current status and future prospects. *Biofuels*, 1, 861-876.

Collings, A.F., Critchley, C., (2005). *Artificial photosynthesis from basic biology to industrial application*. Germany: Wiley-VCH.

Cong, Y., Zhang, J., Chen, F., Anpo, M. (2007). Synthesis and characterization of nitrogen-doped TiO2 nanophotocatalyst with high visible light activity. *The Journal of Physical Chemistry C*, 111, 6976-6982.

Crake, A., Christoforidis, K. C., Kafizas, A., Zafeiratos, S., & Petit, C. (2017). CO2 capture and photocatalytic reduction using bifunctional TiO2/MOF nanocomposites under UV–vis irradiation. *Applied Catalysis B: Environmental*, 210, 131-140.

Dong, F., Guo, S., Wang, H., Li, X., Wu, Z. (2011). Enhancement of the visible light photocatalytic activity of c-doped TiO2 nanomaterials prepared by a green synthetic approach. *The Journal of Physical Chemistry C*, 115, 13285-13292.

Dugandžić, I.M., Jovanović, D.J., Mančić, L.T., Zheng, N., Ahrenkiel, S.P., Milošević, O.B., Šaponjić, Z.V., Nedeljković, J.M. (2012). Surface modification of submicronic TiO2 particles prepared by ultrasonic spray pyrolysis for visible light absorption. *Journal of Nanoparticle Research*. 14, 1-11.

Factorovich M., Guz L., Candal R. (2011). N-TiO2: chemical synthesis and photocatalysis. *Advances in Physical Chemistry*, 2011, 821204.

Fujishima, A., Honda, K. (1972). Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 238, 37-38.

Gan, P., Liu, F., Li, R., Wang, S., & Luo, J. (2019). Chloroplasts-beyond energy capture and carbon fixation: tuning of photosynthesis in response to chilling stress. *International Journal of Molecular Sciences*, 20(20), 5046.

Gázquez, M.J., Bolívar, J.P., Garcia-Tenorio, R., Vaca, F. (2014). A review of the production cycle of titanium dioxide pigment. *Materials Sciences and Applications*, 05, 441-458.

Haggerty, J.E.S., Schelhas, L.T., Kitchaev, D.A. (2017). High-fraction brookite films from amorphous precursors. *Scientific Reports*, 7, 15232.

Hammarstrom, L., Hammes-Schiffer, S. (2009). Artificial photosynthesis and solar fuels. *Accounts of Chemical Research*, 42, 1859-1860.

Hoffmann, M.R., Martin, S.T., Choi, W., Bahnemann, D.W. (1995). Environmental applications of semiconductor photocatalysis. *Chemical Reviews*, 95, 69-96.

Houghton, J. (2004). *Global warming the complete briefing.* USA: Cambridge University Press.

Inoue, T., Fujishima, A., Konishi, S., Honda, K. (1979). Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders. *Nature*, 277, 637-638.

Kaneko, M., Okura I. (2002). *Photocatalysis : science and technology*. Kodansha: Springer.

Kočí, K., Obalová, L., Matějová, L., Plachá, D., Lacný, Z., Jirkovský, J., Šolcová, O. (2009). Effect of TiO2 particle size on the photocatalytic reduction of CO2. *Applied Catalysis B: Environmental*, 89, 494-502.

Kočí, K., Matějů, K., Obalová, L., Krejčíková, S., Lacný, Z., Plachá, D., Čapek, L., Hospodková, A., Šolcová, O. (2010). Effect of silver doping on the

TiO2 for photocatalytic reduction of CO2. *Applied Catalysis B: Environmental*, 96, 239-244.

KočÍ, K., ZatloukalovÁ, K., ObalovÁ, L., KrejČÍKovÁ, S., LacnÝ, Z., ČApek, L., HospodkovÁ, A., ŠOlcovÁ, O. (2011). Wavelength effect on photocatalytic reduction of CO2 by Ag/TiO2 catalyst. *Chinese Journal of Catalysis,* 32, 812-815.

Kumar, S., Karthikeyan, S., Lee, A.F. (2018). g-c3n4-based nanomaterials for visible light-driven photocatalysis. *Catalysts*, 8, 74.

Li, F.B., Li, X.Z., Hou, M.F. (2004). Photocatalytic degradation of 2-mercaptobenzothiazole in aqueous La3+–TiO2 suspension for odor control. *Applied Catalysis B: Environmental*, 48, 185-194.

Linsebigler, A.L., Lu, G., Yates, J.T. (1995). Photocatalysis on TiO2 surfaces: principles, mechanisms, and selected Results. *Chemical Reviews,* 95, 735-758.

Magesh, G., Viswanathan, B., Viswanath, R.P., Varadarajan, T.K. (2009). Photocatalytic behavior of CeO2-TiO2 system for the degradation of methylene blue. *Indian Journal of Chemistry,* 48A, 480-488.

Matějová, L., Kočí, K., Reli, M., Čapek, L., Hospodková, A., Peikertová, P., Matěj, Z., Obalová, L., Wach, A., Kuśtrowski, P., Kotarba, A. (2014). Preparation, characterization and photocatalytic properties of cerium doped TiO2: On the effect of Ce loading on the photocatalytic reduction of carbon dioxide. *Applied Catalysis B: Environmental*, 152-153, 172-183.

Nassoko, D., Li, Y.-F., Li, J.-L., Li, X., Yu, Y. (2012). Neodymium-doped TiO2 with anatase and brookite two phases: mechanism for photocatalytic activity enhancement under visible light and the role of electron. *International Journal of Photoenergy,* 2012, 1-10.

Nie, X., Zhuo, S., Maeng, G., Sohlberg, K. (2009). Doping of TiO2 polymorphs for altered optical and photocatalytic properties. *International Journal of Photoenergy,* 2009, 1-22.

Obregón, S., Kubacka, A., Fernández-García, M., Colón, G. (2013). High-performance Er3+–TiO2 system: Dual up-conversion and electronic role of the lanthanide. *Journal of Catalysis*, 299, 298-306.

Ogura, K., Kawano, M., Yano, J., Sakata, Y. (1992). Visible-light-assisted decomposition of H2O and photomethanation of CO2 over CeO2-TiO2 catalyst. *Journal of Photochemistry and Photobiology A: Chemistry*. 66, 91-97.

Ozcan, O., Yukruk, F., Akkaya, E., Uner, D. (2007). Dye sensitized artificial photosynthesis in the gas phase over thin and thick TiO2 films under UV and visible light irradiation. *Applied Catalysis B: Environmental*, 71, 291-297.

Park, J.H., Kim, S., Bard, A.J. (2006). Novel carbon-doped TiO2 nanotube arrays with high aspect ratios for efficient solar water splitting. *Nano Letters*. 6, 24-28.

Raja, K.S., Smith, Y.R., Kondamudi, N., Manivannan, A., Misra, M., Subramanian, V. (2011). CO2 photoreduction in the liquid phase over pd-supported on TiO2 nanotube and bismuth titanate photocatalysts. *Electrochemical and Solid-State Letters*, 14, F5-F8.

Rajalakshmi, K., Jeyalakshmi, V., Krishnamurthy, K.R., Viswanathan, B. (2012). Photocatalytic reduction of carbon dioxide by water on titania: role of photophysical and structural properties. *Indian Journal of Chemistry*. 51A, 411-419.

Ranjit, K.T., Willner, I., Bossmann, S.H., Braun, A.M. (2001). Lanthanide oxide doped titanium dioxide photocatalysts: effective photocatalysts for the enhanced degradation of salicylic acid and t-cinnamic acid. *Journal of Catalysis*. 204, 305-313.

Rohde, Robert A., Solar radiation spectrum, (http://www.globalwarmingart.com/), licence: https://creativecommons.org/licenses/by-sa/3.0/deed.en.

Rockafellow, E.M., Stewart, L.K., Jenks, W.S. (2009). Is sulfur-doped TiO2 an effective visible light photocatalyst for remediation?. *Applied Catalysis B: Environmental*. 91, 554-562.

Sasirekha, N., Basha, S., Shanthi, K. (2006). Photocatalytic performance of Ru doped anatase mounted on silica for reduction of carbon dioxide. *Applied Catalysis B: Environmental*. 62, 169-180.

Shen, H., Mi, L., Xu, P., Shen, W., Wang, P.-N. (2007). Visible-light photocatalysis of nitrogen-doped TiO2 nanoparticulate films prepared by low-energy ion implantation. *Applied Surface Science*. 253, 7024-7028.

Shi, H., Long, S., Hu, S., Hou, J., Ni, W., Song, C. et al. (2019). Interfacial charge transfer in 0D/2D defect-rich heterostructures for efficient solar-driven CO2 reduction. *Applied Catalysis B: Environmental*, 245, 760-769.

Silija, P., Yaakob, Z., Suraja, V., Binitha, N.N., Akmal, Z.S. (2012). An enthusiastic glance in to the visible responsive photocatalysts for energy production and pollutant removal, with special emphasis on titania. *International Journal of Photoenergy*. 2012, 1-19.

Tahir, M., Amin, N.S. (2013). Recycling of carbon dioxide to renewable fuels by photocatalysis: prospects and challenges. *Renewable and Sustainable Energy Reviews*. 25, 560-579.

Tan, J.Z.Y., Fernández, Y., Liu, D., Maroto-Valer, M., Bian, J., Zhang, X. (2012). Photoreduction of CO2 using copper-decorated TiO2 nanorod films with localized surface plasmon behavior. *Chemical Physics Letters*. 531, 149-154.

Tseng, I.H., Chang, W.-C., Wu, J.C.S. (2002). Photoreduction of CO2 using sol–gel derived titania and titania-supported copper catalysts. *Applied Catalysis B: Environmental*. 37, 37-48.

Tseng, T.K., Lin, Y.S., Chen, Y.J., Chu, H. (2010). A review of photocatalysts prepared by sol-gel method for VOCs removal. *International Journal of Molecular Sciences*. 11, 2336-2361.

Uner, D., Oymak, M.M., İpek, B. (2011). CO2 utilisation by photocatalytic conversion to methane and methanol. *International Journal of Global Warming*. 3, 142-162.

Wang, Y., Li, B., Zhang, C., Cui, L., Kang, S., Li, X., Zhou, L. (2013). Ordered mesoporous CeO2-TiO2 composites: highly efficient photocatalysts for the reduction of CO2 with H2O under simulated solar irradiation. *Applied Catalysis B: Environmental*. 130-131, 277-284.

Wang, M., Wang, D., & Li, Z. (2016). Self-assembly of CPO-27-Mg/TiO2 nanocomposite with enhanced performance for photocatalytic CO2 reduction. *Applied Catalysis B: Environmental*, 183, 47-52.

Wei, Y., Jiao, J., Zhao, Z., Liu, J., Li, J., Jiang, G. et al. (2015). Fabrication of inverse opal TiO2-supported Au@CdS core–shell nanoparticles for efficient photocatalytic CO2 conversion. *Applied Catalysis B: Environmental*, 179, 422-432.

Wojtowicz, J.A. (2001). The carbonate system in swimming pool water. *Journal of the Swimming Pool and Spa Industry*. 4, 54-59.

Wu, J.C.S., Lin, H.-M., Lai, C.-L. (2005). Photo reduction of CO2 to methanol using optical-fiber photoreactor. *Applied Catalysis A: General*. 296, 194-200.

Xiao, Q., Si, Z., Zhang, J., Xiao, C., Yu, Z., Qiu, G. (2007). Effects of samarium dopant on photocatalytic activity of TiO2 nanocrystallite for methylene blue degradation. *Journal of Materials Science*. 42, 9194-9199.

Xiong, Z., Wang, H., Xu, N., Li, H., Fang, B., Zhao, Y. et al. (2015). Photocatalytic reduction of CO2 on Pt2+–Pt0/TiO2 nanoparticles under UV/Vis light irradiation: A combination of Pt2+ doping and Pt nanoparticles deposition. *International Journal of Hydrogen Energy*, 40(32), 10049-10062.

Xu, F., Zhang, J., Zhu, B., Yu, J., & Xu, J. (2018). CuInS2 sensitized TiO2 hybrid nanofibers for improved photocatalytic CO2 reduction. *Applied Catalysis B: Environmental*, 230, 194-202.

Yang, G., Jiang, Z., Shi, H., Xiao, T., Yan, Z. (2010). Preparation of highly visible-light active N-doped TiO2 photocatalyst. *Journal of Materials Chemistry*. 20, 5301.

Yoneyama, H. (1997). Photoreduction of carbon dioxide on quantized semiconductor nanoparticles in solution. *Catalysis Today*. 39, 169-175.

Yurtsever, H. A., (2015). Preparation and characterization of titania based powders and suspensions for photocatalytic applications. PhD Thesis, Graduate School of Engineering and Sciences of Izmir Institute of Technology.

Yurtsever, H. A., Çiftçioğlu, M. (2018). The effect of powder preparation method on the artificial photosynthesis activities of neodymium doped titania powders. *International Journal of Hydrogen Energy*, 43(44), 20162-20175.

Zaleska, A. (2008). Doped-TiO2: a review. *Recent Patents on Engineering*. 2, 157-164.

Zang, L., (2011). Energy efficiency and renewable energy through nanotechnology. USA: Springer.

Zhang, Q.-H., Han, W.-D., Hong, Y.-J., Yu, J.-G. (2009). Photocatalytic reduction of CO2 with H2O on Pt-loaded TiO2 catalyst. *Catalysis Today*. 148, 335-340.

Zhao, Z., Fan, J., Wang, J., Li, R. (2012). Effect of heating temperature on photocatalytic reduction of CO2 by N–TiO2 nanotube catalyst. *Catalysis Communications*. 21, 32-37.

Zhu, J., Zäch, M. (2009). Nanostructured materials for photocatalytic hydrogen production. *Current Opinion in Colloid & Interface Science*. 14, 260-269.