

Inorganic semiconductors as catalysts in the CO₂ photoreduction reaction: a review.

Marcelo Pereira Brasil ^a.

^a Chemistry Institute, University of Campinas, Campinas, Brazil, m202623@dac.unicamp.br.

Abstract. Human activities and the burning of fossil fuels to meet the planet's energy demands have triggered a growing emission of carbon dioxide (CO₂), one of the main causes of the greenhouse effect today. Searching for ways to reduce CO₂ emission or mechanisms that reduce its concentration in the atmosphere has been a challenge for scientists in recent decades. A path that is quite promising is the use of solar radiation to convert CO₂ into high value-added products, through photocatalysis processes, in which the reduction of gas and the oxidation of reducing agents such as water occur. The application of inorganic semiconductors as photocatalysts in CO₂ reduction processes has been extensively studied due to the economic viability that these materials present, in addition to the thermodynamic properties that favor photocatalysis processes. This study focused on understanding the basic principles of photocatalysis and the application of inorganic semiconductors such as sulfides, metal oxides, nitrides and oxynitrides in photocatalysis reactions, giving special attention to photocatalytic CO₂ reduction systems based on titania (TiO₂), an oxide metallic that presents great prominence due to its structure, chemical and thermodynamic properties. A brief historical summary of highly relevant studies using TiO₂ in photocatalysis processes is presented, confirming its potential and outlining future perspectives for studies of photocatalytic reduction of CO₂.

Keywords. Greenhouse effect, Principle of photocatalysis, Photocatalytic conversion of CO₂, Inorganic semiconductors, TiO₂-based catalytic systems.

1. Introduction

In recent years, society has been faced with several changes in the climate and life dynamics of some species of fauna and flora, due to the human influence and the activities developed since the industrial revolution (18th - 19th centuries) to the present day [1]. According to the 35th International Geological Congress, held in 2016, it is possible to affirm that this influence is altering the planet's climate on geological scales, confirming that our planet is in a new era, the Anthropocene [2].

The emission of gases into the atmosphere is one of the factors that most contributes to these intense climate changes. With industrial development and tropical deforestation by burning biomass for agricultural applications, the global emission of carbon dioxide (CO₂), one of the gases that cause the greenhouse effect, has increased extensively between the pre-industrial era and the present day [1]. Data from the Global Monitoring Laboratory (GML) of the National Oceanic and Atmospheric

Administration (NOAA) indicate that the monthly emission of CO₂ into the atmosphere increased by about 22.3% between the years 1980 and 2021, from 340 ppm to 415,68 ppm [3]. This emission growth reflects on the increase in the planet's temperature and contributes to the occurrence of irreversible damage to biodiversity, which compromises agriculture, industry and infrastructure, in addition to corroborating the intensification of natural events such as melting of glaciers, rising sea levels and a major imbalance in aquatic life [4].

Several strategies to mitigate the emission of CO₂ in the atmosphere are being studied and some of them are based on the reduction of CO₂ in products of high added value. The most prominent techniques are electrochemical conversion, thermochemical conversion and photocatalytic reduction [5]. The electrochemical conversion of CO₂ is usually conducted under ambient conditions through the application of an external bias, which promotes its feasibility for large scale applications, however, lower electrode efficiency and stability limit the efficiency of the process, combined with a large

amount of electrical energy for the reaction [6]. The thermal conversion of CO₂ using heterogeneous catalysts presents significant efficiency, but the dependence of several reaction conditions such as elevated temperature and pressure can give the process an extremely high operational cost [7]. Photocatalytic reduction of CO₂ to high value-added products such as carbon monoxide (CO), methanol (CH₃OH), methane (CH₄), formaldehyde (HCHO) and formic acid (HCOOH) is a technique that uses water as a reactant and an extremely abundant source of energy: solar radiation. Due to the accessibility to the reagent and the use of energy from renewable sources, the absence of toxic residues and the non-emission of greenhouse gases during the operational procedure, this technique appears to be the most viable, from an economic and sustainable point of view [8].

Fujishima et al. reported in 1978 studies on the photoelectrocatalytic reduction of carbon dioxide to form organic compounds, in the presence of photosensitive semiconductor powders suspended in water as catalysts [9]. Since then, novel studies have been conducted to increase the efficiency of the photocatalytic reduction of CO₂ and several catalysts have been used in the photocatalytic reduction of CO₂, such as zinc oxide (ZnO), tungsten oxide (WO₃), zirconium oxide (ZrO₂), cadmium sulfide (CdS), gallium phosphide (GaP) and titanium dioxide (TiO₂) [10]. Among the catalysts mentioned, titanium dioxide (TiO₂) stands out extensively, due to its unique properties, such as high chemical stability and activity under ultraviolet light irradiation [11]. Some strategies have been employed to improve the performance of TiO₂-based catalysts in CO₂ absorption, such as surface modifications, doping, morphological modifications, and other techniques [10].

The aim of this study is to summarize the results of studies on the application of inorganic catalysts in the CO₂ photoreduction reaction.

2. Photocatalytic conversion of CO₂

2.1 Principles of photocatalysis

A semiconductor can be defined as a material that presents electrical resistivity at ambient temperatures within the range of 10² to 10⁹ ohm-centimeter and this characteristic makes this type of material extremely useful in the manufacture of electronic devices such as diodes, photovoltaic cells, transistors and in applications containing photocatalytic processes [12].

A photocatalytic process wishes to exploit light to promote chemical transformations. Light illumination excites the electronic transition from the valence band (VB) to the conduction band (CB) of a semiconductor, which has a fully filled VB and a partially filled or empty CB. The generated electrons

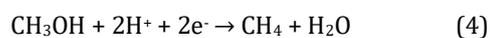
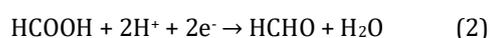
and holes then experience subsequent recombination and are transferred to their acceptors. The potential difference between CB and VB is called bandgap energy. The more negative the CB potential and the more positive the VB potential, the more easily electrons and holes become capable of causing a reducing and oxidizing effect [13] [14].

The photocatalytic reduction of CO₂ occurs by reducing the gas and oxidation of water, thus generating different solar fuels, according to the positions of the conduction and valence bands of the semiconductor used as photocatalyst [15]. The yield of photocatalytic reactions depends significantly on the intensity and wavelength of the absorbed light since the energy of the generated electron-hole pairs varies according to the wavelength of the light and the populations of pairs depend on the intensity of the light. Semiconductors that have bandgap energy small enough to function under irradiation of visible sunlight are widely studied in the photocatalytic reduction of CO₂, since the reaction yield increases with increasing light intensity and decreases with increasing wavenumber of the light absorbed [12] [16].

However, semiconductors that present small bandgap energy and materials in which electrons and gaps that have lifetime of nanoseconds cannot find the substrate allow them to be part of the electrons generated pairing with the gaps, recombining and losing energy, and another small amount of electron migrates to the band surface [12]. Serpone et al demonstrated in 1984 that the transfer of electrons from the CdS conduction band to TiO₂ semiconductive particles in alkaline medium containing bisulfide ions or sulfide ions led to an effective charge separation, transferring the photogenerated electron of CdS conduction band to the TiO₂ conduction band and leaving the gaps in the valence band of CdS [17].

2.2 Photocatalytic CO₂ reduction mechanisms

Photocatalytic reduction is a redox reaction that involves the reduction of CO₂ and the oxidation of reducing agents such as water. To turn CO₂ into carbon monoxide or hydrocarbons, electrons in the semiconductor need to have a more negative chemical potential, while holes need to have a more positive chemical potential [18]. This mechanism was initially proposed by Inoue et al. in 1979 [9] and the following reduction products are formed sequentially:



Several mechanisms have been proposed and validated for CO₂ reduction in different studies. Anpo et al. [19] proposed in 1995 a mechanism for the

formation of CO, CH₄ and CH₃OH on TiO₂-based photocatalysts. Another reaction mechanism was developed and proposed by Subrahmanyam et al. [20] in 1999, for the conversion of CO₂ radicals to formic acid followed by the formation of formaldehyde, methane and methanol. A third reaction mechanism was reported by Shkrob et al. [21] in 2012, in which CO₂ radicals were first converted to glyoxal and then dissociated into aldehyde.

From a thermodynamic point of view, the formation of methane and methanol is more favorable for the reduction of carbon dioxide because these reactions occur at lower potentials. However, kinetic deficiencies make the formation of methane and methanol more difficult than carbon monoxide, formaldehyde, and formic acid because more electrons are needed for the first reaction [22].

2.3 Semiconductors as photocatalysts

The application of inorganic semiconductors such as sulfides, metallic oxides, nitrides and oxynitrides have been widely studied in reactions that are driven by solar energy, due to their significant stability, low cost compared to other photocatalyst materials and light absorption capacity consisting of photons with energy equal to or greater than its bandgap energy [23].

Sulfide-based semiconductors have a valence band formed by the 3p orbitals of sulfur atoms, which gives it a higher location compared to analog oxides, resulting in a more reductive conduction band. In addition to the bandgap energy suitable for various applications, other factors such as surface area and recombination rate indicate an influence on the yield of photocatalytic reactions. Liu et al. studied the catalytic performance of a series of Mo-Co-K sulfide catalysts, prepared by co-precipitation with the addition of some components such as SiO₂, Al₂O₃, TiO₂ and activated carbon to improve the catalytic properties of the catalysts, in the hydrogenation of carbon dioxide in C₂₊ alcohols and other products [24].

Semiconductor metal oxides have excellent stability when used as photocatalysts, due to their resistance to photocorrosion by irradiation. In general, oxides are divided into two distinct groups when employed in photocatalytic reactions. The first group contains octahedrally coordinated transition metal ions, such as Ti⁴⁺, Zr⁴⁺, Ta⁵⁺, V⁵⁺, in addition to various binary oxides such as ZrO₂, Ta₂O₅, among others. The second group is composed of main group metal oxides in a d¹⁰ configuration, such as Ga, Ge, In, Sn and Sb. The properties of metal oxides play a significantly critical role in determining the feasibility of their application in photocatalyzed CO₂ reduction reactions [23]. Mgolombane et al. studied the photoreduction of CO₂ to CH₃OH with the application of nanocomposites of zinc, ZnO, doped ZnO and co-doped ZnO. The research results indicated that the doping of ZnO with Co²⁺ ions facilitated the formation of adsorbed carbonate or CO²⁻ species on the surface of doped

zinc nanocomposites, opening the way for new perspectives in the systematic adaptation of the material's properties for the desired photocatalytic applications [25].

The insertion of nitrogen atoms in metal oxide photocatalysts favors an extension of several optical properties of metal oxynitride, since the 2p orbital of nitrogen has a higher potential energy than the 2p orbital of oxygen. Furthermore, the presence of nitrogen in the photocatalyst structure facilitated the determination of the band gap energy of oxynitrides and nitrides. Metal oxynitrides demonstrate significant activity in reducing CO₂ under irradiation, but precisely controlling the cation ratios in the structures of these materials is a challenge, making bandgap energy adjustment complex and corroborating a lower efficiency in CO₂ reduction [23]. Maiti et al. reported in 2019 calculations based on density functions in structure-function relationships of oxynitrides based on zinc and gallium, exploring various parameters of material properties, such as elemental composition, intrinsic lattice voltage and vacancy defects, to obtain a process of synthesis of stable oxynitride photocatalysts that demonstrate promising activity in the conversion of CO₂ to CO under simulated solar spectrum. The study indicated that the higher CO production rate exceeded that of TiO₂ under the same conditions, thus stimulating future research on oxynitride materials in sustainable photocatalytic activities and in large-scale applications [26].

Studies show that nitride-based catalysts have a high potential to increase selectivity, through the engineering of cocatalysts or hybrid catalysts [23]. Roy et al. reported in 2019 a photocatalyst for CO₂ reduction consisting of a polymeric cobalt phthalocyanine catalyst coupled with mesoporous carbon nitride, which acts as a photosensitizer. The studies indicated that this noble metal-free hybrid catalyst selectively converts CO₂ to CO in organic solvents under ultraviolet light irradiation in the visible region. The in-situ polymerization of phthalocyanine allowed the control of the catalyst charge and was fundamental to achieve the photocatalytic conversion of CO₂ [27].

Among the main inorganic semiconductors mentioned above, TiO₂ has significant advantages in the photocatalytic process of CO₂ reduction. Titanium dioxide-based catalysts have high thermal and chemical stability, good availability, and excellent charge transfer potential. In addition, this material is advantageous because it has a low cost, which from an economic point of view favors the study and applications outside the laboratory scale. These characteristics of several other properties of TiO₂ have made it appreciated and widely studied not only in photocatalysis, but in other catalytic and redox processes.

3. TiO₂-based catalytic systems

3.1 Brief historical summary of studies using TiO₂

The first work using TiO₂ in the photocatalytic reduction of CO₂ was reported in 1979 by Fujishima et al [9]. In 2005, Tamaki et al. reported the absorption of trapped holes formed in TiO₂ nanocrystal films by ultraviolet irradiation, which was measured by extremely sensitive femtosecond and nanosecond spectroscopy, under low-intensity excitation conditions, to avoid the recombination process. This study made it possible to evaluate the rates and yields of photocatalytic oxidation of some alcohols in TiO₂. The authors observed that the developed method can be applied to studies of oxidation reactions in molecules for which the oxidized forms are experimentally difficult to detect [28].

Li et al. demonstrated in 2014, through ultrafast spectroscopy, that charge transfer can occur between photoexcited inorganic semiconductors and MOFs, indicating that this charge transfer suppresses electron-hole recombination in the semiconductor, in addition to providing electrons with a longer lifespan for the process of reducing gas molecules adsorbed on the MOF. The authors also developed a synthesis method and evaluated its photocatalytic efficiency in gaseous reactions using CO₂ as a model system [29]. Xiong et al. reported in 2015 the synthesis of TiO₂ nanoparticles modified by Pt²⁺ ions and (Pt²⁺ - Pt⁰/TiO₂) nanoparticles, using a sol-gel method. The catalysts were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, UV-Vis absorption spectroscopy and photoluminescence spectroscopy. The catalytic activity of each material was analyzed through the photocatalytic reduction of CO₂ with water vapor under ultraviolet irradiation and visible light, in a continuous flow reactor [30].

Fang et al. reported in 2015 a scalable template-free synthesis strategy to manufacture hollow TiO₂ microspheres embedded in CuO on a large scale. The results of the study indicated that the TiO₂ hollow microsphere catalyst incorporated with CuO demonstrated much higher photocatalytic activity towards photo-directed reduction of CO₂ with H₂O to CH₄ compared to a commercial state-of-the-art photocatalyst. The authors pointed out the synthesis strategy as viable for the large-scale production of CuO-TiO₂ hollow microspheres [31]. Reli et al. reported the preparation of anatase-brookite mixtures by preprocessing with ethanol and methanol and the evaluation of the influence of alcohol on photocatalytic activity. The TiO₂ photocatalysts were prepared by the controlled sol-gel process inside reverse micelles and by hot pressurized solvent processing. The efficiency of the prepared photocatalysts was evaluated in the photocatalytic reduction of CO₂ and compared with a

commercial photocatalyst [32].

Jiang et al. proposed in 2018 the use of silver and activated carbon obtained from biomass with high CO₂ adsorption capacity to modify TiO₂, thus composing a TiO₂/AC-Ag ternary composite photocatalyst through ultrasonic and in situ photodeposition methods. The confectioned material showed a sixfold increase in CO yield compared to pure TiO₂ [33]. Kreft et al. reported in 2019 the synthesis of a highly porous copper and TiO₂ aerogel photocatalyst and its application in aqueous CO₂ reduction using external sacrificial electron donors. Complete selectivity towards CO and improved catalyst productivity were observed in the presence of oxygen. The detection of oxygen from the catalyst in the presence of O₂/CO₂ mixtures indicated an unexpected photoadsorption of oxygen on the titania surface. The authors then proposed photooxidation of surface hydroxyl groups to be the electron source for CO₂ reduction, which is supported by consumption of hydroxyl groups, detection of hydroxyl radicals using EPR in situ, and detection of surface peroxide species after the reaction [34].

3.2 Properties and structure of TiO₂

TiO₂ has three crystalline structures that can be found naturally in minerals: anatase, rutile and brookite, in addition to a fourth crystalline phase not found naturally, called TiO₂(B). From a thermodynamic perspective, rutile is the most stable form, while anatase shows the highest performance, due to its high mobility and electron affinity, as it has a more elongated crystal structure, to expose more active sites [23][35].

Studies indicate that the mixture of different crystalline phases of TiO₂ exhibit a greater photocatalytic activity, in relation to the pure phases, in addition to providing synergistic effects to the combined structure. Bouras et al. reported in 2007 that anatase with a small amount of rutile make up an optimal mixture of phases. The increase in photocatalytic activity is attributed to the formation of energy wells, due to the lower band gap energy of rutile, which serves as an electron-hole trap that reduces the recombination of photogenerated electron-hole pairs [35][36].

4. References

- [1] Olah GA, Prakash GKS, Goepfert A. Anthropogenic Chemical Carbon Cycle for a Sustainable Future. *Journal of the American Chemical Society*. 2011 Aug 24;133(33):12881-98.
- [2] Senftle TP, Carter EA. The Holy Grail: Chemistry Enabling an Economically Viable CO₂ Capture, Utilization, and Storage Strategy. *Accounts of Chemical Research*. 2017;50(3):472-5.
- [3] US Department of Commerce N. Global Monitoring Laboratory - Carbon Cycle

- Greenhouse Gases [Internet]. gml.noaa.gov. 2021. Available from: <https://gml.noaa.gov/ccgg/trends/>.
- [4] Technical Summary — Special Report on the Ocean and Cryosphere in a Changing Climate [Internet]. Ipcc.ch. Special Report on the Ocean and Cryosphere in a Changing Climate; 2010. Available from: <https://www.ipcc.ch/srocc/chapter/technical-summary/>.
- [5] Sakakura T, Choi J-C, Yasuda H. Transformation of Carbon Dioxide. *Chemical Reviews*. 2007;107(6):2365–87.
- [6] Daiyan R, Lu X, Ng YH, Amal R. Liquid Hydrocarbon Production from CO₂: Recent Development in Metal-Based Electrocatalysis. *ChemSusChem*. 2017;10(22):4342–58.
- [7] Gao J, Jia C, Liu B. Direct and selective hydrogenation of CO₂ to ethylene and propene by bifunctional catalysts. *Catalysis Science & Technology*. 2017;7(23):5602–7.
- [8] Alper E, Yuksel Orhan O. CO₂ utilization: Developments in conversion processes. *Petroleum*. 2017;3(1):109–26.
- [9] Inoue T, Fujishima A, Konishi S, Honda K. Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders. *Nature*. 1979;277(5698):637–8.
- [10] Shehzad N, Tahir M, Johari K, Murugesan T, Hussain M. A critical review on TiO₂ based photocatalytic CO₂ reduction system: Strategies to improve efficiency. *Journal of CO₂ Utilization*. 2018; 26:98–122.
- [11] Tahir M, Amin NS. Advances in visible light responsive titanium oxide-based photocatalysts for CO₂ conversion to hydrocarbon fuels. *Energy Conversion and Management*. 2013;76:194–214.
- [12] Yang X, Wang D. Photocatalysis: From Fundamental Principles to Materials and Applications. *ACS Applied Energy Materials*. 2018;1(12):6657–93.
- [13] Guo LJ, Wang YJ, He T. Photocatalytic Reduction of CO₂ over Heterostructure Semiconductors into Value-Added Chemicals. *Chemical Record*. 2016;1918–33.
- [14] Serpone N, Borgarello E, Barbeni M, Pelizzetti E. Effect of CdS Preparation on the Photocatalyzed Decomposition of Hydrogen Sulfide in Alkaline Aqueous Media. Vol. 90, *Inorganica Chimica Acta*. 1984.
- [15] Tahir M, Amin NS. Advances in visible light responsive titanium oxide-based photocatalysts for CO₂ conversion to hydrocarbon fuels. *Energy Conversion and Management*. 2013;76:194–214.
- [16] Wu JCS, Lin H-M. Photo reduction of CO₂ to methanol via TiO₂ photocatalyst. Vol. 07, *International Journal Of Photoenergy*. 2005.
- [17] Serpone N, Borgarello E, Gratzel M. Visible Light Induced Generation of Hydrogen from H₂S in Mixed Semiconductor Dispersions; Improved Efficiency through Inter-particle Electron Transfer. *J. Chem. Soc., Chem. Commun*.
- [18] Li K, An X, Park KH, Khraisheh M, Tang J. A critical review of CO₂ photoconversion: Catalysts and reactors. *Catalysis Today*. 2014;224:3–12.
- [19] Anpo M, Yamashita H, Ichihashi Y, Ehara S. Photocatalytic reduction of CO₂ with H₂O on various titanium oxide catalysts 1. Vol. 396, *Journal of Electroanalytical Chemistry*. 1995.
- [20] Subrahmanyam M, Kaneco S, Alonso-Vante N. A screening for the photo reduction of carbon dioxide supported on metal oxide catalysts for C1-C3 selectivity. Vol. 23, *Applied Catalysis B: Environmental*. 1999.
- [21] Shkrob IA, Marin TW, He H, Zapol P. Photoredox reactions and the catalytic cycle for carbon dioxide fixation and methanogenesis on metal oxides. *Journal of Physical Chemistry C*. 2012;116(17):9450–60.
- [22] Wang Y, Xin F, Chen J, Xiang T, Yin X. Photocatalytic reduction of CO₂ in isopropanol on Bi₂S₃ quantum dots/TiO₂ nanosheets with exposed {001} facets. *Journal of Nanoscience and Nanotechnology*. 2017;17(3):1863–9.
- [23] Tan JZY, Gavrielides S, Luo X, Thompson WA, Maroto-Valer MM. Development of photocatalysts and system optimization for CO₂ photoreduction. In: *Nanostructured Photocatalysts: From Materials to Applications in Solar Fuels and Environmental Remediation*. Elsevier; 2020. p. 39–73.
- [24] Liu S, Zhou H, Song Q, Ma Z. Synthesis of higher alcohols from CO₂ hydrogenation over Mo–Co–K sulfide-based catalysts. *J Taiwan Inst Chem Eng*. 2017;76:18–26.
- [25] Mgolombane M, Majodina S, Bankole OM, Ferg EE, Ogunlaja AS. Influence of surface modification of zinc oxide-based nanomaterials on the photocatalytic reduction of carbon dioxide. *Materials Today Chemistry*. 2021;20.

- [26] Maiti D, Meier AJ, Cairns J, Ramani S, Martinet K, Kuhn JN, et al. Intrinsically strained noble metal-free oxynitrides for solar photoreduction of CO₂. *Dalton Transactions*. 2019;48(33):12738–48. photocatalysis. *Applied Catalysis B: Environmental*. 2007;73(1–2):51–9.
- [27] Roy S, Reisner E. Visible-Light-Driven CO₂ Reduction by Mesoporous Carbon Nitride Modified with Polymeric Cobalt Phthalocyanine. *Angewandte Chemie - International Edition*. 2019;58(35):12180–4.
- [28] Tamaki Y, Furube A, Murai M, Hara K, Katoh R, Tachiya M. Direct observation of reactive trapped holes in TiO₂ undergoing photocatalytic oxidation of adsorbed alcohols: Evaluation of the reaction rates and yields. *J Am Chem Soc*. 2006;128(2):416–7.
- [29] Li R, Hu J, Deng M, Wang H, Wang X, Hu Y, et al. Integration of an inorganic semiconductor with a metal-organic framework: A platform for enhanced gaseous photocatalytic reactions. *Advanced Materials*. 2014;26(28):4783–8.
- [30] Xiong Z, Wang H, Xu N, Li H, Fang B, Zhao Y, et al. 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*. 2015;40(32):10049–62.
- [31] Fang B, Xing Y, Bonakdarpour A, Zhang S, Wilkinson DP. Photodriven reduction of CO₂ to CH₄. *ACS Sustainable Chemistry and Engineering*. 2015;3(10):2381–8.
- [32] Reli M, Kobielski M, Matějová L, Daniš S, Macyk W, Obalová L, et al. TiO₂ Processed by pressurized hot solvents as a novel photocatalyst for photocatalytic reduction of carbon dioxide. *Applied Surface Science*. 2017;391:282–7.
- [33] Jiang Z, Zhang X, Yuan Z, Chen J, Huang B, Dionysiou DD, et al. Enhanced photocatalytic CO₂ reduction via the synergistic effect between Ag and activated carbon in TiO₂/AC-Ag ternary composite. *Chemical Engineering Journal*. 2018;348:592–8.
- [34] Kreft S, Schoch R, Schneidewind J, Rabeah J, Kondratenko E v., Kondratenko VA, et al. Improving Selectivity and Activity of CO₂ Reduction Photocatalysts with Oxygen. *Chem*. 2019;5(7):1818–33.
- [35] Scanlon DO, Dunnill CW, Buckeridge J, Shevlin SA, Logsdail AJ, Woodley SM, et al. Band alignment of rutile and anatase TiO₂. *Nature Materials*. 2013;12(9):798–801.
- [36] Bouras P, Stathatos E, Lianos P. Pure versus metal-ion-doped nanocrystalline titania for