The Application of TiO_2 for Photoreduction of CO_2

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ABSTRACT

Greenhouse gas emission mostly accounts for global warming effect, hence the urgency to realize CO_2 removal efficiently and harmlessly to the environment. Base on all of these requirements, utilization of abundant solar energy to achieve CO_2 reduction seems the be the best choice. In this review, mechanisms of CO_2 photoreduction is briefly introduced, including electrochemical potential analysis and chemical reaction mechanism. Efficiency measurements in this filed are summarized, mainly divided into two groups: catalyst-based measurement and light-based measurement. Applications of TiO_2 on CO_2 reduction will follow. Subsequently, the modifications on TiO_2 specifically for its efficiency and selectivity are discussed in details.

KEYWORDS

TiO_2; CO_2 photoreduction; measurement; efficiency; selectivity; doping; heterostructure.

1 Introduction

Global warming effect have been worrying people all around the world these years. Most of the researchers hold the point that CO_2 is the main substance which influence the global warming effect[1,2], for the reason that CO_2 emission is incredibly high these years, and higher than ever[3]. The scientist are pursuing adequate method to relieve this effect, and as the reason mentioned before, the research are chiefly focusing on CO_2 removal.

A lot of scientists are trying to achieve that goal by electrocatalysis[4–7]. However, electrochemistry methods consume a considerable amount of energy, which could be used elsewhere. Thus, to find some other way to realize the removal of CO_2 is a challenging but attractive problem.

In 1972, Fujishima observed the water splitting effect on the surface of TiO_2 without electricity but only illumination[8]. After that important discovery, TiO_2 were heatedly researched and modified as a kind of photocatalyst used in many fields. Til now, TiO_2 is still a very important and widely used photocatalyst of the application in water splitting[9], oxidation of waste water[10] and so on.

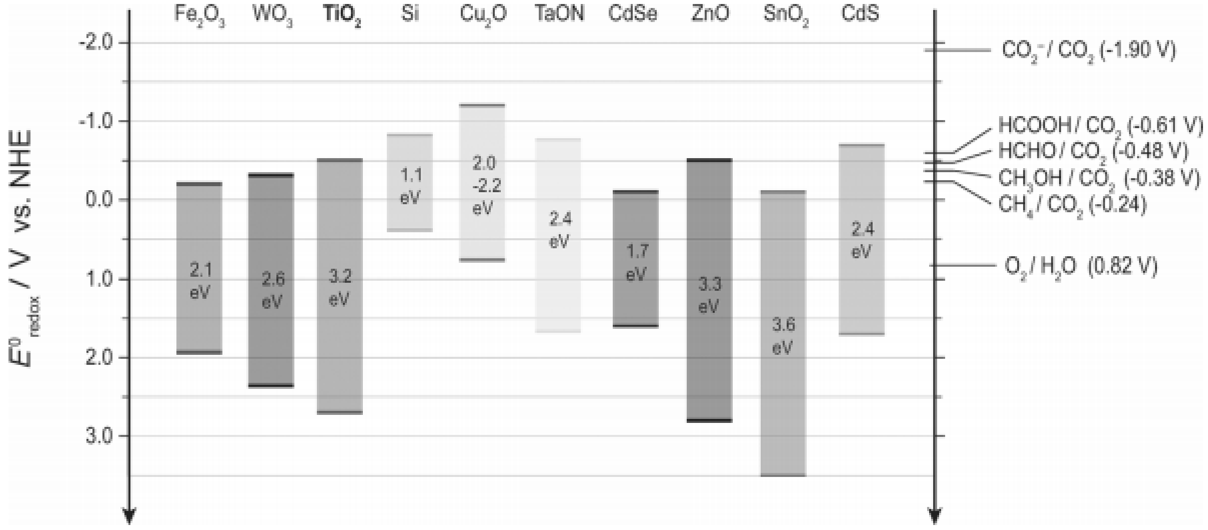


Figure 1. Conduction band, valence band potentials, and band gap energies of various semiconductor photocatalysts relative to the redox potentials at pH 7 of compounds involved in CO_2 reduction. Adapted from Ref. [14].

It's natural to come up with the idea of applying TiO_2 on CO_2 removal. Specifically, TiO_2 can probably be the "photocatalyst" for CO_2 reduction into many other organic matter like CH_4[11], CH_3OH[11], HCOOH[12], etc. But actually TiO_2 does not act as catalyst in CO_2 reduction. As the definition goes, catalyst cannot change the thermal properties of a reaction, but only the dynamic properties of it. CO_2 is chemically inert, which means its electrochemical potential versus NSE(Normal Standard Electrode) is actually too negative(-1.8V)[13] to be reduced. Electrochemical potentials of different substances are showing in Figure 1[14]. Thus, CO_2 reduction process is definitely not a photocatalytic process, but a process named photosynthesis or photoreduction.

Although TiO_2 is a wise choice as a photocatalyst, its practical performance remains unsatisfied. First of all, the efficiency of photoreduction is low, as the potential of the CB (conduction band) of TiO_2 is barely more negative than the multi-electron process of CO_2 reduction (Figure 1), and kinetically this photoreduction is not so fast. Plus, the photoreduction process is a hole-scavenger-needed process[15]. The reduced process would come to an end when the hole scavengers run out, which means this process is not so ideal that we still need to provide additional man-made energy for that process.

This article is going to discuss the mechanism of photoreduction, and then summary for some applications and modifications of TiO_2 of CO_2 photoreduction in recent years.

2 Mechanism

Mechanisms related to the photoreduction are band theory and thermodynamic analysis. To know more about the mechanisms allows us a more accurate design on band structures of the materials, in order to increasing the energy reduction efficiency; and, gives us a chemical way to lower the energy barrier of certain process to accelerate the reaction.

2.1 Mechanism of photoreduction

In band theory, if an incident photon comes, the electrons in VB (Valence Band) might be excited into the CB (Conduction Band). At the same time, a hole generated in VB. If the CB electrons are in a more negative electrochemical potential than that of any CO_2 reduction process, then they are favored to move downward (less negative) to lower the energy of this system. Therefore, the photoreduction takes place.

As we know, the energy is given by a discrete process. That is why the term “photon” exists. So, the photoreduction is a discrete process as well. But all catalytic processes are continuous. This is another reason why this process cannot be named “photocatalysis”.

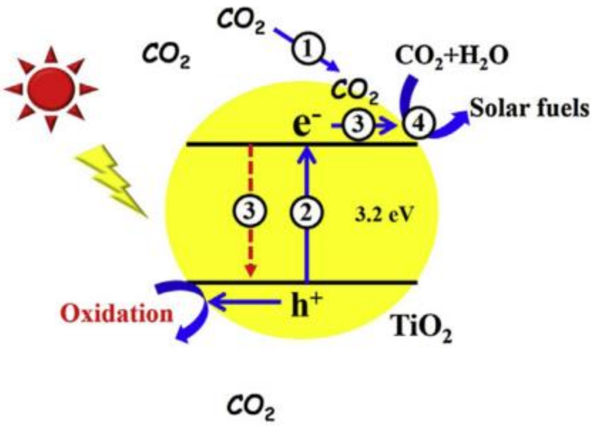


Figure 2. Schematic diagram for CO_2 photoreduction process on TiO_2. Firstly, CO_2 molecules adsorption. Secondly, photogeneration of electrons and holes. Thirdly, separation (blue line) or recombination (red dotted line) of photoexcited electrons and holes. Fourthly, reaction between active electrons/ holes and reactants like CO_2 molecules and water molecules. Adapted from Ref. [16].

Photoreduction is an intrinsically difficult process. Basically, the whole process can be divided into four steps. First of all, CO_2 molecules adsorption ought to be achieved. Thus, it hugely influences the consequent reduction. Secondly, electrons and holes are photoexcited from VB to CB, resulting in reactive charge carriers generation. Thirdly, separation or recombination of electrons and holes are both possible, so the two process seems to be conflictive. If one was weaken, the other would be enhanced. How to realize a better separation of charge carriers is hot research field recently. Finally, reaction would happen, when active electrons move closer to adsorptive CO_2 molecules.

2.2 Mechanism of CO_2 reduction

As what was discussed before, CO_2 is hard to have a reduced reaction, as the electrochemical potential of its single-electron process is too negative, and only multi-electron process can be realizable. The reduced processes and corresponding electrochemical potential (versus NHE, at Ph=7) found in literatures are listed as follow[16]:

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \qquad E^0=-0.61V \qquad (1)$$

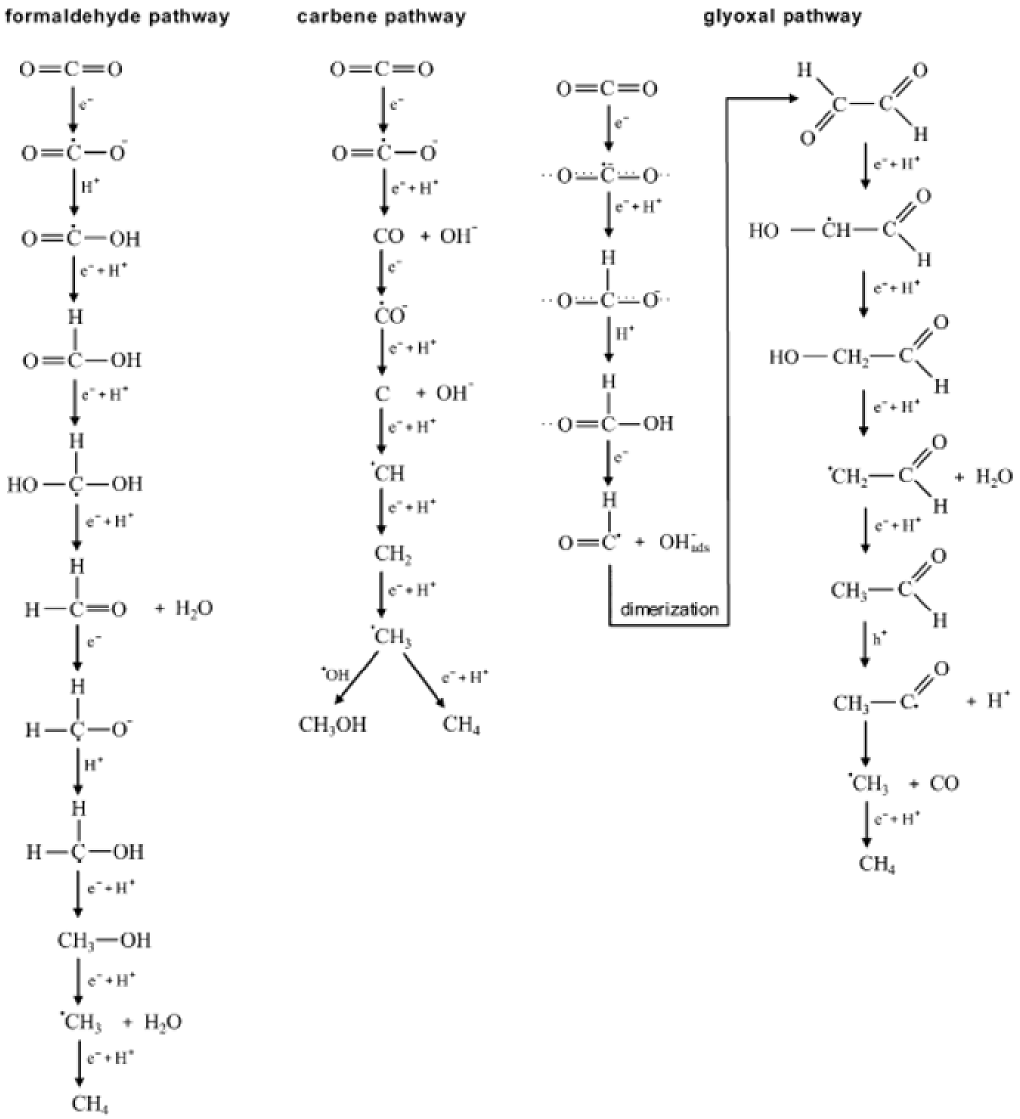
$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad E^0=-0.53V \qquad (2)$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \qquad E^0=-0.48V \qquad (3)$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \qquad E^0=-0.38V \qquad (4)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E^0=-0.24V \qquad (5)$$

However, we should pay attention to the fact that the energy barrier for a chemical reaction is not absolutely unchangeable. Here are two common method about activation of inert CO_2 molecule. Firstly, adsorption will influence the distribution among atoms in molecules, and accordingly influence in chemical bonding in CO_2 molecule occur[17,18], thus the energy barrier for CO_2 reduction is tuned. Secondly, CO_2 molecules can form active radicals which are reactive with other molecules[19].



Scheme 1. Three proposed chemical pathways for CO_2 photoreduction. Adapted from Ref. [20].

The reaction path research also provides us useful information. Here, we introduce three kinds of pathways: the formaldehyde pathway, the carbene pathway, and the glyoxal pathway (Scheme 1)[20]. The first mechanism is preferred within a high dielectric medium like water. The carbene pathway is a favored reaction when carbon dioxide radical is attached to the semiconductor by the carbon atom. The third pathway revealed that the recycle of CO_2 might be the reason for poor quantum efficiency of CO_2 reduction. This leads to a critical step toward understanding the mechanism of this reaction.

3 Efficiency measurement

Til now, there has never been a perfect efficiency measurement method which can be accepted by all of the researchers. Because a "perfect" measurement ought to be only intrinsic-property -based, but the method adopted now are either base on the amount of the catalyst, or the intensity of illumination. Therefore, more subjective methods are needed, especially which aim at real-life problems. In that case, a solar spectrum, and normal pressure and temperature are needed to be achieved.

Herein, we state some of the common measurements divided into two groups: catalyst-based measurement and light-based measurement.

3.1 Catalyst-based method

To measure how much production we have is a common measurement which can be seem in reaction dynamic analysis. And here we called it, the rate of formation of a product. The formula commonly adapted is showing below[20]:

$$\text{Rate} = \frac{[\text{Product}]}{\text{Time}[\text{Catalyst}]} \tag{6}$$

We should notice that, CO_2 is everywhere in the air, so it is not a suitable object for measurement, but H_2 or other product that is only related to this redox reaction(corresponding to CO_2 reduction) can be considered. Also, we ought to confirm that whether the true photoreduction happened or not. If not, the measurement conducted becomes meaningless. Yang et al. demonstrated carbon residues play an important role in formation of CO by isotopically labeled $^{13}CO_2$. They proposed two possible chemical pathways to explain why the ratio of CO_2 versus $^{13}CO_2$ can be so high as approximately 6, and both pathways involve carbon residues as reactant[21]. This indicates we need scrutiny to analysis the result of production rate efficiency, maybe by adding additional test of the whole product to eliminate the participation of carbon residues.

There are still five more point that we should emphasis: (1) All kinds of by-product ought to be calculated as well, or some mistakes about the reaction rate may happen; (2) This kind of measurements give us a saturation curve; (3) In most cases, co-catalyst helps a lot for increasing the efficiency, but it is only account for a small part in the total mass without discussing about its fraction; (4) The measurement is somewhat time-dependent, which means the initial time measurement begins can do a unneglected influence to the results; (5) Because this rate measurement ignores the incident photon, hence cannot generate comparable results among different laboratories, for the reason that it is almost impossible to have the same spectra and the same incident intensities[20].

To measure the turnovers is another way dependent on the amount of catalyst. There are two different aspect, TON(turnover number), and TOF(turnover frequency) or TOR(turnover rate). TON is a dimensionless measure that expresses how many times that a site involved in the catalytic process during illumination[20,22]. That is,

$$\mathrm{TON} = \frac{N}{N_{\mathrm{a}}} \tag{7}$$

N_a represents the number of catalytically active sites. As it is hard to be measured, so usually, it can be replaced by surface area determined by Brunauer-Emmett-Teller (BET) measurements.

But due to the uneven distributions of active sites on the surface of catalyst, surface area is not always a good representation of the number of catalytically active sites.

TOF is defined as the number of photoinduced reaction per catalytically active site per time period[20,22]. It differentiates from TON just by a dividing time dimension just as below,

$$\mathrm{TOF} = \frac{1}{N_{\mathrm{a}}}\frac{dN}{dt} \tag{8}$$

Nevertheless, all turnovers do not care about the photon flux, hence suffer the same problem as the rate of reaction. That is a turnover increasing just by simply increasing the intensity of incident irradiation.

3.2 Light-based method

Quantum efficiency measures how many photons can be used to generate electron-hole pairs. Specifically, that is the number of product entities formed (alternatively the number of reactant entities consumed) divided by the number of irradiation photons[23], so it can be defined as below:

$$\phi = \frac{N_{\mathrm{product/reactant}}}{N_{\mathrm{photon}}} \times 100\% \tag{9}$$

The number of the entities should involve all parts in the catalytic system, and the number of the photons is within a specific wavelength range[23].

If we adequately control the experiment condition: the same spectrum, the same intensity of illumination, the same amount of the catalyst, and the same amount of the reactants, we are able to have some results which are comparable among different laboratories with this measurement.

The power conversion efficiency measures the conversion efficiency from photon energy to chemical energy. Therefore, it can be express as a ratio of energy store in product (measured by combustion of product) versus power of photon flux[20].

$$\eta = \frac{\Delta H_{\text{combustion}}}{P_{\text{photon}}} \times 100\% \tag{10}$$

Due to the fact that illumination excess cannot be absorbed, this measurement of efficiency also shows a saturation curve.

4 Photoreduction of CO_2 on TiO_2

In this part, we will deal with some discussion related to applications and modification of TiO_2 on CO_2 reduction. It may not be a detailed analysis, but rather be a general one, for the purpose that it will be as complete as it can to contain the frontiers in this field.

4.1 Photocatalytic properties of TiO_2

TiO_2 exists particularly in four different crystallographic structures: rutile (tetragonal), anatase (tetragonal), brookite (orthorhombic), and TiO_2(B) (monoclinic)[24]. Among them, rutile and anatase structure are the most common structures in TiO_2 photocatalyst. The band gaps of rutile and anatase are 3.03eV and 3.20eV[25], respectively.

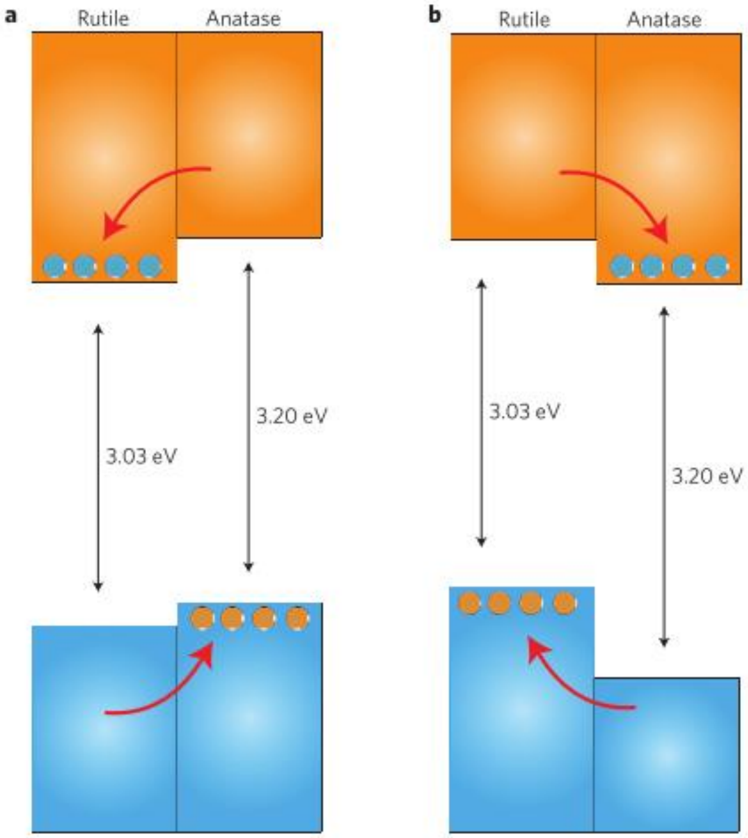


Figure 3. Two proposed band alignments of anatase/rutile interface, the latter was satisfactorily proved. a. Type-II heterostructure based on rutile structure; b. Type-II heterostructure base on anatase structure. Blue and orange dots represents electrons and holes, respectively. Adapted from Ref. [25].

Recent research has proved that the mixture of these two structures can reach a higher level of photocatalytic performance[26,27]. Many researchers found their path trying to explain the reason for enhanced photocatalytic properties in that mix-phase structure. Scanlon et al. demonstrate that the electron affinity of anatase TiO_2 is higher than rutile TiO_2 (Figure 3b). A type-II band alignment exists between them, resulting in a strong charge carrier separation between the two phases[25]. Then, the enhancement of catalytic performance makes sense.

4.2 Modification of TiO_2 for CO_2 photoreduction

Pure TiO_2 is not always good enough for photoreduction of CO_2. So we need a couple of modifications such as band gap engineering, nanostructure engineering, surface modification, in order to have some improvement in various aspects.

4.2.1 Efficiency enhancement

There are two particular views that would lead to an efficiency improvement. One is the energy providing end (EPE), which relates to either increasing the absorbance of solar energy, or enlarge the energy pulses (higher energy photons). The other is the energy receiving end (ERE) or reaction end, that is, trying to weaken the bonding of CO_2 molecules, consequently lower the activation energy.

Doping is a good example for modification on EPE. It usually increases the quantum efficiency by narrowing the band gap, then a better absorbance of solar spectrum would be achieved. And that is usually achieved by adding extra bands just above VB[20]. Wang et al. reported a P-doped TiO_2 NTs with a reduced band gaps (3.02-3.16eV), achieving a preferable photoreduction of CO_2 to CH_3OH[28]. Nevertheless, non-metal doping might also bring some new charge carrier recombination center.

Dye molecules enhanced EPE by providing more reactive electrons. Organic dye molecules often have a narrower band gap (between HOMO and LUMO) than that of semiconductors, so their VB electrons are more likely to be excited and then inject into the CB of semiconductors. Ozcan et al. provided evidence that a dye-sensitized, Pt promoted TiO_2 films are capable of CO_2 photoreduction under visible light illumination[29]. In a recent work, with a kind of H_2 evolving

Co^{III} catalyst and another CO-producing Re^{I} catalyst , a visible-light-induced dye-sensitized TiO_2 system for CO_2 reduction can be established[30], which considers both EPE and ERE enhancement.

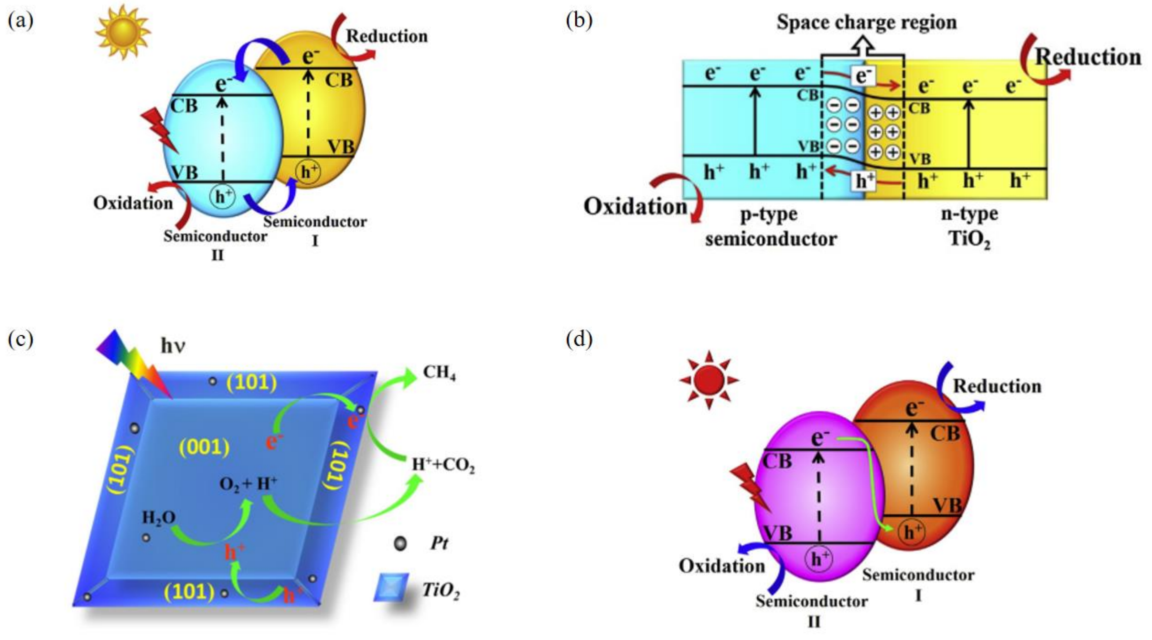


Figure 4. Schematic diagrams of different heterostructures. (a) Conventional type-II heterostructure; (b) P-N junction; (c) Surface junction [between (001) and (101) on TiO_2]; (d) Z-scheme heterojunction. Figure (a), (b) and (d) are Adapted from Ref. [16]. Figure (c) is Adapted from Ref. [31].

Here is another large group of methods for efficiency enhancement - heterojunction construction, focusing mainly on EPE. Conventional type-II heterojunction (Figure 4a) and P-N junction (Figure 4b) have already been widely adopted[16]. Their basic idea is, making opposite charge carriers move toward different directions or substances. Because of the difference between the energy of different facets on TiO_2, heterojunctions between different facets exist (Figure 4c)[31]. A heterojunction between (001) and (101) on anatase TiO_2 has been established by Zhou al, and it exhibits its best photocatalytic activities with 32% (011) facet exposure[32]. In a word, charge carriers separation would lower the probability of their recombination, hence the utilization of both kinds of reactive charge carriers, and that's why heterojunction help in photoreduction.

As we know, the reduction potential of TiO_2 is not negative enough to have a high reaction rate. Z-scheme heterostructure is one of the best solution on this problem. It has a normal band gap as other semiconductor, but it provides a more negative potential (Figure 4d). Absolutely, this will lead to a more powerful ability to make the CO_2 reduction happen. A $ZnIn_2S_4$ NSs/TiO_2 NBs direct Z-scheme CO_2 reduction system was established by Yang et al. with a CH_4 production rate of 1.135 μ mol g^{-1} h^{-1}, which is about 39-times higher than that of bare $ZnIn_2S_4$[33].

Quantum dots also help to establish heterojunction with TiO_2. For CdS QDs/TiO_2, photoexcited electrons of semiconductor inject into the CB of QDs, but photogenerated holes still left in VB of semiconductor[34].But for SnO_2 QDs/TiO_2, it is quite the opposite[35]. If this process has been proceed, charge carriers move to different direction: toward quantum dots, or semiconductor. Then the separation of charge carriers are realized.

Adjustment on ERE is not going to be ignored. Adsorption of CO_2 interferes the chemical bonding among CO_2 atoms, specifically, it would weaken the bonding, and make it more reactive. Alkali addition on surface of semiconductor would enhance the adsorption of CO_2[18]. Consequently, the activation of CO_2 is achieved in consequence. Definitely, The more active CO_2 molecules are, the easier for CO_2 reduction to happen.

4.2.2 Selectivity enhancement

Metal doping seems to be a good way to achieve an enhanced CH_4 selectivity. The doped Co change the construction of CB and VB of TiO_2, by adjusting the molar ratio of Co/Ti. By increasing the cobalt species, more oxygen vacancies were obtained, Co-decorated TiO_2 show a remarkable selectivity of CH_4, because the increasing Co-doping create more oxygen vacancies so that more and more excited electrons are trapped in the vacancies, of which electrochemical potential could only induced CO_2 reduced to CH_4[36] [according to equation (2) and (5), the redox potential of CO is more negative compared with CH_4]. Moreover, there are Pt-doping[37], Cu-doping[38] and La-doping[39] TiO_2 available for this kind of selectivity modification.

Non-metal doping might lead to a different preferred product. Wang et al. have prepared a P-doped TiO_2 NTs which exhibit a good selectivity of CH_3OH[28]. Carbon-based materials would also help in selectivity. Li et al. reported a g-C_3N_4 NDs decorated brookite TiO_2 quasi nanocube (BTN) with better CH_4 selectivity compared to g-C_3N_4 or BTN alone[40].

5 Conclusions

In this review, a misunderstanding is corrected. CO_2 reduction with TiO_2 under illumination is exactly not a catalytic process. Yet the chemical pathways of the reduction are not fully understood, different conditions seem to have their own preferred pathways.

As the photoreduction process is still a process similar to catalysis, the measurements adopted are almost all related to catalytic process measurements. However, we should emphasis that there has never been an agreement on the measurement, because of their dependence either on the amount of the catalyst or the intensity of the irradiation. A solar spectrum is a reasonable choice for standard measurements in the future.

Table 1. Different modifications on TiO_2 for CO_2 reduction.

Material	Reaction environment	Major product	R_{max}[a]	Minor products	Ref.
P-TiO_2 NT@Ti plate	CO_2 and H_2O gases	CH_3OH	280	-	[28]
RuBpy.Pt(in).TiO_2[d]	690 Torr CO_2 gas	CH_4	~0.25	-	[29]
surface heterostructure anatase TiO_2[e]	$KHCO_3$ (CO_2)	CH_4	1.58	-	[31]
$ZnIn_2S_4$ NS/TiO_2 NB	CO_2 and H_2O gases	CH_4	1.135	-	[33]
SnO_2 QD/TiO_2 hollow spheres	CO_2, H_2O, HCl gases[b]	CH_3OH	1.61	CH_4, HCHO	[35]
Cu-BTN[f]	CO_2 and H_2O gases[c]	CH_4	17.81	CO	[38]
Pt-(BTN-CNDs)[g]	CO_2 and H_2O gases[c]	CH_4	31.8	CO	[40]

[a] Maximum formation rate reported for the major product(s), in μmol g^{-1} h^{-1}, unless stated otherwise. [b] Generated by HCl and $NaHCO_3$. [c] Generated by H_2SO_4 and $NaHCO_3$. [d] RuBpy.Pt(in).TiO_2: dye-sensitized Pt promoted TiO_2. RuBpy is a kind of dye molecule, expressed as Tris(2,2'–bipyridyl) ruthenium(II) chloride Molecular. [e] 51% (001) and 49% (101) facets exposing ultrafine anatase TiO_2. [f] Cu decorated brookite TiO_2 quasi nanocubes (BTN). [g] Pt loaded on a substrate made of brookite TiO_2 quasi nanocubes (BTN) and g-C_3N_4 nanodots (CND).

Anatase and rutile are the most common crystal structures of TiO_2 when it is used as photocatalyst. A mix-phased structure of the two usually exhibit a better performance. Doping, heterojunction construction and other kinds of modifications are efficient ways to enhance pure TiO_2, both in efficiency and selectivity. A electron-scale characterization might be critical to unveil the mechanism behind these methods, and more complicated and delicate band gap engineering is likely to be helpful to achieve a higher photoreduction performance. A summary of different modifications on TiO_2 has been summarized in Table 1.

With all these efforts, we are able to get closer to the real nature of photosynthesis, and figure out a near future filled with low-carbon and renewable "green energy".

ABBREVIATIONS

NHE, normal hydrogen electrode; CB, conduction band; VB, valence band; TOF, turnover frequency; TOR, turnover rate; TON, turnover number; NB, nanobelt; ND, nanodot; NS, nanosheet; NT, nanotube; QD, quantum dots; BTN, brookite TiO_2 quasi nanocube; EPE, energy providing end; ERE, energy receiving end.

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