The Application of TiO$_2$ for Photoreduction of CO$_2$

MOZHEYANG*†£

†School of Material Science and Engineering, University of China, Beijing, P.R. China. £Chinese Academy of Sciences, Beijing, P.R. China.

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$_3$OH,$^{11}$ 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 (-1.8 V)$^{13}$ 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:\textsuperscript{16}:

\begin{align*}
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{HCOOH} \quad E^0=\text{-0.61V} & (1) \\
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{CO} + \text{H}_2\text{O} \quad E^0=\text{-0.53V} & (2) \\
\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- & \rightarrow \text{HCHO} + \text{H}_2\text{O} \quad E^0=\text{-0.48V} & (3) \\
\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad E^0=\text{-0.38V} & (4) \\
\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad E^0=\text{-0.24V} & (5)
\end{align*}

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\textsuperscript{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\textsuperscript{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$^{20}$:

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

(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,

\[
TON = \frac{N}{N_a}
\]  

(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\textsuperscript{20,22}. It differentiates from TON just by a dividing time dimension just as below,

$$\text{TOF} = \frac{1}{N_a} \frac{dN}{dt}$$

(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\textsuperscript{23}, so it can be defined as below:

$$\phi = \frac{N_{\text{product/reactant}}}{N_{\text{photon}}} \times 100\%$$

(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\textsuperscript{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\(^{20}\).

\[
\eta = \frac{\Delta H_{\text{combustion}}}{P_{\text{photon}}} \times 100\%
\]  

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\textsuperscript{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\textsubscript{2} is higher than rutile TiO\textsubscript{2} (Figure 3b). A type-II band alignment exists between them, resulting in a strong charge carrier separation between the two phases\textsuperscript{25}. Then, the enhancement of catalytic performance makes sense.
4.2 Modification of TiO₂ for CO₂ photoreduction

Pure TiO₂ is not always good enough for photoreduction of CO₂. 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 CO₂ 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 VB²⁰. Wang et al. reported a P-doped TiO₂ NTs with a reduced band gaps (3.02-3.16eV), achieving a preferable photoreduction of CO₂ to CH₃OH²⁸. 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 TiO₂ films are capable of CO₂ photoreduction under visible light illumination²⁹. In a recent work, with a kind of H₂ 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\textsuperscript{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\textsuperscript{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)\textsuperscript{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\textsuperscript{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\textsubscript{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\textsubscript{2} reduction happen. A ZnIn\textsubscript{2}S\textsubscript{4} NSs/TiO\textsubscript{2} NBs direct Z-scheme CO\textsubscript{2} reduction system was established by Yang et al. with a CH\textsubscript{4} production rate of 1.135 $\mu$ mol g\textsuperscript{-1} h\textsuperscript{-1}, which is about 39-times higher than that of bare ZnIn\textsubscript{2}S\textsubscript{4}\textsuperscript{33}.

Quantum dots also help to establish heterojunction with TiO\textsubscript{2}. For CdS QDs/TiO\textsubscript{2}, photoexcited electrons of semiconductor inject into the CB of QDs, but photogenerated holes still left in VB of semiconductor\textsuperscript{34}. But for SnO\textsubscript{2} QDs/TiO\textsubscript{2}, it is quite the opposite\textsuperscript{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\textsubscript{2} interferes the chemical bonding among CO\textsubscript{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\textsubscript{2}\textsuperscript{18}. Consequently, the activation of CO\textsubscript{2} is achieved in consequence. Definitely, The more active CO\textsubscript{2} molecules are, the easier for CO\textsubscript{2} reduction to happen.

4.2.2 Selectivity enhancement

Metal doping seems to be a good way to achieve an enhanced CH\textsubscript{4} selectivity. The doped Co change the construction of CB and VB of TiO\textsubscript{2} by adjusting the molar ratio of Co/Ti. By
increasing the cobalt species, more oxygen vacancies were obtained, Co-decorated TiO\textsubscript{2} show a remarkable selectivity of CH\textsubscript{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\textsubscript{2} reduced to CH\textsubscript{4}\textsuperscript{36} [according to equation (2) and (5), the redox potential of CO is more negative compared with CH\textsubscript{4}]. Moreover, there are Pt-doping\textsuperscript{37}, Cu-doping\textsuperscript{38} and La-doping\textsuperscript{39} TiO\textsubscript{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\textsubscript{2} NTs which exhibit a good selectivity of CH\textsubscript{3}OH\textsuperscript{28}. Carbon-based materials would also help in selectivity. Li et al. reported a g-C\textsubscript{3}N\textsubscript{4} NDs decorated brookite TiO\textsubscript{2} quasi nanocube (BTN) with better CH\textsubscript{4} selectivity compared to g-C\textsubscript{3}N\textsubscript{4} or BTN alone\textsuperscript{40}.

5 Conclusions

In this review, a misunderstanding is corrected. CO\textsubscript{2} reduction with TiO\textsubscript{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.
Anatase and rutile are the most common crystal structures of TiO₂ 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 TiO₂, 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 TiO₂ 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”.

Table 1. Different modifications on TiO₂ for CO₂ reduction.

<table>
<thead>
<tr>
<th>Material</th>
<th>Reaction environment</th>
<th>Major product</th>
<th>R_{max}^{[a]}</th>
<th>Minor products</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-TiO₂ NT@Ti plate</td>
<td>CO₂ and H₂O gases</td>
<td>CH₃OH</td>
<td>280</td>
<td>-</td>
<td>[28]</td>
</tr>
<tr>
<td>RuBpy.Pt(in).TiO₂^{[d]}</td>
<td>690 Torr CO₂ gas</td>
<td>CH₄</td>
<td>~0.25</td>
<td>-</td>
<td>[29]</td>
</tr>
<tr>
<td>surface heterostructure anatase TiO₂^{[e]}</td>
<td>KHCO₃ (CO₂)</td>
<td>CH₄</td>
<td>1.58</td>
<td>-</td>
<td>[31]</td>
</tr>
<tr>
<td>ZnIn₂S₄ NS/TiO₂ NB</td>
<td>CO₂ and H₂O gases</td>
<td>CH₄</td>
<td>1.135</td>
<td>-</td>
<td>[33]</td>
</tr>
<tr>
<td>SnO₂ QD/TiO₂ hollow spheres</td>
<td>CO₂, H₂O, HCl gases^{[b]}</td>
<td>CH₃OH</td>
<td>1.61</td>
<td>CH₄, HCHO</td>
<td>[35]</td>
</tr>
<tr>
<td>Cu-BTN^{[f]}</td>
<td>CO₂ and H₂O gases^{[c]}</td>
<td>CH₄</td>
<td>17.81</td>
<td>CO</td>
<td>[38]</td>
</tr>
<tr>
<td>Pt-(BTN-CNDs)^{[g]}</td>
<td>CO₂ and H₂O gases^{[c]}</td>
<td>CH₄</td>
<td>31.8</td>
<td>CO</td>
<td>[40]</td>
</tr>
</tbody>
</table>

[a] Maximum formation rate reported for the major product(s), in μmol g⁻¹ h⁻¹, unless stated otherwise. [b] Generated by HCl and NaHCO₃. [c] Generated by H₂SO₄ and NaHCO₃. [d] RuBpy.Pt(in).TiO₂: dye-sensitized Pt promoted TiO₂. 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 TiO₂. [f] Cu decorated brookite TiO₂ quasi nanocubes (BTN). [g] Pt loaded on a substrate made of brookite TiO₂ quasi nanocubes (BTN) and g-C₃N₄ nanodots (CND).
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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