Review

Recent Advances in Photo-catalytic Materials for Artificial Photosynthesis

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Abstract: Artificial photosynthesis is copying in practically less complex structure to achieve the consequences of natural photosynthesis. The process includes coupling solar powered driven water splitting and CO_2 reduction. It takes place in a way that dispenses with the requirement for an external, sacrificial electron donor is one of the colossal difficulties for the utilization of renewable energy and a sustainable development. For all intents and purposes, "CO_2 reduction" is more emerging than "water splitting" since it not just adds to worldwide carbon cycling for carbon unbiased natural powers, mimicking what genuine leaves do (characteristic carbon reduction), additionally mitigating worldwide atmosphere changes. However, as CO_2 is a generally dormant and stable exacerbate, its diminishment is entirely testing. The photo catalytic dwindling of CO_2 has been generally expected for quite a while and additionally water splitting. For heterogeneous photo catalyst, numerous endeavors still concentrate on TiO_2-based materials while different photo catalysts, for example, $LiNbO_3$, $ZnGa_2O_4$, $ALa_4Ti_4O_{15}$ (A=Ca, Sr, and Ba) etc. have additionally been accounted for as of late. Nevertheless, the advance accomplished in this field had not been as sensational as that in water splitting for a few decades in view of the low efficiencies, limited photo catalyst and/or requiring the utilization of sacrificial reducing agents. The study finds out current gaps inside of the advancement of recent photo-catalytic materials for artificial photosynthesis.

Keywords: Photo catalytic materials; artificial photosynthesis; carbon-dioxide reduction

1. Introduction

In photosynthesis system, the energy achieved from sunlight is eventually used to convert CO_2 into glucose that's kept in the type of chemical energy. The approach of artificial photosynthesis would even be completed via the photo reduction of CO_2 to deliver hydrocarbons. This would imply that solar energy can be instantly changed and stored as chemical energy with the help of a photo-catalyst. The photo catalytic reduction of CO_2 requires multiple electron transfers and can lead to the formation of many exclusive products relying on the detailed response pathway adopted and the quantity of electrons transferred, which determines the final oxidation state of the carbon atom. Carbon monoxide, formic acid, formaldehyde, methanol, methane, ethane, and oxygen have been observed in many experiments [1-6].

Energy and environment are the two most imperative issues that are of serious dilemma to cutting-edge society. Greenhouse gases like CO_2, CH_4, and CFCs are the foremost factors of global warming[7]. The atmospheric attention of CO_2 has steadily expanded owing to human activities and this quickens the greenhouse effect. The reduction of CO_2 with the aid of artificial photosynthesis is believed to be one of the vital possible choices that emits O_2 utilizing atmospheric CO_2 and water in the presence of a photo-catalyst. Although the state-of-the-art for the production of beneficial chemicals from CO_2 using sunlight energy is still far from practical consideration, rich knowledge has been accumulated to understand the key factors that determine the catalytic performances. This study reveals the recent advances of semiconductor based photo catalysts like TiO_2, $LiNbO_3$, $ALa_4Ti_4O_{15}$ (A =Ca, Sr, and Ba) and $ZnGa_2O_4$ and their usage in artificial photosynthesis for decreasing of greenhouse effect.

2. Principle of semiconductor photo-catalysts for artificial photosynthesis

The semiconductor-based photo catalysis for the reduction of CO_2 to H_2O includes 3 primary steps (Fig. 1). In the first step, electron-hole pairs are produced when a semiconductor photo-catalyst is illuminated through a suitable light source with its energy equal or higher than the band-gap energy (Eg) of the semiconductor. Then, the generated electrons and holes migrate to the surface of the semiconductor or a co-catalyst involved with the semiconductor in the second step (Fig. 1, iia). It must be stated that best a fraction of carriers can attain the outside of the semiconductor or co-catalyst. A significant fraction of electron-hole pairs recombine together (Fig. 1, iib), with the power being released in the type of heat or photon. In the third step, the photo caused electrons reduce CO_2, which is adsorbed on catalyst surfaces, into CO, HCOOH, CH_2OH or CH_4. At the same time, the holes oxidize H_2O to O_2. The first and second steps are the same as those in the splitting of H_2O. The reduction of H_2O might also proceed in competition with that of CO_2 [8] .

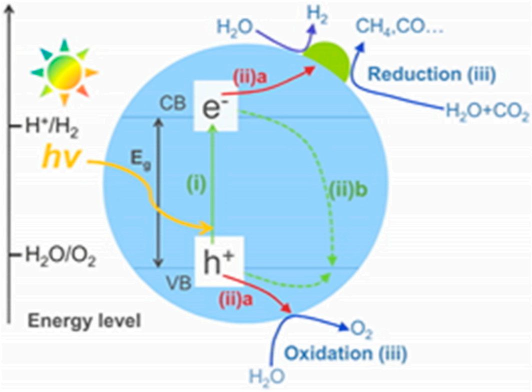

Figure 1. Schematic representation of basic mechanism for the photo catalytic reduction of CO_2 with H_2O on TiO_2[8].

For most photo catalytic reactions including H_2O splitting, the photo catalytic efficiency for CO_2 reduction is most commonly determined with the assistance of the efficiencies of the light harvesting, the charge separation and the surface reaction. In precise, the acceleration of electron-hole separation is of paramount importance for practically all of the photo catalytic reactions. That is also a key hindrance in the photo-catalytic discount of CO_2.

Taking the thermodynamics into consideration, CO_2 is with no doubt one of the most stable molecules among carbon compounds. The molecule consists of a linear connection of a carbon and two oxygen atoms (O=C=O) and it does not have a dipole moment. Thus, in evaluation of Gibbs free power for the preferred carbon compounds ($\Delta G^o= -51$ kJ mol^{-1} for CH_4, $\Delta G^o= -137$ kJ mol^{-1} for CO and $\Delta G^o = -166$ kJ mol^{-1} for CH_3OH), the full of life steadiness of the CO_2 molecule ($\Delta G^o= -394$ kJ mol^{-1}) appears to be a robust issue [9]. This issues makes CO_2 reduction an incredibly endothermic process, even more complicated than the water splitting reaction ($\Delta G^o= -228$ kJ mol^{-1}) for liquid H_2O.

With respect to electronic system of the reducing of CO_2, CO_2 can be decreased by getting one or a few electrons to end up the comparing reducing structures. Equation (1) reveals that the one-electron exchange to form •CO (at pH 7 in an aqueous solution, versus NHE[10]) is very much endothermic and unfavorable. At the same time, development of $\bullet CO_2^-$ may be the initial step for the photo reduction of CO_2. The trial information uncovered that adsorbed CO_2 was photo chemically decreased to shape the carbonate anion radical ($\bullet CO_2^-$) [11,12], it is recommended that the extraordinary connection between the photo-catalyst surface and CO_2 is critical. A short time later, the carbonate anion radical ($\bullet CO^-$) is further lessened by accepting multiple electrons with protons, position anion (HCO^-), carbon monoxide (CO), formaldehyde (HCHO), methanol (CH_3OH) and methane (CH_4) are developed as the results of the photo catalytic reaction of CO_2, as appeared in (2)~(6)[8].

$$CO_2 + e^- \rightarrow CO \qquad E^o = -1.90\ V \qquad (1)$$

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

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad E^o = -0.53\ V \qquad (3)$$

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

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \qquad E^o = -0.38\ V \qquad (5)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E^o = -0.24\ V \qquad (6)$$

3. Recent photo-catalysts for artificial photosynthesis

Now a days, numerous reported photo-catalysts are built with metal complex, natural mixes, and semiconductors combined with different co-catalysts, for example, metal complex, metal particles, and compounds. Regularly, the reported photo catalysts for the decrease of CO_2 could be ordered into two classifications: homogeneous and heterogeneous structure. In this study, we concentrate on the heterogeneous photo catalysts. In 1979, Fujishima and other co-authors. inspected the utilization of photo-catalyst powders for CO_2 reduction[13]. Little measures of formic acid, formaldehyde, methyl acid, and methane were created. From that point forward, different other photo-catalytic system that utilize heterogeneous photo-catalysts have been examined. In spite of the fact that there are numerous issues, for example, low movement of impetuses and low selectivity of the items, further advancement of photo catalysts is a vital target.

An effective photo-catalyst would have acquired to overcome the most three important mechanistic challenges which involve (i) the enough band gap energy for the reduction capabilities of CO_2; (ii) the suitable catalytic sites for the adsorption and stimulation of CO_2; (iii) the effective multi electron transmission with protons (or hydrogen radicals). The study will also spotlight some valuable cutting-edge semiconductor photo-catalysts that can enhance CO_2 reduction and artificial photosynthesis by using facilitating the electron-hole separation.

Table 1. The band gap of some recent photo-catalysts in aqueous solution for artificial photo synthesis.

Semiconductor	Band gap (eV)
TiO_2	3.2
$LiNbO_3$	3.78
$BaLa_4Ti_4O_{15}$	3.85
$CaLa_4Ti_4O_{15}$	3.82
$SrLa_4Ti_4O_{15}$	3.79
$ZnGa_2O_4$	4.4-5

From the list, TiO_2 has drawn a lot of responsiveness due to the fact its great photo activity for its low band gap. Unluckily, TiO_2 will not be the quality for all purposes and performs instead poorly in processes associated with solar light driven photo catalysis. A number of metal oxide complexes like, $LiNbO_3$, $ZnGa_2O_4$, $ALa_4Ti_4O_{15}$ (A=Ca, Sr, and Ba) had been explored to exploit their photo catalytic activity in the solar spectrum also. These novel semiconductors have proved to be among the most effective photo catalysts for reactions, decreasing CO_2 and the generation of O_2 through artificial photosynthesis[3,6,7].

3.1 TiO_2

TiO_2 has developed as a standout amongst the most fascinating photo catalytic materials in the present day period for an widespread variety of utilizations from environment to wellbeing.TiO_2 is naturally and chemically latent, ecological well disposed, ease, nontoxic and stable as for photo erosion and chemical corrosion and this has prompted it's far reaching use in photo catalytic applications.

Since the earliest report from Fujishima and co-author, TiO_2 and Ti-based materials have been concentrated profoundly because of the ease, strength and execution [13]. In 1983, Halmann and co-authors assessed the CO_2 diminishment capacity of TiO_2, $SrTiO_3$, and $CaTiO_3$ photocatalysts under characteristic daylight illumination [2].The light energy transformation efficiencies were evaluated to be 0.001~0.016% as it were. The utilization of Cu and Ag as co-catalysts was accounted for by Wu and co-authors [14]. CO_2 was photo-catalytically diminished to methanol under UV illumination. The UV-light affected diminishment of CO_2 to CH_4 utilizing different metal-kept (Pd, Rh, Pt, Au, Cu, and Ru) TiO_2 particles in water has been investigated. The Pd-stored TiO_2 (Pd-TiO_2) was the most productive photo-catalyst in such frameworks. Photo-reduction of vaporous CO_2 to CO with hydrogen over Rh-stacking TiO_2 was examined by Kohno et al.[11].

Table 1. The comparison of the reaction intermediates, products and reaction media for CO_2 photo reduction with H_2O on the different photo catalysts from the literature.

Catalysts	Reaction intermediates	Products	Reaction Media	References
TiO_2-brookite	CO_2•, HCOOH	CO, CH_4,	H_2O vapor	[4]
TiO_2-P25	$HCOO^-$, CO_3^{2-}	CH_4	H_2O solution	[15]
Pt/TiO_2	HCO_3^-	CH_4	H_2O vapor	[16]
CuO/TiO_2	C residue	CH_4	H_2O vapor	[4]

A few studies have been directed to investigate the surface response intermediates in the CO_2 photo reduction over exposed TiO_2. The photograph impetuses, response media, response intermediates, and items are outlined in Table 1. Table 1 demonstrates that there are a variety of feasible response intermediates, to a great extent relying upon the response media. In a strong gas response frameworks including CO_2 and H_2O vapor, CO_2, C•, CO, $HCO_3$and HCOOH are the essential intermediates. CO_2 and HCOOH can be changed over to CO, while C•, CO and $HCO_3^-$are considered as the intermediates for the generation of hydrocarbons (e.g., CH_4, C_2H_4, C_2H_6). In a strong fluid response framework including broke down CO_2 in water, $CO^{2-,}$ CH_3•, COOH•, and HCHO are the normal intermediates, which can be changed into CH_4, CH_3OH, HCOOH and CH_3CH_2OH.

Yet, a substantial limitations of TiO_2 photo catalysts is the huge recombination of photo generated electon-hole pair and its huge band gap. Considering that of the latter it may possibly most effective take in photons with light wavelengths shorter than about 400 nm in the UV or near-UV wavelength regime, which accounts for lower than 5% of the complete solar power irradiation [17]. Even though TiO_2 based photo catalysts can operate as strong photo catalysts, they cannot be used for powerful solar energy harvesting and conversions. For that reason many improved ways, such as metal or non-metal doping, floor sensitization, semiconductor coupling, beneficial metallic deposition, and growing crystal defects had been carried out with the intention to broaden the spectral response range and increase the photo catalytic quantum affectivity of TiO_2 [18].

3.2. $LiNbO_3$

$LiNbO_3$ have wider band gap (3.78 eV) [5]. $LiNbO_3$ has strong remnant polarization (70 μc/cm^2) [19].Compared with numerous tried semiconductors (i.e., ZnO, Fe_2O_3, CdS, ZnS, and TiO_2), $LiNbO_3$ can more rapidly reduce CO_2 than the others. Although, $LiNbO_3$ (3.78 eV) has a larger band gap than TiO_2 (3.2 eV)[5], it can produce more photo-catalytic product than TiO_2 due to remnant polarization[20].

Figure 3 compares the capability of the valence and conduction bands of $LiNbO_3$ and TiO_2 in connection to the cell potential of the transformation of CO_2 and water into formic acid and formaldehyde. The half-equation for the reduction of CO_2 and the oxidation of water are likewise considered. This figure demonstrates that TiO_2 drives the response of CO_2 and water to formic acid and formaldehyde[21], valence band openings oxidize water and conduction band electrons can't lessen CO_2 to CO_2^-. $LiNbO_3$ additionally drives the response of CO_2 and water to formic acid and formaldehyde, however the valence band gaps don't oxidize water [19].Conduction band electrons of $LiNbO_3$ are, in any case, profoundly lessened and hence diminish CO_2 to $CO_2{}^-$ (1.9V v's Standard Hydrogen Electrode or SHE) or $CO_2{}^{2-}$ (1.45V v's Standard Hydrogen Electrode or SHE) not at all like TiO_2 . The response undertaking of $LiNbO_3$ permits an alternate response pathway due to its extremely decreasing conduction band electrons [5].

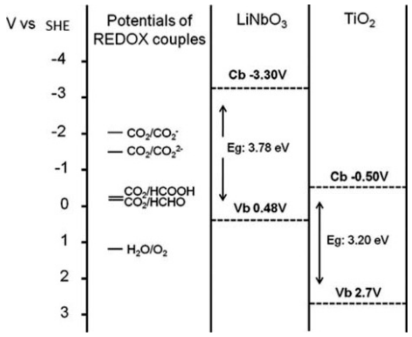

Figure 2. Band positions of $LiNbO_3$ and TiO_2 vs. Standard Hydrogen Electrode (SHE) in relation to the redox reactions of artificial photosynthesis [5,21].

3.3. Ag loaded $ALa_4Ti_4O_{15}$(A = Ca, Sr, and Ba)

Ag co-catalyst loaded $ALa_4Ti_4O_{15}$ (A = Ca, Sr, and Ba) photo catalysts with (3.79-3.85 eV) of band gaps and layered perovskite structures showed pursuits for CO_2 reduction to produce CO and HCOOH by way of bubbling CO_2 gas into the aqueous suspension of the photo catalyst powder with none sacrificial reagents[22].

Ag co-catalyst loaded $BaLa_4Ti_4O_{15}$ is the most lively photo catalyst. A liquid-segment chemical reduction procedure is better than impregnation and in situ photo deposition methods for the loading of the Ag co-catalyst. CO is the important reduced product rather than H_2 even in an aqueous medium on the optimized Ag/ $BaLa_4Ti_4O_{15}$ picture catalyst. Evolution of O_2 in a stoichiometric ratio (H_2+CO: O= 2:1 in a molar ratio) indicated that water is consumed as a reducing reagent (an electron donor) for the CO_2 reduction accompanied with water oxidation was executed making use of the Ag/$BaLa_4Ti_4O_{15}$ reduction. Hence, an uphill reaction of CO_2 photo catalyst [3].

Table 2 demonstrates impacts of co-catalysts, the loading technique, and the loading quantity on photo catalytic reduction of CO_2 diminishment in liquid media over $ALa_4Ti_4O_{15}$ (A = Ca, Sr, and Ba) photo catalysts. Simple $ALa_4Ti_4O_{15}$ (A = Ca, Sr, and Ba) demonstrated irrelevant workouts for CO_2 reduction.

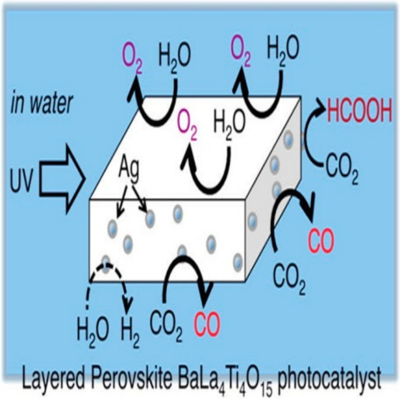

Figure 3. Photo-catalytic mechanism of layered perovskite $BaLa_4Ti_4O_{15}$ photo catalyst

Loading pretreated Ru and Au co-catalyst on $BaLa_4Ti_4O_{15}$ improved photo catalytic activity for water spliting, however not CO_2 reduction, in light of the fact that these co-catalysts are very powerful for H_2 creation by water splitting. When a Cu co-catalyst was loaded, photo catalytic activities for water splitting and CO_2 reduction increased. In spite of the fact that the measures of responded electrons and holes> Ag, Ag was the most dynamic co-catalyst for CO_2 were substantial in the request of Au > Cu > Ru reduction. The Ag co-catalyst was likewise convincing for CO_2 decreasing over $CaLa_4Ti_4O_{15}$ and $SrLa_4Ti_4O_{15}$ photo catalyst[3].

Table 2. Effects of co-catalyst, the loading method and the loading amount on photo catalytic reduction of CO_2 in aqueous media over $ALa_4Ti_4O_{15}$ (A = Ca, Sr, and Ba) photo catalysts[3].

Photo catalyst	Band Gap/ eV	Co-catalyst (%wt)	Loading Method	H_2 activity/μmolh^{-1}	O_2 activity/μmolh^{-1}	CO activity/μmolh^{-1}	HCOOH activity/μmolh^{-1}
$BaLa_4Ti_4O_{15}$	3.9	None		5.3	2.4	0	0
$BaLa_4Ti_4O_{15}$	3.9		Impregnation	58	29	0.02	0
$BaLa_4Ti_4O_{15}$	3.9	Ru (0.5)	Photo deposition	84	41	0	0
$BaLa_4Ti_4O_{15}$	3.9	Cu (0.5)	photo deposition	96	45	0.6	0
$BaLa_4Ti_4O_{15}$	3.9	Au (0.5)	photo deposition	110	51	0	0
$BaLa_4Ti_4O_{15}$	3.9	Ag (1.0)	photo deposition	10	7.0	4.3	0.3
$CaLa_4Ti_4O_{15}$	3.9	None		1.3	0.6	0.07	0
$CaLa_4Ti_4O_{15}$	3.9	Ag (1.0)	photo deposition	5.6	2.1	2.3	1.3
$SrLa_4Ti_4O_{15}$	3.8	None		0.8	0.5	0.06	0
$SrLa_4Ti_4O_{15}$	3.8	Ag (1.0)	photo deposition	2.7	1.8	1.8	0.5

3.4. $ZnGa_2O_4$

The spinel type oxide $ZnGa_2O_4$, with a wide band gap of (4.4–5.0 eV), can efficiently decomposes H_2O to H_2 and O_2, without any sacrificial reagents, under UV irradiation. Since the reduction of CO_2 requires a reduction potential higher than that of H^+, the wide band gap of $ZnGa_2O_4$, which is capable of generating photoelectrons with a high reduction potential, should result in the efficient reduction of CO_2 [9,23]. Indeed, $ZnGa_2O_4$ possessing various morphologies, such as meso-porous, nano-cube, and ultrathin nanosheet, has been used in the photocatalytic reduction of CO_2 with H_2O. In addition, high crystallinity in a photo-catalyst has a positive effect on its activity due to the elimination of defects, which usually act as recombination centers for photo generated pairs [24,25].

The photocatalytic conversion of CO_2 by H_2O, which can be regarded as artificial photosynthesis, is an arduous reaction making use of electrons generated by light energy. The generation of H_2 from the reduction of protons usually competes for the photo-excited electrons and takes precedence over the reduction of CO_2, because the redox potential of H_2 (0. 41 V vs. NHE, at pH 7) is more positive than that of CO/CO (0.51 V vs. NHE, at pH 7). In order to achieve the conversion of CO_2 rather than the production of H_2 by H_2O over heterogeneous photo catalysts, it is extremely important to improve the selectivity of generated electrons toward the reduction of CO_2 [26]. Moreover, a stoichiometric amount of O_2 should be evolved if H_2O functions efficiently as an electron donor. Although various metal oxide photo catalysts have been reported for CO_2 reduction in H_2O, only a few materials, i.e., Zn-doped Ga_2O_3 [25], $ALa_4Ti_4O_{15}$ (where A = Ca, Sr and Ba), showed higher selectivity for CO_2 reduction and simultaneously produced O_2 stoichiometrically. Wang and co-authors showed, Ag-modified $ZnGa_2O_4$ also suggests high activity and selectivity toward CO production in the photo catalytic change of CO_2 with H_2O. The stoichiometric progress of O_2 watched demonstrates that H_2O can work efficiently as an electron donor during the photo-catalytic conversion of CO_2. The crystallinity of the $ZnGa_2O_4$ catalyst increments, and the surface area reduces, with increasing calcination temperature and time. Probably the maximum quantity of CO is produced over $ZnGa_2O_4$ calcined at 1123 K for 40 h. Change of the catalyst with an Ag co-catalyst through the chemical scale down method likewise enhances the photo catalytic activity of $ZnGa_2O_4$ [27].

4. Conclusion

CO_2 reduction to produce usable products is an important topic from the viewpoint of not only an environmental issue but also artificial photosynthesis. If one thinks artificial photosynthesis accompanied by light energy conversion, water has to be used as an electron donor and a hydrogen source for the CO_2 reduction. A photo-catalytic system is a candidate for the CO_2 reduction of an artificial photosynthesis in an aqueous medium as well as an electrochemical system combined with a solar cell. The photo-catalytic reduction of CO_2 has been studied for a long time as well as water splitting. When homogeneous photo is efficiently reduced to form CO in the presence of electron donors. It has been reported that TiO_2 photo-catalysts give HCOOH, HCHO, CH_3OH, and CH_4, depending on co-catalysts loaded on the photo-catalysts. Mixed metal oxides such as, $LiNbO_3$, $ZnGa_2O_4$ and $ALa_4Ti_4O_{15}$ (A = Ca, Sr, and Ba) have also been testified as photo catalyst for CO_2 reduction and O_2 production leading to artificial photosynthesis even in the presence of a sacrificial reagent and co-catalysts in many cases.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:
CB: Conduction Band
SHE: Standard Hydrogen Electrode
NHE: Normal Hydrogen Electrode
VB: Valance Band

References

1. Carraro, M.; Sartorel, A.; Toma, F.; Puntoriero, F.; Scandola, F.; Campagna, S.; Prato, M.; Bonchio, M. Artificial photosynthesis challenges: Water oxidation at nanostructured interfaces. *Photocatalysis* **2011**, 121-150.
2. Halmann, M.M.; Steinberg, M. *Greenhouse gas carbon dioxide mitigation: Science and Technology*. CRC press: 1998.
3. Iizuka, K.; Wato, T.; Miseki, Y.; Saito, K.; Kudo, A. Photocatalytic reduction of carbon dioxide over ag cocatalyst-loaded $ALa_4Ti_4O_{15}$ (A= Ca, Sr, and Ba) using water as a reducing reagent. *Journal of the American Chemical Society* **2011**, *133*, 20863-20868.
4. Liu, L.; Zhao, C.; Li, Y. Spontaneous dissociation of CO_2 to CO on defective surface of Cu (i)/TiO_{2-x} nanoparticles at room temperature. *The Journal of Physical Chemistry C* **2012**, *116*, 7904-7912.
5. Stock, M.; Dunn, S. $LiNbO_3$—a polar material for solid-gas artificial photosynthesis. *Ferroelectrics* **2011**, *419*, 9-13.
6. Wang, Z.; Teramura, K.; Hosokawa, S.; Tanaka, T. Highly efficient photocatalytic conversion of CO_2 into solid CO using H_2O as a reductant over ag-modified $ZnGa_2O_4$. *Journal of Materials Chemistry A* **2015**, *3*, 11313-11319.
7. Nath, R.K.; Zain, M.F.M.; Kadhum, A.A.H. Artificial photosynthesis using $LiNbO_3$ as photocatalyst for sustainable and environmental friendly construction and reduction of global warming: A review. *Catalysis Reviews* **2014**, *56*, 175-186.
8. Xie, S.; Zhang, Q.; Liu, G.; Wang, Y. Photocatalytic and photoelectrocatalytic reduction of CO_2 using heterogeneous catalysts with controlled nanostructures. *Chemical Communications* **2016**, *52*, 35-59.
9. Kubacka, A.; Fernández-García, M.; Colón, G. Advanced nanoarchitectures for solar photocatalytic applications. *Chemical Reviews* **2011**, *112*, 1555-1614.
10. Indrakanti, V.P.; Kubicki, J.D.; Schobert, H.H. Photoinduced activation of CO_2 on Ti-based heterogeneous catalysts: Current state, chemical physics-based insights and outlook. *Energy & Environmental Science* **2009**, *2*, 745-758.
11. Kohno, Y.; Hayashi, H.; Takenaka, S.; Tanaka, T.; Funabiki, T.; Yoshida, S. Photo-enhanced reduction of carbon dioxide with hydrogen over Rh/TiO_2. *Journal of Photochemistry and photobiology A: Chemistry* **1999**, *126*, 117-123.
12. Lunsford, J.H.; Jayne, J.P. Formation of CO_2-radical ions when CO_2 is adsorbed on irradiated magnesium oxide. *The Journal of Physical Chemistry* **1965**, *69*, 2182-2184.
13. Inoue, T.; Fujishima, A.; Konishi, S.; Honda, K. Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders. *Nature* **1979**, *277*, 637-638.
14. Tseng, I.-H.; Wu, J.C.-S. Chemical states of metal-loaded titania in the photoreduction of CO_2. *Catalysis Today* **2004**, *97*, 113-119.
15. Dimitrijevic, N.M.; Vijayan, B.K.; Poluektov, O.G.; Rajh, T.; Gray, K.A.; He, H.; Zapol, P. Role of water and carbonates in photocatalytic transformation of CO_2 to CH_4 on titania. *Journal of the American Chemical Society* **2011**, *133*, 3964-3971.
16. Uner, D.; Oymak, M.M. On the mechanism of photocatalytic CO_2 reduction with water in the gas phase. *Catalysis today* **2012**, *181*, 82-88.
17. Gueymard, C.A. The sun's total and spectral irradiance for solar energy applications and solar radiation models. *Solar energy* **2004**, *76*, 423-453.

18. Yang, Y.; Zhong, H.; Tian, C.; Jiang, Z. Single-step preparation, characterization and photocatalytic mechanism of mesoporous Fe-doped sulfated titania. *Surface Science* **2011**, *605*, 1281-1286.
19. Yang, W.-C.; Rodriguez, B.J.; Gruverman, A.; Nemanich, R. Polarization-dependent electron affinity of $LiNbO_3$ surfaces. **2004**.
20. Yang, K.; Richards, P.; Shen, Y. Generation of far-infrared radiation by picosecond light pulses in $LiNbO_3$. *Applied Physics Letters* **1971**, *19*, 320-323.
21. Bockris, J.M.; Dandapani, B.; Cocke, D.; Ghoroghchian, J. On the splitting of water. *International Journal of Hydrogen Energy* **1985**, *10*, 179-201.
22. Kudo, A.; Miseki, Y. Heterogeneous photocatalyst materials for water splitting. *Chemical Society Reviews* **2009**, *38*, 253-278.
23. Fan, W.; Zhang, Q.; Wang, Y. Semiconductor-based nanocomposites for photocatalytic H_2 production and CO_2 conversion. *Physical Chemistry Chemical Physics* **2013**, *15*, 2632-2649.
24. Kitano, M.; Hara, M. Heterogeneous photocatalytic cleavage of water. *Journal of Materials Chemistry* **2010**, *20*, 627-641.
25. Maeda, K.; Domen, K. New non-oxide photocatalysts designed for overall water splitting under visible light. *The Journal of Physical Chemistry C* **2007**, *111*, 7851-7861.
26. Teramura, K.; Wang, Z.; Hosokawa, S.; Sakata, Y.; Tanaka, T. A doping technique that suppresses undesirable H_2 evolution derived from overall water splitting in the highly selective photocatalytic conversion of CO_2 in and by water. *Chemistry–A European Journal* **2014**, *20*, 9906-9909.
27. Wang, Z.; Teramura, K.; Hosokawa, S.; Tanaka, T. Highly efficient photocatalytic conversion of CO_2 into solid CO using H_2O as a reductant over Ag-modified $ZnGa_2O_4$. *Journal of Materials Chemistry A* **2015**, *3*, 11313-11319.