REVIEW ARTICLE

Photocatalytic Reduction of Carbon Dioxide: Issues and Prospects

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Abstract: *Background*: The conversion of carbon dioxide into worthwhile chemicals through photo-catalysis has been a matter of attraction for the last four decades among the scientific community. However, the conversion rate has not yet been achieved to the desired efficiency due to the inevitable barriers associated with the process making it as a Holy Grail. This presentation deals with the identification and critical evaluation of the hurdles that pulls back the photocatalytic processes on track and the recent advances in the scientific field that pertain to the photocatalytic conversion of carbon dioxide in the near future.

Methods: We explored the content of more than 200 original research articles that are relevant to the desired topic and extracted the current knowledge on the so called photo-catalytic reduction of carbon dioxide. We have approached all the articles in a perspective way rather than a word to word recent advances in the field and found out the major limitations that have to be rectified.

Results: The issues related to the state-of-the-art of carbon dioxide reduction are described in separate sections in detail. Mechanistic aspects should to be revisited with the help of advanced instrumentation facilities. Major problem associated is finding the appropriate material, hence efficient material should be engineered to overcome the high energy barrier associated with the reduction process. Product analysis as well as efficiency determination are highly susceptible to errors. It is very difficult to compare the work produced by any two labs between each other!

Conclusion: There are so many hurdles associated invariably with the photocatalytic carbon dioxide reduction process which must be rectified in order to create an energy, sustainable society using direct sunlight as a primary energy source just as plants do. It could happen only by the collaborative research effort from various groups, irrespective of the implicit bias among the scientific community.

Hariprasad Narayanan

1. INTRODUCTION

It's almost a century after the publication of the mind blowing article "The photochemistry of the future" by the pioneer chemist Giacomo Ciamician, who challenged the scientists of that decade to imagine a chemical industry producing chemicals in such a way that plants do using solar energy, the primary energy source [1,13]. During the Past 40 years, several scientists [2-19] have made a significant contribution towards the storage of solar energy into chemical bonds. The efforts have not yet achieved Ciamician's vision.

The planet earth receives ~ 4.3 x 10^{20} J/h of energy from the sun while the requirement of energy for the earth is around 4.7 x 10^{16} J/h and it shows that if one can harness completely the solar energy for one hour, it will be sufficient to satisfy the energy need of the world for more than a year [17].

There are many ways to harness the solar energy and convert it into useful electrical energy. One of them is to store solar energy in chemical bonds, that is, the conversion of carbon dioxide and water into value added chemicals and fuels. The reduction of carbon dioxide with water to give methanol is a thermodynamic uphill process with the free energy change of +689 kJ/mol and that of water reduction to yield hydrogen and oxygen also associated with a free energy change of +457.2 kJ/mol

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Current Catalsis

[17]. This implies that greater effort will be needed to overcome the energy barrier for converting carbon dioxide than the water splitting. In spite of this unfavourable condition, enormous efforts have been expanded around the globe to convert carbon dioxide into chemical and value added fuels. It has received considerable attention in recent times due to its similarity to photosynthesis. There are various other routes available for carbon dioxide conversion with specific advantages and disadvantages over photo-catalytic route.

The photocatalytic conversion rate so far reported is up to few tens of micromoles per gram per hour, which is far from the levels required for the industrialization of the process. One of the primary reasons is that the carbon dioxide in its ground state is a linear molecule which is stable and the activation of this linear molecule for chemical conversion requires high overpotential. The first electron transfer to the carbon dioxide to produce carbon dioxide anions radical which needs high reduction potential up to -1.9 V vs Normal Hydrogen Electrode (NHE). The conduction band bottom of currently known photocatalysts is more positive than the first electron reduction potential. So, urgent need is a photocatalyst with conduction band edge more negative potential with necessary band gap for visible light absorption. The visible light absorption of the photocatalyst can be achieved by means of sensitization and band gap engineering, *etc*. But these possibilities have not provided any desired results. Since the photocatalytic process is a multielectron transfer process, the reaction rate depends upon each of the electron transfer steps, namely photon absorption, charge separation, surface reaction, electron-hole recombination, transfer of electron to the adsorbed substrate and desorption of the substrates and each of them must be sequentially taking place for the formation of multielectron reaction products like methanol, ethanol, formaldehyde. To the best of the author's knowledge, no photocatalyst reported so far does both activation and visible light absorption in an appropriate way. At least one wants to achieve a 10% quantum efficiency or comparable to photosynthetic rate, then only the dream can be realized.

Another hurdle associated with the efficiency is the measures like Quantum Efficiency, Turnover Rate, Turnover Number, Turnover Frequency, which reflects reactivity of the system, used for comparison and appropriate selection of materials in photocatalysis. These measures are based on either in terms of catalyst systems or in terms of illumination employed. In a reaction like photocatalysis, the illumination based measures is not directly reflecting the activity of the catalyst since the activity not only depends upon the illumination but also on many other factors.

The illuminated beam itself undergoes multiple events like scattering, reflection, etc., hence the calculation of the exact number of photons absorbed by the photocatalyst is difficult. Hence, one wants to develop a new efficiency scale for representing the activity of the photocatalyst and it must be based on photocatalyst as well as the illumination and independent of these individual parameters. The new scale must be based on the number of successful photons absorbed by the photocatalyst, which only truly gives the quantum efficiency.

The reaction rate can be increased by catalyst modification or by adding sacrificial reagent to the system. In the case of CO_2 reduction, none of the above methods has not been yielding the desired result. The role of sacrificial reagent on the PCR of carbon dioxide is limited for a few hours and it also absorbs the light from the illumination source. The degradation of sacrificial reagent may affect the reaction mechanism of carbon dioxide reduction itself because the proposed mechanism for carbon dioxide reduction involves radical species. If nanoarchitecture will be a solution, the large scale production of catalyst with well-defined size, shape, surface, porosity, defects, and assemblies are the challenges. The doping and aliovalent substitution of nanomaterials may lead to photochemical deactivation of the catalyst.

Major limitation associated with carbon dioxide reduction is the accuracy of the analytical measurements employed. The photocatalytic process is a multielectron transfer process, hence the reaction leads to the formation of a variety of products like carbon monoxide, methane, higher hydrocarbons, alcohol, aldehydes, carboxylic acid etc., with some intermediates. The identification and quantification of the products are needed for the best selection of photocatalyst, comparison and elucidation of reaction mechanisms. Currently there is no standard analysis method that has been developed for product analysis of carbon dioxide reduction. Hence the results of these measurements also include the products derived from the carbon contamination invariably present in the reaction sys-

tem. Isotope labelling is the solution, but there is also a chance of contamination.

Current developments in carbon dioxide reduction research is not enough for the real implementation of the process. The maximum yield has been reached up to some micromoles. Let's look at the present scenario, with the current pace, 1.1×10^8 kg of TiO_2 would be required for the production of methanol from carbon dioxide and water, assuming a catalyst activity of $1\mu mol_{product} \, g_{cat}^{-1} \, h^{-1}$ and production rate $1 kg \, s^{-1}$ [19].

The main objective of this write up is to analyze the issues associated with the state-of-the-art photocatalytic reduction of carbon dioxide into chemicals and fuels.

2. ACTIVATION OF CARBON DIOXIDE: THE HOLY GRAIL

Carbon Dioxide, the highest oxidation product of carbon, is a stable ($\Delta G^0 = -394$ kJ/mol), linear, non-polar molecule with C−O bond length of 1.16Å and bond strength D = 532 kJ/mol. Even though it is a nonpolar molecule, CO_2 contains polar bonds due to the electronegativity difference between carbon and oxygen. The molecular properties of CO_2 are assembled at Table **1**.

Because of the structure, the molecule is susceptible to both nucleophilic and electrophilic attack through carbon and oxygen centers respectively. The first ionization potential of carbon dioxide (13 eV) is higher compared to that of water (12.6) and ammonia (10) [21]. This indicates the noticeable electrophilicity of the central carbon atom.

From the perspective of Molecular Orbital Theory, the energy of the lowest unoccupied antibonding orbital (LUMO) has been estimated at 3.8 eV, indicates the high electron affinity with respect to the central carbon atom, hence it is susceptible to attack by nucleophile and to the reduction while that of highest occupied molecular orbital (HOMO) is susceptible to attack by electrophile due to its high localized electron density as oxygen in-plane lone pairs. It also interacts weakly with Lewis and Bronsted acids [21, 22a].

Carbon dioxide consists of two degenerate HOMO and LUMO levels. The degenerated frontier orbitals of CO_2 show similarity with the d-

Table 1.   Properties of Carbon Dioxide Molecule. Reproduced with permission from Ref [20]. ©2015 American Chemical Society.

Molecular Properties	
Molecular weight	44.0098 g/mol
Density	1.976 g/L (gas at 0 ℃ and 760 mm Hg);
	0.914 g/L (liquid at 0 ℃ and 34.3 atm);
	1.512 g/L (solid at -56.6 ℃)
Point group	$D_{\infty h}$
Diploe moment	0 D
Dielectric constant	1.000922 (gas)
Sublimation point	-78.4 ℃
Melting Point	-56.56 ℃ (triple point)
Vapor pressure	760 mm Hg at -78.2 ℃
Viscosity	0.0147 mN·s·m^{-2} (gas)
Solubility in water	0.614×10^{-3} mole fraction at 25 ℃ and 100 kPa CO_2 partial pressure
Acidity(pKa of H_2CO_3)	$pK_{a1} = 6.35$, $pK_{a1} = 10.33$ at 25 ℃
Enthalpy, $\Delta_f H^o$ (298.15 K)	-393.522 kJ·mol^{-1}
Heat capacity, C_p^o	37.129 J·K^{-1}·mol^{-1}
Entropy, S^o (298.15K)	213.795 J·K^{-1}·mol^{-1}

orbitals and f-orbitals of transition metals and lanthanides respectively. The molecule has four electrons with the same energy in the HOMO, which are ready to be released. It has also four unoccupied states to which four electrons can transfer (Fig. **1**). The degeneracy will break if one of four electrons are transferred or released [20]. Simultaneous addition or transfer of electrons does not occur in the case of carbon dioxide, hence the activation is a Holy Grail.
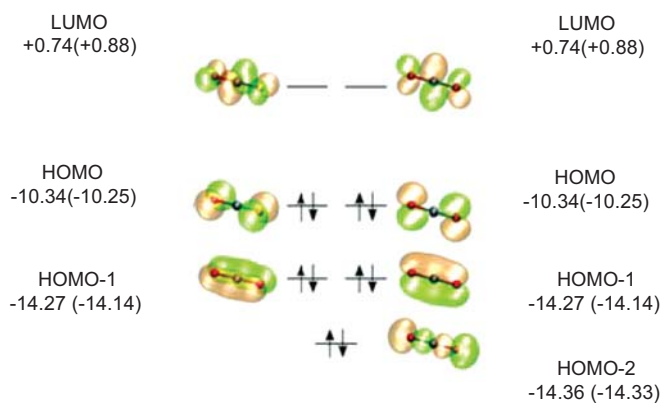
Fig. (1). Frontier molecular orbitals for ground state CO_2. The unit of orbital energy is eV in vacuum (in water, PCM). Reproduced with permission from Ref [20]. ©2015 American Chemical Society.

Activation of the molecule or substrate is to increase the degree of reactivity in the molecule by means surface reactions and it is a key step in any catalytic reaction. The overall rate of the catalytic reaction depends on the activation of the substrate or molecule. In many catalytic reactions, activation of the substrate is the rate limiting step. The main steps of carbon dioxide activation are: (i) bending of OCO bond (ii) elongation of two or one of the CO bond in CO_2 (iii) polarization of the CO_2 molecule. These three are not separate pathways, they take place simultaneously. The schematic representation is given in Fig. (**2**).
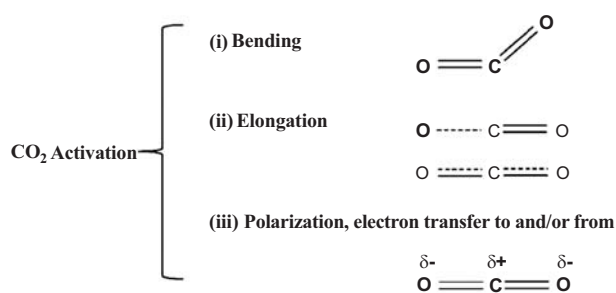
Fig. (2). Carbon Dioxide Activation Types. Reproduced with permission from Ref [20]. ©2015 American Chemical Society

Since it is a stable molecule, one wants to supply additional energy to convert the linear structure to bent form, i.e., CO_2 to $CO_2^{-\bullet}$. Because of the high LUMO level of carbon dioxide, the transfer of one electron to free CO_2 is thermodynamically unfavourable, requires a very negative redox potential up to the order of -1.9V vs Normal Hydrogen Electrode (NHE). In photocatalytic route, no semiconductor possesses the conduction band potential required for CO_2 activation, there is a need to supply additional overvoltage which will lead to another energy dilemma.

One of the prominent ways to reduce the barriers is to adsorb the substrate on the catalyst surface. The adsorptive interaction between catalyst surface and CO_2 molecule change the molecular structure from linear to bent. The bending of the carbon dioxide depends on the nature of catalyst surface. Carbon dioxide adsorbs on a metal surface by nine different ways [22b]. The interaction of CO_2 with the metal surface is beyond the scope of this document. CO_2 interacts with semiconductor surface in different ways as shown in Fig. (**3**).
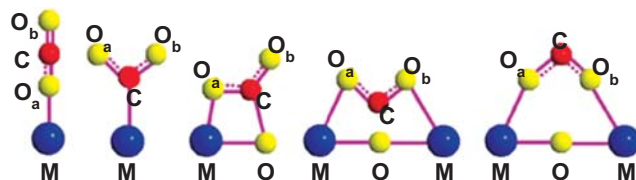
Fig. (3). Possible ways of adsorption of CO_2 on semiconductor surfaces. Reproduced with permission from Ref [23]. ©2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

CO_2 interacts with semiconductor surface either with oxygen or through carbon. The photoelectron produced on the catalyst surface add to the LUMO level of the chemically stable carbon dioxide leading to the formation of $CO_2^{-\bullet}$. The first electron transfer changes the geometry of CO_2 from linear to bent shape $CO_2^{-\bullet}$. The structural arrangement of linear CO_2 to bent shape involves the change in hybridization from *sp* to *sp²* at carbon, characterized by high overpotential, signifying a substantial kinetic barrier to the reaction. Once formed, the bent $CO_2^{-\bullet}$ undergo two electron reduction rather than one. The $CO_2^{-\bullet}$ anion radical formation has a significant role in the reduction of carbon dioxide. The formation of $CO_2^{-\bullet}$ alone does not lead to CO_2 reduction. The decrease in the OCO bond angle via surface interactions facilitates the charge transfer to CO_2 by lowering its LUMO. Theoretical

studies provide a clear picture of energy level variation of molecular orbitals as a function of OCO angle called Walsh diagram. The variation in the energy of LUMO with respect to OCO bond angle is shown in Fig. (**4**).
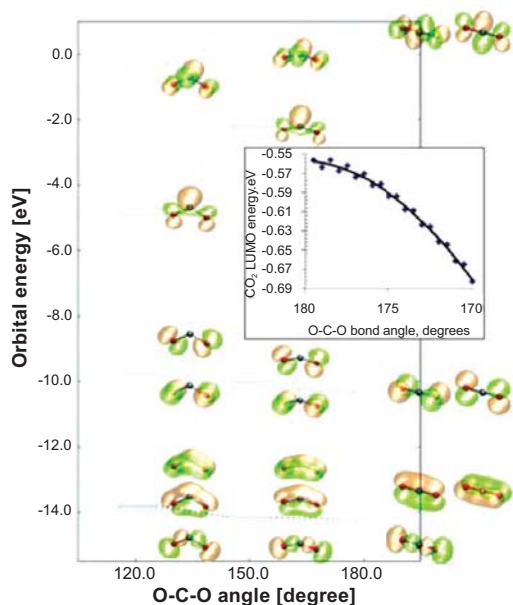

Fig. (4). Variation of the energy of LUMO w.r.t the bond angle of gaseous CO_2. Reproduced with permission from Ref [20] and [24]. ©2015 American Chemical Society and ©2009 Royal Society of Chemistry.

The most stable state is the linear carbon dioxide with 180° bond angle. The energy of frontier orbital changes with the decrease in the bond angle. Anionic $CO_2^{-\bullet}$ radical shows a bent geometry with a bond angle 134° while that of neural and cationic molecule possess linear geometry. The decrease in the bond angle can be characterized by means of IR spectroscopy.

It has been already established that rutile (100) crystal face is active for photocatalytic reduction of CO_2 while the crystal lattice (110) was found to be inactive towards the reaction [25]. The interaction between TiO_2 and CO_2 has been studied using a wide variety of spectroscopic techniques and quantum mechanical modelling. For convenience, all mechanisms related to semiconductors expressed in terms of TiO_2 as a representative. The carbon dioxide can attach to the TiO_2 surface either through oxygen or by carbon atom. It is suggested that attachment through two oxygen atoms is more stable due to the bidentate nature of CO_2 ligand. The Ti^{3+} formed at the surface reduces the CO_2 to corresponding radical. The oxygen vacan-

cies can also reduce CO_2 to CO and one of the oxygen atoms in the carbon dioxide heals the vacancy. Adsorbed hydrogen atoms on the surface of TiO_2 reduces the bound $CO_2^{-\bullet}$. Fig. (**5**) shows the activation of carbon dioxide on titanium dioxide surfaces.
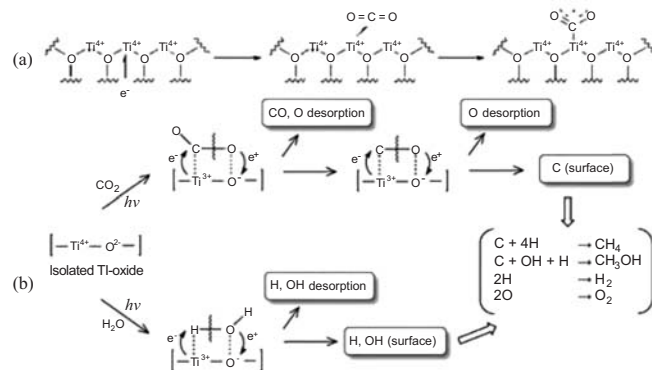
**Fig. (5).** (a) Bending and concurrent the formation of $CO_2^{-\bullet}$ of CO_2 on TiO_2 surfaces (b) Photocatalytic reduction of CO_2 on the anchored TiO_2 species. Reproduced with permission from Ref [26, ©2015 American Chemical Society & 27, ©2012Royal Society of Chemistry]

The carbon dioxide activation depends on the nature of the solvent used. Solvent modify the surface charge of semiconductors as well as the charges on the substrate. It also depends on the pH of the solution because the same molecule exhibits different geometry at varying pH. The pH also controls the surface charges of semiconductors in solution. The point zero charge (PZC) of TiO_2 is 6.3 that means the TiO_2 surface is more positive when the pH of the solution is below the PZC and more negative when it is above the PZC. The change in pH of the solution changes the mode of adsorption of the carbon dioxide on the semiconductor surfaces hence the reaction pathway. Carbon dioxide also exhibits a speciation at various pH. In alkaline medium, CO_2 exists as HCO_3^- ion, which in turn adsorb on the surface of catalyst leads to a different adsorption mechanism. At higher pH, CO_3^{2-} is the predominant species, that is, the surface of semiconductor may be saturated with the bicarbonate ion (See Fig. **6**). These three forms show different properties in solution, which shows that the mechanism of CO_2 activation may differ at different pH.

Since the pzc changes with the semiconductor, the adsorption mode of CO_2 on any particular semiconductor surface has also been different. This

leads to the formation of different reduction products with individual semiconductors used. In short, the activation mechanism changes with the individual semiconductor employed.
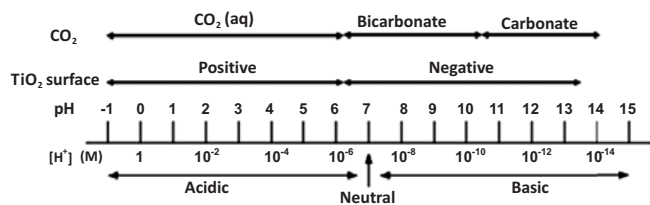
Fig. (6). CO_2 (speciation) and TiO_2 (surface charge) at different pH.

The exact mechanism of activation of carbon dioxide is still unrevealed. Great research efforts are needed to overcome this bottleneck problem in terms of both experimental and computational research. Quantum mechanical modelling gives a better insight to the activation mechanism. Once one identifies the appropriate material which will adsorb even gaseous carbon dioxide and transfer it into the corresponding radical anion, yield products with greater than 10% silver bottom efficiency, in a similar way of ammonia synthesis, then the rest becomes history.

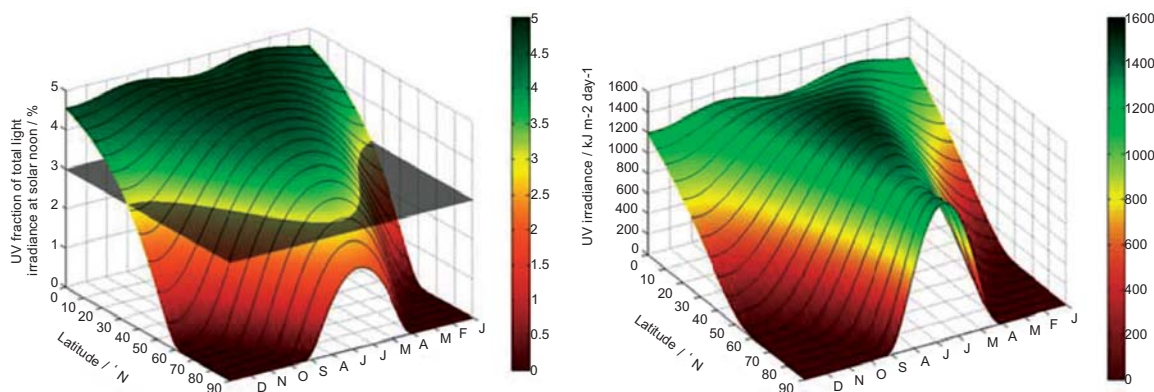## 3. SOLAR ENERGY AS AN ENERGY SOURCE

The utilization of solar energy is the main attraction for photocatalytic reduction of carbon dioxide. Otherwise, the large overpotential required for the reduction of carbon dioxide itself, creates a large barrier in the process. The sunlight if it is free of cost, abundant and easily available, is advantageous. The sunlight that falls on the earth's surface in an hour has enough energy to run the entire world for a year. Therefore, solar energy conversion becomes one of the leading research interest in the 21st century [28].

The conversion of solar energy is a difficult process. The great barrier is associated with the conversion process as well as for industrial implementation. Photovoltaic research is there for converting solar energy to electricity, which is also associated with storage and transportation issues. The efficiency of photovoltaic cell reached the desired level of industrial implementation, but the process economics are high. The solar cells are said to be a pollution free technology that means it does not emit carbon dioxide into the atmosphere, hence it is also termed as a carbon neutral technology. In the real sense, the solar cells or any other solar energy converting processes are not a carbon neutral technology. Creation and appending the parts of solar cells are made by means of fossil fuel energy and it also causes the emission of CO_2, sulfur hexafluoride, CFC like greenhouse gases, which possess 23,700 and 10000 times higher global warming potential than carbon dioxide respectively [29]. Similarly, other solar energy conversion processes also depend on fossil fuels for the production materials. The main attraction of photocatalysis is that the carbon dioxide footprint is comparatively low as compared to the other carbon dioxide conversion techniques.

Most of the studies in carbon dioxide reduction are carried out by the UV light source rather than sunlight. The UV content of the sunlight is only about 3-6% [30] and it varies with time, latitude, and seasons (Fig. **7**). Hence the exploration of UV light from sunlight is difficult.

A very few studies have been carried out using

Fig. (7). Changes in the UV irradiation as a function of latitude, time and day of the year Reproduced with permission from Ref. [31] ©2014 by the American Chemical Society.

the natural sunlight as an energy source, especially Varghese *et al*., reported the maximum yield [32]. The wavelength range of the incident light influences the product yield, maximum efficiency was reported at a wavelength of 254 nm as compared with that of 354 nm [33, 34]. In a real life point of view, the UV light utilization using a lamp imposes an extra burden to the energy challenge.

The irradiation of ultraviolet light below wavelength 315 nm initiates the photochemical reaction of gaseous products like methane, carbon monoxide and formaldehyde via free radical reactions and affects the interpretation of analysis of products. The increased amount of product yield below wavelength 315 nm may be because of the photochemical reaction taking place in the gaseous phase of the reaction system. Methane produced by the photocatalytic reduction of carbon dioxide combined with the hydroxyl radicals to form a variety of products like HCHO, CO and ultimately CO_2 and other gaseous products also undergo photochemical reaction below wavelength 315 nm [35, 36]. Hence, one can never presume that all the detected gaseous products are formed directly from CO_2 or carbon artifact, photochemical dissociation of methane itself contributes to the CO and HCHO formation. The schematic representation of oxidation of methane in the presence of hydroxyl radicals is given in Fig. (**8**).
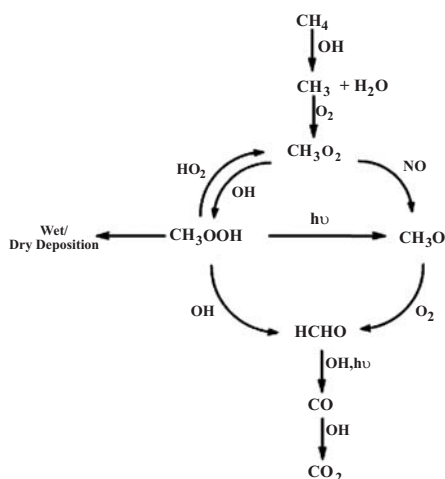
Fig. (8). Oxidation pathways of methane in presence of hydroxyl radical. Reproduced with permission from [35] ©2006 John Wiley & Sons, Inc.

The carbon dioxide molecule itself undergoes dissociation in the presence of high energy ultraviolet radiation to carbon monoxide, which is the predominant source of carbon monoxide in the up-

per atmosphere. The UV irradiation problem can be solved up to a particular extent by placing the lamp horizontally to the liquid reaction system, thereby the direct interaction between gaseous products and UV light can be avoided.

The top of the hemisphere receives around $1360 W/m^2$ of energy. Since the earth is spherical and rotating, $1360 W/m^2$ gets spread out to an average of $340 W/m^2$ [37]. The above mentioned problem also applies to the liquid phase photocatalytic reduction of carbon dioxide, in such a way that, the photons reached on the surface of the solvent not exactly equals with the energy absorbed by the photocatalyst, it undergoes multiple scattering as in the atmosphere. Hence the majority of the photon flux reached on the earth's surface are not available for the photocatalytic reaction system [38].
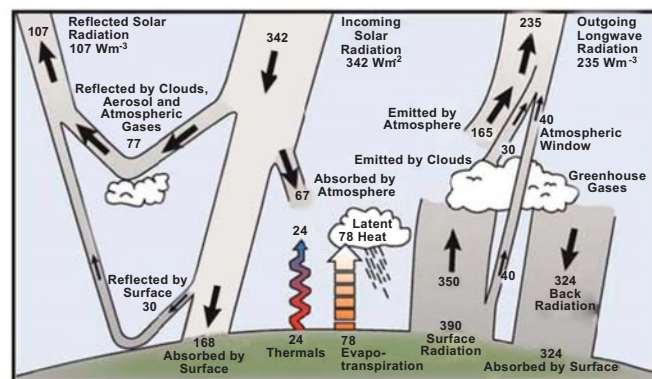
Fig. (9). Solar Radiative Flux at earth's surface. Reproduced with permission from [39]. ©1997 American Meteorological Society.

It is clear that the energy reached on the earth's surface which is different from the energy reached at the top of the atmosphere (See Fig. **9**). The intensity of the sunlight varies constantly with the environmental factors such as geographic region and seasons, latitudes, geographical regions, aerosol concentration and cloud cover [31]. One can utilize the available sunlight reached on the earth's surface more efficiently using appropriate reactor designs [40-45]. The responsibility of a photoreactor is to capture the solar radiation and transmit it to the photocatalyst surface in a better way. Thus, failure may happen if the design of reactor is not proper even if one have the champion photocatalyst. The reactor should be made in such way that it transmits more amount irradiated light even in the presence of diffused sunlight. A number of innovative reactor designs for CO_2 reduction have

been assayed. Recently, photocatalytic hydrogen generation was achieved on compound parabolic concentrator (CPC) under direct solar irradiation in presence wastewater as sacrificial reagent [46]. The benefit of CPC technology is that it will concentrate all types of radiation, irrespective of whether it is diffused or not, into the central tube containing photocatalyst and the substrates. This type of reactor can be used on cloudy days which efficiently concentrate the diffused light towards the photocatalytic reactor. Moreover, it does not need any solar tracking like facilities, the only need is to arrange the CPC at an angle equivalent to the latitude of that particular region [47]. The applicability of this type of reactor geometry yet to be tested for CO_2 reduction both in the aqueous solution as well as gaseous form. Normally the CO_2 reduction is carried out in batch type of reactor, which will give better yield, but not applicable to the pilot plant scale. Koci *et al* studied the effect of reactor geometry on the photoreduction carbon dioxide using two annular batch reactors [45]. The study reveals that the product yield depends on the reactor diameter as well as the volume of the liquid phase and confirmed that perfect mixing was not taking place in the annular reactor. The highest yield of the products was achieved when the lamp placed just near the surface of the liquid in the reactor. Therefore, from the above it is evident that the macroscopic parameters play an important role in the photocatalytic reduction of carbon dioxide. Further insight investigations are required to overcome the barriers associated with the solar energy utilization [48]. Collaborative efforts from scientists belonging to various disciplines are required for the successful utilization of carbon dioxide, water and sunlight together! [49]

4. PHOTOCATALYTIC REDUCTION OF CO_2 ON SEMICONDUCTOR SURFACES

The process starts with the absorption of a photon with energy greater than the bandgap of the semiconductor. The absorption of light moves an electron from the valence to the conduction band, the absence of electron in the valence band creates a positive center called hole. The electron and hole carried out the reduction and oxidation processes respectively, leading to the formation of a redox couple (Fig. **10**). The life time of charge carrier in any semiconductor influences the reaction rate. By increasing the lifetime of charge carriers using re-

spective method, one can utilize the electron in an efficient way. The commonly used methods for increasing the life of charge carriers are cation or anion doping and use of sacrificial reagents etc. These methods, up to an extent reduce the electron hole recombination.
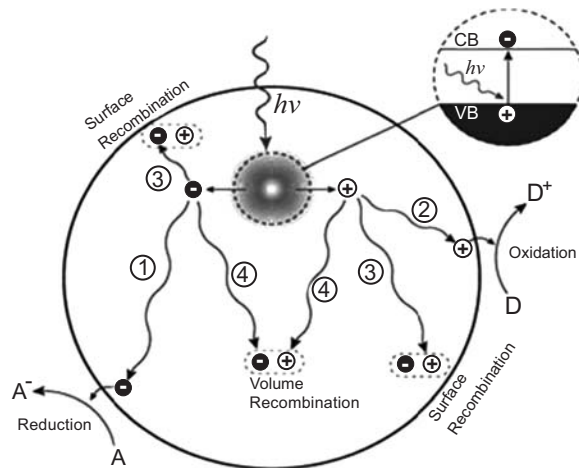
Fig. (10). Photoinduced generation of electrons and holes and their reaction cum recombination pathways. Reproduced with permission from ref [50]. ©1995 American Chemical Society.

The electron and hole can be utilized into a variety of means.

a) For producing electricity (Photovoltaics)

b) For the production of useful chemicals and fuels (Solar fuels generation)

c) For removing pollutants from water and air (Photo-oxidation)

d) For photoelectrolysis of water (Photoelectrochemistry)

The utilization of electron through photocatalytic way is promising approach because it stores the solar energy in chemical bonds, which can be used later as fuels for energy generation [51]. In photovoltaics even though it is a well-established field, the energy storage is the main problem and the transmission of solar electricity through grids are also associated with the dissipation of energy as heat.

In the case of carbon dioxide reduction, the generated conduction band electron reduces the CO_2 molecule to carbon dioxide anion radical, which initiates the reduction step. The initiation step involves a large reduction potential up to -1.9V vs NHE. The carbon dioxide undergoes a

multielectron reduction in the protonated environment into various products at lower reduction potentials. Valence band hole gives rise to oxygen through water oxidation, thus generated hydrogen ion converted to hydrogen gas by conduction band electrons ultimately reduces the carbon dioxide molecule. The band alignment diagram of various semiconductors with respect to vacuum level and the NHE for selected semiconductors at pH 0 is given in Fig. **11**, along with the possible multielectron transfer processes (Table **2**).

bon dioxide multielectron transfer for interpreting the mechanism (Table **2**). This aspect should be changed because the multilelectron transfer reduction potentials of carbon dioxide varies with the solvent used especially in organic solvents. Recently, Pegis *et al* have studied the solvent effect on the standard reduction potentials of CO_2/CO and CO_2/CH_4 couples in acetonitrile and N, N-Dimethylformamide and reported that carbon dioxide reduction potentials undergo some changes according to the solvent used (Table **3**).
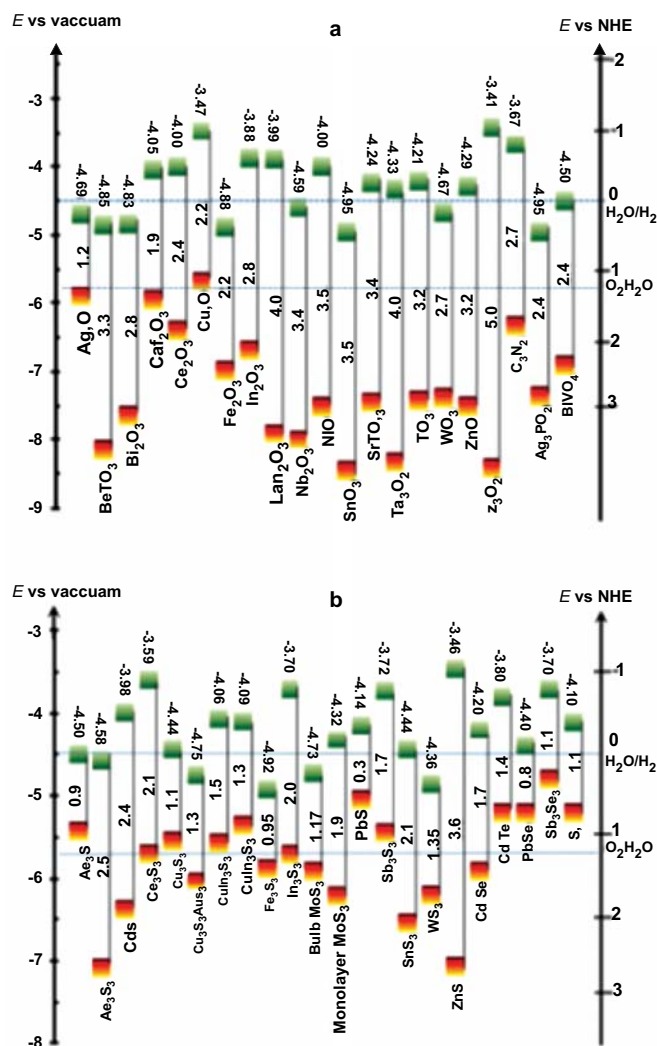
Table 2.   **The reduction potential (E_0) of CO_2 for various products.**

Reduction Reaction	E_0 (V) vs. NHE
CO_2 (aq) + e− → $CO_2^{-\bullet}$ (aq)	−1.9
$CO_2^{-\bullet}$ (aq) + e− → CO_2^{2-} (aq)	−1.2
CO_2 (g) + 2H⁺ + 2e⁻ → HCOOH	−0.52
CO_2 (g) + 2H⁺ + 2e⁻ → HCOOH	−0.58
CO_2 (g) + H⁺ + 2e⁻ → HCO_2^- (aq)	−0.43
CO_2 (g) + 4H⁺ + 4e⁻ → HCHO (aq) + H_2O	−0.51
CO_2 (g) + 6H⁺ + 6e⁻ → CH_3OH (g) + H_2O	−0.38
CO_2 (g) + 8H⁺ + 8e⁻ → CH_4 (g) + 2H_2O	−0.24
2CO_2 (g) + 8H⁺ + 8e⁻ → CH_3COOH (g) + 2H_2O	−0.31
CO_2 (g) + 10H⁺ + 10e⁻ → CH_3CHO (g) + 3H_2O	−0.36
2CO_2 (g) + 12H⁺ + 12e⁻ → C_2H_5OH (g) + 3H_2O	−0.33
3CO_2 (g) + 16H⁺ + 16e⁻ → CH_3CH_2CHO (g) + 5H_2O	-0.32
3CO_2 (g) + 16H⁺ + 16e⁻ → CH_3COCH_3 (g) + 5H_2O	-0.31
3CO_2 (g) + 18H⁺ + 18e⁻ → C_3H_7OH (g) + 5H_2O	-0.31
3CO_2 (g) + 18H⁺ + 18e⁻ → $CH_3CH(OH)CH_3$ (g) + 5H_2O	-0.30

Fig. (11). Band alignment of various semiconductors with respect to vacuum level and the NHE at pH 0. Reproduced with permission from Ref [53]. ©2015 Royal Society of Chemistry.

Band edge positions of semiconductors vary according to the nature of the solvent used and the solution pH. Most of the non-aqueous studies invariably use the above reduction potentials of car-

Table 3.   **Thermodynamic cycle for determining the standard reduction potentials of O_2/H_2O, CO_2/CO and CO_2/CH_4 in MeCN and DMF. Reproduced with permission from ref [52]. ©2015 American Chemical Society.**

Reduction Reaction	MeCN E_0 (V vs Fc$^{+/0}$)	DMF E_0 (V vs Fc$^{+/0}$)
O_2 + 4H⁺ + 4e⁻ → 2H_2O	1.29	+0.60
CO_2 (g) + 8H⁺ + 8e⁻ → CH_4 (g) + 2H_2O	-0.12	-0.73
CO_2 (g) + 2H⁺ + 2e⁻ → CO + H_2O	+0.15	-0.48

Now there are various questions left unanswered!

a) How is that one observing the reduced CO_2 species like CO, HCOOH, CH_3OH, CH_4 even though the first electron transfer associated with high energy barrier?

b) Whether the LUMO level of CO_2 is altered in the adsorbed state?

c) On what types of sites, this reduction in the energy of LUMO level of CO_2 can take place?

d) The above mentioned reaction and corresponding reduction potentials are applicable only to the gaseous CO_2 molecules. Can one use the same for liquid phase reactions?

e) Which is more important, activation of CO_2 on semiconductor or the reduction potential?

f) Which is the source of $CO_2^{-\bullet}$ anion radical detected in the reaction mixture?

Let us imaginatively look at one or more possible mode of adsorption of carbon dioxide on semiconductor surfaces. It is known that CO_2 adsorption on stoichiometric defect free TiO_2 is not strong enough, hence the LUMO level alteration cannot take place on the surface. Anion defected anatase surface would adsorb carbon dioxide more effectively than the defect free surfaces [17]. If carbon dioxide adsorption on the surface through oxygen, then it can lower the barrier and give rise to the dissociation CO_2 to CO. The oxygen released from the CO_2 heals the vacancy. CO_2 can also adsorb bidentately with titanium ions through oxygen atoms. The mechanisms are already discussed in the section 2. Hence the photocatalyst should have good adsorption sites and necessary band alignment w.r.t CO_2 reduction and water splitting since both are competitive process. Extracting the exact mechanism of CO_2 reduction, one must consider the oxidation half reaction also, both are interdependent chemical processes. The oxygen produced in the valence band consumes the electrons forming the superoxide radical which in turn produces hydroxyl radicals, the second largest oxidant after fluoride ion respectively (Table **4**).

The hydroxyl radical oxidizes the reduced products of carbon dioxide reduction, leading to a decrease in the overall efficiency of the process in terms of product yield. The low dissolved oxygen level in the CO_2 reduction process accounts for this aspect. Many reports do not consider this possibility and reports the efficiency without any investigations on the competitive reactions. The oxidation half reaction is also important for hydrogen ion generation from water oxidation, which further reduces the CO_2. The exact interdependency of these two reactions is still unclear. Calculating the activity of the photocatalyst with respect to the CO_2 reduction does alone not make any sense because the electron produced in the conduction band also utilized by H^+ and O_2 present within the reaction system. Hence the catalyst based activity measures should consider all the viable processes that take place in the system, at least electronic processes.

Table 4.   Oxidation potentials of some common oxidants.

Oxidant	Oxidation Potential (V)
Fluoride Ion	2.87
Hydroxyl Radical	2.80
Ozone	2.07
Hydrogen Peroxide	1.77

Metal loaded semiconductor has been a promising route to increase the carbon dioxide adsorption on the surface of the catalyst [54]. The metal deposited on the surface facilitates the electron transfer from the d state of the metal to the pi* orbital of CO_2, thereby reduces the bong angle of CO_2 below $180°$. The reduced bond angle or the bent structure easily undergoes nucleophilic as well as electrophilic attack leading to the reduction products. The presence of metal ions on the surface not only promotes the first electron transfer process, but also facilitates the subsequent multielectron transfer reactions and the rate comparative reactions by shifting the absorption region of semiconductor towards visible through a phenomenon called Surface Plasmon Resonance (SPR) [55,56]. Ag, Pt, Cu nanoparticles, which are effectively excited by visible light within a narrow size interval compared to other metal nanoparticles and it can be tuned by changing the size, surroundings and modification of nanoparticles. Excess of deposit metals on the surface can act as a center for electron-hole recombination as well as reducing the catalytic active centers on the photocatalyst leads to a decrease in the rate of formation of products.
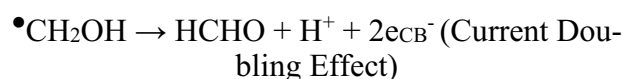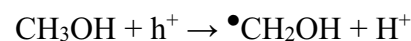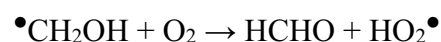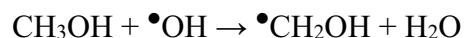
Therefore, significant improvement in the photo-activity is possible only at low dopant concentrations. It further activates the competitive processes on the photocatalyst surfaces, however, the exact involvement of these processes are still not known. The surface metal ion activates the carbon dioxide molecule in a different way as that of semiconductors, leading to a relatively high product yield compared to the bare photocatalyst. The earth's abundance and cost of the metals are the main problems which adversely affect the process economics, hence the metal doping increases the overall cost of the process. Hence the practical implementation is not possible with the metal doped photocatalyst even though it's a promising route for the conversion of carbon dioxide into chemical and fuels.

Use of sacrificial reagent has been another method to increase the availability of conduction band electrons via the oxidation of the sacrificial reagent by holes. Commonly used sacrificial reagents are TEOA, TEA or alcohols. However, the life time sacrificial reagents are too short within the system. It should be noted that most of the commonly used sacrificial reagents are same as that of the reduction products of carbon dioxide! Hence a part of the reduced product also oxidized by scavenging the holes and other radicals leading to a lower product yield. The absorbed light energy also used for the degradation of sacrificial reagents which influences the energy balance of the reaction unfavorably. The undesired side product formed after the oxidation of sacrificial reagents makes the system cruder, poisons the catalyst by adsorbing on the active sites and it absorbs a rational amount of the irradiated light. If formate ion is used as a sacrificial agent, $CO_2^{-\bullet}$ anion radical

will be the reduction intermediate via current doubling effect. This may also be the source of ESR detected $CO_2^{-\bullet}$ anion radical in solution! The increase in product yield in presence of sacrificial reagent is due to the better charge separation due to the suppression of oxidation ability. If sacrificial reagent suppresses the oxidation ability, then (1) where did the CO_2 gets sufficient hydrogen ions for reduction reaction? (2) What is the fate of sacrificial reagents in the reduction system? (3) Whether the oxidation products of sacrificial reagents interfere with the reduction products? Since the process associated with the free radical mechanism the hydrogen source may be the oxidation product of sacrificial reagent. For example, if methanol is used as a sacrificial reagent, the oxidation of methanol produces formaldehyde along with two hydrogen ions and single electron radical will transferred to the conduction band of the semiconductor, the process is called current doubling effect (See Fig. **12**) [57].

$$HCOO^- + h^+ \rightarrow CO_2^{-\bullet} + H^+$$

$$CO_2^{-\bullet} \rightarrow CO_2^{\bullet} + 2e_{CB}^- \text{(Current Doubling Effect)}$$
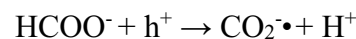
Two electrons produced will transferred to the conduction band of the semiconductor. If methanol is used as sacrificial reagent then the reaction proceeds through the same way,

$$CH_3OH + {}^{\bullet}OH \rightarrow {}^{\bullet}CH_2OH + H_2O$$

$${}^{\bullet}CH_2OH + O_2 \rightarrow HCHO + HO_2^{\bullet}$$

$$CH_3OH + h^+ \rightarrow {}^{\bullet}CH_2OH + H^+$$

$${}^{\bullet}CH_2OH \rightarrow HCHO + H^+ + 2e_{CB}^- \text{(Current Doubling Effect)}$$

Hydrogen ion formation through the oxidation
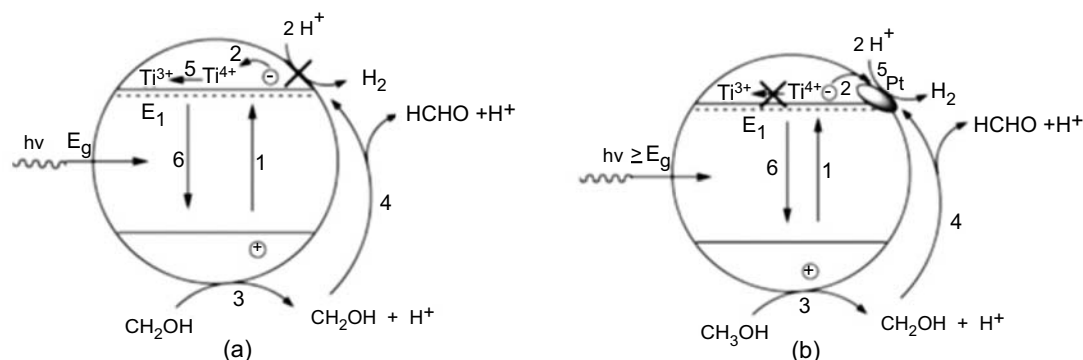
Fig. (12). Processes involved in the photocatalytic H_2 evolution from aqueous methanol solution both in the presence and absence of metal deposition. Reproduced with permission from Ref. [57]. ©2013 American Chemical Society.

of methanol is easier compared to water oxidation. This leads to an enhanced hydrogen concentration near the active sites of photocatalyst adsorbed by carbon dioxide, which results in a better formation of products. Sacrificial donors like Triethyl amine produces highly reactive intermediates like imines and enamines, which will further complicate the overall reaction. Sacrificial reagents provide only the initial hype otherwise addition of reagent in equal interval of time is required. Hence the production of chemicals and fuels by sacrificing a chemical entity is not a viable economic process. Recently, CO_2 converted to formic acid using a recyclable sacrificial donor was reported elsewhere using tricyclic tertiary amine 10-endo-anti-11-aza-10-methoxy-11-methyltricyclo [4.3.1.1^{2,5}] un-7-decane through a photochemical pathway (Fig. **13**) [58-61].

Incorporation of heteroatoms (N, P, and S) in the semiconductor lattice offers a promising route towards the production of solar fuels, but the improvement in the photocatalytic activity is marginal with respect to the bare semiconductor in most of the cases but the yield is more in the case of metal deposited heteroatom doped semiconductor systems [62]. A significant breakthrough in the photocatalytic reduction of gas phase CO_2 saturated with water vapor using natural sunlight has recently been reported by Varghese *et al* [32], using nitrogen doped titanium dioxide nanotube arrays catalyzed with Cu/Pt nanoparticles to methane and other hydrocarbons at high rates (160μL/g/h) with a quantum efficiency of 0.74%. Doping with greater than 1% of any hetero atom changes the lattice structure ulti-

mately reduces the photocatalytic activity. Heteroatom incorporation does not change the position of conduction band or reduction potential of any particular semiconductor hence the increase in product yield only due to the decrease in carrier charge combination and it does not contribute anything towards the thermodynamic activation of carbon dioxide. The large scale production of doped semiconductor with similar pore size, surface area, composition, etc. is also another hurdle hence affects the reproducibility of the result.

Increasing visible light activity alone does not contribute to the carbon dioxide reduction process. The state-of-the-art methods of increasing visible light activity do not change the reduction potential of the photocatalyst towards more negative or changes only up to 1 mV! It needs a stable photocatalyst with a moderate band gap to absorb the visible light with necessary band edge positions with respect to the carbon dioxide activation potential. This can be achieved through band gap engineering and if it happens then the above mentioned catalyst modifications can increase the reaction rate tremendously.

5. MEASURES OF EFFICIENCY

Since the carbon dioxide reduction is a complex process, the efficiency depends upon a number of factors such as electron migration through band gap, electron transfer reactions, adsorption of substrate on the semiconductor surface, surface reactions, nature of solvent medium, illumination source, reactor geometry and a number of other
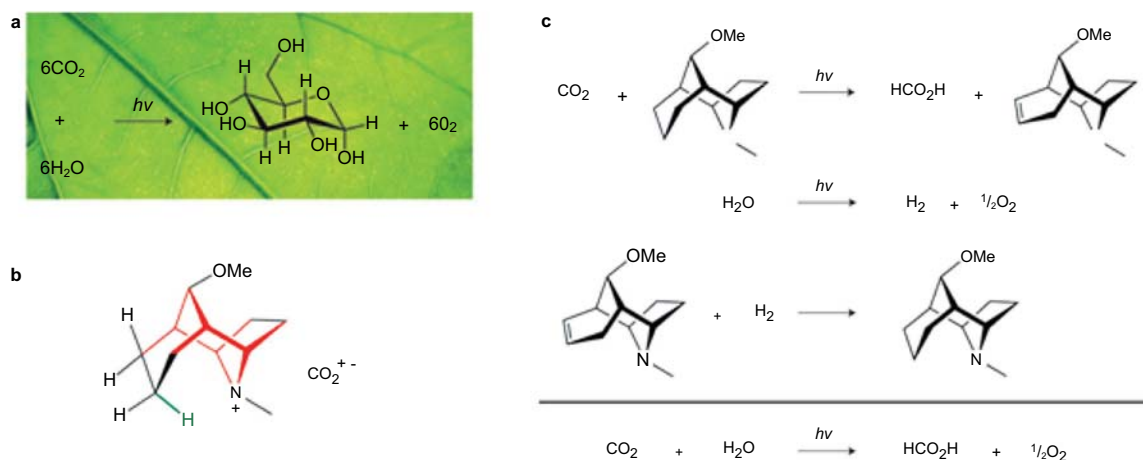

Fig. (13). Photochemical reduction of carbon dioxide into formic acid using tricyclic tertiary amine as a sacrificial donor (a) Plant photosynthesis (b) amine radical cation formed from tricyclic amine (c) regeneration of amine by hydrogenation using Pd catalyst. Reproduced with permission from Ref. [58, 59]. ©2011 McMillan Publishers Ltd.

processes. The conduction band electrons not only reduce the carbon dioxide, but also takes part in the hydrogen production as well as in superoxide formation which is produced from the non-stoichiometric oxygen evolved during the oxidation of water adsorbed on the semiconductor surface. Charge carriers also react with sacrificial agents, sensitizers, by product formed during the process. Hence the actual efficiency of the photocatalyst depends on the overall reactions, but the currently achieved efficiency is limited to a particular reaction or a site. For example, in carbon dioxide reduction process, the efficiency is measured only in terms of the amount of products formed during the reduction. The other reactions are excluded from the efficiency measures. So the reported efficiencies do not give any idea about the actual efficiency of the photocatalyst. In light based efficiency measures, one only measuring the light absorbed by the reaction medium and it is different from the light absorbed by the photocatalyst. The illuminated light undergoes multiple reflection and scattering before it reaches the photocatalyst surface. It is also absorbed by the sacrificial reagents or sensitizers present in the reaction system and the choice of wavelength absorbed by the system and the semiconductor also may be different. Increased light absorption, sometimes facilitates the charge carrier recombination. With all this prospect, it is evident that the efficiency measures used in photocatalysis should be revisited. The new efficiency scale should be based on photocatalyst as well as the illumination and independent of these individual parameters and also consider the overall reaction process, then only one can compare different photocatalyst systems and to elect the champion photocatalyst.

6. PRODUCT ANALYSIS

Reduction of carbon dioxide produces a number of products like alcohols, acids, aldehydes etc. Since the photocatalytic reduction is a multielectron process, the products formed in the reaction system consist of many compounds, both in liquid (alcohols, aldehydes, acids etc.) as well as gaseous state (CO, CH_4, and unreacted CO_2 etc.). The exact identification and quantification of these products are required for the analysis of the overall reaction efficiency and hence the design of a better photocatalyst. Normally used analytical techniques are GC, HPLC, LC-MS, IR, IEC, UV-Vis, ^1H or ^{13}C NMR.

Once a product is formed in the reaction system, it undergoes oxidation through valence band holes and thereby initiate free radical reactions in the system which produces a large number of by-products. Hence, one or two analytical methods is not enough for identification and quantification, a combo of all state-of-the-art techniques can be used for analysis. But the actual problem is that the quantity of many products formed during the reaction is below the minimum detectable limit and the other products formed may interfere with each other by reactions inside the analysis column which leads to a misinterpretation of results. The intensity of any peak in the chromatographic system will highly depend on the nature solvent medium used. Hong and coworkers [63] examined the different chromatographic techniques used for the analysis of CO_2 reduction products, in a better way and proposed a new set of techniques for the accurate quantification of reduction products with low detection limits on the basis of their findings (See Fig. **14**). They also examined the effect of organic additives such as sacrificial reagents, photosensitizers in the analysis using GC and HPLC. It has been found that alcohol analysis using GC is more sensitive towards most of the organic additives and that of acid and aldehyde by HPLC are unaffected by the organic additives except DMF and TEOA for formic and acetic acid respectively.
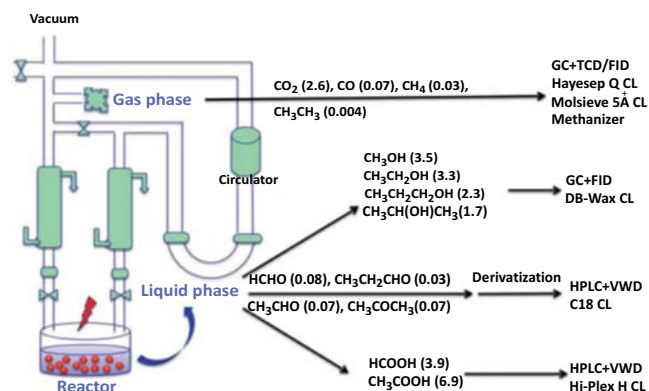
Fig. (14). Gas and liquid phase analysis of CO_2 reduction products proposed by Rang Xu and coworkers. Reproduced with permission from Ref. [63] ©2013 Royal Society of Chemistry.

Use of different preparative methods for improving the activity of photocatalyst towards CO_2 reduction induces some undesired trouble in the product analysis. Preparation methods usually involve the use of organic solvent, high temperature method or vacuum annealing. These methods im-

part some carbon impurities on the photocatalyst surfaces. The carbon residues also take part in the reaction resulting in an elevated rate of photoconversion. Many reports in the literature claiming higher rates may be due to the presence of carbon impurities present in the system. Suppose, some sample contains 1% of carbon residue per 0.1g of the photocatalyst, then the photoproduction rate after irradiation will be up to some tens of micromoles which is far greater than many reported values [63]. Hence a systematic assay of the products was needed for the evaluation of the photoactivity for the design of better photocatalyst. Cleaning the surface before the reduction process to minimize the effect of such artifacts is highly recommended. These problems can simply be overcome by the incorporation of $^{13}CO_2$ tracer experiments best analyzed using ^{13}C NMR or GCMS [64-67]. Yang *et al* [68], performed a comprehensive study of the undesired role of carbon artifacts through FTIR measurements using isotopically labelled CO_2. Prior to isotopically labeled experiments one must be careful about the purity of the isotope used because usually low grade samples of $^{13}CO_2$ contain trace amounts $^{13}CH_4$. Hence purity should be confirmed prior to the experiment otherwise it leads to contaminated results!

5. TITANIUM DIOXIDE RUT

Titanium dioxide and its modification have been a matter of attraction since the publication of the work by Teichner and coworkers in 1971 [69, 70] followed by Fujishima's breakthrough article in 1972 [2]. Now the term titanium dioxide becomes a synonym of semiconductor based photocatalysis research. Several new photocatalysts have been introduced into the field, even though the majesty of TiO_2 has not been affected by them. After the introduction of a new material, every scientist has enthusiasm of how it works with respect to that of TiO_2. This is true for the case of materials like zeolites [71,72], double layered hydroxides [73], heteropoly acids [74], graphene [75-80], carbon nitride [81-84], carbon nanotubes [85,86], metal nano clusters [87], metal organic framework [88], quantum dots [89], supramolecular compounds [90] and metal complexes [91]. The interesting point is that almost all possible elements are also incorporated in the TiO_2 matrix for increasing the photoactivity of it towards the visible light region. The dark side is that these modifications

have not led to yield the products at an appreciable level with desired efficiency.

Titanium dioxide has been the prime photocatalyst in the solar fuel generation process [92]. Many reports are available in the literature on the photocatalytic conversion of CO_2 to fuels using titanium dioxide and its derivatives [93-115]. The prime reason for the use of titanium dioxide as a photocatalyst for various applications of photocatalysis is its stability. It is stable under vigorous conditions like high acidic pH, hence it is not susceptible to photocorrosion whereas most of the semiconductors would fail and the incorporation of the low percentage of heteroatoms or metal for the improvisation of the visible light activity does not affect the crystal lattice of TiO_2 matrix. Titanium dioxide, largely used in the photooxidation of organic compounds due to the higher oxidation potential of valence band holes. It is less favorable in the case of carbon dioxide reduction mechanism due to the low reduction potential. The conduction band position of TiO_2 (-0.1V vs NHE) is more positive compared to the $CO_2/CO_2^{-\bullet}$(-1.9V) reduction potential.

Anatase form of TiO_2 is the most studied titanium dioxide polymorph for CO_2 reduction in which the conduction band lies at -0.1V (pH 7) with a band gap of 3.2 eV [116]. Other polymorphs rutile [117], brookite [118] and TiO_2 (B) [119,120] also have been investigated for CO_2 reduction, however, their potential as a photocatalyst not yet fully revealed. The common belief is that anatase form is more photoactive than the others. Many research groups revisited this concept and revealed the mystery in different ways and found that other phases are also active under specific regimes [121,122]. Hence, one can compare the photoactivity of these polymorphs only with respect to a particular substrate. Generalized comparisons of these polymorphs are not valid because the photoactivity depends on the nature of substrate adsorption on the photocatalyst.

Liu *et al* studied the conversion of carbon dioxide in the nanocrystal form of titanium dioxide polymorphs and compared the activity using in situ DRIFT and photoactivity measurements [123]. It is found that defect free oxygen deficient surface of brookite showed the highest yield for CO and CH_4 (Fig. **15**). This shows that the surface interface showed a crucial role in photocatalytic reduc-

tion. The yield of product depends on the extent of adsorption of carbon dioxide on the photocatalyst. Anpo *et al* also studied the photoactivity of single crystal surface of Ti terminating rutile (100) and oxygen terminating rutile (110) and found after careful kinetic measurements that the TiO_2 (100) facet was 7.4 times more active than TiO_2 (110) in reducing CO_2 [25]. This is due to the fact that the transfer of d electrons to the LUMO of CO_2 is more favourable in Ti terminating surface. It is already known that carbon dioxide adsorbs strongly in steps sites, hence the creation of proper step active sites would lead to better carbon dioxide adsorption on the surface which facilitate the electron transfer from the photocatalyst to the CO_2 and thereby increases the product yield.
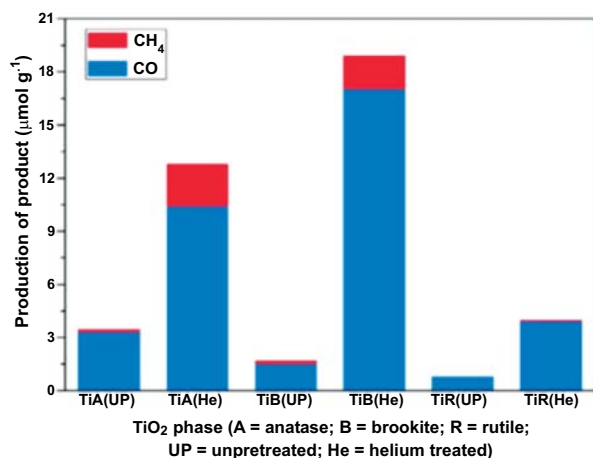
Fig. (15). Production of CO and CH_4 on the untreated and the treated titania polymorphs Reproduced with permission from ref [123]. ©2012 American Chemical Society.

Titanium oxide nanomaterials also have been studied extensively for CO_2 reduction in the last decade [125-128]. Most of the studies conducted due to the common belief that the semiconductor nanomaterials increase the visible light activity. In a real way, the belief is no longer true, it's one of the misconceptions in photocatalysis. Decreasing particle size from bulk to nano level increases the bandgap and their by decreases the visible light activity. Most of the semiconductor nanoparticles and clusters active only under UV irradiation below 320 nm. The Ti-oxide highly dispersed TiO_4 single unit site absorbs only UV light under the wavelength 230-280 nm (Fig. **16**) [27]. The absorption of that particular wavelength creates an electron-hole pair within the single site unit contributed to the high and unique photocatalytic ac-

tivity. Incorporation of titanium dioxide single site photocatalyst into the zeolite matrix, thus a promising route towards the carbon dioxide conversion. However, it suffers by the lower product yield.
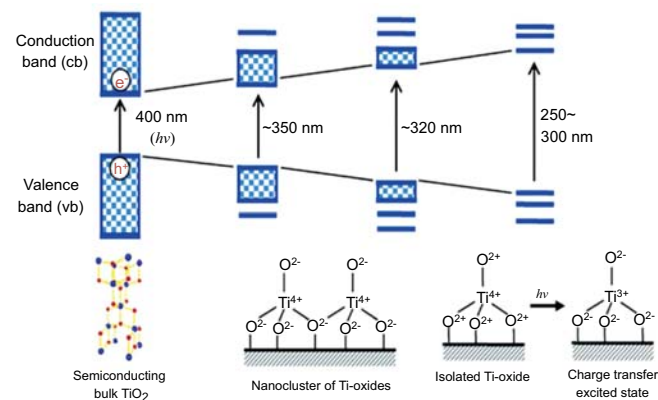
Fig. (16). Bandgap diagram of different titania structures. Reproduced with permission from Ref. [27]. ©2012 Royal Society of Chemistry.

By comparing the yield of the product by the different titanium dioxide structures for the conversion of CO_2 (see Table **5**), one can find that the product yield is too low as compared to the other material structures. Table **5** shows the product and product yield irrespective of their reaction conditions.

TiO_2 Degussa P25 (presently Evonik) is the most used material for CO_2 reduction, normally used as a standard reference material in thermodynamically "downhill" photocatalytic processes. It is a mixture of two polymorphs of titanium dioxide, namely anatase (80%) and rutile (20%) and the particle size up to some nanometers. Recently, Ohtani *et al* found that Degussa P25 also contains trace amount of amorphous titanium dioxide [165].

The superior photocatalytic activity of P25 makes it as a standard reference in photocatalytic oxidation processes. The mechanism of superior activity of P25 is still a controversy among the photocatalytic community [166]. When scientists realize that CO_2 can also reduce by the photocatalytic phenomenon, the followers used P25 as the reference material, even though it's not a champion photocatalyst for CO_2 reduction. In a process like CO_2 reduction, the product yield depends on many factors interdependently as compared to the normal photocatalytic oxidation processes (See Table **6**) [167]. The electron as well as proton transfer plays a crucial role in the thermodynamic uphill processes such as water or carbon dioxide splitting into valuable fuels that means the reaction led not alone by light irradiation.

Table 5.   Photocatalytic reduction of carbon dioxide with product yield greater or equal to 100 (μL h^{-1}gcat^{-1}) irrespective of the reaction conditions.

Photocatalyst	Product (yield, $\mu l\ h^{-1}\ g_{cat}^{-1}$)	References	Year
TiO_2 Anatase Film	CO (240)	129	2012
Au (0.25%) /Pt (0.75%)/TiO_2 nanofiber	CH$_4$ (110) CO (54)	130	2013
Cu/Pt$_2$/TiO_2 nanotube	CH$_4$ (166)	131	2012
Pt (0.21%)/TiO_2	CH$_4$ (420)	129	2012
Pt (0.94%)/TiO_2	CH$_4$ (1400)	129	2012
Pt (1.3%)/TiO_2 single crystal	CH$_4$ (630)	129	2012
Pt (2.5%)/TiO_2	CH$_4$ (63)	129	2012
Au (1.5%)/TiO_2	CH$_4$ (210)	132	2014
Au (0.5%)/Cu (1%)/P25	CH$_4$ (2200)	132	2014
Cu (1.5%)/P25	CH$_4$ (280)	132	2014
Pt (0.5%)-red P-g-C_3N_3	CH$_4$ (300)	133	2013
Ni/SiO_2-Al_2O_3 (AM 1.5 filter)	CH$_4$ (55,000)	134	2014
NiO (AM 1.5 filter)	CH$_4$ (13,000)	134	2014
Fe_2O_3 (AM 1.5 filter)	CO (7200)	134	2014
CoO (AM 1.5 filter)	CO (2500), CH$_4$ (170)	134	2014
Ni/SiO_2-Al_2O_3 (λ> 420nm)	CH$_4$ (13,000)	134	2014
NiO (λ> 420nm)	CH$_4$ (210), CO (170)	134	2014
Au_3Cu/$SrTiO_3$/TiO_2	CO (730)	135	2015
Hex-$ZnIn_2S_4$	MF (190)	136	2013
Cub- $ZnIn_2S_4$	MF (160)	136	2013
MIL-101 (Fe)	HCO$_2$- (150)	137	2014
NH$_2$- MIL-101 (Fe)	HCO$_2$- (450)	137	2014
NH$_2$- MIL-53 (Fe)	HCO$_2$- (120)	137	2014
CdS-Co-ZIF-920,1	CO (2400)	138	2015
CeO_2-TiO_2 composites	CH$_4$ (1800-2100) CO (12000-13100)	139	2013
Au/Pt-TiO_2 nanotube	CH$_4$ (114), CO (17)	140	2013
Ag/Zn-Ga_2O_3	CO (117), H$_2$ (16.2), O$_2$ (70.1)	141	2014
In_2O_3/g-C_3N_4	CH$_4$ (1990) with Pt	142	2014
Cu based MOF	CH$_3$OH (263ppm g^{-1}h^{-1})	143	2013
C_3N_4/Ru complex	HCOOH (375-483)	144	2013
Porphyrin/Graphene	C_2H_2 + CH$_4$ (170 μmol m^{-2}h^{-1})	145	2014
Ru/RuX$_2$-TiO_2	CH$_4$ (900)	146	1987
23.3 wt % AgBr-TiO_2	CH$_4$ (128.56) CH$_3$OH (77.87)	147	2011

	C₂H₅OH (13.28) CO (32.14)		
CdS/TiO₂ nanotubes	CH₃OH (159.5)	148	2012
Bi₂S₃/TiO₂ nanotubes	CH₃OH (224.6)	148	2012
GaP/TiO₂	CH₄ (118)	149	2014
Ru (0.5%)/ TiO₂	CH₄ (200) H₂ (250)	150	2006
3 wt % CuO/TiO₂	CH₃OH (2655)	151,152	2005,2009
2 wt % CuO/TiO₂	CH₃OH (1000) O₂ (20)	153,154	2002,2004
2 wt% Cu/TiO₂/SBA-15	CH₄ (627)	155	2009
0.1% Y-TiO₂	HCHO (382.62)	156	2011
3 wt % Ag TiO₂	H₂ (100) CH₄ (6) C₃H₆ (14)	157	
CeF₃/TiO₂	CH₃OH (162)	158	2014
Pt/TiO₂	CH₄ (277.2) C₂H₆ (12.4) H₂ (389.2) O₂ (785.3)	159	2014
Pt/MgO/TiO₂ nanotubes	CH₄ (100.22 ppm/hr cm²) CO (10.4 ppm/hr cm²)	160	2014
In/TiO₂	CH₄ (244) CO (81)	161	2015
N-TiO₂/Ni	CH₃OH (482)	162	2010
N-TiO₂/Pt-Cu	CO (111 ppm/h cm²)	32	2009
N-TiO₂ nanotubes	CH₃OH (1132.6) HCHO (921.6) HCOOH (12475.8)	163	2012
C/TiO₂	HCOOH (2610.98)	164	2011

The CO_2 adsorption and the concurrent reaction with the electrons highly depends on the nature of the material surfaces. Not all the semiconductors have the similar surface arrangement, therefore, the reaction pathway and the interaction of CO_2 moiety with surfaces varies according to the materials used. The product and yield vary within the titanium dioxide compounds itself [124]. Since the CO_2 reduction doesn't only depend on the visible light activity of the photocatalytic material, but also many other factors described in Table **6**, so the benchmarking of titanium dioxide P25 for CO_2 reduction seems to be irrelevant and any comparison of reactions is only possible after the implementation of a standard procedure. A new benchmark system has to be evolved instead of TiO_2 P25 because it is not a pure single component system. Recently, scientific efforts are reported in the literature for benchmarking the photocatalytic material for electrochemical water splitting reactions [168-170]. It would be a surprising

fact that such kinds of effort are not seen in the CO_2 reduction field especially in the electrocatalytic CO_2 reduction.

Table 6. Factors that determine the photoactivity of a semiconductor surface. Reproduced with permission from Ref. [167] ©2015 American Chemical Society.

Properties	Factors	Impacts
Optical	Band gap	Photonic Efficiency
Electronic	Carrier Mobility	Quantum Efficiency
Structural and Morphological	Surface Area	Multiple Ways
	Crystallinity/ Crystal Faces	Multiple Ways
	Particle Size	Multiple Ways
	Defects	Multiple Ways
	Crystal Phase	Multiple Ways
Surface Chemical	Acid-Base character Surface Groups	Multiple Ways

The innovation of new materials, alternative to TiO_2 has been in progress. Many materials like carbon nitride, $BiVO_4$ offer a better activity than that of TiO_2 but it lacks the in detail in situ and operando studies. The interaction of CO_2 with these two materials has not been revealed in full swing. New studies on these materials for CO_2 reduction

do not consider the nature of interaction with CO_2 (adsorption mechanism, since it varies with materials) and the followed reaction pathways. The rational modelling of these materials under real conditions is still missing, limiting the generation of alternative or next generation photocatalytic materials. Since the photocatalytic reaction is too complex, the use of state-of-the-art techniques and methods are needed to overcome the barriers associated with process and to find an alternative photocatalytic material for solar fuel generation. The combination of theoretical modelling, time resolved spectroscopies, surface science methodologies and radical chemistry is needed for the successful understanding of the mechanism of solar fuel generation both in terms of thermodynamics and kinetics [171].

6. PERSPECTIVES

Photocatalytic reduction of carbon dioxide is an immediate need in the energy as well as environmental points of view. The amount of product formed during the reaction still suffered by lower yield say up to some micromoles. A complete revisit to each individual process associated with the carbon dioxide reduction is required for elucidating the reaction pathways and preparing a suitable mechanism. At this point, the scientist should deviate from the conventional TiO_2 route [167,172]. The mechanistic studies using TiO_2 are highly encouraged due
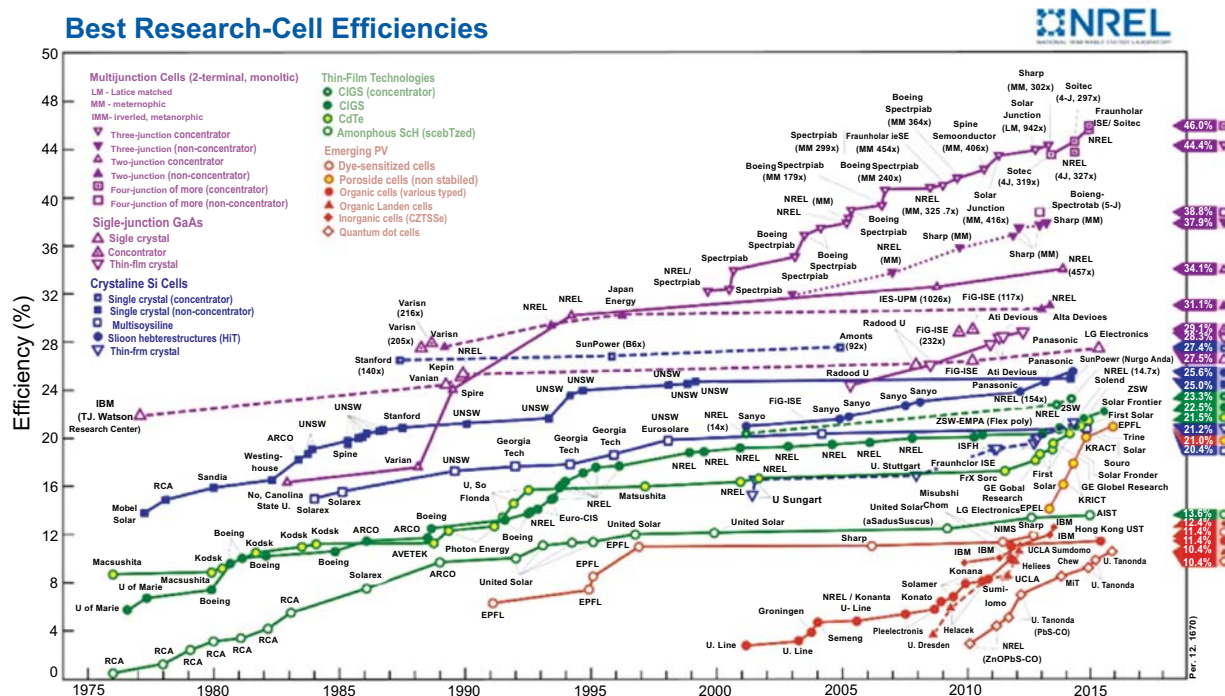
Fig. (17). Best Solar Cell Efficiencies. This plot is courtesy of the National Renewable Energy Laboratory, Golden, CO.

to its appreciable stability in most of the vigorous medium compared to other photocatalysts.

Most of the studies have not explained the source of product formed during the reduction reaction, whether it is from the artifact or not. Isotopic study or blank run is recommended to all CO_2 reduction processes in order to reveal the exact carbon source thereby avoiding the bias in CO_2 reduction. A standard experimental procedure is an immediate need in the carbon dioxide reduction process. Only with the standard methods one can compare the efficiency of material innovated from the different research groups, and also to choose the prominent candidate as the champion photocatalyst. Now different groups normalize the reaction efficiency in different ways, no standard method is also available for the normalization of efficiency of the CO_2 reduction process. Standard method and normalization of efficiency is needed for developing an efficiency chart for selection of best photocatalysts as in the photovoltaics. In photovoltaics field, the National Renewable Energy Laboratory (NERL) maintains a plot that combines all research cell efficiencies reported so far since 1976 (Fig. **17**) [173]. The plot includes the current state of the art efficiencies that are reported on a standardized basis based on Standard Test or Reporting Conditions defined by IEC 60904-3 edition 2 or ASTM G173 at 25^0C.

The reaction rate and the product yields are low compared to the natural photosynthesis. The catalyst is deactivated in the operation stage itself. Hence the quantum efficiencies are often very low. For the real life implementation of the photocatalytic reduction of CO_2 or so called artificial photosynthesis, one has to prepare catalyst systems which will be more effective in the visible region and also give more than 10% quantum efficiency [174]. Osterloh in 2008, has excellently depicted a pictorial representation on the selection of materials for water splitting reaction (Fig. **18**) [174, 175]. The materials represented in the Fig. **20** are also relevant to the CO_2 reduction process. The figure clearly depicts that if a photocatalyst is said to be economic, it has to give at least 10% quantum efficiency in the visible region of the electromagnetic spectrum. To the best of the author's knowledge, no material which has been identified to satisfy both criteria as shown in the shaded part of the figure.

Photo-fuel cell is an attractive route to reach the solar energy conversion in an effective way. It offers a spatial separation of redox reactions, the anode catalyst oxidise the water and the cathode catalyst reduces the H^+ ions to H_2 using holes and electrons respectively. The theoretical efficiency is found to be 32% when the device is based on a single bandgap absorber that constitute a semiconductor [176]. The same principle is also applied for CO_2 reduction by Hurst *et al*. in 2010. In that, water oxidation catalyst ejects electrons and holes when irradiated by light and the concurrently formed electron undergoes a series of reduction reactions to produce H_2, which will further react with the CO_2 to yield fuels (Fig. **19**) [177]. The reaction is suffered by the rapid deactivation of the water oxidation ligands. The discovery of visible light active, durable, cost effective water oxidation molecular photo-catalyst and stable ligands accelerate the yield of fuels. The present scenario does
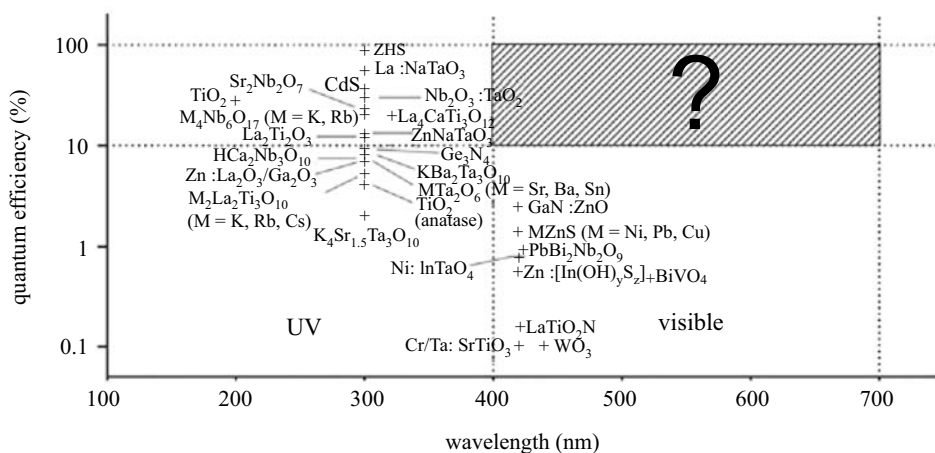

Fig. (18). Quantum efficiencies of various materials used for photocatalytic water splitting reaction. Reproduced with permission from [174]. ©2010 The Royal Society.

not offer such a kind of materials and stable and self-reparable ligands. More research effort is needed. [178].

Swiegers and coworkers put forward an idea towards the efficient production of hydrogen from solar energy based on a bio-inspired photosynthetic mechanism [178, 179]. The set-up consists of two electrons separated by a plastic membrane which allows the one directional transfer of protons. In this, the manganese impregnated membrane is attached to the ruthenium based DSSC (Dye Sensitised Solar Cell) which absorbs visible light irradiation and transfer an electron into the TiO_2 nanoparticles. The water oxidation catalyst (Mn_4O_4) also absorbs light and grab electrons from water. The electrons are transmitted to the cathode

by means of an external circuit and the protons passed through the H^+ conducting nafion membrane further reduced to H_2 at the cathode by the electrons (See Fig. **20**). This cell is too inefficient to produce hydrogen economically. If succeeded, one can make 15 times more hydrogen compared to the conventional hydrogen evolution pathways. The realization of this idea and incorporating this to CO_2 reduction process offers a significant research avenue.

In a similar way, Seger *et al* investigated methanol as a source of hydrogen in a PEFC with TiO_2 photoanode and Pt cathode with no applied bias [180]. The acidified methanol oxidized under UV irradiation on TiO_2 and the H^+ formed is transported to the Pt cathode through the nafion membrane.
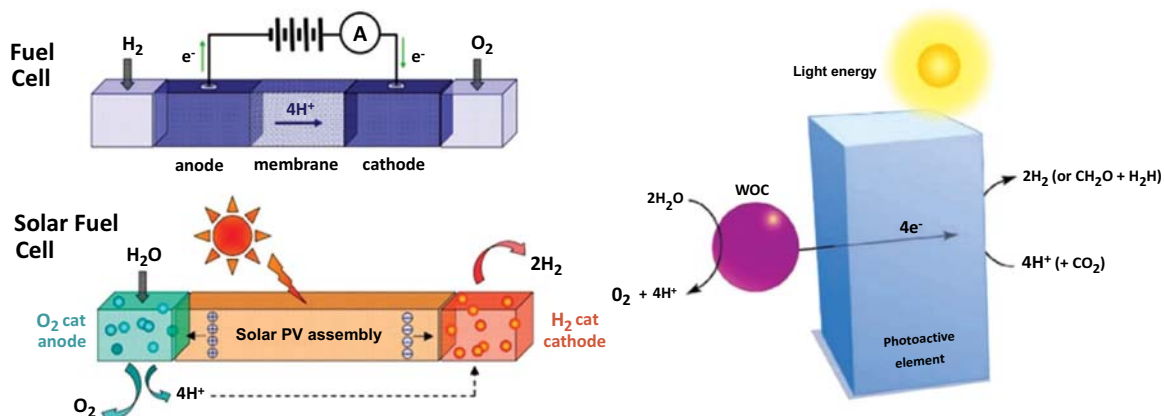
Fig. (19). Solar fuel cells based on the concept of a Polymer Electrolyte Fuel Cell (PEFC). Reproduced with permission from ref [176, 177]. ©2006 National Academy of Science (left) ©2010 American Association for the Advancement of Science (right).
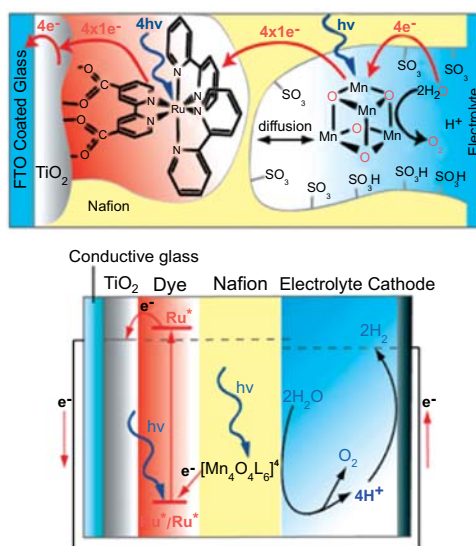
Fig. (20). Photoanode consisting of titania sensitized Ru dye coated over a nafion layer doped with manganese based water oxidation catalyst along with the cross sectional arrangement of photoelectrochemical cell. Reproduced with permission from Ref. [179] ©2010 American Chemical Society.

The hydrogen ion is reduced to H_2 with a rate of 69 μL h^{-1} cm^{-2}. Kim *et al* also studied the nafion layer-enhanced photocatalytic conversion of CO_2 [181]. The main role of nafion membrane is to enhance the proton activity. It also prevents the re-oxidation of the CO_2 reduction products. The current efficiency of solar fuel cells restricts this process from real-life implementation.

Since water oxidation is one of the key steps in the photocatalytic reduction of carbon dioxide, any breakthrough in water splitting research also contributes to the CO_2 reduction process. Materials used for water splitting reactions and its pros and cons were excellently reviewed elsewhere [175, 182-186]. Recently more research has been concentrated on hydrogen evolution reaction [187-191] and the evolved hydrogen is channeled for the CO_2 reduction [192-205]. Some reports also used CH_4 as a reductant, instead of water and externally channeled hydrogen [199, 201]. Such kind of CO_2 reduction systems is innovative but one cannot term it as photocatalytic even though the hydrogen produced ex situ by photocatalytic water splitting. Photocatalytic process involves generation and combined utilization of charge carriers within the reaction system and the in-situ generation of hydrogen ions from water oxidation and consecutive reduction to hydrogen, which is directly used for CO_2 reduction on the surface of a photocatalyst.

The artificial photosynthetic systems should make use of the state-of-the-art microscopic and spectroscopic techniques for the in-situ experimental studies. Chromatography based analytical measurements do not give any insight into the mechanism of photocatalytic reaction. It only helps to identify the products formed during the process or the reaction pathways. Most of the product formed are also under the detectable limit of chromatographic measurements or the product formed during the reaction will interface with each other over the chromatographic column. The unreacted carbon dioxide should be vented out properly, otherwise it will adversely affect the chromatographic column during the continuous operation.

Incorporation of XANES, XES like spectroscopic techniques give a detailed information on the reaction mechanism of the surface photocatalytic reactions. It reveals the chemical environment, charge transfer and charge symmetry with respect to the particle size and impurity level, which will throw light on the surface reaction mechanism of the photocatalytic reaction. X-ray photoelectron technique is another important tool in photocatalytic research while the exact potential of that technique is not fully explored. Casalongue *et al* directly probed the relationship between the adsorbed chemical species on the surface and the electrochemical potential in the case of polymer electrolyte membrane fuel cells using ambient pressure X-ray photoelectron spectroscopy (See Fig. **21**) [206]. It is found that non-hydrated hydroxyl species were the protuberant surface species and the exclusion of hydration increases the reactivity of oxygen species on the surface of the electrode. This type of in situ experiments can also be useful in solar energy conversion processes, which may throw light on the dark shaded CO_2 reduction mechanism and many other processes.
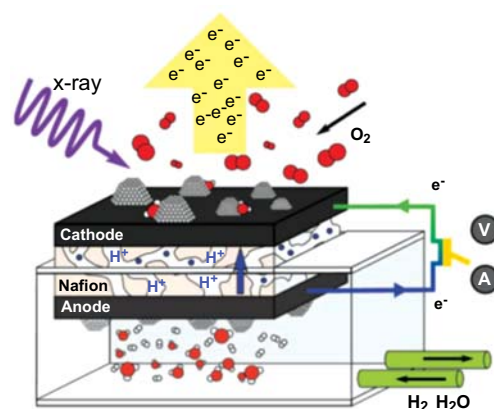
Fig. (21). Schematic representation of a PEM fuel cell set-up for in situ APXPS investigations Reproduced with permission from Ref. [206]. ©2013 Macmillan Publishers Limited.

For in-situ experiments most commonly used microscopic and spectroscopic techniques are environmental transmission electron microscopy (E-TEM) [207-209], In-situ vibrational spectroscopic [210-212], ambient pressure X-ray photoelectron spectroscopy [206,210,213], X-ray absorption spectroscopy [213,214-217], and Raman spectroscopy [218]. Making use of this in-situ experiments, the solar fuel generation processes will get a new dimension to the state-of-the-art beliefs. Moreover, the catalysts structure, coverage and composition also change with time, the combination of ultrafast of in-situ spectroscopic techniques reveal the structure and catalytic activity relationships (See Table **7**) [217].

The potential of electroanalytical techniques such as cyclic voltammetry and impedance spectroscopy is also not fully explored in photocatalytic studies which is primarily used for the rapid screening and high throughput evaluation of photocatalysts. The use of in-situ analytical techniques used for heterogeneous catalysis is extensively reviewed elsewhere [213-218].

The main advantage of in-situ experiments is; one can avoid the artifacts or interference from sample transfer or ion beam cleaning when using surface sensitive techniques. The applicability of this online techniques to the artificial photosynthesis is highly recommended. It will help to map the entire photocatalytic reaction leading to better understanding of the overall photocatalytic processes. Commonly used microscopic techniques analyze the photocatalytic material prior to the experiments while the properties of photocatalyst vary in solution or restructured with respect to the solvent medium. Most of the present literature does not consider this type of changes or postulates that the reaction rate decreases without any scientific evidences for the catalyst deactivation. This kind of changes can be monitored using in-situ experiments by mapping the entire life span of the catalyst during the photocatalytic process. It also reveals the deactivation mechanism of photocatalysts which will help us to modify the catalyst surface. Most of the laboratories suffered by the in-situ setup due to its high cost. One can at least do the characterization of photocatalyst prior and after the reaction or one can design the experiment in such a way that conducting the same experiment in different times and characterize the catalyst. This kind crude methods will impose impurities to the samples while transferring.

Separation of products formed during the reaction imposes an additional challenge to the photocatalytic conversion process. Recently, Alexis Bell and Meenesh Singh proposed an effective method for synthesizing pure liquid ethanol from carbon dioxide, which uses a saturated salt electrolyte [219, 220]. According to the theoretical calculations, the system would be capable of producing 15.27 million gallons of ethanol per year per square kilometer. The suggestion is based on an effect known as salting out. They used an electrolyte supersaturated with caesium carbonate, the attraction between the salt and water weakens the water-ethanol interaction which leads to the for-

Table 7.   Some of In situ used techniques and applications in the solar fuel generation. Extracted from Ref [211,216, 218].

Method	Applications
AP-XPS	Mainly used for studying the elemental compositions, the redox state of the surface and the subsurface region etc.
HP-STM	Elucidating the surface structure.
SFG-FTIR	Identifying the reaction intermediates and molecular nature of active sites.
EPR	Detection and identification of paramagnetic centers and free radicals
TA	It will give a reaction up to femto to the microsecond. Effective tool for unravelling at the kinetics of a single step from the subsequent reaction steps under relevant reaction conditions and probing the charge carrier dynamics and lifetimes. Ultrafast TA was used for probing the hole transfer kinetics.
XAS,EXAFS, NEXAFS	Extracts the evidence about the chemical state environment like the oxidation state, symmetry or the local charge distribution. It also gives the local environment of atoms (coordination number, distance between the neighboring atom etc.) absorbing the incident radiation.
KPFM	Used for the investigation of surface potential of materials
Electrochemical Impedance Spectroscopic Methods	Reveals the chemistry at electrolyte / semiconductor interfaces
AFM, SECM, STM	Visualization of catalyst structure in operando conditions. Provide finest details of the surface atom by atom.
TEM	In situ TEM reveals atomic level structure activity relationships of photocatalysts under reaction conditions.
EELS	Used in gas composition studies and simultaneous atomic structural characterization of the particles during the reaction.
Raman Spectroscopy	Used to study the spectral features of solar fuel materials under reaction conditions.

mation of a micro-emulsion that can be separated by means of a liquid-liquid separator (Fig. **22**).

The main challenge in front of the proposers is to make this idea in a cost effective manner. If it is experimentally proven, then it will be a break-
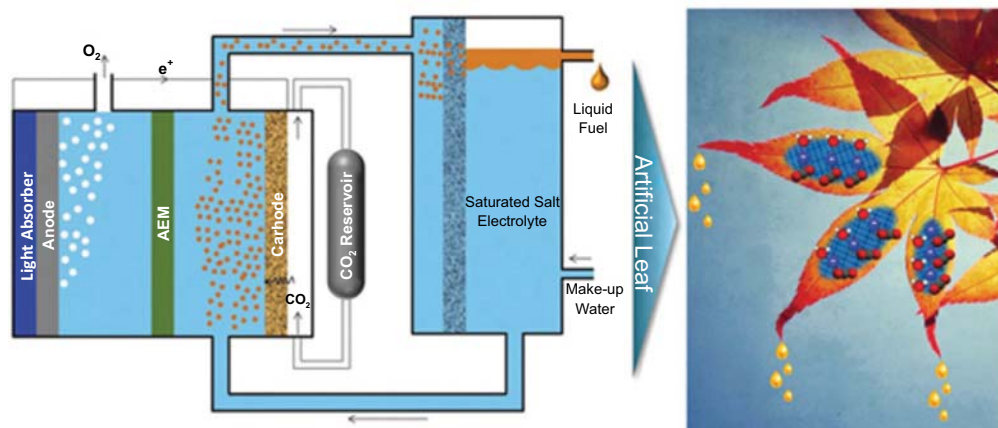
Fig. (22). Proposed system incorporated with the liquid-liquid extractor for the conversion of carbon dioxide into pure liquid ethanol fuel. Reproduced with permission from Ref. [219]. ©2016 Royal Society of Chemistry
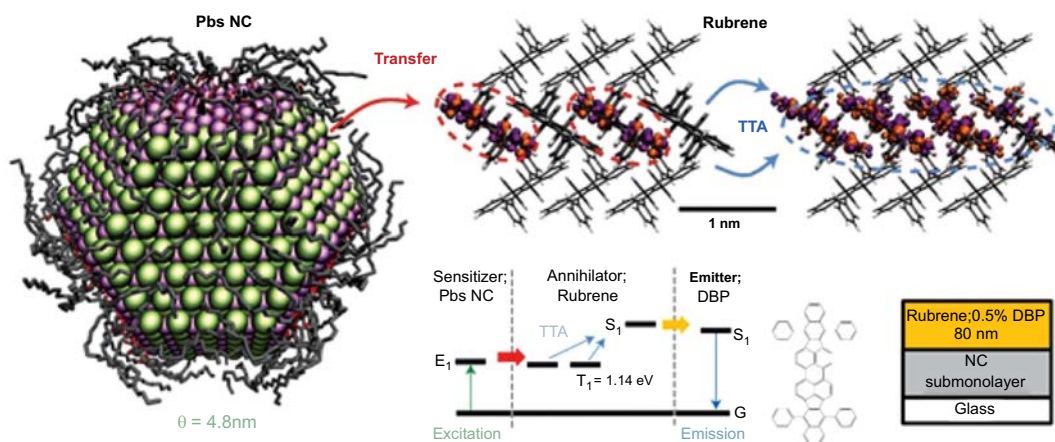
Fig. (23). Schematic representation of quantum dot sensitized upconversion of IR to Visible light via triplet-triplet annihilation. Reproduced with permission from [224] © 2015 Macmillan Publishers Limited.

through in artificial photosynthesis where the greatest challenge is to separate alcohols from water due to its high solubility and crossover [221].

Generally, the natural photosynthetic process is associated with the absorption of light in the near infrared region of the electromagnetic spectrum. Most of the semiconductors are not activated by the absorption of light near infrared region due to the bandgap values. One way to make the artificial photosynthesis efficient would be to increase the visible light absorption of the photocatalyst. Studies are reported for activating the photocatalyst using light near infrared region [222, 223]. A recent study reports the strategy for converting the infrared light into visible light using quantum dots films [224, 225]. The film was made up of a lead sulphide semiconductor quantum dot glazed with a single layer of fatty acids that make the surface inactive. The top crystalline layer was made up of

rubrene, an organic molecule. The top layer absorbs infrared light and transfers it in the bottom layers (See Fig. **23**). The energy inside the system exists in the form of excitons which diffuse over the rubrene through a process called triplet-triplet annihilation. When it is irradiated with infrared radiation, glowing of the film occurred which is the direction of the production of visible during the process. It claims that the collision of two low energy excitons creates a high energy exciton or singlet, which can further emit visible light. If it is possible to create the materials in large scale, then it will be an asset to the artificial photosynthesis process if and only if the champion photocatalyst is discovered.

7. CONCLUSION

Carbon dioxide reduction is a promising route to the sustainable solar energy conversion. The

existing level of knowledge does not permit the design of economically viable process for the conversion carbon dioxide into chemicals and value added fuels. It could happen only by the collaborative research effort from various groups, irrespective of the implicit bias among the scientific community. The material development and the lack of a standard procedure has been the bottleneck. The material should give at least 10 % quantum efficiency in the visible region of the solar spectrum. Currently, all such CO_2-to-fuel research efforts have been scattered around the various parts of the globe. A global initiative is needed for the resurrection of CO_2-to-fuel technology in a real life process and it should be targeted on the policy makers as well as the general audience. The global initiative should be like a compound parabolic concentrator in which all the scattered research efforts concentrated into a central point. The current pace shows that the plants will face a tight competition from the CO_2-to-fuel solar business in the near future!

LIST OF ABBREVIATIONS

AFM	=	Atomic Force Microscopy
AP-XPS	=	Ambient Pressure X-Ray Photoelectron Spectroscopy
CPC	=	Compound Parabolic Concentrator
DMF	=	N, N-dimethylformamide
EELS	=	Electron Energy Loss Spectroscopy
EPR	=	Electron Paramagnetic Resonance or electron spin resonance (ESR)
EXAFS	=	Extended X-ray Absorption Fine Structure
$Fc^{+/0}$	=	ferrocenium/ferrocene couple
HOMO	=	Highest Occupied Molecular Orbital
HP-STM	=	High-Pressure Scanning Tunneling Microscopy
IR	=	Infra Red
KPFM	=	Kelvin Probe Force Microscopy
LUMO	=	Lowest Occupied Molecular Orbital
MeCN	=	Acetonitrile
MOT	=	Molecular Orbital Theory
NEXAFS	=	Near Edge X-Ray Absorption Fine Structure
NHE	=	Normal Hydrogen Electrode
PCR	=	Photocatalytic Reaction
PZC	=	Point of Zero Charge
SECM	=	Scanning Electrochemical Microscopy
SFG-FTIR	=	Sum Frequency Generation Vibrational Spectroscopy
SPR	=	Surface Plasmon Resonance
STM	=	Scanning Tunneling Microscopy
TA	=	Transient Absorption
TEM	=	Transmission Electron Microscopy
UV light	=	Ultraviolet light
XANES	=	X-Ray Absorption Near Edge Structure
XAS	=	X-Ray Absorption Spectroscopy
XES	=	X-ray emission spectroscopy

CONFLICT OF INTEREST

The authors have no conflict of interest to disclose.

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