

# PHOTOCATALYTIC DECONTAMINATION OF AIR (DEGRADATION OF AIR POLLUTANTS, CO<sub>2</sub> REDUCTION)

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## Keywords

*Photocatalysis, Air pollutant degradation, Semiconductor photocatalysts, Environmental remediation, CO<sub>2</sub> reduction*

## Abstract

Photocatalysis provides a renewable platform to address both environmental and energy problems by converging air cleaning or less harmful products. This chapter overviews the principles of gas-phase photocatalysis, highlighting mechanistic similarities and differences between oxidative pollutant degradation and reductive pollutant conversion. Photocatalytic oxidation of major pollutants including volatile organic compounds (VOCs), nitrogen oxides (NOX), and sulfur oxides (SOX). The reductive reactions provide transferable insights for carbon dioxide (CO<sub>2</sub>) reductions. CO<sub>2</sub> photoreduction is highlighted, with discussion devoted to mechanistic insight, material design pathways including defect engineering, doping, heterojunction engineering, cocatalyst loading and organic interlayers, and control of selectivity and product proof standards. Case studies are included to show recent progress in increasing efficiency and stability. This chapter concludes by providing a critical account of current limitations and suggesting potential futures for developing scalable photocatalytic systems capable of sustaining simultaneously both clean technologies for air and sustainable CO<sub>2</sub> utilization.

Received -  
16<sup>th</sup> September 2025

Online Available -  
21<sup>st</sup> October 2025

## 1. Introduction

Air pollution is a serious environmental and public health concern of the 21st century. The rapid industrialization, urbanization process, and continuously increasing world's energy demand have led to the widespread release to the atmosphere of NOX, SOX, VOCs, carbon monoxide (CO), and greenhouse gases like CO<sub>2</sub>. These pollutants are harmful to human health and pose long-term risks to future generations[1, 2]. For example, atmospheric concentrations of CO<sub>2</sub> have now surpassed 420 ppm, well above pre-industrial levels and recognized as a major driver of climate change. These pollutants reduce air quality in ways that are both unpleasant and dangerous, threatening the well-being of ourselves, our children, and our grandchildren. While the dangers are clear, focusing only on the negative aspects of pollution can hide the possibilities for scientific progress and sustainable solutions[3]. The United States (Tier 3) prioritizes stricter NOX reduction, while the European Union (Euro 6) enforces balanced limits on CO, NO<sub>x</sub>, HC, and PM.

Asian countries such as Japan, China, and India largely align with Euro norms but differ in focus, with Japan emphasizing HC control and India allowing comparatively higher NOX[4]. Despite these regulations, significant challenges remain in effectively controlling emissions worldwide.

Photocatalysis is seen as a promising approach for tackling environmental and energy challenges. It uses solar or artificial light under mild conditions to enable the simultaneous removal of harmful air pollutants and the conversion of toxic air pollutants into fuels or chemical feedstocks. Since Fujishima and Honda first reported photoelectrochemical water splitting on TiO<sub>2</sub> electrodes in 1972, TiO<sub>2</sub> has been extensively studied because of its stability, low cost, and ability to produce reactive oxygen species (ROS) that can break down organic contaminants[5]. The photocatalytic process for the treatment of airborne contaminants in the gas phase by the use of semiconductor photocatalysts represents an exciting new technology for environmental remediation based on photocatalysts based on TiO<sub>2</sub>, ZnO or graphitic carbon nitride, which decomposes or degrades



airborne contaminants in the gas phase upon illumination by UV or visible light. The semiconductor is illuminated by the light source producing electron-hole pairs that then migrate to the surface of the semiconductor, where they subsequently react with the adsorbed oxygen and water molecules producing ROS, including hydroxyl radicals ( $\bullet\text{OH}$ ), superoxide anion ( $\text{O}_2\bullet^-$ ). The reactive oxygen species that are produced in this process are regarded as highly oxidative and have been shown to be effective for reducing a wide variety of air pollution agents including VOCs, NOX, SO<sub>2</sub>, CO, odorous gases, and they can also affect microorganisms [6, 7]. As a result, gas-phase photocatalysis has become particularly attractive for indoor air purification, industrial emission treatment, and general air pollution control. In air decontamination, oxidative reactions dominate, as photogenerated holes oxidize surface hydroxyl groups or water molecules to form  $\bullet\text{OH}$ , while electrons reduce oxygen molecules to  $\text{O}_2\bullet^-$ . These highly reactive intermediates then degrade organic pollutants VOCs or convert NO to nitrate.

In this context, photocatalytic reduction of CO<sub>2</sub> follows a reductive pathway in which electrons are used to activate CO<sub>2</sub> molecules, while holes oxidize water to provide the necessary protons. Thus, although pollutant degradation and CO<sub>2</sub> reduction operate on different chemical principles, both rely on the same underlying challenge: extending the lifetime of charge-carriers and directing them toward desired surface pathways. Z. Rao et al. developed a new gas-phase capture method that revealed the distinct roles of ROS in VOC photodegradation. The  $\bullet\text{OH}$  dominated the removal of o-xylene and styrene through ring-opening and mineralization, while  $\text{O}_2\bullet^-$  governed acetaldehyde degradation and acid formation. In ethanol conversion, photogenerated holes ( $h^+$ ) and lattice oxygen played the main roles, whereas  $\text{O}_2\bullet^-$  was primarily responsible for toluene and ketone transformations [8, 9].

Recently, focus has shifted from simply using pure TiO<sub>2</sub> for gas phase pollutant removal to modifying semiconductor systems that can both air pollutants and convert them into useful or less harmful products, emphasizing photocatalysis as a technology with both

environmental and energy advantages. As an illustration, the photocatalytic process can selectively and efficiently convert CO<sub>2</sub> into C1 products such as methane (CH<sub>4</sub>), C2 products such as CO, and methanol (CH<sub>3</sub>OH), as well as multi-carbon (C<sub>2</sub>+) products such as ethanol (C<sub>2</sub>H<sub>5</sub>OH). These compounds could help lower greenhouse gas levels while also providing renewable fuels and chemical feedstocks.

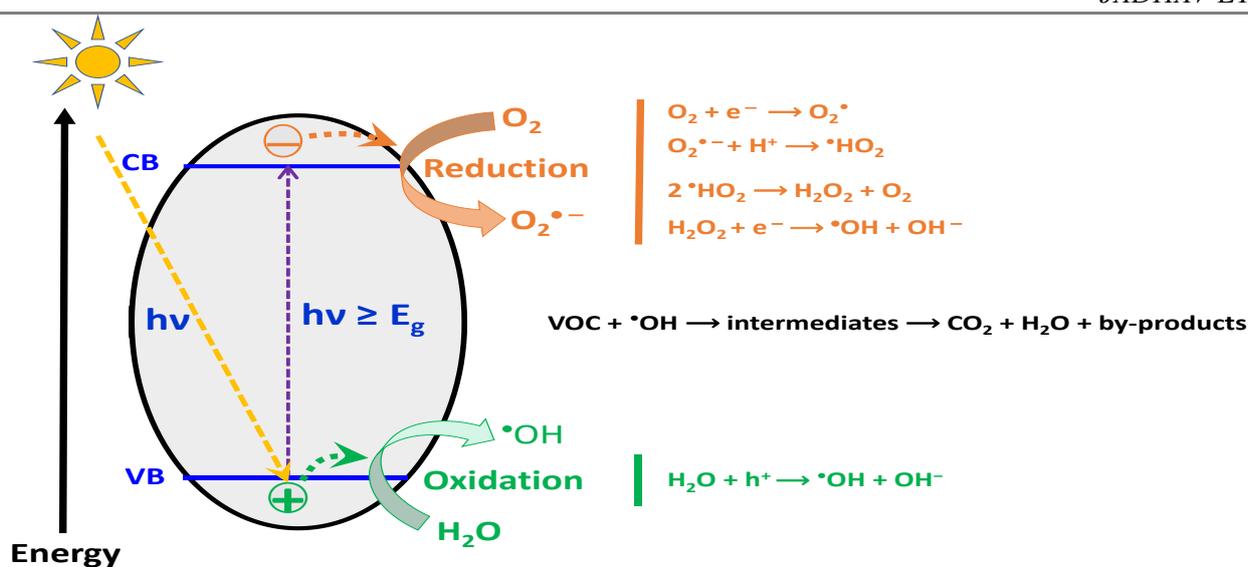
This chapter opens with an overview of the principles of gas-phase photocatalysis and the similarities and disparities of pollutant oxidation and reduction. It then surveys the photocatalytic oxidation of major air pollutants, including VOCs, NOX, and SOX, to demonstrate how experience from oxidative processes can inform approaches to CO<sub>2</sub> activation. Principal subheadings deal with CO<sub>2</sub> photoreduction, including reaction mechanisms, materials design approaches, selectivity, and product authentication. Case studies are included to reflect recent innovations, and the chapter concludes with current challenges and directions to make CO<sub>2</sub> conversion scalable and sustainable.

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## 2. Fundamentals of photocatalytic redox reactions

### 2.1 Photoinduced charge dynamics and surface chemistry

The basic principle of photocatalysis is the generation of electron-hole pairs upon absorption of light, where the photon energy is equal to or greater than the band gap ( $E_g$ ) of the semiconductor. In this process, electrons are excited from the valence band (VB) to the conduction band (CB), leaving behind positively charged holes in the VB. The photogenerated electron-hole pairs can migrate to the catalyst surface, where they participate in redox reactions with adsorbed species. Alternatively, these charge carriers may recombine, releasing their energy as heat or light, which decreases photocatalytic efficiency. Thus, the performance of a photocatalyst is largely determined by the efficiency of charge separation and the ability of carriers to reach the surface before recombination occurs. The mechanism of charge generation, migration, and separation is schematically illustrated in Figure 5.1.



**Figure 5.1:** Schematic illustration of the principle of photocatalytic oxidation and reduction in gas-phase air pollutants [10].

Category	Air pollutant	Reaction Pathway	Reaction products	Ref.
<b>Oxidation reaction</b>	VOCs (Toluene, formaldehyde, Ethyl acetate etc.)	VOCs + Free radical ( $\bullet\text{OH}/\text{O}_2^{\bullet-}$ ) $\rightarrow$ $\text{CO}_2 + \text{H}_2\text{O} + \text{by products}$	$\text{CO}_2 + \text{H}_2\text{O}$	[11]
	CO	$2\text{CO} + \text{O}_2^{\bullet-} \rightarrow 2\text{CO}_2$	$\text{CO}_2$	[12]
	NO	$\text{NO}_{(\text{ads})} + \bullet\text{OH}_{(\text{ads})} \rightarrow \text{HNO}_{2(\text{ads})}$ $\text{HNO}_{2(\text{ads})} + \bullet\text{OH}_{(\text{ads})} \rightarrow \text{NO}_{2(\text{ads})} + \text{H}_2\text{O}$ $\text{NO}_{2(\text{ads})} + \bullet\text{OH}_{(\text{ads})} \rightarrow \text{HNO}_{3(\text{ads})}$	$\text{NO}_2$ and $\text{HNO}_3$	[13]
<b>Reduction-reaction</b>	$\text{NO}_x$	$\text{NO}_3^- + 9\text{H}^+ + 8e^- \rightarrow \text{NH}_3 + 3\text{H}_2\text{O}$	$\text{NH}_3$	[14]
	$\text{CO}_2$	$\text{CO}_2 + 2e^- + 2\text{H}^+ \rightarrow \text{CO} + \text{H}_2\text{O};$ $\text{CO}_2 + 4\text{H}^+ + 4e^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$ $\text{CO}_2 + 6\text{H}^+ + 6e^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$ $\text{CO}_2 + 8e^- + 8\text{H}^+ \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	$\text{CO}, \text{CH}_4,$ $\text{HCHO},$ $\text{CH}_3\text{OH},$ $\text{HCOOH},$	[15]
<b>Mixed pathways</b>	$\text{O}_2$	$\text{O}_2 + e^- \rightarrow \text{O}_2^{\bullet-};$ $\text{O}_2^{\bullet-} + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2;$ $\text{H}_2\text{O} + h^+ \rightarrow \bullet\text{OH} + \text{H}^+$ $\bullet\text{OH} + \bullet\text{OH} \rightarrow \text{H}_2\text{O}_2$	$\text{H}_2\text{O}_2$	[16]

**Table 5.1:** Pollutant degradation pathways in gas-phase photocatalysis

## 2.2 Oxidizing and reducing agents

The photogenerated  $h^+$  and  $e^-$  can initiate redox reactions directly with adsorbed species or indirectly through the generation of reactive intermediates. Generally, two types of reactions take place on the photocatalyst surface: oxidation and reduction.

- Oxidants: Oxidative reactions are typically driven by photogenerated holes or  $\bullet\text{OH}$  from water or hydroxide.
- Reductants: Reduction processes are mediated by photogenerated electrons in CB or  $\text{O}_2\bullet^-$  or Surface-trapped electrons that promote reduction of metal ions or gaseous pollutants.

These reactions play a central role in gas-phase photocatalysis, enabling both pollutant degradation and the transformation of molecules into value-added fuels. Accordingly, Table 5.1 summarizes representative pollutants, the dominant reactive species involved, and the typical final products, classified according to whether their degradation is primarily driven by oxidation, reduction, or mixed pathways.

## 2.3 Band edge potentials and redox capability

Photocatalytic oxidation or reduction potential is also founded upon its band edge positions with respect to redox potential. The suitability of materials for photocatalysis including their electronic properties is described in Chapters I and II. A detailed discussion is provided on the energy band position for selecting suitable photocatalysts for redox reactions. As an example, VB for  $\text{TiO}_2$  (+2.7 V vs. NHE) is sufficiently high such that it would oxidize water into  $\bullet\text{OH}$ , while its CB (-0.5 V vs. NHE) is sufficiently low such that it would reduce  $\text{O}_2$  into  $\text{O}_2\bullet^-$ . Photocatalysts with low values for their band gap such as g-C<sub>3</sub>N<sub>4</sub> have CB potential values appropriate for reducing  $\text{CO}_2$  but low VB oxidation positions. Thus, thermodynamic pairing of CB and VB with those for redox pollutants controls oxidation, reduction, or both-pathway predominance.

## 3. Reactor modes in gas-phase photocatalysis

Reactor engineering provides an interface between photocatalytic materials and their measurable performance in suitable gas-phase environments.

Even if a photocatalyst is an extremely effective charge separator with high activity in a model laboratory experiment, its real potential is not confirmed until there is a sharply defined reactor mode in conjunction with a standard test method. The design of the reactor influences photon distribution, mass transfer, and residence time, while the test methods guarantee the reproducibility and comparison of results across different laboratories. Reactors for gas-phase photocatalysis are mainly classified by their flow mode (batch vs. continuous) and geometry/illumination approach (annular, flat plate, monolith, etc.). Each has special advantages and limitations.

Batch reactors are commonly used because of their simplicity and their ability for precise measurement of evolution of reactant and product in relation to time. However, their use is very often limited by product accumulation and mass-transfer obstruction in a way that a disturbance in apparent kinetics occurs. Flow reactors, contrary to batch reactors, experience continuous consumption of reactants with simultaneous effluent disposal in a way that mass transportation is favored and circumstances are made closer to real applications.

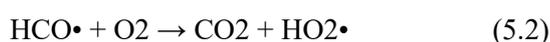
## 4. Oxidation-based photocatalytic degradation

Oxidation pathways are the cornerstone of photocatalytic degradation of air pollutants. Oxidizing agents mineralize pollutants or convert them into less hazardous forms. The high reactivity and lack of selectivity of oxidative species allow them to target a broad range of contaminants, including  $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{CO}$  and VOCs.

### 4.1 Volatile organic compounds removal

VOCs are dangerous pollutants released from both natural and human-made areas, including industrial plants, passenger cars, and residential combustion. They pose considerable dangers to both human health and the environment. VOCs can generally be characterized by having relatively high vapor pressures at room temperature (approximately 133.322 Pa) and boiling points between 50-250°C, which allows them to evaporate easily to the atmosphere [10]. VOCs contain a variety of chemicals that vary in their reactivity and toxicity, including aromatic hydrocarbons, saturated and

unsaturated alkanes, alcohols, aldehydes, ketones, halogenated hydrocarbons, non-methane hydrocarbons, and VOCs containing nitrogen, oxygen, and chlorine. The chemical compound, concentration, and emissions source will affect overall influence on human health and the surrounding environment [27]. Indoor concentrations of VOCs, including formaldehyde, acetaldehyde, toluene, chlorobenzene, vinyl chloride, ketones, and esters, can be 5-10 times higher than outdoors, because of the solvents used in household and industrial-based products. Their photocatalytic degradation reaction occurs via adsorption to the catalyst surface, radical attack, and mineralization reactions. For instance, formaldehyde is oxidized via formate intermediates to form CO<sub>2</sub>. The reaction mechanisms for the photocatalytic degradation of formaldehyde are described in the following reactions. According to Chen et al. the photocatalytic degradation of formaldehyde over Cu-TiO<sub>2</sub> composites under visible light follows a stepwise pathway[28]. The initial step involves the oxidation of formaldehyde to form dioxymethylene, which subsequently forms the formate species that acts as the critical intermediate in this process. The rate-limiting step is the decomposition of formate, in which CO<sub>2</sub> and H<sub>2</sub>O is formed as products. Interestingly, this is primarily driven by •OH as opposed to the O<sub>2</sub>•<sup>-</sup>.



#### 4.2 Carbon monoxide oxidation

The CO is a toxic gas produced from incomplete combustion in vehicles, industries, and residential heating. Its strong binding to hemoglobin disrupts oxygen transport. CO also contributes to urban air pollution and smog, making its efficient removal vital for air purification and environmental protection[29]. The photocatalytic oxidation has emerged as a promising green approach to mineralize CO into CO<sub>2</sub>. The general principle of CO photocatalytic oxidation involves the generation of reactive oxygen species upon light excitation of semiconductor photocatalysts such as TiO<sub>2</sub>, CeO<sub>2</sub> or their modified forms[30, 31]. These reactive species actively participate in the stepwise oxidation of CO, which

typically begins with CO adsorption on the catalyst surface, followed by electron transfer and reaction with oxygen intermediates to yield CO<sub>2</sub>. On the surface of TiO<sub>2</sub> photocatalyst, the dominant mechanistic pathway involves CO reacting with adsorbed superoxide species, producing carbonate-like intermediates that subsequently decompose into CO<sub>2</sub> [32].

A secondary pathway is the direct oxidation of CO by photogenerated holes or •OH, though this route is generally less favorable than the superoxide-assisted mechanism. The main elementary steps can be expressed as:



Instead of this, •OH generated at the surface may oxidize CO directly:



Oxygen availability is a key factor influencing the process. Molecular O<sub>2</sub> not only serves as the oxidant but also scavenges electrons, thereby reducing recombination and sustaining ROS generation. Under oxygen-deficient conditions, CO oxidation slows significantly, whereas water vapor can promote the reaction by generating additional •OH[33]. Oxygen vacancies (OV) in TiO<sub>2</sub> and related semiconductors enhance CO adsorption and O<sub>2</sub> activation[32]. Vacancies also tune the electronic structure, extend light absorption, and provide preferential adsorption sites for CO and O<sub>2</sub>, thereby lowering the reaction barrier. This can lead to higher CO<sub>2</sub> yields. Similarly, heterojunction systems such as improve charge separation and broaden light absorption, both of which further enhance CO photooxidation[34]. Alloy or plasmonic modifications, such as Pt–Ru/TiO<sub>2</sub> or plasmonic NPs systems, have also shown superior performance by stabilizing intermediates, improving charge transfer, and preventing catalyst deactivation[35, 36]. Therefore, the reaction primarily proceeds via superoxide radical-mediated pathways, with formate- or carbonate-like intermediates playing crucial roles in the transformation to CO<sub>2</sub>.

Type	Flow mode	Catalyst form	Advantages	Limitations	Ref.
Batch (Static)	Closed/non-flow	Powder or thin film	<ul style="list-style-type: none"> <li>No catalyst loss</li> <li>Simple design</li> <li>Controllable experimental parameters</li> </ul>	<ul style="list-style-type: none"> <li>Less product yields</li> <li>Non-scalable</li> <li>Difficult to understand and control the reaction mechanism</li> <li>Unsuitable for continuous treatment</li> </ul>	[17]
Continuous Flow	Steady-state	Immobilized films	<ul style="list-style-type: none"> <li>Enable continuous operation</li> <li>Scalable compared to batch reactors</li> <li>Suitable for continuous emission treatment</li> </ul>	<ul style="list-style-type: none"> <li>Short residence time produces low yield due to incomplete reaction,</li> <li>Require precise optimization of experimental parameters</li> <li>Complex setup compared to batch reactor.</li> </ul>	[18]
Flat-Plate	Batch or flow	Transparent thin films	<ul style="list-style-type: none"> <li>Scalable</li> <li>Mechanically stable</li> <li>Uniform light distribution</li> </ul>	<ul style="list-style-type: none"> <li>Limited light penetration</li> <li>Limited scalability</li> </ul>	[19]
Annular	Continuous	Coated on inner/outer wall	<ul style="list-style-type: none"> <li>Uniform irradiation and large interaction area in compact design</li> <li>High degradation efficiency even at very short gas residence time</li> </ul>	<ul style="list-style-type: none"> <li>Limited scalable</li> <li>Heat control issues</li> <li>Limited surface area than monolith</li> </ul>	[20]
Monolith / Honeycomb	Continuous	Wash-coated channels	<ul style="list-style-type: none"> <li>Larger geometric surface area</li> <li>Uniform distribution of gas flow</li> <li>Mass transfer</li> <li>Thermal stability</li> </ul>	<ul style="list-style-type: none"> <li>Limited commercial viability</li> <li>Scalability challenges</li> </ul>	[21, 22]
Membrane	Continuous	Porous coatings	<ul style="list-style-type: none"> <li>Selective permeation</li> <li>Compact design</li> <li>Low catalytic loss</li> </ul>	<ul style="list-style-type: none"> <li>Membrane fouling</li> <li>High cost and diffusion-limited reaction rates</li> </ul>	[23, 24]
Fluidized-bed	Continuous	Suspended powders	<ul style="list-style-type: none"> <li>Enhance heat and mass transfer</li> <li>Extreme fluidized regimes enabling throughput and scalability</li> </ul>	<ul style="list-style-type: none"> <li>Catalyst loss</li> <li>High pressure drops</li> <li>Complex operation</li> <li>Costly auxiliary equipment</li> </ul>	[25]
Packed-bed	Continuous	Pellets or	<ul style="list-style-type: none"> <li>Simple design</li> </ul>	<ul style="list-style-type: none"> <li>Uneven reactant</li> </ul>	[26]

		powders	<ul style="list-style-type: none"> <li>• Enhance heat and mass transfer</li> <li>• Mild operating conditions</li> <li>• Good scalability</li> </ul>	<ul style="list-style-type: none"> <li>• Mass transfer limitations</li> <li>• Catalyst degradation</li> <li>• Non-uniform light distribution in thick coatings</li> </ul>	
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**Table 5.2.** Reactor types used in gas-phase photocatalysis, advantages and limitations.

### 4.3 Nitrogen oxides oxidation

The NO and NO<sub>2</sub> are key precursors to photochemical smog and ground-level ozone, making their effective removal a pressing environmental challenge. Photocatalytic oxidation offers a sustainable pathway, converting these species into nitrate, which ideally remains adsorbed on the catalyst surface or can be washed away. However, selectivity remains a critical issue: incomplete oxidation often produces transient by-products such as NO<sub>2</sub> or nitrous acid (HONO), both of which are hazardous pollutants[37-39]. Surface modification approaches, including incorporation of basic sites, transition-metal doping, and OV engineering, have been widely explored to enhance NO adsorption, O<sub>2</sub> activation, and charge separation. Collectively, these defect and surface engineering strategies represent a promising pathway toward selective and efficient NO<sub>x</sub> removal under practical environmental conditions[40]. For example, OV have emerged as key structural defects that significantly enhance photocatalytic NO oxidation[41]. Acting as electron-rich active sites, OV promote strong NO adsorption and stabilize it as NO- intermediates. Simultaneously, they facilitate O<sub>2</sub> activation, generating reactive oxygen species such as •O<sub>2</sub>- and •OH, which drive the deep oxidation of NO into harmless nitrate/nitrite while suppressing toxic NO<sub>2</sub> formation. Moreover, OV improve visible-light absorption, promote charge separation, and extend carrier lifetimes, thereby boosting photocatalytic efficiency. Thus, OV engineering through strategies like various dopants such as Ce, Cu, Fe etc. doping represents a promising pathway for designing highly efficient catalysts for air purification.

## 5. Reduction-based photocatalytic degradation

Photocatalytic reduction transfers greenhouse and harmful gases (CO<sub>2</sub> and NO<sub>x</sub>) into fuels (CH<sub>4</sub> and methanol) or benign molecules like N<sub>2</sub> and NH<sub>3</sub>.

These technologies use solar energy and surface-active sites on semiconductors to reduce hazardous emissions while also providing avenues for sustainable energy and resource recovery. The primary challenges are efficiency, selectivity, and long-term stability.

### 5.1 NOX reduction

Transformation of harmful nitrogen oxides by photocatalytic reactions as a green pathway for the production of beneficial products, such as harmless nitrogen gas or ammonia[42]. The photocatalytic reduction occurs via a different pathway as compared to the photocatalytic oxidation pathway, which could possibly create secondary pollutants, such as NO<sub>2</sub> and HONO. The reduction occurred on the semiconductor photocatalysts surface such as TiO<sub>2</sub>, ZnO, or other catalysts through photogenerated electrons to cleave the N–O bond directly[2]. In recent years, researchers have focused on approaches such as heterojunction engineering to boost charge separation, transition metal introduction to lower reaction barriers, and OV or single-atom site alteration to optimize NO adsorption and electron transport[43]. Co-catalysts to assist with selectivity for either N<sub>2</sub> or NH<sub>3</sub> for photocatalytic NO<sub>x</sub> reduction are also preferable and have included noble metals and metal sulfides[44]. The reduction pathway has not been fully explored compared to the oxidation pathway which has been previously explored; nonetheless, the photocatalytic reduction of NO<sub>x</sub> for air purification and sustainable nitrogen resource use could be an exciting opportunity.

### 5.2 CO2 reduction

Global CO<sub>2</sub> emissions have risen from the burning of fossil fuels. According to the IEA's detailed forecast, emissions increased by 6% to 36.3 gigatons. In response, high CO<sub>2</sub> emissions have become a major

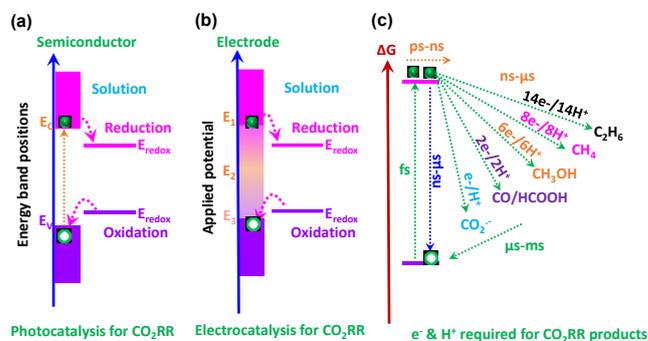
issue for sustainable environments that deal with CO<sub>2</sub> chemistry. The chemistry in which the CO<sub>2</sub> molecule is transferred to value-added products such as one-carbon and multi-carbon. However, in terms of green chemistry research goals, producing value-added products such as stable C1 molecules or C-C coupling from C1 molecules is one of the most difficult research targets in chemistry.

Photocatalysis is the major emerging process for the selective conversion of CO<sub>2</sub> molecules to C1 or C2 products. In these processes, the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) occurs by providing electrons from catalysts. Therefore, the redox potential of the reactants is a key factor in photocatalysis (energy band position in semiconductors) and electrocatalysis (electrode potential) according to thermodynamic requirements, as displayed in Figure 5.2.

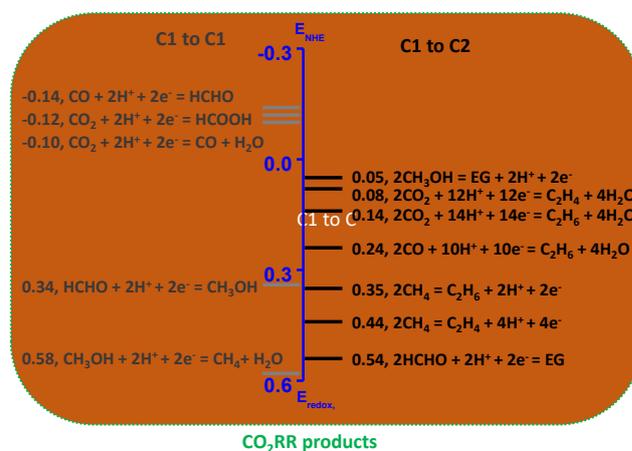
In the artificial photosynthesis process or electrocatalysis process, C1 or C2 product formation rates depend on the redox potentials and the contribution of e<sup>-</sup> and H<sup>+</sup> couples, as shown in Figure 5.2 and 5.3. Finally, these products help to balance carbon in the atmosphere. In particular, methanol, ethanol, and methane from CO<sub>2</sub> reduction have important applications in industries and as future energy sources. A recent report suggests that methanol may be the gasoline of the future. The economics of methanol may be attractive to meet the growing energy demand in developing nations. Artificial photosynthesis enables the closing of the industrial carbon cycle and is the ultimate technology to combat climate change while providing a suitable source of reduced carbon feedstock. For example, CH<sub>3</sub>OH (20 MJ/kg) and CH<sub>4</sub> (55.5 MJ/kg) have high energy density stored in their chemical bonds, which is much higher than current batteries (0.1–0.7 MJ/kg)[45]. Importantly, in the context of this proposal, the electrochemical process utilizes CO<sub>2</sub> gas, which passes across a gas diffusion electrode where it is reduced.

The limited surface-active sites, low CO<sub>2</sub> solubility, weak local CO<sub>2</sub> interaction at the catalyst surface, selectivity challenges from band position (photocatalysis), dominant H<sub>2</sub>O environment at the electrode (electrocatalysis), and sluggish multielectron transfer remain major obstacles in CO<sub>2</sub>RR. To overcome these, strategies such as defect engineering to enrich active sites, ionic liquids or salts to enhance CO<sub>2</sub> solubility, band structure tuning

for improved selectivity, surface modification to balance H<sub>2</sub>O/CO<sub>2</sub> adsorption, and co-catalyst integration to accelerate electron transfer have been proposed. Together, these approaches provide a pathway toward efficient, selective, and stable CO<sub>2</sub> conversion systems.



**Figure 5.1:** (a) Energy-band positions of semiconductor and redox potentials level (b) electrode applied potentials ( $E_1$ ,  $E_2$ ,  $E_3$ ) and substrate redox potentials ( $E_{\text{redox}}$ ), and (c) Energy diagram of the different CO<sub>2</sub> reduction products, illustrating the number of e<sup>-</sup> and H<sup>+</sup> required for CO<sub>2</sub>RR products[46].



**Figure 5.3:** The redox potentials for conversion of CO<sub>2</sub> to C1 or C2 products [46].

## 6. Coupled oxidation-reduction processes

In gas-phase photocatalysis, both oxidation and reduction reactions happen at the same time on the catalyst surface. While photogenerated holes drive oxidation pathways for pollutants such as VOCs, CO, or NO<sub>x</sub>, photogenerated electrons are responsible for reduction reactions, such as CO<sub>2</sub> → CO/CH<sub>4</sub> or NO → N<sub>2</sub>. These two pathways can work together to utilize charge carriers effectively, improve energy conversion efficiency and decrease the formation of harmful by-products [27, 47]. Coupled redox

reactions represent a promising method to enhance photocatalytic performance by connecting the removal of environmental pollutants with the production of useful products. This dual role exemplified through photocatalysis has broader implications beyond environmental detoxification, including for sustainable energy and carbon utilization.

### 7. Factors Affecting redox pathways

Various inherent and external factors together influence photocatalytic redox reactions efficiency. From a materials perspective, factors such as band edge alignment, defect states, surface area, and crystallographic orientation, are all decisive parameters influencing charge carrier generation and transportation. From an external standpoint, multiple factors- such as light intensity, wavelength, pollutant concentration, gas rate, and humidity-will all vary the balance of oxidation-reduction processes[11, 48]. Furthermore, strategies such as co-catalyst deposition and heterojunction engineering can precisely direct charge carriers to the desired reaction and ultimately lead to selectivity for targeted products while minimizing unwanted byproducts. Therefore, an understanding of these interdependent parameters will assist in the rational design of photocatalysts that can achieve not only high efficiency but controlled redox reactions in representative operational environments.

### 8. Environmental and practical implications

The advancement of effective and selective photocatalytic systems is of much importance to environmental and practical implications. Through both oxidation and reduction of air pollutants, or sustainably producing fuels and value-added chemicals under mild conditions, they may make industrial processes more sustainable, and reduce our reliance on fossil fuel sources. However, in order to transition new photocatalytic materials from laboratory demonstrations to upon costs on the floor of the factory into industry, factors such as catalyst stability, scalability of the synthesis methods, expense and slant to be used with existent infrastructure must be assessed. These sought considerations will facilitate transition of photocatalytic technology from fundamental studies

to eventual deployment honed of intrinsic research, lead to cleaner energy cycles, and enhanced environmental quality.

### 9. Challenges and future perspectives

Although substantial advancements have been made, multiple challenges must be overcome before photocatalysis approaches practical usage. Most notably, scalability remains a challenge because what can work well in the lab does not translate to the field with limitations of mass transport, variability in sunlight, and fouling of the catalyst. Another important challenge is selectivity, as CO<sub>2</sub> reduction usually affords a mixed product stream, and therefore specific engineering of active sites needs to occur in order to drive specific pathways or products. Durability can also limit time to operate, as photo-corrosion, fouling, and deactivation limit catalyst lifespan. Also, a lack of established guidelines for reporting procedures, especially isotope-labeling and apparent quantum yield, restricts objective comparison across studies. Additionally, photocatalysis maybe be the most efficacious when used as a hybrid system - as part of an adsorptive, filtering, or electrochemical interface-rather than stand-alone. Overall, combining materials innovation, rigorous evaluation, and systems integration to address these intertwined challenges will be imperative to advancing the ultimately photocatalysis closer to environmental and energy applications on real-world scales.

### 10. Conclusion

Decontaminating air pollutants via photocatalysis holds promise as a pathway to simultaneously reduce environmental pollution and address challenges around sustainable energy. Semiconductor photocatalysts used solar or artificial light to degrade harmful pollutants in the air including VOCs, NO<sub>x</sub>, SO<sub>x</sub>, and CO, and convert CO<sub>2</sub> into value-added products (CO, CH<sub>4</sub>, CH<sub>3</sub>OH, or higher hydrocarbons) at the same time. This synergy provides the opportunity to mitigate air pollution impacts and also contributes to closing the carbon cycle for renewable fuels and chemicals. To date, tremendous advances in the design of materials via defect engineering, doping, heterojunctions, and cocatalysts have improved charge separation, light

absorption, and selectivity. However, major hurdles remain, including scalability, durability, standardization of performance testing, and methods to integrate photocatalysis with hybrid systems. As look to the future, overcoming these challenges through interdisciplinary approaches with materials engineering, reactors/engineering, and integration into systems will be critical to develop a successful, scalable and durable photocatalytic technology. Development of photocatalytic technology can lead to viable use of clean air, reduced greenhouse gas emissions, and sustainable energy production on a global scale.

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