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## Solar Driven Gas Phase Advanced Oxidation Processes for Methane Removal – Challenges and Perspectives

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# **Solar driven gas phase advanced oxidation processes for methane removal – challenges and perspectives**

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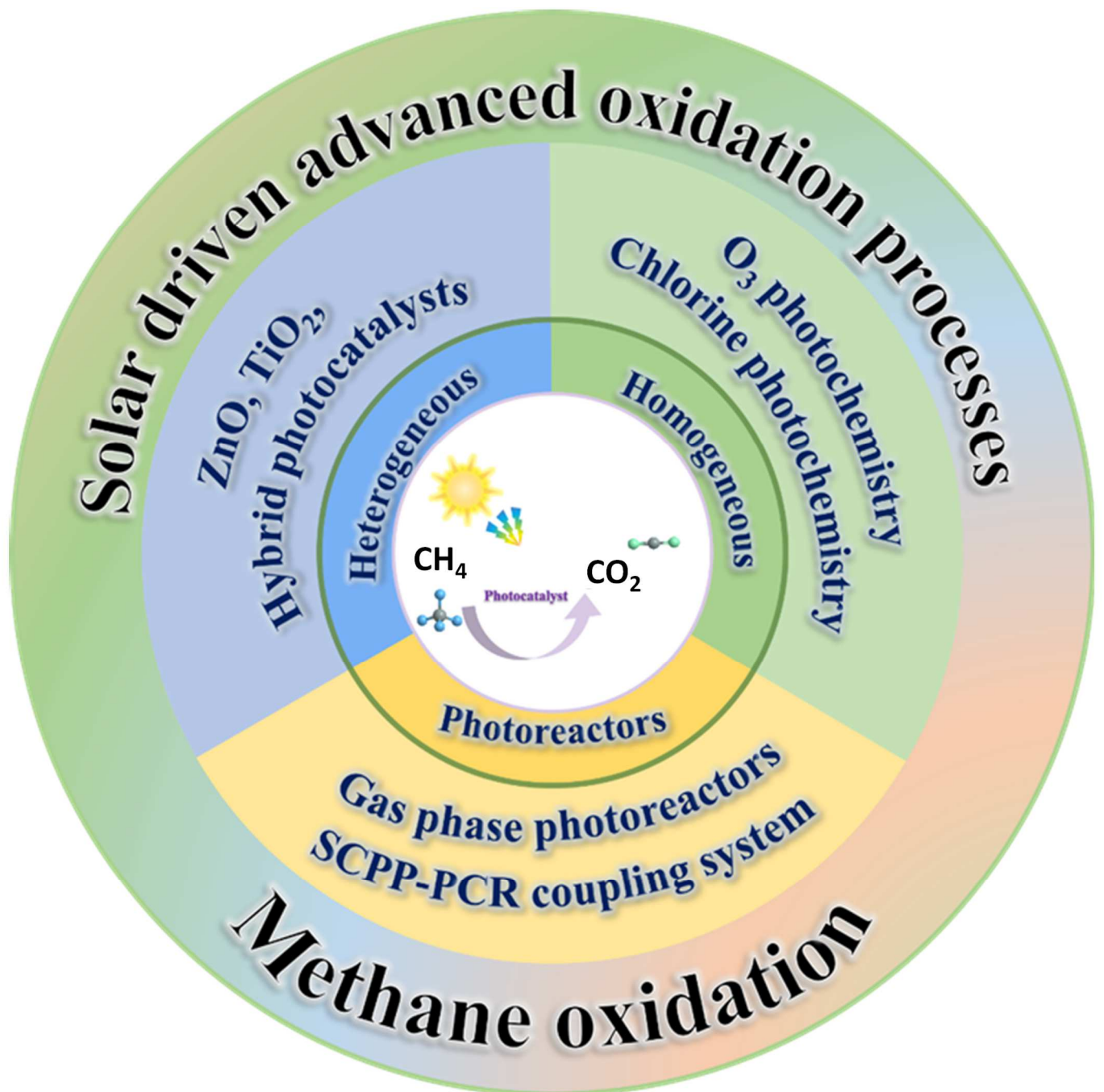
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Frontispiece

# Abstract

Methane (CH<sub>4</sub>) is a potent greenhouse gas and the second highest contributor to global warming. CH<sub>4</sub> emissions are still growing at an alarmingly high pace. To limit global warming to 1.5°C, one of the most effective strategies is to reduce rapidly the CH<sub>4</sub> emissions by developing large-scale methane removal methods. The purpose of this perspective paper is threefold. (1) To highlight the technology gap dealing with low concentration CH<sub>4</sub> (at many emission sources and in the atmosphere). (2) To analyze the challenges and prospects of solar-driven gas phase advanced oxidation processes for CH<sub>4</sub> removal. And (3) to propose some ideas, which may help to develop solar-driven gas phase advanced oxidation processes and make them deployable at a climate significant scale.

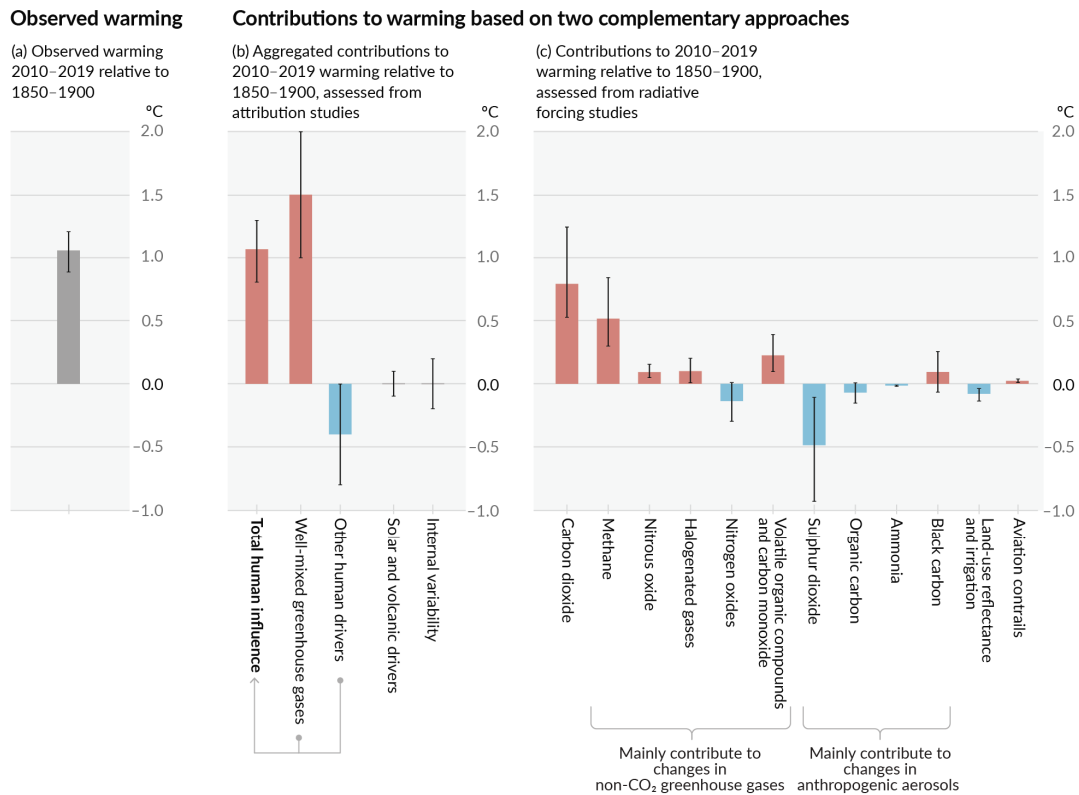
**Keywords:** Photocatalysis; Ozone; Chlorine; Photoreactor; Methane oxidation; Advanced oxidation process

## 1. Introduction

### 1.1 Why focus on removing CH<sub>4</sub> greenhouse gas?

Economic development is often accompanied by the sacrifice of the environment. Since the industrial revolution, human activities have produced a large amount of greenhouse gases (GHGs), thus resulting in the greenhouse effect. CH<sub>4</sub> is a potent GHG. For a 100-year time horizon, CH<sub>4</sub> has a global warming potential (GWP) 27-35 times higher than that of CO<sub>2</sub><sup>[1]</sup>. It also has a short residence time in the atmosphere with a GWP 84 times higher than that of CO<sub>2</sub> over 20 years.

At present, CO<sub>2</sub> is the main cause of the greenhouse effect (about 0.75°C global warming), while about 0.5°C global warming is caused by CH<sub>4</sub><sup>[2]</sup>, as shown in Figure 1.

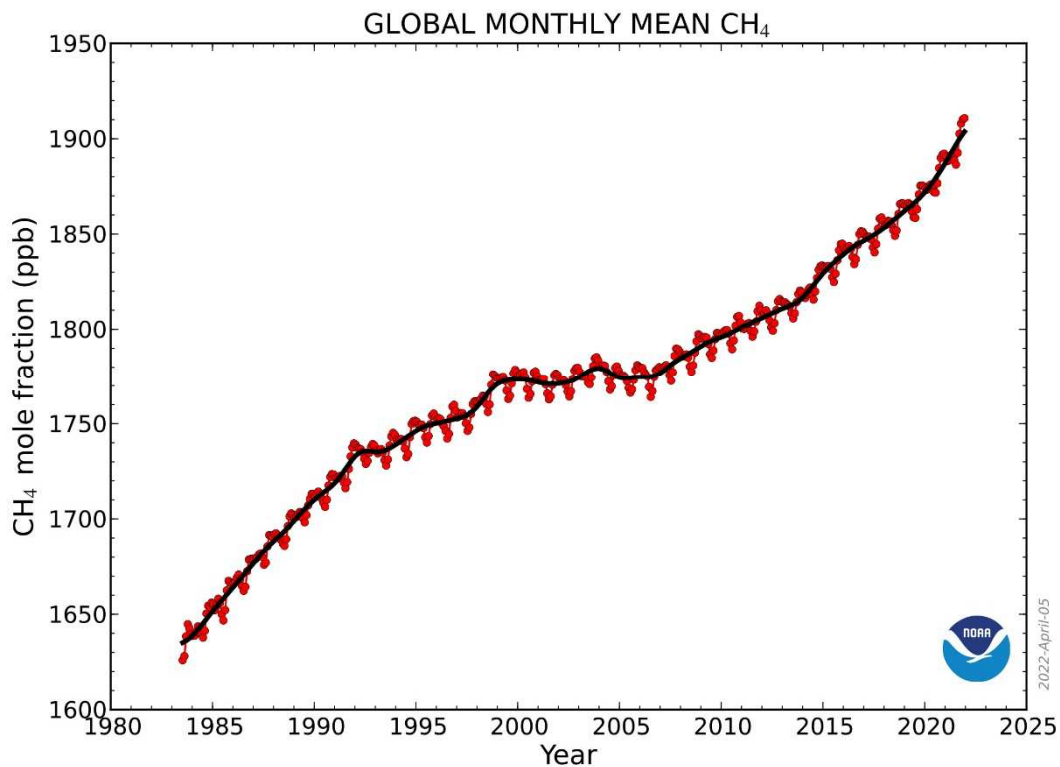


**Figure 1. Assessed contributions to observed warming in 2010–2019 relative to 1850–1900. Reproduced with permission. Copyright 2021, IPCC.**

Apart from the attention and efforts that have been put towards CO<sub>2</sub>, it is more and more important and urgent to focus on CH<sub>4</sub>, too. We need to investigate in two directions - CH<sub>4</sub> emissions and CH<sub>4</sub> already in the atmosphere.

In general, CH<sub>4</sub> emission sources can be classified into two categories: natural sources of CH<sub>4</sub> (~ 40%) and anthropogenic sources of CH<sub>4</sub> (~ 60%). In November 2021, during the 26<sup>th</sup> conference of parties (COP 26) in Glasgow, UK, more than 100 countries signed the global methane pledge committing to reduce anthropogenic methane emissions by 30% comparatively to 2020 levels by 2030.

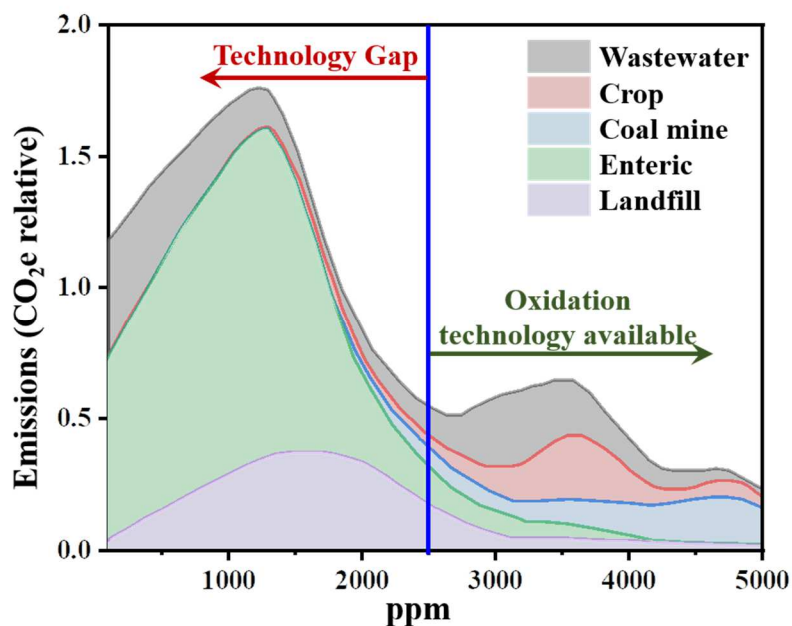
Considering CH<sub>4</sub> already in the atmosphere, its concentration averaged at 1,895.7 ppb during 2021, or around 162% greater than pre-industrial levels. Meanwhile, CH<sub>4</sub> continues accumulating in the atmosphere at an alarmingly high rate. According to the US National Oceanic and Atmospheric Administration (NOAA), in 2020 and in 2021 the annual increases in atmospheric methane (respectively 15.3 and 17 ppb) were the largest annual increases ever recorded since systematic measurements began, as shown in Figure 2. [3]



**Figure 2. CH<sub>4</sub> trend:** This graph shows globally-averaged, monthly mean atmospheric methane abundance determined from marine surface sites since 1983. Values for the last year are preliminary (NOAA Global Monitoring Laboratory).

Limiting global warming below 1.5°C as targeted by the Paris agreement will require not only stopping CO<sub>2</sub> emissions but also reducing the emissions of CH<sub>4</sub><sup>[4]</sup> and removing CH<sub>4</sub> from the atmosphere<sup>[5]</sup>.

## 1.2 Technology gap



**Figure 3. Relative amount of CH<sub>4</sub> emissions at different concentrations from various emission sources.**

CH<sub>4</sub> is better known as a fuel or platform chemical, when its concentration is higher than 0.25% (e.g., 2500 ppm), rather than a potent GHG. Mature technologies are available in this concentration range to utilize it as a fuel or platform chemical.

However, the majority of CH<sub>4</sub> emissions (e.g., from agriculture, landfill, and wastewater) are dilute and in concentrations lower than 2500 ppm. Concentration of CH<sub>4</sub> in the atmosphere is even lower (i.e., 1895.7 ppb). No mature technology is available to utilize or remove CH<sub>4</sub> in these concentrations.

Novel technologies are needed to fill this technology gap. Researchers are learning from the fate of CH<sub>4</sub> in the natural atmosphere. Currently, in the troposphere, the principal natural CH<sub>4</sub> sinks are hydroxyl radicals<sup>[6]</sup>, chlorine atoms<sup>[7]</sup>, minerals in soils and dust<sup>[8]</sup>, soil microbes, plants, and trees. Enhancing or mimicking those natural sinks is the strategy of some early attempts to develop removal technologies for low concentration methane. For example, several

advanced oxidation processes, which produce hydroxyl radicals and chlorine atoms, can transform CH<sub>4</sub> into CO<sub>2</sub>, water vapor, and small amounts of volatile compounds, all of which are much less potent GHGs than the precursor. Relevant chemistry is summarized in Table 1. The basic principles of these conversions are well established and they happen naturally in the atmosphere.

**Table 1. Main advanced oxidation processes to transform methane**

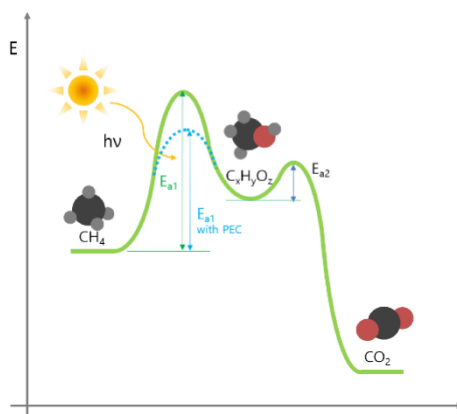
	Heterogeneous photocatalysis	Ozone based photochemistry	Chlorine based photochemistry
Main oxidizing reactive species	hydroxyl radical ( $\cdot\text{OH}$ )	hydroxyl radical ( $\cdot\text{OH}$ )	Chlorine atom (Cl)
Oxidation reactions of methane	$\text{CH}_4 + \text{O}_2 + (\cdot\text{OH or Cl}) \rightarrow \text{CO}_2 + (\text{H}_2\text{O or HCl});$		

As the vast majority of GHG removal work focuses on CO<sub>2</sub>, research into CH<sub>4</sub> removal has been gaining momentum in recent years, particularly those based on the above-mentioned advanced oxidation processes. There is early stage research (including conceptual proposals<sup>[9]</sup>, numerical analysis<sup>[10]</sup>, and experimental work<sup>[11]</sup>) spanning the areas of materials (e.g., TiO<sub>2</sub> and Ag/ZnO photocatalysts<sup>[11a, 12]</sup>, zeolite catalyst<sup>[9b]</sup>), processes (e.g., Cl atoms generated from NaCl of natural sea-spray aerosols<sup>[13]</sup>) and reaction systems (e.g., hydroxyl radical reactions and photolysis modules in ventilation systems<sup>[14]</sup>).

### **1.3 Solar driven gas phase advanced oxidation processes can be good options**

We learned from CO<sub>2</sub> removal that removing low concentration CO<sub>2</sub> at a large scale is energy intensive<sup>[15]</sup>. This applies to CH<sub>4</sub> removal, too. Therefore, among those above-mentioned advanced oxidation processes, the ones that can be driven by solar energy are more attractive.





**Figure 4. Schematic energy diagram of methane oxidation with a photocatalyst. Reproduced from ref.<sup>[16]</sup> with permission from Catalysts, copyright 2021.**

For example, photocatalysis is an ideal way to replace traditional thermal catalysis in some particular applications<sup>[17]</sup>. It employs photons to drive chemical processes instead of thermal energy, and most importantly, photocatalysis enables difficult chemical reactions to occur at mild temperature conditions. Due to the chemical inertness of CH<sub>4</sub> molecules, converting CH<sub>4</sub> via thermal catalysis requires large activation energy. Photocatalysis reaction can generate high-energy charge carriers in the process, which can pre-activate CH<sub>4</sub> and substantially reduce the activation energy<sup>[18]</sup>. This pre-activation process enables thermodynamically unfavorable reactions at room temperature, and overcomes traditional thermodynamic barriers (Figure 4)<sup>[16]</sup>. Compared with thermal catalysis, photocatalytic reactions can theoretically avoid harsh reaction conditions.

This perspective article focuses on solar driven advanced oxidation processes - analyses their challenges, summarizes the state-of-the-art progress, and proposes further solutions.

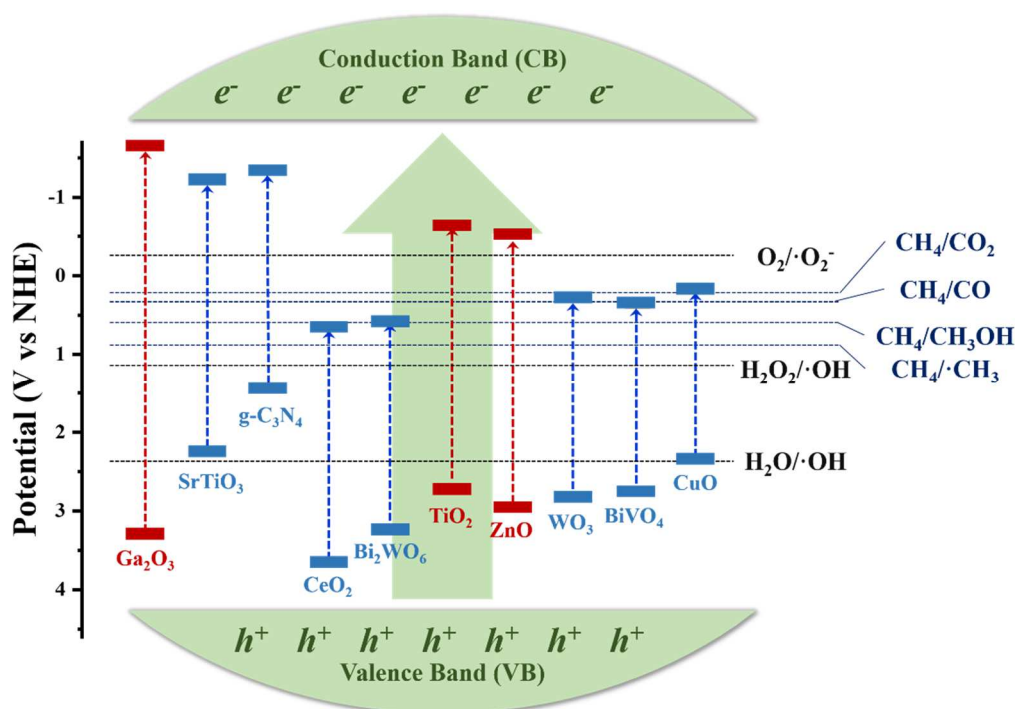
## **1.4 Challenges in Solar driven gas phase advanced oxidation processes**

There are hurdles to overcome in transforming these established principles and early concepts into validated technologies. Two crucial aspects are – (1) Efficacy. We need highly efficient photocatalysts or photochemical processes for the extremely diluted target gas. (2) Upscaling. The scale of any GHG removal technology needs to be significant to have a climate impact while the generation of airflow on a large scale is energy intensive.

In order to respond to all these challenges, this perspective article is organized in the following structure – Section 2, Catalysts in heterogeneous photocatalysis for CH<sub>4</sub> oxidation; Section 3, Processes of homogenous photochemistry for CH<sub>4</sub> oxidation and Section 4, Photoreactors for large scale CH<sub>4</sub> oxidation. Each section is started with the state-of-the-art and is completed with future perspectives.

## **2. Catalysts in heterogeneous photocatalysis for CH<sub>4</sub> oxidation**

Photocatalyst is a key part of a photocatalytic process, which refers to a kind of substance that can induce photocatalytic oxidation-reduction reactions under light irradiation. The primary criterion for a suitable photocatalyst is that it fulfills the thermodynamic requirements of CH<sub>4</sub> oxidation. The common and widely accepted way to present and discuss thermodynamic requirements for photocatalysis is a diagram (as shown in Figure 5) that contains two sets of information: 1) the band structure of electronic energy in photocatalysts, and 2) the redox potentials of the relevant chemical reactions<sup>[18b, 19]</sup>.



**Figure 5. Positions of conduction band and valence band edges of various semiconductors and redox potentials of relevant chemical reactions, with respect to NHE.**

The positions of redox potentials of the relevant chemical reactions indicate their thermodynamic requirements. The redox potentials of oxidizing CH<sub>4</sub> to different products are  $E^\circ(\text{CH}_4/\text{CO}_2) = 0.17 \text{ V}$ ,  $E^\circ(\text{CH}_4/\text{CO}) = 0.32 \text{ V}$ ,  $E^\circ(\text{CH}_4/\text{CH}_3\text{OH}) = 0.65 \text{ V}$ , and  $E^\circ(\text{CH}_4/\cdot\text{CH}_3) = 0.83 \text{ V}$ , versus the normal hydrogen electrode (NHE). The oxidation of CH<sub>4</sub> is initiated by radicals that attack the C-H bond. The redox potentials of commonly involved radicals are  $E^\circ(\text{O}_2/\cdot\text{O}_2^-) = -0.33 \text{ V}$ ,  $E^\circ(\text{H}_2\text{O}_2/\cdot\text{OH}) = 1.07 \text{ V}$ , and  $E^\circ(\text{H}_2\text{O}/\cdot\text{OH}) = 2.30 \text{ V}$ , vs. NHE. [18]

The positions of conduction band (CB) and valence band (VB) edges of various semiconductors indicate their thermodynamic capability to generate active radicals and drive a chemical reaction.<sup>[20]</sup> In this case, the CB of the semiconductor is thermodynamically required to be located higher than the reduction potential of  $\text{O}_2/\cdot\text{O}_2^-$ , while the VB needs to be located below the oxidation potentials of  $\text{H}_2\text{O}_2/\cdot\text{OH}$  and  $\text{H}_2\text{O}/\cdot\text{OH}$ .<sup>[21]</sup>

Therefore, Figure 5 has clearly displayed the thermodynamic requirements for methane oxidation and the thermodynamic capabilities of various photocatalysts. The most suitable photocatalysts for photocatalytic oxidation of CH<sub>4</sub> are TiO<sub>2</sub>, ZnO and Ga<sub>2</sub>O<sub>3</sub>. Recent progress in the field agrees with this and the best results mostly came from photocatalysts based on TiO<sub>2</sub>, ZnO and Ga<sub>2</sub>O<sub>3</sub>.

## 2.1 TiO<sub>2</sub>

Since Japanese scientists Fujishima and Honda discovered that TiO<sub>2</sub> single crystal electrodes were able to split water in 1972, systematic research on TiO<sub>2</sub> photocatalysis has kicked off<sup>[22]</sup>. TiO<sub>2</sub> is the most widely used semiconductor photocatalyst, which is chemically stable, environmentally friendly, and inexpensive.

The vast majority of current work on TiO<sub>2</sub> photocatalyst for CH<sub>4</sub> oxidation is in the field of CH<sub>4</sub> conversion<sup>[22]</sup>, where CH<sub>4</sub> is seen as a platform chemical and appears in high concentrations. The emphasis in this area is on selectivity and avoiding overoxidation to CO<sub>2</sub><sup>[22]</sup>. This makes the research results not directly applicable for oxidation of low concentration CH<sub>4</sub> to CO<sub>2</sub>, but can be inspiring as in some cases there are in-depth discussions into some catalysts and their mechanism of over-oxidation. For example, Song *et al.*<sup>[23]</sup> demonstrated that a platinum decorated TiO<sub>2</sub> photocatalyst was a ‘bad’ sample because of heavy over-oxidation, but this can be a ‘good’ starting point for a different application (i.e., total oxidation of low concentration CH<sub>4</sub>).

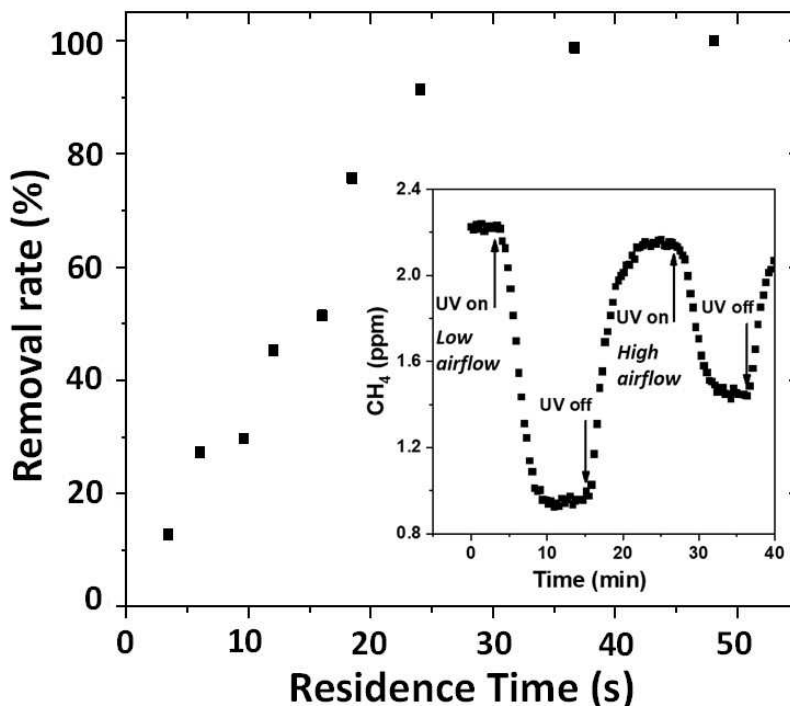
There are scattering of publications in the last decade working towards total oxidation of low concentration CH<sub>4</sub> on TiO<sub>2</sub>. Kleinschmidt and Haeger *et al.* investigated the kinetics of the

oxidation reactions from CH<sub>4</sub> to fully oxidized CO<sub>2</sub>, in a concentration range from 2000 to 15000 ppm<sup>[24]</sup>.

Jin *et al.* evaluated the feasibility of photocatalytic oxidation of ventilation air CH<sub>4</sub> for coal mining fugitive emissions abatement. Results showed that the simulated ventilation air (with CH<sub>4</sub> concentration in the range from hundreds of ppm to 3000 ppm) can be oxidized at ambient temperature by photocatalytic reaction with commercial TiO<sub>2</sub>, however, the reaction rate was slow<sup>[25]</sup>.

To the best of our knowledge, there is no reported research on the photocatalytic oxidation of ~ 2 ppm atmospheric methane. We made the first attempt recently. A flow through photocatalytic reactor was developed to test ~ 2 ppm atmospheric CH<sub>4</sub> in a continuous flow mode, using commercial TiO<sub>2</sub> (P25) as the photocatalyst illuminated by 20 W/m<sup>2</sup> UV light (similar to UV intensity in solar radiation).

As shown in the inset of Figure 6, under an airflow of 0.4 L/min, which is equivalent to a residence time of 12 seconds, the removal rate of CH<sub>4</sub> is 46%. Faster airflows lead to shorter residence time and give lower removal rates. Slower airflows result in longer residence time and provide higher removal rates, which can be as high as 98% when residence time is longer than half a minute (Figure 6).



**Figure 6. Photocatalytic removal of ~ 2 ppm atmospheric CH<sub>4</sub> in a bench top continuous flow reaction system.**

## 2.2 ZnO

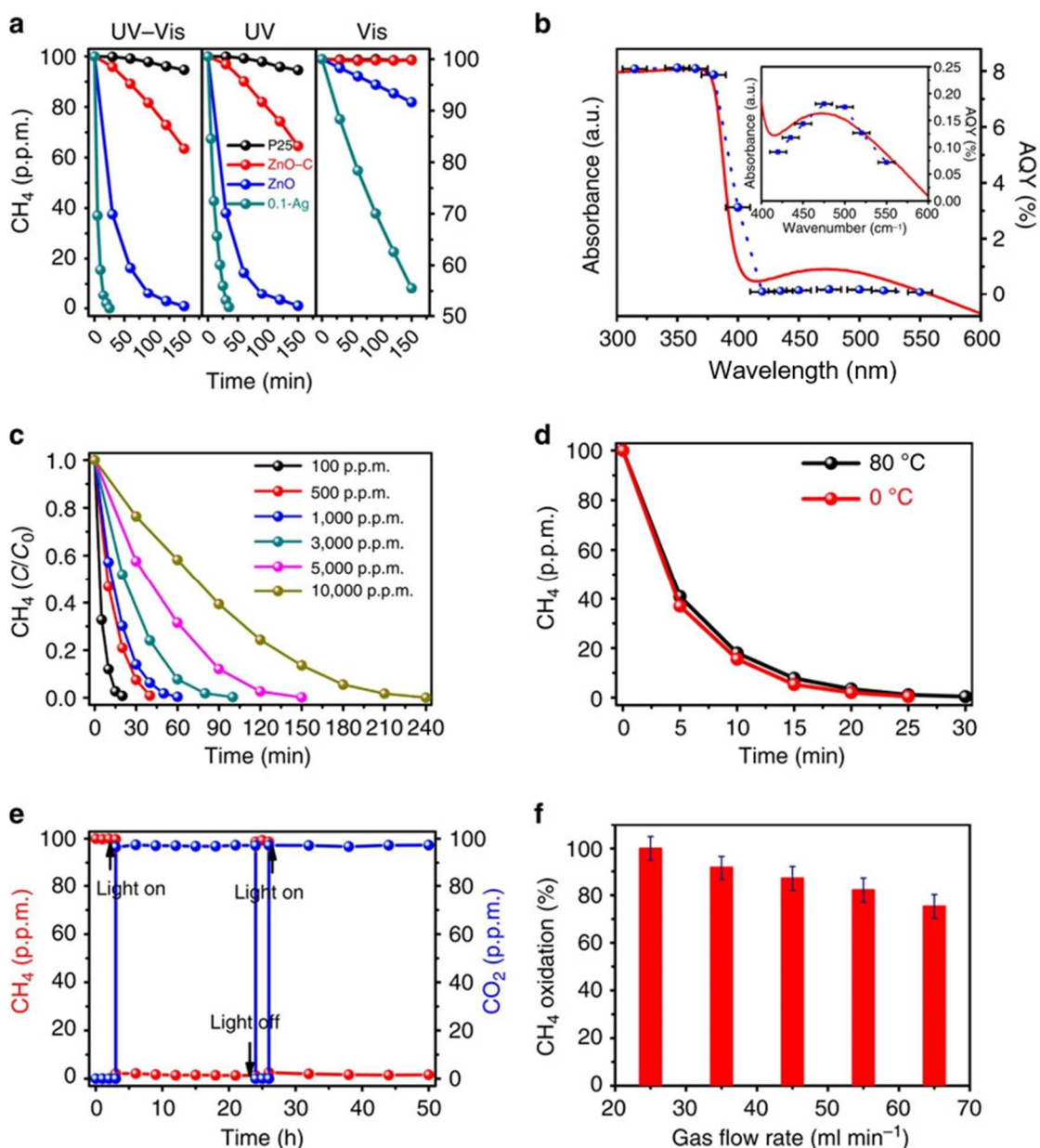
In the field of photocatalytic conversion of CH<sub>4</sub>, where CH<sub>4</sub> is seen as a platform chemical and appears in high concentrations, ZnO has also emerged as a promising photocatalyst<sup>[26]</sup>. It shows many advantages such as suitable optical band structure and electronic properties. ZnO has three different crystalline forms, namely wurtzite, zinc blende, and rock salt structures, among which the wurtzite ZnO crystal structure (the most common because of its high thermodynamic stability) appears most often in CH<sub>4</sub> conversion.

Chen Yi *et al.*<sup>[11a]</sup> extended the research into photocatalytic oxidation of CH<sub>4</sub> in much lower concentrations (100 ~ 10000 ppm). In their study, as shown in Figure 7, 200 – 300 nm sized commercial ZnO can already oxidize a considerable amount of CH<sub>4</sub> at a concentration of 100 ppm. They demonstrated that by reducing their size to ~ 20 nm, ZnO nanoparticles

exhibited high activity for methane oxidation under simulated sunlight illumination, and a small amount (0.1 wt%) of nano silver decoration further enhances the photocatalytic oxidation of CH<sub>4</sub> via the surface plasmon resonance. They achieved a quantum yield of 8% at wavelengths <400 nm and over 0.1% at wavelengths ~470 nm on the silver decorated ZnO nanoparticles.

In addition to the batch-wise test in a fixed-bed mode, they also tested photocatalytic oxidation of CH<sub>4</sub> in a continuous flow mode, which is even more relevant to future practical applications. For 100 ppm CH<sub>4</sub>, 1 – 2 seconds of residence time is sufficient to achieve > 80% removal rate.

The CH<sub>4</sub> concentrations they tested are in the range of 100 to 10000 ppm, and fit well with the concentration range where the technology gap is. This shows great promise for CH<sub>4</sub> GHG removal.

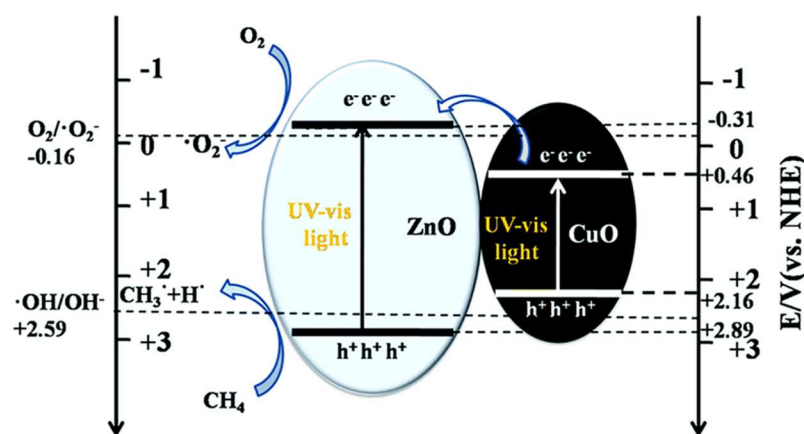


**Figure 7.** (a) Photocatalytic oxidation of methane in a fixed-bed mode with full arc (UV–vis), ultraviolet and visible light illumination, respectively. (b) Ultraviolet–visible diffuse reflectance spectrum and AQYs of the 0.1-Ag sample plotted as a function of wavelength of the incident light. (c) Time evolution of the methane photo-oxidation over the 0.1-Ag sample in the fixed-bed mode under full arc illumination with various initial CH<sub>4</sub> concentration. (d) Influence of the temperature on the methane photo-oxidation activities over the 0.1-Ag sample under full arc illumination. (e) Methane photo-oxidation activity over the 0.1-Ag sample under full arc illumination and a flow-gas mode with gas flow rate of 25 ml min<sup>-1</sup>. (f) Influence of the gas flow rate on the rate of methane oxidation under the flow-gas mode with ± 5% error bars calculated from the sample introduction uncertainty. Reproduced from ref. [11a] with permission from Nature Communications, copyright 2016.



## 2.3 Hybrid photocatalysts

Both TiO<sub>2</sub> and ZnO meet most of the criteria for an ideal photocatalyst, but there are weak points, such as limitation to ultraviolet light and recombination of charge carriers<sup>[20b, 27]</sup>. Introducing co-catalysts or heterojunctions to form hybrid photocatalysts is a promising strategy to overcome these weaknesses<sup>[28]</sup>. The primary criterion for a suitable hybrid photocatalyst is the same as for a single semiconductor (i.e., it needs to fulfill the thermodynamic requirements of CH<sub>4</sub> oxidation).

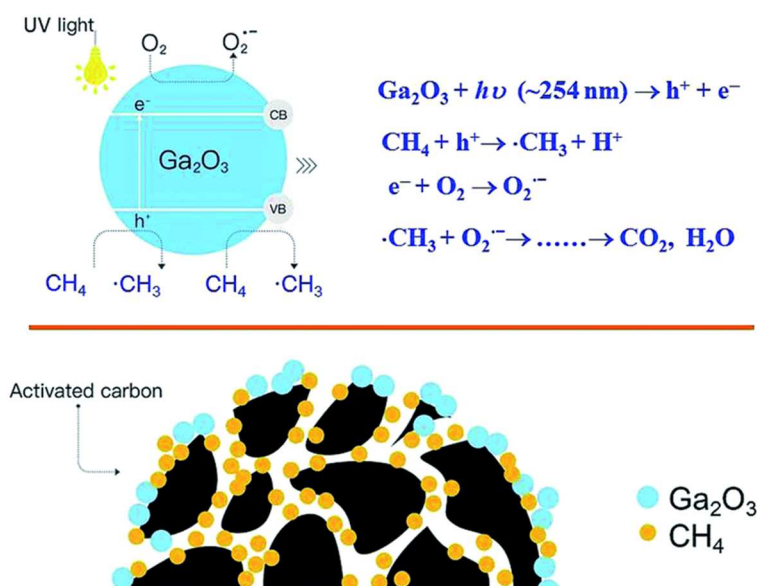


**Figure 8. Schematic of the cocatalytic function of CuO on CH<sub>4</sub> oxidation over ZnO under simulated solar light illumination. Reproduced from ref. <sup>[29]</sup> with permission from Journal of materials chemistry A, copyright 2019.**

Li *et al.*<sup>[29]</sup> successfully synthesized a CuO/ZnO photocatalyst for total oxidation of CH<sub>4</sub>, as shown in Figure 8. The band edge potential of CuO is not suitable to activate the O<sub>2</sub>, but it has a narrow bandgap of 1.7 eV, so the CuO/ZnO composite can absorb much more solar light. Part of *e*<sup>-</sup> in the CB of CuO can be excited to the CB of ZnO, thereby activating the oxygen molecular to generate free radicals.

Wei *et al.*<sup>[30]</sup> prepared β-Ga<sub>2</sub>O<sub>3</sub> supported on activated carbon (AC) composites for efficient photocatalytic oxidation of CH<sub>4</sub> to CO<sub>2</sub> under UV irradiation, as shown in Figure 9.

Among them, AC can enhance the adsorption of CH<sub>4</sub> molecules, thereby transferring CH<sub>4</sub> to the catalytic active component β-Ga<sub>2</sub>O<sub>3</sub>. β-Ga<sub>2</sub>O<sub>3</sub> has a wide bandgap that meets the requirements for strong oxidizing ability and effectively promotes the separation of photogenerated electron-hole pairs. The synergistic effect improves photocatalytic performance.



**Figure 9. Proposed mechanism for photocatalytic oxidation of CH<sub>4</sub> over Ga<sub>2</sub>O<sub>3</sub>/AC composites. Reproduced from ref.<sup>[30]</sup> with permission from RSC advances, copyright 2017.**

## 2.4 The prospect of photocatalysts for low-concentration CH<sub>4</sub>

Learned from the above existing research and the fact that CH<sub>4</sub> GHG is often extremely diluted (e.g., < 2500 ppm), the following aspects could be the major topics for future development on photocatalysts for this application.

High surface area is always a favorable feature for an ideal photocatalyst and this is more desirable to dealing with low-concentration CH<sub>4</sub>. Nano-engineered or mesoporous photocatalysts can be good options. In the authors' research group, more than ten years of research experience has been accumulated in the area of nano-engineering mesoporous TiO<sub>2</sub><sup>[31]</sup>.

It is thermally stable, highly crystalline, reactive, and has large surface area<sup>[32]</sup>, which are all desirable properties as a photocatalyst alone or as a support for more advanced hybrid photocatalysts. Ongoing research is focusing on hybrid photocatalysts based on this mesoporous TiO<sub>2</sub>. Another option is that photocatalysts can be loaded to high surface area supports, for example, porous frameworks (MCM-41<sup>[33]</sup>), and glass fiber mesh/cloth<sup>[34]</sup>.

Enhancing CH<sub>4</sub> adsorption would be another strategy to improve the oxidation of low-concentration CH<sub>4</sub>. The activated carbon (AC) supported β-Ga<sub>2</sub>O<sub>3</sub> composite<sup>[30]</sup> mentioned earlier is a good example. Surface modification of photocatalysts to increase the affinity with CH<sub>4</sub> could be another possible way to enhance CH<sub>4</sub> adsorption.

Visible light utilization is the key to make photocatalysis more applicable. It is one of the major goals that researchers in the field are pursuing. Solar driven photocatalysis for CH<sub>4</sub> GHG removal relies even more on visible light utilization. The encouraging thing is that the cutting-edge progress in this direction is developing so rapidly. Any exciting progress made by someone can inspire the development of visible light photocatalysts for CH<sub>4</sub> GHG removal.

As shown in the above examples (i.e. Ag/ZnO, CuO/ZnO and Ga<sub>2</sub>O<sub>3</sub>/AC), hybrid photocatalysts can be designed to address every challenge discussed above. For example, efficient photocatalysts can be loaded and spread into porous and high surface area substrates to increase photocatalytic surface and enhance CH<sub>4</sub> adsorption; different semiconductors can be utilized to construct heterojunctions to fulfill the thermodynamic requirements for methane oxidation and to expand the visible light utilization; co-catalysts can be combined with semiconductors to boost adsorption and reaction.

### 3. Processes of homogenous photochemistry for CH<sub>4</sub> oxidation

As mentioned earlier, researchers are learning from the natural CH<sub>4</sub> sinks in the troposphere, for example, hydroxyl radicals and chlorine atoms (as summarized in Table 1). These are all homogenous photochemistry processes. Mimicking those natural sinks is also a strategy to develop removal technologies for low concentration CH<sub>4</sub>.

#### 3.1 Ozone (O<sub>3</sub>) photochemistry

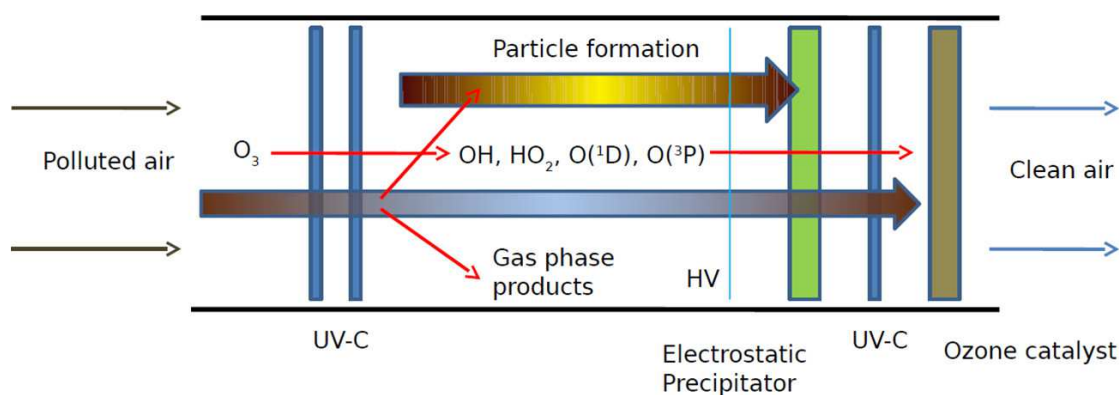
Ozone is a powerful oxidant capable of reacting with a wide range of organic and inorganic compounds. It has a higher oxidation potential ( $E^\circ = 2.08$  eV), second only to fluorine ( $E^\circ = 2.87$  eV) and hydroxyl radicals ( $E^\circ = 2.30$  eV). Since ozone can absorb ultraviolet light of 200~400 nm, its photolysis can promote the generation of highly active substances such as O $\cdot$  and  $\cdot$ OH, which can improve the pollutants removal and mineralization<sup>[35]</sup>.

During photocatalytic oxidation, the formation pathway of hydroxyl radicals is described in Equation 1. In the case of ozone photolysis, oxidants (e.g., O $\cdot$ , Equation 2) will be generated. Ozone can react with H<sub>2</sub>O to generate hydroxyl radicals through electron-hole pairs, light irradiation, or active sites on catalysts<sup>[36]</sup> (Equation 3). Ozone decomposition is primarily carried out by the following five-step chain reaction, as shown in Equations 4-7<sup>[37]</sup>.





To the best of our knowledge, there is no existing publication that demonstrates the removal of low concentration  $\text{CH}_4$  using ozone photolysis. Several most relevant studies are presented here. Li *et al.* and Jin *et al.* studied  $\text{CH}_4$  oxidation using ozone with the assistance of either thermal catalysis or solid catalysts<sup>[38]</sup>. Johnson *et al.* demonstrated a gas-phase advanced oxidation process. They used ozone and UV-C light to produce *in situ* radicals to oxidize air pollution (e.g., propane, cyclohexane, benzene, isoprene, aerosol particle mass), as shown in Figure 10<sup>[14]</sup>. This process and set-up can be adapted to investigate the removal of low concentration  $\text{CH}_4$  using ozone photolysis.



**Figure 10. Photochemical air purification process used in the prototypes. Ozone is added to the airstream, and  $\text{HO}_x$  radicals are generated with UV-C lamps. Particles form and are removed by the electrostatic precipitator. Gas-phase products are removed in a second stage of radical chemistry. Finally, excess ozone is removed using a catalyst. Reproduced from ref.<sup>[14]</sup> with permission from Environmental Science & Technology, copyright 2014.**

### 3.2 Chlorine ( $\text{Cl}^\bullet$ ) photochemistry

In the troposphere, chlorine atoms ( $\text{Cl}^\bullet$ ) are also an important oxidant<sup>[39]</sup>, about 2.5% of

the total CH<sub>4</sub> is oxidized by Cl<sup>•</sup><sup>[40]</sup>. In some polluted coastal areas, Cl<sup>•</sup> accounts for ~10 to >20% of total marine boundary layer CH<sub>4</sub> oxidation<sup>[41]</sup>. Although the <sup>•</sup>OH oxidizes about 90% of CH<sub>4</sub>, it is interesting to target the Cl<sup>•</sup> sink because the speed of CH<sub>4</sub> reaction with Cl<sup>•</sup> is 16 times faster than the one of CH<sub>4</sub> with <sup>•</sup>OH<sup>[42]</sup>. The rate constant of the reaction between CH<sub>4</sub> and Cl<sup>•</sup> is 1.07×10<sup>-13</sup> cm<sup>3</sup> s<sup>-1</sup><sup>[43]</sup>, while the rate constant of the reaction between CH<sub>4</sub> and hydroxyl radicals is 6.20×10<sup>-15</sup> cm<sup>3</sup> s<sup>-1</sup><sup>[44]</sup>.

Polat *et al.* demonstrated a photochemical method for efficient removal of ~ 2 ppm CH<sub>4</sub> via Cl<sup>•</sup> initiated oxidation. The following reactions outline the mechanism of Cl<sup>•</sup> induced CH<sub>4</sub> oxidation technology<sup>[11b]</sup>.

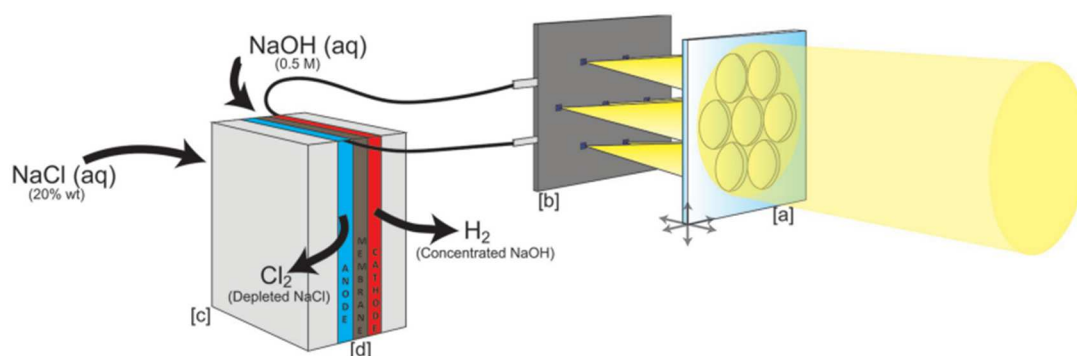


### **3.3 The prospect of homogeneous photochemistry for low-concentration CH<sub>4</sub>**

Compared to heterogeneous photocatalysis, homogeneous photochemistry processes have the advantage of avoiding several potential rate-limiting steps (e.g., gas diffusion towards the solid surface, adsorption and desorption at the gas-solid interface, and surface reactions). This advantage can be more profound when we consider lower concentrations of target gas (e.g.,

low concentration  $\text{CH}_4$  in this context). Therefore, homogeneous photochemistry processes should be more advantageous for large scale applications of low concentration  $\text{CH}_4$  GHG removal. The next question is how we can produce a large amount of ozone or chlorine. Here we take chlorine as an example, as it reacts much faster with  $\text{CH}_4$  than ozone.

It is possible to generate  $\text{Cl}^\bullet$  by UV photolysis of chlorine gas ( $\text{Cl}_2$ ), which is produced at a large scale by the chlor-alkali processes (e.g., electrolysis of sodium chloride salt ( $\text{NaCl}$ ) aqueous solutions, or electrolysis of melted  $\text{NaCl}$ ). These processes can all be integrated with solar cells to utilize solar energy, as shown in Figure 11<sup>[45]</sup>.



**Figure 11. Solar chlor-alkali device overview. a) Optical planar concentrator, lenses array. b) Triple-junction Gas-based solar cells mounted on PCB. c) Electrolyzer 3D printed metallic flow plates. d) Electrochemical cell, composed of a nickel cathode and a DSA insoluble anode, separated by a cation exchange membrane. Reproduced from ref.<sup>[45]</sup> with permission from Global Challenges, copyright 2017.**

It is also possible to generate a large amount of  $\text{Cl}^\bullet$  from Iron (III)/Iron (II) photo-catalyzed reaction by UV at 365 nm, a natural catalytic process<sup>[46]</sup>. It involves the illumination of an acidified aqueous solution of Fe (III), which induces a photochemical reduction of Fe (III) to Fe (II) and the formation of  $\text{Cl}^\bullet$ . Under the marine boundary layer, the Fe (II) species formed are re-oxidized and  $\text{FeCl}_3$  is rapidly regenerated, making a profit from abundant sea brine which contains  $\text{NaCl}$  and provides excess chloride ions<sup>[47]</sup>. Wittmer *et al.* demonstrated

photochemical activation of  $\text{Cl}^*$  by dissolved iron in artificial sea-salt aerosol droplets or by highly dispersed iron oxide ( $\text{Fe}_2\text{O}_3$ ) aerosol particles exposed to gaseous  $\text{HCl}$ <sup>[13]</sup>.

## **4. Photoreactors for large scale $\text{CH}_4$ removal**

In order to demonstrate the feasibility of solar-driven gas phase advanced oxidation processes, the design of photoreactors is an equally critical area. It can scale up the laboratory tests and enable industrial applications.

### **4.1 Photoreactors at $\text{CH}_4$ emission sources where there are defined outlets**

There are two areas of tackling  $\text{CH}_4$  GHG, e.g., reducing the emissions of  $\text{CH}_4$  at their sources and removing atmospheric  $\text{CH}_4$  from the open air. The methodologies in these two areas are different because of the different scenarios.

When there are defined outlets available, many existing designs of various gas phase photoreactors are applicable, for example, solar-driven tubular reactor to treat polluted airstreams<sup>[48]</sup>, and internal-illuminated monolith photoreactor<sup>[49]</sup>. There are comprehensive review articles available<sup>[50]</sup> and any new progress in the field can feed into the development of photoreactors for applications at  $\text{CH}_4$  emission sources.

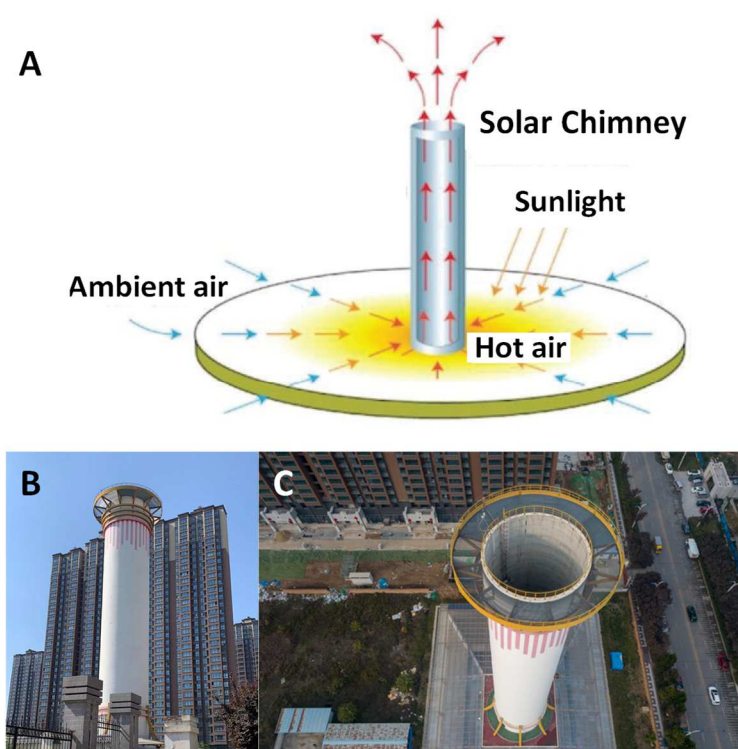
### **4.2 Photoreactors for large scale $\text{CH}_4$ removal in the open air**

In the open air, sufficient airflow is required to process extremely dilute  $\text{CH}_4$ . de Richter et al. proposed a method to perform large scale  $\text{CH}_4$  oxidation using a solar chimney as an air



moving device and coupling it with photocatalytic and/or photochemical processes<sup>[9a]</sup>.

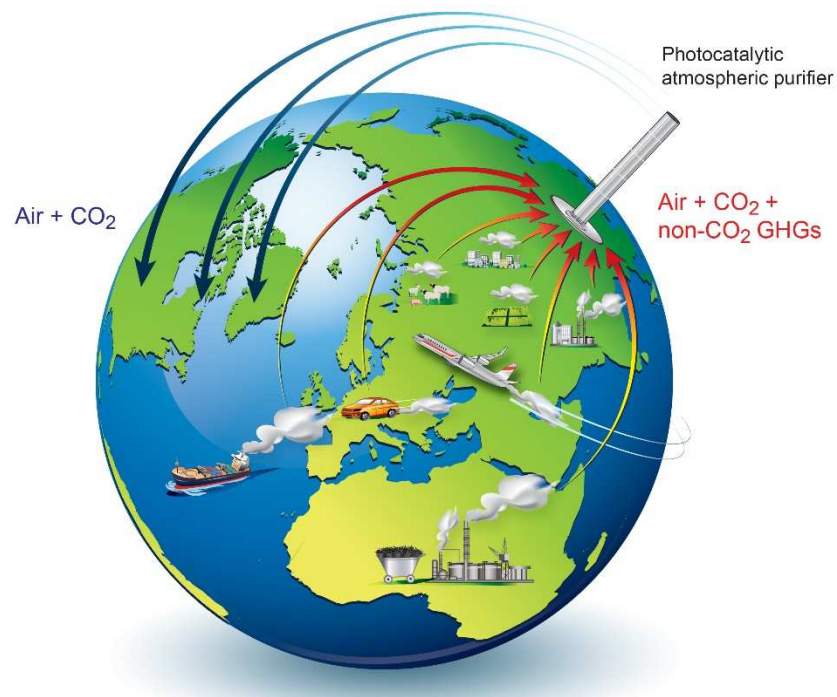
A solar chimney (SC, as shown in Figure 12A) involves, a) a large greenhouse used as a solar collector where the air is heated to create an artificial updraft; b) a tall tower or chimney in the centre of the greenhouse to build up the stack effect<sup>[9a, 51]</sup>. One SC prototype has been built in 2018 in the city of Xi'an in China<sup>[52]</sup>, with the purpose of air purification as shown in Figures 12B and 12C.



**Figure 12: A) A scheme of the working principle of solar chimney; B) and C) Photographs of the SC prototype currently visible in the city of Xi'an, China. Pictures taken by one of the co-authors.**

The solar collector and the chimney can be much larger and taller than this prototype. Then turbines can be added at the bottom of the chimney to generate electricity. This makes it a solar chimney power plant (SCPP). A prototype SCPP with a 46,760 m<sup>2</sup> solar collector and a 195 m high chimney was built and fully tested in 1982-1989<sup>[53]</sup> in Manzanares, Spain.

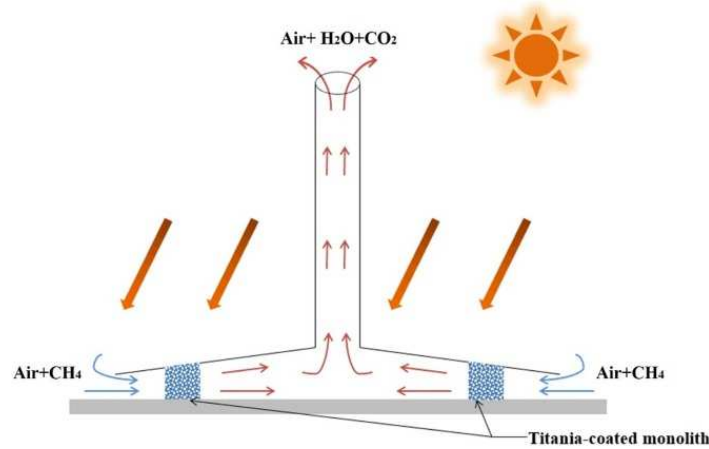
For both SC and SCPP, photocatalytic and/or photochemical processes can be coupled under the solar collector and/or in the chimney, where a large amount of airflow can be processed, as shown in Figure 13<sup>[9a]</sup>.



**Figure 13: Artist's representation of the GHG removal technologies by photocatalytic-SCs. Reproduced from ref.<sup>[9a]</sup> with permission from Progress in Energy and Combustion Science, copyright 2017.**

Ming *et al.* used computational fluid dynamics (CFD) models to investigate the performance and influencing factors of photocatalytic oxidation of CH<sub>4</sub> under SCPP-photocatalytic reactor (PCR) system<sup>[10a]</sup>, as shown in Figure 14. The PCR was designed based on a honeycomb monolithic photoreactor. The flow characteristics of the system under different PCR dimensions were also analyzed, in which the pore diameter and length of the PCR had the largest effects on flow performance, including pressure drop, flow velocity and volume flow rate. When the channel diameter of the honeycomb PCR was 4 mm and its length

is 8 m, the SCPP-PCR system can remove 21,312 g CH<sub>4</sub> per day.

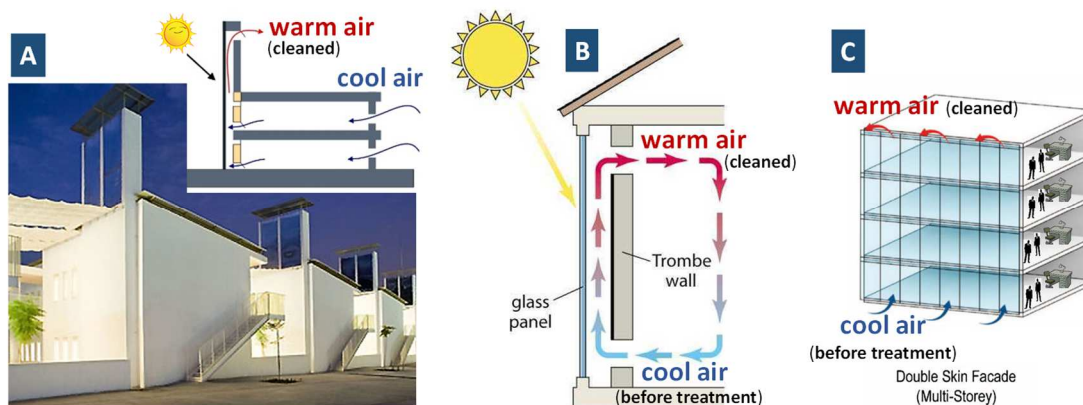


**Figure 14. Solar chimney power plant integrated with a photocatalytic reactor (SCPP-PCR) for atmospheric methane removal. Reproduced from ref.<sup>[10a]</sup> with permission from Solar Energy, copyright 2021.**

Huang *et al.*<sup>[10b]</sup> evaluated the feasibility of an SCPP-PCR as a large-scale photocatalytic reactor for removing atmospheric CH<sub>4</sub>. They calculated the potential of CH<sub>4</sub> removal in relation to the dimensions and configuration of SCPP and different types of photocatalysts (e.g., TiO<sub>2</sub>, Ag-doped ZnO). Night operation strategies and further improvements were also discussed.

### 4.3 The prospect of photoreactors development

Capital investment and land footprint could be some potential hurdles before giant SC/SCPP can be widely applied. With the same principle as SC, there are other three formats of solar updraft devices (namely Trombe wall, double skin façade, and ventilation solar chimney, Figure 15). When combined with advanced oxidation processes, they can provide more versatile applications for the above-mentioned two scenarios (e.g., at CH<sub>4</sub> emission sources and in the open air).



**Figure 15. Other three formats of solar updraft: A) ventilation solar chimney, B) Trombe wall, and C) double skin facade.**

In the future development of global GHG removal, direct air capture (DAC) systems may play an important role. Once DAC plants exist, we would have a large amount of airflow. Therefore, de Richter et al. proposed that, to profit from this existing infrastructure, CH<sub>4</sub> removal processes could be integrated to enhance the capture/removal of GHGs, as shown in Figure 16<sup>[54]</sup>. Progresses in the fields of heterogeneous photocatalysts, homogeneous photochemical processes and photoreactors will all be critical to making this strategy feasible.



**Figure 16. A hypothetical industrial DAC device with added photocatalyst, proposed to oxidize CH<sub>4</sub>. Reproduced from John Bradley<sup>[55]</sup>.**

There are other nature mimicking ideas<sup>[5b]</sup> that may be inspiring for researchers to design other photoreaction systems, which can be deployed at a large scale.

## 5. Conclusion

In this perspective, we focus on heterogeneous photocatalysts, homogeneous photochemical processes, and photoreactors for CH<sub>4</sub> greenhouse gas removal. By summarizing some recent progress and future prospects, we try to inspire some solutions to fill the technology gap of removing low concentration (< 2500 ppm) CH<sub>4</sub>, which appears in the atmosphere and from a wide range of CH<sub>4</sub> emissions.

The achievements so far include conceptual proposals, numerical analysis and early stage experimental work, spanning the areas of photocatalysts, photochemical processes and reaction systems.

The fundamental challenge is that any GHG removal technology needs to be deployed at climate relevant scale. Therefore, it is important that solar driven gas phase advanced oxidation processes can remove low concentration methane at a large scale. This requires cheap and efficient photocatalysts, as well as cheap and large reaction systems.

It is positive to envisage that there are potential solutions. The cutting-edge progress in newer and better photocatalysts is developing so rapidly thanks to the large photocatalysis research community. Any exciting progress can be adapted to improve CH<sub>4</sub> GHG removal. For homogeneous photochemical processes, there is a lot to learn from the natural hydroxyl radical

and chlorine sinks of CH<sub>4</sub> happening all the time in the atmosphere. To make any solar-driven gas phase advanced oxidation process deployable at a climate significant scale, big ideas and collective efforts are needed.

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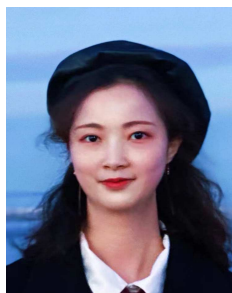


Methane (CH<sub>4</sub>) is a potent greenhouse gas and the second highest contributor to global warming. Developing large-scale methane removal methods is one of the most effective strategies to reduce rapidly the CH<sub>4</sub> emissions and thus to limit global warming. We analyzed the challenges and prospects of solar-driven gas phase advanced oxidation processes for CH<sub>4</sub> removal.

Author biographies:



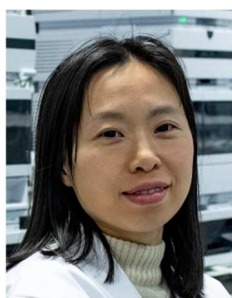
Jie Zhang graduated from Weifang University of Science and Technology in 2020 with a Bachelor's degree. She is currently a master's degree student in Prof Xiaohua Lu's group at the School of Chemical Engineering of Nanjing Tech University. Her research interests include photocatalysis and the high-value utilization of biomass materials.



Yuyin Wang received her B.Sc. degree from YangZhou University of in 2020. Currently, she is studying for a Ph.D. under the supervision of Dr Wei Li in the University of Edinburgh. Her research mainly focuses on catalytic processes and materials for methane oxidation.



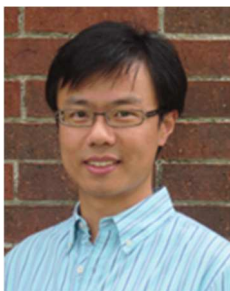
Yun Wang, majoring in chemical engineering and technology, completed his bachelor's degree in 2021 at Weifang University of Science and Technology. In the same year, he joined Prof Xiaohua Lu's research group at in Nanjing Tech University and is currently focusing on photocatalytic removal of non-CO<sub>2</sub> greenhouse gases from the atmosphere.



Dr Yang Bai is a Senior Analytical Officer in the School of GeoScience at the University of Edinburgh. She studied chemical engineering at the Nanjing University of Technology and obtained B.Eng. in 2003 and Ph.D. in 2009. Her research interests are in the areas of methane emissions and greenhouse gas removal.



Prof Xin Feng holds Ph.D. in chemical engineering from Nanjing University of Technology, is currently a professor in the School of Chemical Engineering, Nanjing Tech University. Mainly engaged in the research of low dimensional nanomaterials for composites and catalysis.



Prof Jiahua Zhu received his Ph.D. in Chemical Engineering from Lamar University, joined the Department of Chemical and Biomolecular Engineering at the University of Akron as an assistant professor in 2013. He is currently a professor in the School of Chemical Engineering, Nanjing Tech University. Current research directions include basic research on carbon-based nanocomposites, and explore their applications in emerging fields such as energy conversion, catalysis, and environmental remediation.



Prof Xiaohua Lu holds Ph.D. in chemical engineering from Nanjing University of Technology, is currently a professor at the School of Chemical Engineering, Nanjing University of Technology, deputy director of the Academic Committee of the State Key Laboratory of Materials Chemical Engineering. In 1999, he was awarded the National Fund for Distinguished Young Scholars, Chief Scientist of the 973 Project, German Humboldt Scholar, National Education System Model Worker and National Model Teacher, "Chinese Doctorate Recipient with Outstanding Contribution" by the State Education Commission.



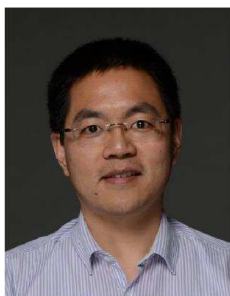
Prof Liwen Mu received his Ph.D. from the Nanjing University of Technology in 2012. From 2015 to 2019, he worked as a postdoctoral fellow at the University of Akron in the United States and Luleå University of Technology in Sweden. He is currently a professor in the School of Chemical Engineering, Nanjing Tech University. His current research focuses on biomass conversion and utilisation.



Prof Tingzhen Ming, Chair Built Environment and Energy Engineering, School of Civil Engineering and Architecture, Wuhan University of Technology. Subject Editor of Journal of Thermal Science. His research interests are: CFD, heat and mass transfer, urban planning, building and environment, pollutant dispersion. Prior to join in WHUT, He worked as an associate professor at Huazhong University of Science and Technology. Prof. Ming published over 150 journal papers, 3 books in Elsevier Academic Press, Springer Press, and Science Press (China).



Dr Renaud de Richter is a scientific advisor to Methane Action. He graduated from the organic chemistry department of the engineering school of chemistry of Montpellier, France in 1985 with a Master's degree in chemistry. Renaud received his PhD degree in 1989 from University of Science and Technology in Montpellier, France. His current research interests include the application of photocatalytic chemistry and processes for environmental protection to fight climate change and for remediation purposes.



Dr Wei Li joined the University of Edinburgh in 2021 as a Senior Lecturer in Chemical Engineering. He studied chemical engineering at the Nanjing University of Technology, obtaining his B.Eng. and Ph.D. in 2008. His first employment started at The University of Hong Kong (Department of Chemistry), followed by research positions at the Ludwig-Maximilians-Universität München (Department of Physics) and the University of Liverpool. Before he joined UoE, Dr Li also had worked at the National Graphene Institute, University of Manchester, and Aston University. His expertise includes nanoengineering of photocatalytic materials and reaction engineering of photocatalytic processes.