# Global Warming, Energy Transition and Sustainable Agriculture: The Role of Photocatalytic Materials in shaping the future

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The growing need for sustainable agricultural practices impacts various aspects since fertilizer production, pesticide management, until addressing greenhouse gas emissions ($N_2O$, $NO_x$, $CH_4$, and $CO_2$). In common, all these problems need to be addressed by sustainable solutions that reduce associated environmental impacts. Innovative approaches include the development of photocatalytic materials that harness sunlight for catalyzing reactions, which include contaminant oxidation reactions, the reduction of $CO_2$ and $N_2$ to chemicals, and, ultimately, the conversion of biomasses to valuable products. However, the technology level is still incipient, facing the challenge's size, proportional to the massive size of agricultural demand, requiring an oriented process to understand which applications are, in fact, closer to society. From pesticide decontamination to solar-based nitrogen reduction to fertilizers, there is a long road with plenty of possibilities for photocatalysis–agriculture nexus.

## Introduction

Agriculture, a vital human activity, is significantly influenced by modern chemical methods, though the wider public may not fully grasp the implications. The sector's growth relies on agrichemicals, including nutrients like fertilizers and protective agents like pesticides [1]. However, the development of the role of catalytic materials, crucial for agricultural productivity, remains underappreciated. The "green revolution," initiated by advancements like the Haber-Bosch process for ammonia production, revolutionized farming practices, significantly boosting global food production and population growth (Figure 1) [2]. It highlights the strong, yet often overlooked, connection between catalytic materials and agricultural advancement. The increasing demand for agricultural production has led to a reliance on monocultures and crops for animal feed, subsequently raising the need for fertilizers and specific pesticides. While this approach addresses immediate needs, it often results in ecological imbalances such as water eutrophication and greenhouse gas emissions. Additionally, climate change has exacerbated pest problems, necessitating more pesticide use, which sometimes contaminates food. These factors contribute to a public perception of agricultural chemistry as harmful, underscoring the need for a new paradigm in agriculture that minimizes chemical use and improves resource efficiency [3].

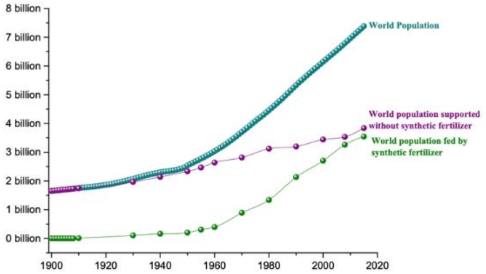

**Figure 1.** The impact of synthetic nitrogen fertilizers on the global population, estimating how many people could be sustained with and without these fertilizers, which are predominantly produced using the Haber-Bosch process. The data suggests that over half of the world's population depends on synthetic nitrogenous fertilizers for food production. Based on a dataset from Our World in Data [4], under Creative Commons license.

Thus, there is a growing interest in integrating photocatalysis with agricultural processes, leveraging sunlight as a renewable energy source. While the potential for light-driven reactions in agriculture is vast, the development of necessary catalytic materials and economic feasibility remain largely unexplored. Current research primarily focuses on using semiconductors in oxidative reactions to remove pesticides from water. Additionally, exploring various reactions, such as greenhouse gas treatment and energy conversion, is crucial in this field. A review of the literature [5] shows that photocatalytic materials present various current applications in agriculture, such as degrading pollutants, especially pesticides, and treating animal medicines and hormones. They may also be explored for direct use as inorganic pesticides on plants. In addressing environmental concerns, these materials can help to reduce greenhouse gases like $NO_x$, $N_2O$, $CH_4$, and $H_2S$. In biorefining, they can play a role in cellulose bleaching and glycerol reforming. Additionally, they can contribute to $CO_2$ photoreforming for energy storage and in converting $N_2$ to $NH_3$, an environmentally friendly alternative to the conventional Haber-Bosch process for fertilizer production (Figure 2).

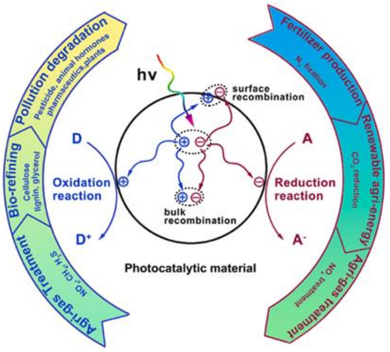

**Figure 2.** Overview of possible reactions driven by photocatalysts, considering the oxidative ($h^+$) and reductive ($e^-$) contributions of excitons.

However, the difficulties remain unsolved despite substantial research conducted in the previous decades. Nevertheless, the substitution of more dangerous agrichemicals with newer ones that have more excellent biodegradability tends to restrict the use of these technologies. This limitation arises due to the need to consider the specific conditions of the agricultural setting, such as the presence of liquid effluents containing numerous components, large volumes of water, and extensive environmental contamination. Alternatively, there are opportunities pertaining to the agricultural value chain, specifically exploring the conversion of byproducts (such as residues, fibers, and fermentation products) into higher-value commodities through the utilization of sunlight. The photocatalytic processes have the potential to be used in the biorefining of agricultural products and the generation and conversion of valuable chemicals and energy. These techniques have the potential to enhance the overall energy efficiency in agriculture and, hence, decrease the carbon footprint. These catalysts can also be applied to reduce greenhouse gases, which can then be converted into nutrients for the soil. Furthermore, it is crucial to consider the future outlook for fertilizer consumption, which may hold significant value in the advancement of photocatalytic materials despite being in its early stages of development. It is necessary to thoroughly address the numerous opportunities by analyzing the application needs and enhancing the sustainability of present agricultural supply operations.

Heavy investment in material design in recent years highlights photocatalysis as a promising solution for sustainable agriculture. Early studies used simple semiconductor materials as photocatalysts, but subsequent advancements include doping, cocatalysts, sensitizers, heterojunctions, and nanostructuring. While efforts like doping and heterojunction have been made to improve photocatalytic performance, practical usage is still far off. $TiO_2$ and ZnO are still the most investigated photocatalysts for the abovementioned applications, although they have a broad bandgap, limiting solar irradiation absorption. In recent years, innovative photocatalytic materials such as MOFs, layered double hydroxides, g-$C_3N_4$, and perovskites have gained popularity. Due to their unique topologies, these materials are intriguing. The adaptable morphology and structure allow for flexible regulation of photocatalytic properties. Geometrical structure engineering enhances photocatalytic activity by facilitating electron-hole separation and transmission due to reduced size. Research has focused on 0D (QD), 1D, 2D, and porous structures, which exhibit exceptional features. To create effective photocatalysts, numerous strategies are used to customize the materials' components, electrical, and geometric structures simultaneously.

Despite extensive research on photocatalytic materials and all the listed opportunities, their use in agriculture remains limited to the lab scale due to low efficiency and stability. Challenges exist in building efficient photocatalysts on a large scale, as well as pilot-scale solar plants are necessary to prove the benefits before commercialization in agriculture. The lack of demonstrations in higher TRL (>6) is a critical point that needs to be attacked by the whole researcher community.

### ***References***

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