



Photocatalyzed Production of Urea as a Hydrogen–Storage Material by TiO₂–Based Materials

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Abstract: This review analyzes the photocatalyzed urea syntheses by TiO_2 -based materials. The most outstanding works in synthesizing urea from the simultaneous photocatalyzed reduction of carbon dioxide and nitrogen compounds are reviewed and discussed. Urea has been widely used in the agricultural industry as a fertilizer. It represents more than 50% of the nitrogen fertilizer market, and its global demand has increased more than 100 times in the last decades. In energy terms, urea has been considered a hydrogen-storage (6.71 wt.%) and ammonia-storage (56.7 wt.%) compound, giving it fuel potential. Urea properties meet the requirements of the US Department of Energy for hydrogen-storage substances, meanly because urea crystalizes, allowing storage and safe transportation. Conventional industrial urea synthesis is energy-intensive $(3.2-5.5 \text{ GJ ton}^{-1})$ since it requires high pressures and temperatures, so developing a photocatalyzed synthesis at ambient temperature and pressure is an attractive alternative to conventional synthesis. Due to the lack of reports for directly catalyzed urea synthesis, this review is based on the most prominent works. We provide details of developed experimental set-ups, amounts of products reported, the advantages and difficulties of the synthesis, and the scope of the technological and energetic challenges faced by TiO₂-based photocatalyst materials used for urea synthesis. The possibility of scaling photocatalysis technology was evaluated as well. We hope this review invites exploring and developing a technology based on clean and renewable energies for industrial urea production.

Keywords: TiO₂–based materials; photocatalysis; urea; hydrogen storage; ammonia storage; green ammonia; nitrate reduction; carbon dioxide reduction

1. Introduction

Synthetic nitrogen–based fertilizers such as urea (CO₂(NH₂)₂) have become essential for intensive agriculture and global food production. The industrial production of urea began in the 1920s with the development of the Bosch–Meiser process, and since then, its global demand has been increasing year after year. Approximately 90% of urea is used as a fertilizer, and the remaining percentage represents its uses as an additive in different industries. Urea can be used as a ruminant feed additive [1,2] or chemically synthesized to make urea–based herbicides or pesticides [3–5]. Other non–fertilizer uses of urea include manufacturing plastic materials, additives in fire retardants, tobacco products, some wines, and the cosmetic industry [6]. Urea is even used in fuels, helping reduce NOx gases in combustion engines through selective catalytic reduction (SCR) systems [7,8]. However,



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). one of the most exciting uses of urea is in energy storage technology because urea can be considered a hydrogen and ammonia storage material.

Previous research has widely documented different energy storage technologies, their classifications, properties, and applications [9–11]. A convenient energy storage technology is chemical energy storage (CES), which can use reversible chemical reactions to store and use energy. Most studies on CES technologies are based on hydrogen energy storage (HES) because hydrogen gas (H₂) is considered a clean energy carrier [12]. The combustion of hydrogen with oxygen produces water vapor, and from the reverse reaction, it is possible to produce green hydrogen:

$$2 \operatorname{H}_2 + \operatorname{O}_2 \to 2 \operatorname{H}_2 \operatorname{O} \tag{1}$$

$$2 \operatorname{H}_2 \operatorname{O} \to 2 \operatorname{H}_2 + \operatorname{O}_2 \tag{2}$$

CES allows the indirect availability of hydrogen, as it occurs in aqueous solutions of ammonia (NH₃) or methanol (CH₃OH). Unlike carbon–based hydrogen–storage substances, nitrogen compounds can develop cleaner combustion because their reaction products are nitrogen (N₂), water, and a low concentration of CO₂, as in the case of urea (CO(NH₂)₂) combustion [13,14]:

$$2 \operatorname{CO(NH_2)}_2 + 3 \operatorname{O}_2 \to 2 \operatorname{N}_2 + 2 \operatorname{CO}_2 + 4 \operatorname{H_2O}\left(\Delta \hat{H}^0_{rxn} = -635 \text{ kJ mol}^{-1}\right)$$
(3)

The energy interest in urea arises when it simultaneously considers its capacity to store ammonia (52.7 wt.%) and hydrogen (6.71 wt.%). There are also other hydrogen-storage compounds with a higher percentage of hydrogen than urea, such as ammonia (17.6 wt.%), hydrazine (11.2. wt.%), and methanol (12.6 wt.%) or cyclohexane (7.2 wt.%), which could be like liquid fuels. However, they still face problems about safety because they are flammable, toxic, or environmentally hazardous substances [15]. Urea, on the other hand, has better properties than some liquid fuels, such as energy density (16.9 MJ L⁻¹) and high solubility (1079 g L⁻¹), and it also overcomes the disadvantages of toxicity and volatility [16]. Urea is a stable compound at room temperature and atmospheric pressure, non–flammable, crystallizable, and storable in granules or pellets, allowing easy and safe storage and transportation [15].

Urea is an interesting candidate for alternative fuels since it reaches the goals set by the United States Department of Energy (US DOE), which has defined requirements that hydrogen–storage materials must meet to be used as fuels [17]. Some goals of the US DOE projected for the year 2025 for hydrogen–storage materials include [18]:

- High storage capacity, a minimum of 6.5 wt.% of H₂ abundance, and 50 g L⁻¹ of H₂ availability in the material;
- Low cost, less than USD 266 per kilogram of hydrogen;
- Operating ambient temperature between $-40 \,^\circ\text{C}$ and $60 \,^\circ\text{C}$;
- Low toxicity, non–explosive, and possibly inert storage for water and oxygen.

Therefore, urea is an attractive alternative for fuel applications, suitable for electrooxidation systems such as direct combustion cells where urea degradation produces nontoxic compounds such as CO_2 , N_2 , and H_2 , according to Equation (2) [14]. Moreover, it is possible to use urea (U) mixed with ammonium nitrate (NH₄NO₃, AN) to produce fuel (UAN fuel), which consists of 60% AN, 15% urea, and 25% water by mass, generating a gas effluent composed of 73% water, 21.6% N₂, and 5.4% CO₂ [19]. Another fuel option is a mixture of ammonium hydroxide (NH₄OH, AH) with urea (AHU fuel) with relatively clean combustion effluent products [13]. The combustion reactions for UAN and AHU are presented below:

$$3 \text{ NH}_4 \text{NO}_3 + \text{CO}(\text{NH}_2)_2 + 5.56 \text{ H}_2 \rightarrow 4 \text{ N}_2 + 13.56 \text{ H}_2\text{O} + \text{CO}_2 \left(\Delta \hat{H}^0_{rxn} = -446 \text{ kJ mol}^{-1}\right)$$
(4)

$$NH_4OH + 0.3 CO(NH_2)_2 + 1.4 H_2O + 1.3 O_2 \rightarrow 0.8 N_2 + 4.6 H_2O + 0.3 CO_2 \left(\Delta \hat{H}^0_{rxn} = -571 \text{ kJ mol}^{-1}\right)$$
(5)

Despite the advantages and possible uses of urea as a hydrogen–storage material and fuel, its use has not yet been massively exploited. One of the main problems is that its industrial production continues to be energy–intensive. This paper revisits one of the least explored urea synthesis alternatives, photocatalyzed synthesis by TiO_2 –based materials. Few studies have investigated the photocatalyzed synthesis of urea using TiO_2 –based materials, which were analyzed in this review, evaluating the systems used, amounts of products formed, difficulties, advantages, disadvantages, and projections of this technology as a natural alternative to industrial production.

2. Industrial Synthesis of Urea and Alternative Syntheses

The industrial production of urea from CO_2 and NH_3 began in 1922 with the development of the Bosch–Meiser process. According to this process, about 0.750 tons of CO_2 must be consumed to produce a ton of urea. However, urea is not recognized as a storage or capture species of CO_2 since 2.27 tons of CO_2 –eq are released per ton of CO_2 [20]. Nowadays, the industrial process continues to use the same reactions tied to a pressure higher than 100 atm and temperatures above 170 °C to form ammonium carbamate, which subsequently dehydrates to generate urea and water [21] as presented in the following reactions:

$$2 \operatorname{NH}_3 + \operatorname{CO}_2 \rightleftharpoons \operatorname{NH}_2 \operatorname{COONH}_4 \tag{6}$$

$$\mathrm{NH}_{2}\mathrm{COONH}_{4} \rightleftharpoons \mathrm{H}_{2}\mathrm{O} + \mathrm{CO}(\mathrm{NH}_{2})_{2} \tag{7}$$

There are few reports of urea synthesis under ambient conditions. A proposed alternative to industrial synthesis is to form urea by negative corona discharge in the gas phase, in which electronegative ammonia anions and radicals can reduce CO₂ into solid urea with an 82.16% yield at 1 atm and 20 °C [22]. Catalysts such as hematite (α -Fe₂O₃) nanowires [23], zinc oxide (ZnO) [24], and cupric oxide (CuO) [25] have been used to produce urea as well. The catalysts as α -Fe₂O₃ adsorb H₂, N₂, and CO₂ to form urea under the influence of magnetic fields with high yield from >600 ppm to 11,243 ppm depending on catalyst, gas flow rates, and magnetic field. In terms of the use of catalysts, transition metals such as palladium (Pd), nickel (Ni), ruthenium (Ru), cobalt (Co), rhodium (Ro), and gold (Au), among others, have been used to convert amines into urea by oxidative carbonylation [26], and techniques such as catalysis in ionic liquids [27–29]. These syntheses are more sustainable alternatives to the reagent phosgene (COCl₂) used for synthesizing compounds from amines such as urea and its derivatives. However, they have not yet been used at industrial levels.

Phosgene has been used to produce urea and urea–based compounds. This powerful reagent is used to generate carbonyl groups due to its highly electrophilic center, which is nucleophilically attacked by alcohols and amines, allowing the formation of compounds of agrochemical interest, such as urea [30], as described in the following reaction:

$$COCl_2 + 4 NH_3 \rightarrow CO(NH_2)_2 + 2 NH_4Cl$$
(8)

Although the compounds synthesized with phosgene show good yields (60–90%), it is a highly toxic compound, and the Chemical Weapons Convention has strictly regulated its use and manufacturing. Phosgene was even used as a chemical weapon in World War I (1914–1918), known as "white star". Nowadays, phosgene substitutes have been used to design new synthesis routes to urea or urea derivatives. Some alternatives to phosgene have been catalysts or reagents such as dimethyl carbonate, dimethyl sulfate, ethylene carbonate, bis(4–nitrophenyl) carbonate, 1–1–carbonylbisimidazole, S,S–dimethyldithiocarbonate, among others [27,31,32]. However, these alternative syntheses have not been developed on an industrial scale for urea. The electrochemical synthesis of urea has shown a high potential to be considered an alternative to industrial production. The first report was presented in 1995 by M. Shibata, K. Yoshida, and N. Furuya [31]. Their work opened a new field of exploration for this type of synthesis with the main advantage of controlling the electrochemical potential for forming urea from nitrate ions (NO₃⁻) as a nitrogen source and CO₂ as a carbon source. However, electrochemical synthesis still has the disadvantage of the costs of the metals used for the electrode coating, such as gold (Au) or platinum (Pt). Additionally, a lack of information on the selectivity or formation of by–products in the reports presented for urea synthesis has not allowed an objective evaluation of the scalability of this technology.

The production of urea from urine is considered a possible sustainability synthesis [32,33] since a human excretes 1.5 L per day of urine with an average urea concentration of 22–23 g per liter of urine [15]. Still, the main challenge is separating and stabilizing the urea from feces and other components in the wastewater. Another sustainable approach to urea production is using bacteria that catabolize the arginine [34,35]. Although urea production from urine could be a viable alternative route, further development of this technology is still required, especially in optimizing substrate stabilization.

Recent proposals for urea production consider industrial systems powered by solar and wind energy as sustainable alternatives [36-38] or biomass as NH₃ and CO₂ sources [39]. However, these systems produce energy from non–conventional renewable sources to power cells and reactors used for urea synthesis, which continue to be based on the classical industrial synthesis of carbamate formation and subsequent dehydration (see Equations (6) and (7), respectively).

Few studies propose using direct solar or radiant energy for urea synthesis by photocatalysis. One of the latest publications in this field presents the simultaneous photocatalyzed reduction of NH₃ and CO₂ on palladium nanoparticles with promising results [40]. This review analyzes a hardly explored alternative route to industrial urea synthesis: photochemical production using TiO₂-based materials. We revisit the papers that have reported the simultaneous photochemical reduction of CO₂ and nitrogen species such as NH₃, NO₃⁻, NO₂⁻, or N₂ to form urea using TiO₂ surfaces. It has been observed that urea generation by photocatalysis can be performed at ambient pressure and room temperature, emerging as an attractive and viable alternative to developing and evaluating the current alternative syntheses.

3. Developments in the Photocatalyzed Production of Urea Using TiO₂–Based Materials

Urea production by photocatalysis was first reported in 1998 by S. Kuwabata, H. Yamauchi, and H. Yoneyama [41]. This research group presented the simultaneous reduction of CO_2 and nitrate ion (NO_3^-) using titanium dioxide nanocrystals (Q–TiO₂) with sizes ranging from 1.0 to 7.5 nm, which were immobilized in a film of polyvinylpyrrolidone gel (Q–TiO₂/PVPD). A 500 W high–pressure mercury arc lamp was used as a light source for the experiments, in which wavelengths below 300 nm were removed with a glass filter.

S. Kuwabata et al. [41] reported a concentration of about 1.9 mM urea in a 5 h photocatalysis using a Q–TiO2/PVPD film in polypropylene carbonate (PC) solutions saturated with CO₂ in the presence of LiNO₃ and using 2–Propanol as an electron donor species. However, when using Q–TiO₂ colloidal and TiO₂ P–25 colloidal, under the same conditions, they obtained an approximate concentration of 7.3×10^{-2} mM and 3.3×10^{-2} mM, respectively.

The results obtained by the Q–TiO₂/PVPD film were promising since a lower concentration of urea was expected as a product because of the belief that the use of the Q–TiO₂ photocatalyst particles fixed in a polymeric film reduces the area exposed to the solution as opposed to using suspended photocatalyst particles. S. Kuwabata et al. [41] justified their results by studying the photo–oxidation of the urea formed, determining that urea and 2–propanol compete for active sites on the surface of Q–TiO₂, degrading and decreasing their concentration in the solution. According to research, using Q–TiO₂ in suspension increases the collision frequency and interaction between urea and the catalyst surface. The

interface interaction generates a more significant reaction and increases the degradation of the already–formed products.

However, the concentration of the products formed by the urea degradation via photooxidation does not contribute directly to the secondary reactions leading to by–products such as methanol, ammonia, acetone, and hydrogen. The concentrations observed for the by–products remain proportional to urea formation, as shown in Table 1, whose results were obtained after photoreductions were made for 5 h.

Table 1. Amounts of products obtained by the photoinduced reduction of nitrate ions and carbon dioxide using different kinds of titanium dioxide photocatalysts. Adapted from S. Kuwabata et al. [41].

Catalwat	<u> </u>	Amount of Products (µmol)								
Catalyst	Solvent	Urea	Acetone	Methanol	NH_4^+	H ₂	Ti ₃ +			
Q-TiO ₂ /PVPD	PC	5.6	61.0	1.2	2.7	0.18	0.14			
Q–TiO ₂ coloidal	PC	0.22	2.5	0.12	0	0	0			
P–25 TiO ₂ /PVPD	PC	2.3	30.1	0.04	1.2	0.08	_			
P–25 Coloidal	PC	0.1	1.1	0.05	0	0.06	_			
P–25 TiO ₂ /PVPD	H ₂ O	0	0.07	0	0	0.01	-			

S. Kuwabata et al. [41] used reduced species such as NH_2OH or NO_2 , replicating the experimental conditions for the Q–TiO₂/PVPD film, reaching urea concentrations close to 5.6 and 2.9 mM, respectively, in 1 h. These results concluded that the limiting step of photocatalyzed urea production is the formation of reduced NO_3^- ions species.

B.-J. Liu, T. Torimoto, and H. Yoneyama [42] subsequently generated urea reaching concentrations of 3 mM using a film of TiO₂ nanocrystals embedded in SiO₂ matrices (Q–TiO₂/SiO₂). This experiment proposed the photochemical reduction of CO₂ saturated in a LiNO₃ solution, using 2–propanol as an electron donor. The system was irradiated for 5 h with a 500 W mercury arc lamp.

B.-J. Liu et al. [42] reported that urea selectivity regarding other products, such as formate (HCO_2^-) and carbon monoxide (CO), is influenced by the type of solvent used in the reaction and its dielectric constant (see Table 2). This research group previously reported a systematic study of the photoinduced reduction of CO_2 in solvents such as carbon tetrachloride, dichloromethane, 2–propanol, ethylene glycol monoethyl ether, acetonitrile, sulfolane, propylene carbonate, and water, obtaining in this last one a complete reduction of CO_2 to formic acid [43].

Table 2. Amount of product obtained by the photoinduced reduction reaction of lithium nitrate in solvents saturated with carbon dioxide. Adapted from T. Torimoto et al. [43].

Cal and	Dielectric Constant,	Amount of Products (mM) ^(a)							
Solvent	ε	Urea	NH ₃	HCO ₂ -	CO				
Ethylene glycol monoethyl ether	29.6	1.00	0.20	0.80	0.50				
Acetonitrile	37.5	1.15	0.15	0.70	0.20				
Sulfolane	43.0	1.00	0.20	0.40	0.25				
PC	69.0	0.85	0.25	0.10	0.05				
Water	78.5	2.75	0.75	0.10	0.05				

^(a) Calculated from data reported in diagrams and considering 5 cm³ as solution volume used in the cell.

The results presented by B.-J. Liu et al. [42] showed that the NO₃⁻ ion reduction reaction is the determining step in producing urea and NH₃ as synthesis products. Urea and NH₃ concentrations increase by increasing the concentration of NO₃⁻ as opposed to the concentration of HCO₂⁻ that remained relatively constant. Similar results were presented by S. Kuwabata et al. [41] using TiO₂ particles supported on a surface, justifying that the Q–TiO₂/SiO₂ film has a higher photocatalytic activity since the particles have a negative change in the edge of the conduction band caused by the effect of the quantization and the specific surface area estimated at 290 m² g⁻¹.

In 2005, a new proposal for the photochemical synthesis of urea arose at the hands of D.G. Shchukin and H. Möhwald [44]. They proposed using microenvironments to synthesize complex compounds, allowing dimensions, structure, and morphology specificity. These microenvironments correspond to polyelectrolyte capsules, consisting of polyamine hydrochloride (PAH) and polystyrene sulfonate (PSS), which allow permeability to inorganic macromolecules and nanoparticles, depending on the solvent, pH, or ionic strength of the means. Under this methodology, it was possible to perform the photocatalyzed urea synthesis on TiO₂ nanoparticles, using CO_2 and NO_3^- ions as a precursor, where polyvinyl alcohol (PVA) fulfills the role of electron donor. Figure 1 shows an assembly scheme for these spherical microreactors.



Figure 1. Schematic illustration of the photocatalytic spherical microreactor assembly. Adapted from D.G. Shchukin et al. [44].

D.G. Shchukin and H. Möhwald [44] reported a concentration close to 1.1 mM of urea, using spherical microreactors with a 2.2 μ m diameter in an aqueous solution saturated with CO₂ in the presence of 0.1 M NaNO₃, followed by 5 h of irradiation with a 200 W Xg–He lamp. It was possible to observe a slight increase in urea concentration at 1.7 mM when incorporating copper (Cu) nanodeposits on TiO₂ particles. A simultaneous photocatalysis was expected both on the TiO₂ particles and on the surface of the Cu, which increased the reduction of the NO₃⁻ to NH₄⁺ ions, considered the determining step for urea formation.

The results of D.G. Shchukin and H. Möhwald [44] suggest that the main advantage of using microreactors is controlling reagents in the volume determined for the reaction. Furthermore, the confinement and the ability to control the input of substances give the possibility of modeling biochemical processes of living cells.

Later, E.A. Ustinovich et al. [45] reported urea synthesis by the photoinduced reduction of CO_2 in the presence of NO_3^- ions, using TiO₂ stabilized in perfluorodecalin (PFD:TiO₂) emulsions and 2–propanol as electron donor species. A 120 W high–pressure mercury vapor lamp was used as a light source. After one hour of irradiation, the concentration of urea was 0.54 mM and 1.1 mM using PFD:TiO₂ and PFD:TiO₂/Cu, respectively. The high efficiency and selectivity observed in urea formation, as observed in Table 3, are attributed to a high concentration of CO_2 in the oleic phase, granting favorable conditions to stabilize intermediary species, allowing the formation of C–N bonds [46].

Table 3. Photoproduction ratio of urea and formate from 0.1 M NaNO₃ solution with CO₂ saturated using different TiO₂ photocatalysts. Adapted from E.A. Ustinovich et al. [45].

Catalyst	Amount of Pro				
Catalyst —	Urea	Formate	Urea-Formate Katio		
TiO ₂	0.28	0.11	2.5		
TiO ₂ /Cu	0.40	0.050	8.0		
PFD:TiO ₂	0.58	0.15	3.9		
PFD:TiO ₂ /Cu	1.12	0.025	45		

^(a) Calculated from data reported in diagrams.

E.A. Ustinovich et al. [45] demonstrated that PFD emulsions could dissolve a considerable amount of O_2 and CO_2 , 45 mL/100 mL and 134 mL/100 mL, respectively, which usually demand high pressures. This methodology allowed the accumulation of different organic compounds, whether substrates, intermediates, or products, favoring light–induced reactions.

It is important to note that E.A. Ustinovich et al. [45] established that using concentrations higher than 1.0 M NaNO₃ as a source of N does not significantly increase urea concentration. Hence, this concentration is the saturation limit value of NaNO₃ for solutions used in photocatalyzed urea production.

One of the latest publications on photocatalyzed urea production using TiO₂ was presented by B. Srinivas et al. [21]. The research group studied urea synthesis using KNO₃ solutions as a source of N in the presence of 2–propanol or oxalic acid as electron donor, producing CO₂ in–situ as a reaction product. After 6 h of UV irradiation, using a 250 W high–pressure mercury lamp, it was possible to obtain urea concentrations close to 0.20, 0.10, and 0.31 mM, using TiO₂, iron titanate (Fe₂TiO₅), and iron titanate supported on proton exchange zeolite Socony Mobil–5 (Fe₂TiO₅/HZSM–5) as a photocatalyst, respectively.

B. Srinivas et al. [21] showed that using iron titanates supported in HZSM–5 promotes the separation of photoinduced charges, enhancing urea selectivity. Additionally, zeolites presented high adsorption of CO_2 and NH_3 , which, according to the research, was produced in–situ on the catalyst surface. The condensation for urea formation is facilitated by the adsorption property in the zeolite that inhibits the polymerization of the products.

In a recent report by H. Maimaiti et al. [47], the photocatalyzed synthesis of urea was performed on carbon nanotubes (CNTs) with Fe/Ti³⁺–TiO₂ composite as catalyst (Ti³⁺–TiO₂/Fe–CNTs). This research group has established that urea synthesis from the simultaneous reduction of N₂ and CO₂ in H₂O is related to the arrangement of Ti³⁺ sites and oxygen vacancies on the catalyst surface. The Ti³⁺ sites act as the active center of N₂ and oxygen vacancies acts as the active center for CO₂ on the Ti³⁺–TiO₂ surface. H. Maimaiti et al. [47] state that urea formation is achieved by adsorption and activation, converting the N₂ and CO₂ molecules into a cyclic intermediate that is transformed into two urea molecules. This research reports a urea yield of 710.1 μ mol L⁻¹ g⁻¹ after 4 h of reaction using a 300 W high–pressure mercury lamp as the light source.

Although the trend indicates the use of photocatalysts fixed on a surface which enables better control over the reaction solution, and then the separation of the catalyst from the reaction solution, H. Maimaiti et al. [47] propose using a catalyst supported on CNTs to improve the dispersion in water. However, the catalysts used have an Fe core, which allows their rapid and simple separation from the reaction solution using an external magnetic field.

Table 4 summarizes the highest urea concentration obtained by each reported work, according to the experimental set–up proposed by each author mentioned above. Since the photocatalyzed urea syntheses were performed under different experimental conditions, a direct comparison of the results obtained is limited. Table 4 shows the urea concentration normalized by the irradiation time used in each work. The reaction yields or quantum yields could not be considered for comparing results because these data were not reported in most of the works studied.

When urea concentration is normalized by hours of irradiation, it is possible to observe how the solution or support used plays an essential role in stabilizing the reagents and intermediate species. For example, PFD emulsions allow the dissolving of high concentrations of gaseous substrates at room pressure, increasing the availability of CO₂, favoring urea formation, and stabilizing TiO₂ particles. Moreover, using reduced species such as NO or NH₂OH as a nitrogen source favors the generation of intermediate species, modifying selectivity by by–products, as S. Kuwabata et al. [41] reported.

Contrary to what was thought, using supported TiO_2 particles, in some cases, favors urea synthesis. Modifying the size of the supported particles allows changing the semiconductor band–gap. It should be considered that reactions on supported catalysts are

governed by diffusion phenomena and can be controlled more easily. In addition, the use of support surfaces makes it possible to avoid particle aggregation in solution, reduce irradiation shielding, and prevent reactions depending on particle collision phenomena, allowing, in turn, better adsorption and even increasing the spatial selectivity of reactants and products.

Author	Catalyst	C Source	N Source	Solvent	Illumination Time, h	Urea, mM	Urea, mM h ⁻¹
S. Kuwabata et al. [41]	Q-TiO ₂ /PVPD	CO ₂ , sat.	NH ₂ OH 0.020 M ^(a)	PC	1	5.7 ^(a,c)	5.7
BJ. Liu et al. [42]	$Q-TiO_2/SiO_2$	CO ₂ , sat.	LiNO ₃ 0.020 M	H_2O	5	2.75 ^(b)	0.55
D.G. Shchukin et al. [44]	Cu/TiO ₂ -PVA-PAH/PSS (2.2 µm diameter)	CO ₂ , sat.	NaNO ₃ 0.1 M	H ₂ O	5	1.72 ^(c)	0.34
E.A. Ustinovich et al. [45]	Cu/TiO ₂ :PFD	CO ₂ , sat.	NaNO ₃ 1.0 M	PDF:H ₂ O	1	1.1 ^(c,d)	1.1
B. Srinivas et al. [21]	Fe ₂ TiO ₅ (10wt%)/HZSM-5	2–propanol $1 v/v\%$	KNO ₃ 0.016 M	H ₂ O	6	0.31 ^(e)	0.052
H. Maimaiti et al. [47]	Ti ³⁺ -TiO ₂ /Fe-CNTs	CO_2 (100 mL min ⁻¹ flow rate)	N2 (100 mL min ⁻¹ flow rate)	H ₂ O	4	0.710 ^(f)	0.178

Table 4. Amount of urea synthesized by photocatalysis.

^(a) Calculated from 3 cm³ volume of propylene carbonate solution used in the cell. ^(b) Calculated from data reported in charts and considering 5 cm³ as solution volume used in the cell. ^(c) Estimated value from data reported in charts. ^(d) Reported in mmol L⁻¹ h⁻¹, the normalized value per hour of irradiation is presented. ^(e) Converted from ppm to mmol L⁻¹. ^(f) Converted from μ mol L⁻¹ g⁻¹ and considered 1 g of catalyst.

The above is critical in scaling these technologies because separating and recovering a suspended catalyst from an aqueous solution using filtration systems or more complex unit operations could increase production costs. The use of catalysts with magnetic properties that could be removed from the reaction solution by applying a magnetic field is a possible solution for the use of suspension catalysts.

The confinement of the reaction space in low–scale photoreactors such as microcapsules or microreactors allows the control of the diffusion, input, or output flow of reactants and products and the specificity of the synthesis, stereochemistry, and functionalization of the products formed. The spherical microreactors evaluated produce lower mobility of the compounds, enhancing the interaction between the reactant species and the photocatalyst particles and increasing the concentration of the desired products.

A constant flow of the gases used as a source of C and N is a relevant factor. Considering the low solubility of gases in aqueous media and the time necessary to perform the photocatalytic reduction studied, a high and constant concentration of C and N sources is required to optimize the urea production flow. As presented in Section 6 of this review, in many photocatalyzed system reports, the by–products tend to be the higher concentration.

Even though each experimental set–up proposed has an improvement or an innovation to the photocatalysis technology, there are still many edges to explore in urea synthesis photocatalyzed by TiO_2 -based materials.

4. Use of Titanium Dioxide in Urea Photocatalyzed Synthesis

TiO₂ is an *n-type* semiconductor, widely used in photovoltaic cells, electrochemical sensors, biological applications, and environmental remediation, mainly for its chemical stability, optical/electronic properties, commercial availability, low cost, and low toxicity [48,49].

 TiO_2 is commonly found in three polymorphic forms: rutile, anatase, and brookite. Each crystal phase assembles as octahedra with six oxygen anions shared by three titanium (IV) cations. Each TiO_2 crystal phase has a different shape, structure, density, and refractive index. In turn, metastable anatase and brookite structures can be thermally restructured into stable rutile. Although the rutile crystal phase has the highest structural stability [50], it is hard to find and is a challenge for industrial manufacturing [51]. Regarding the optical properties of TiO_2 , it has been determined that the refractive indexes for rutile and anatase phases are 2.7 and 2.5, respectively [50]. The values of index refraction for TiO_2 are associated with the oxidized metals with the ability to scatter photons. Therefore, the rutile reflects light more efficiently [50,52]. However, the most remarkable property of TiO_2 is its ability to absorb light in the ultraviolet (UV) region, which is approximately 4% of the solar spectrum [53–55].

TiO₂'s ability to absorb UV light is due to its wide band–gap of 2.96, 3.02, and 3.2 eV for the brookite, rutile, and anatase, respectively [56]. When TiO₂ absorbs UV light, an electron (e^-) is excited by absorbing photonic energy (hv), equal to or greater than the semiconductor band–gap. This absorbed energy causes the photoexcited electron to jump from the valence band (VB) to the conduction band (CB), generating a hole (h^+) in the valence band, as it is described in the following equation [56]:

$$\mathrm{TiO}_2 + hv \to h^+ + e^- \tag{9}$$

Photoexcited electrons migrate to the surface, becoming reduction centers for electronaccepting species (A). Similarly, the holes generated in the VB can be considered oxidation sites for electron donor species (D). However, there is also the possibility that electrons and holes are recombined within the semiconductor and do not reach its surface, decreasing the efficiency of the catalyst, as shown in Figure 2A.

Catalyst doping and co–doping reduce the recombination phenomenon [56] and narrow the band–gap [57]. The modifications on the TiO₂ surface can be: (1) The incorporation of a metallic element such as copper [58], iron [59], palladium [60], or gold [61], among others. Non–metallic doping is also possible, such as nitrogen [62], carbon [63], graphene [64], fluorine [65], or sulfur [66], among others. (2) Generating a composite or a heterojunction with another semiconductor with a lower band–gap, increasing the availability of photogenerated electrons since they can be stabilized in the lower energy conduction band and even increase the sensitivity of the system to the absorption of wavelengths of lower energy [67]. (3) Using a sensitizing dye (S), such as an organometallic compound, that can inject electrons into the semiconductor conduction band when the oxidant energy level of the dye (S*) is more negative than the conduction band [68]. Figure 2B illustrates the possibilities for doping the catalyst.

Figure 3 compares the charge transfer when TiO_2 is doped with a metal or nonmetal. Metallic species can narrow the band–gap of TiO_2 and plasmon resonances of metal nanoparticles, allowing an increase in visible light absorption [57]. In addition, metals can act like an "electron trap" by capturing photogenerated electrons, increasing their surface availability and increasing the charge transfer efficiency [69]. A non–metal species can produce half–filled states below the CB, reducing the band–gap of the TiO_2 [57].

On the other hand, the band–gap narrowing can be modified by intrinsic defects in TiO_2 such as oxygen vacancies, Ti interstitials, Ti vacancies, impurities, and interfacial defects. Oxygen vacancies are the most common type of intrinsic defect in TiO_2 and are formed by removing neutral O_2 atoms from the TiO_2 lattice, increasing the electrons, and creating Ti^{3+} ions in the lattice [57]. Therefore, oxygen vacancies are considered the main active sites in TiO_2 and are relevant for the photocatalyzed reduction of CO_2 and nitrogen compounds for urea synthesis, as will be discussed in Section 5.

Figure 4 shows the position of the bands for some semiconductors with a photochemical response relative to the CO₂ reduction potentials [70] and NO₃⁻ [71]. The band position of TiO₂ favors the formation of NH₃ from NO₃⁻, a necessary step for the formation of urea. Although other semiconductors can absorb radiant energy and perform the reduction of nitrate ions, not all have the same qualities as TiO₂. The properties of TiO₂, such as chemical stability, production costs, low toxicity, or oxygen vacancy, have made it one of the most widely used photocatalysts in the last two decades [72].



Figure 2. Charge transfer diagram for TiO₂. (**A**) Schematic representation of band–gap and the e^-/h^+ pair transfer on a photoexcited TiO₂ surface. (**B**) Effect on charge transfer for a semiconductor, according to metal doping, composite semiconductor (CS), or dye–sensitized (S). Adapted from Liu et al. [69].



Figure 3. Conduction band (CB) and valence band (VB) narrowing to TiO₂ by doping. (**A**) Undoped, (**B**) metal–doped, and (**C**) non–metal doped. Adapted from R. Nair et al. [57].



Figure 4. Band–edge position of different semiconductors with photocatalytic properties. Band position relative to CO_2 y NO_3^- reduction energy levels. Adapted from L. Wei et al. [70] and S. Garcia-Segura et al. [71].

TiO₂ nanoparticles suspended in aqueous solutions have proven efficient in degrading by photoinduction: organic compounds, drugs, cosmetics, and sometimes heavy metals [73]. However, according to the methodologies described in this review, these photochemical systems may have low control over reaction products [74], as in the case of urea formation. Furthermore, the development of the reactions can be affected by the loss of radiant energy, which must cross the bulk solution where the reactions are carried out until reaching the surface of the catalyst to achieve the photoexcitation of the electrons. Photocatalyzed systems require electron donor species, usually organic molecules [68], which are oxidized and could produce unwanted by–products, interfering with the expected reactions.

TiO₂ and TiO₂–based photocatalysts have been widely used for the photochemical conversion of both CO₂ [70,74] and nitrogenous species such as NO₃⁻ [75–80], NO₂⁻ [81–85], N₂ [86–91], and NH₃/NH₄⁺ [92–94], among others, to give rise to species of higher energy value or industrial interest. However, few studies have proposed the simultaneous photochemical conversion of CO₂ and nitrogen species to obtain more complex compounds such as urea. Therefore, there are still possibilities to explore new synthesis routes for urea, which represents a high value for the industry by using TiO₂–based materials.

5. Proposed Reactions and Mechanism for Photocatalyzed Urea Synthesis

Urea synthesis from NH₃ and CO₂ is known as the Bazarov reaction and is the basis of large–scale industrial production. The first reaction to form carbamate from NH₃ and CO₂ is fast and exothermic (see Equation (5)). The second reaction is a slow and slightly endothermic reaction of carbamate dehydration to form urea (see Equation (6)). The standard Gibbs free energy change at 25 °C and 1 atm for carbamate formation from NH₃ and CO₂ and subsequent dehydration are -23.8 kJ and +16.7 kJ, respectively [22]. The overall reaction of urea synthesis from NH₃ and CO₂ is exothermic, with a Gibbs free energy value of -7.1 kJ.

However, the reactions involved in urea synthesis have limitations, such as elevated temperatures (170–220 °C), because the reactions are performed only in a liquid phase [95]. Moreover, high pressure (125–250 bar) is needed to force the gaseous reagents into the reaction solution [95]. Adding, the NH₃/CO₂ ratio is another important parameter that is used in industrial synthesis in a higher than the stoichiometric ratio. Since NH₃ is more soluble than CO₂, it is possible to form an ammonia–enriched azeotrope NH₃–CO₂ (ratio greater than 3 mol mol⁻¹), which favors the formation of urea and decreases the required

pressure to perform the reaction [95]. Therefore evaluating new synthesis routes for urea at ambient temperature and pressure is an attractive challenge.

On the other hand, the mechanism of the photocatalyzed urea synthesis is not well known, mainly because of the limited development and scant reports. The work of S. Kuwabata et al. [41] suggests that urea should be formed by simultaneously reducing CO_2 and NO_3^- . This reduction would require 16 e^- to produce 1 mol of product, according to the following multi–electron reaction:

$$2 \text{ NO}_{3}^{-} + \text{CO}_{2} + 18 \text{ H}^{+} + 16 e^{-} \rightarrow \text{CO}(\text{NH}_{2})_{2} + 7 \text{ H}_{2}\text{O}$$
(10)

The following reactions for urea formation are also proposed, depending on the source of carbon or nitrogen used in the photocatalyzed synthesis studied:

$$2 \text{ NO}_3^- + \text{CO} + 16 \text{ H}^+ + 14 e^- \to \text{CO}(\text{NH}_2)_2 + 6 \text{ H}_2\text{O}$$
(11)

$$2 \text{ NO}_3^- + \text{HCOOH} + 16 \text{ H}^+ + 14 e^- \rightarrow \text{CO}(\text{NH}_2)_2 + 7 \text{ H}_2\text{O}$$
 (12)

$$2 \text{ NH}_2\text{OH} + \text{CO}_2 + 4 \text{ H}^+ + 4 e^- \rightarrow \text{CO}(\text{NH}_2)_2 + 3 \text{ H}_2\text{O}$$
(13)

$$2 \text{ NO} + \text{CO}_2 + 10 \text{ H}^+ + 10 \text{ } e^- \to \text{CO}(\text{NH}_2)_2 + 3 \text{ H}_2\text{O}$$
(14)

Forming urea in each reaction is feasible by multi–electron reduction of the substrates. These reductions are possible thanks to the participation of semiconductors that allow this electron transfer. It has been reported that TiO_2 –based semiconductors used in quantum sizes have a photochemical activity more significant for multi–electron reactions [41,96]. It has been calculated that the crystal phase of pure anatase with a diameter of 3 nm can store an average of about six to nine electrons per TiO_2 particle that are needed to photoreduce nitrate or ammonia using five or eight electrons, respectively [97]. The nitrate and ammonia reduction mechanism by electrons photoexcited from TiO_2 are as follows in Scheme 1:

$$NO_{3} - \frac{2H^{+}, 2e^{-}}{H_{2}O} NO_{2}^{-} \frac{2H^{+}, 2e^{-}}{H_{2}O} NO^{-} NO^{-} NH_{2}OH \xrightarrow{3H^{+}, 2e^{-}}{H_{2}O} NH_{4}^{+} NH_{4}^{-} NO^{-} N_{2}O_{2}^{-} \xrightarrow{2H^{+}}{H_{2}O} N_{2}O \xrightarrow{2H^{+}, 2e^{-}}{H_{2}O} N_{2}O \xrightarrow{2H^{$$

Scheme 1. Mechanisms of nitrate and nitrite ion reduction by a multi–electron transfer process on a TiO₂ surface to produce N₂ gas and ammonia. Adapted from H. Mohamed et al. [97].

The agglomeration of nanoscale TiO_2 can occur easily, decreasing its photocatalytic performance. Usually, carbon nanotubes are used to support the TiO_2 to avoid agglomeration, allowing dispersion due to the one–dimensional morphology and stability. Moreover, the carbon nanotubes can improve the transfer of photoexcited electrons and the adsorption of electron acceptor molecules [98–101].

The importance of controlling the pH of the solution has also been reported, considering the requirement of H⁺ to reduce nitrogen species such as NO_3^- [102,103]. When TiO₂ is used in a reaction solution with a pH value below the point of zero charge (pHpzc) of 6.25, electrostatic interaction between species such as NO_3^- and the surface of TiO₂ is favored [78]:

$$TiOH = TiO^{\mp H^+}(pH > 6.25)$$
(15)

$$TiOH + H^+ \leftrightarrows TiOH_2 (pH < 6.25)$$
(16)

D.G. Shchukin et al. [44] introduced that the limiting step for photochemical urea synthesis corresponds to reducing NO_3^- to NH_4^+ . The ammonium formed should react with the $CO^{\bullet-}$ radical ion to produce urea [20]. B. Srinivas et al. [21] also coined the concept of a radical ion according to the electron donor used, either oxalic acid or 2–propanol. Using

oxalic acid, the formation of the radical ion $\text{CO}_2^{\bullet-}$, a species with a high reduction power $\left(E_{\text{CO}_2/\text{CO}_2^-}^0 = -1.8 \text{ V}\right)$, is described in the following reaction:

$$C_2O_4^{2-} + h^+ \to CO_2 + CO_2^-$$
 (17)

The CO₂ formed in Equation (14) diffuses in the aqueous solution producing carbonic acid, dissociating, and releasing protons into the solution. Afterward, NO_3^- ions can be adsorbed on the surface of TiO₂, where the reduction occurred, to give rise to NH_4^+ by ten photogenerated electrons, depending on the reaction:

$$NO_3^- + 4C_2O_4^{2-} + 10 H^+ \to NH_4^+ + 8CO_2 + 3H_2O$$
(18)

To avoid or reduce NH_4^+ formation, B. Srinivas et al. [21] propose using TiO₂ supported in the zeolite. This support would give stability to the intermediate species of NO_3^- ion reduction by the following proposed mechanism in Scheme 2:

$$2 \text{ H}^{+} + 2 \text{ e}^{-} + \text{NO}_{3}^{-} \xrightarrow{2\text{H}^{+} + 2\text{e}^{-}} \text{NO}_{2}^{-} + \text{H}_{2}\text{O} \xrightarrow{\text{[HO-N-OH]}} \text{[HO-N-OH]} \xrightarrow{-\text{H}_{2}\text{O}} \text{[N=O]} \xrightarrow{2\text{H}^{+} + 2\text{e}^{-}} \text{[H-N-OH]} \xrightarrow{2\text{H}^{+} + 2\text{e}^{-}} \text{[NH}_{2}\text{]} \xrightarrow{\text{NH}_{2}^{-}} \text{[NH}_{2}\text{]} \xrightarrow{\text{NH}_{2}^{-}} \text{[HO-N-OH]} \xrightarrow{-\text{H}_{2}\text{O}} \text{[N=O]} \xrightarrow{2\text{H}^{+} + 2\text{e}^{-}} \text{[H-N-OH]} \xrightarrow{2\text{H}^{+} + 2\text{e}^{-}} \text{[NH}_{2}\text{]} \xrightarrow{\text{NH}_{2}^{-}} \text{[NH}_{2}\text{]} \xrightarrow{\text{NH}_{2}^{-}} \text{[HO-N-OH]} \xrightarrow{-\text{H}_{2}\text{O}} \text{[N=O]} \xrightarrow{2\text{H}^{+} + 2\text{e}^{-}} \text{[H-N-OH]} \xrightarrow{2\text{H}^{+} + 2\text{e}^{-}} \text{[NH}_{2}\text{]} \xrightarrow{\text{NH}_{2}^{-}} \text{[NH}_{2}^{-}} \xrightarrow{\text{NH}_{2}^{-}} \text{[NH}_{2}^{-}} \xrightarrow{\text{NH}_{2}^{-}} \text{[NH}_{2}^{-}} \xrightarrow{\text{NH}_{2}^{-}} \xrightarrow{$$

Scheme 2. Speculative mechanism and representation of intermediate species stabilization during nitrate reduction and the prevention of ammonia oxidation over TiO₂–zeolites. Adapted from B. Srinivas et al. [21].

Regarding the by–products, S. Kuwabata et al. [41] propose that in photoinduced reduction reactions, in which 2–propanol (CH₃CH(OH)CH₃) is used as an electron donor, acetone (CO(CH₃)₂) is formed as the main product (Equation (16)). The formation of acetone is thermodynamically favored with a ΔG of reaction estimated at –1059 kJ mol⁻¹

$$CH_3CH(OH)CH_3 \to CO(CH_3)_2 + 2H^+ + 2e^-$$
 (19)

Using other carbon or nitrogen sources also allows obtaining a negative ΔG for forming acetone from 2–propanol. However, high energy may be required to overcome the activation energy barrier that involves a reduction with multiple electrons as the hydration of N₂ to NH₃, where its ΔG is -159 kJ mol⁻¹ [41].

Besides, using 2–propanol as an electron donor implies the formation of the radical ion $(CH_3)_2$ C–OH, which could capture the holes of the valence band of TiO₂, generating acetone, and in turn, it would remain reacted to produce CO₂ in the solution, as described in the following reactions:

$$(CH_3)_2 CHOH + h^+ \to H^+ + (CH_3)_2 \cdot COH$$
⁽²⁰⁾

$$(CH_3)_2 \cdot COH \xrightarrow{h^+,e^-} H_2 + CO(CH_3)_2$$
 (21)

$$CO(CH_3)_2 + h^+ \to CO_2 + H_2O \tag{22}$$

Subsequently, it is assumed that the CO_2 and NH_4^+ species generated in–situ react to form ammonium carbamate, which by dehydration produces urea. B. Srinivas et al. [21] have proposed two speculative mechanisms to describe this process. In the first mechanism, amino acid formation and subsequent dehydration are formed. In the second mechanism, an amide will be obtained by hydroxylation with a hydroxyl radical, followed by an amination, carbamate form, and its subsequent urea dehydration. The proposed speculative mechanisms are developed in Scheme 3:



Scheme 3. The speculative mechanisms for urea synthesis via amino acid and amide formation. Adapted from B. Srinivas et al. [21].

The use of zeolites to support photocatalyst particles would have the double function of adsorbing both reactants and products, given the stereochemical selectivity of zeolite. B. Srinivas et al. [21] report the polymerization and condensation of products from urea and ammonium are not observed when using zeolites as support, unlike using TiO₂ in suspension where the products could continue to react, producing by–products. Scheme 4 shows the speculative mechanism of urea formation using TiO₂ supported on zeolites.



Scheme 4. Schematic representation of urea formation on TiO₂ supported on zeolites under illumination, Adapted from B. Srinivas et al. [21].

Surface defects on TiO_2 are essential as active and adsorption sites for CO_2 and nitrogen compounds. H. Maimaiti et al. [47] suggest that Ti^{3+} sites and oxygen vacancies act as the active centers for N_2 and CO_2 molecules, respectively. Then, if N_2 and CO_2 are on the same plane, the photocatalysis may be activated simultaneously to form a C–N ring intermediate in situ and subsequently to form urea. Figure 5 shows the mechanism of photocatalyzed reduction for N_2 and CO_2 molecules on TiO_2 .



Figure 5. Mechanism of the photocatalyzed reduction of N_2 and CO_2 simultaneously to form urea on the TiO₂ surface. Adapted from H. Maimaiti et al. [47].

When the N₂ molecule is absorbed on Ti³⁺ sites, the photoexcited electrons can form active intermediates such as -N=N-, -HN-NH-, H₂N-. In turn, CO₂ is bent by oxygen vacancy adsorption, and the C=O bond is broken. A C-H bond is formed by the effect of active electrons and protons. The Ti³⁺-TiO₂ structure acts as a photocatalyst with double active sites [47]. Defects on the TiO₂ surface such as oxygen vacancies can easily be formed by electron bombardment, sputtering, or the thermal annealing of the surface to high temperatures [104], but an excess of crystal defects increases the recombination rate of e^-/h^+ pair photoinduction [47].

The photocatalytic activity of TiO₂ (anatase, rutile, and brookite) are governed by the defects present on the surface, which are not sensitive to their morphology and particle size; however, it strongly depends on the crystal phases. Figure 6 illustrates the dependence between band–edge position, e^-/h^+ pair photoinduction, and the crystal phases.



Figure 6. Band–edge position and photoinduced e^-/h^+ pair by the defects on anatase, rutile, and brookite TiO₂. Adapted from A. Yamakata et al. [105].

When electrons are trapped at the defects, their reactivity decreases, so the recombination with holes also reduces. Therefore the lifetime of holes becomes longer, then the photocatalytic oxidation activity increases. If the polymorphism of TiO_2 is compared for the photocatalyzed reductions of nitrogen compounds and CO_2 to form urea, the arrangement favoring reductions is required. Anatase exhibits the highest reduction activity since most electrons survive as free or shallowly trapped [105]. In turn, rutile shows higher oxidation activity, and brookite shows higher activity in several reactions because both electrons and holes are reactive.

H. Maimaiti et al. [47] reported modifications to the band–edge by incorporating defects by thermal annealing. The highest concentration of urea reported was obtained when TiO_2 was calcined at 400 °C. Figure 7 shows the band–gap shift.



Figure 7. Band–edge position of Ti^{3+} – TiO_2 relative to photocatalyzed reduction reactions. Heat treatment temperature (°C) applied to the catalyst: (**A**) 600, (**B**) 500, (**C**) 400, (**D**) 300, and (**E**) 200. Adapted from A. Yamakata et al. [105].

Despite approximating the mechanism of urea formation by the photoinduced reduction of CO_2 and NO_3^- , there is still no complete clarity of its generation due to scarce reports. A possible way to study the mechanisms is to perform a free energy diagram through density functional theory (DFT) calculations for the proposed structures, as has been reported for electrocatalytic studies of urea formation from CO_2 and NO_3^- [106]. However, in this type of study, it is necessary to consider the factors that favor the formation of urea by photocatalysis about the production of other by–products. This will depend as much on the experimental set–up, catalyst defects, carbon or nitrogen source, electron donor substances, and even the source of radiant energy used.

6. Distribution of Reported Products

Table 5 compiles the distribution of products formed in the photocatalyzed urea synthesis reported by each author studied in this review. The products have been ordered based on the photocatalyst, irradiation time, carbon and nitrogen source, electron donor, and solvent used.

The concentrations in mM presented in Table 5 were obtained from the data available in tables and charts reported by the authors cited. The considerations made to get the concentrations indicated in this table are described according to superscript letters.

The acronyms used in Table 5 correspond to Polyvinylpyrrolidinone (PVPD), Propylene carbonate (PC), Acetonitrile (Ac), Ethylene glycol monoethyl ether (Eg), Sulfolane (Sf), Poly (vinyl alcohol) MW ~15,000 (PVA), Poly (allylamine hydrochloride) MW ~50,000 (PAH), Poly (styrene sulfonate) MW ~70,000 (PSS) and Proton–exchange Zeolite Socony Mobil–5 (HZSM–5).

Even though it is not possible to produce isolated urea in all the cases studied, it is possible to appreciate how the different photocatalytic arrangements and the modification of the experimental conditions have allowed specialization in urea formation through the years of research reducing the presence of by–products.

The highest urea concentration (approx. 4.56 mM) was obtained using Q–TiO₂/PVPD as a photocatalyst. However, under the experimental conditions, urea formation can be considered a by–product against the acetone concentration (28.40 mM approx.).

Considering the duration of the photocatalysis made it possible to produce a urea concentration of approximately 1.1 mM in 1 h, using PFD:TiO₂/Cu as a photocatalyst, the properties of which were described previously. This system allowed the authors to reduce the presence of other species derived from the reduction of nitrate ions such as formate, whose approximate concentration was 0.03 mM, allowing it to be considered as a reaction by–product.

In all experimental set–ups where CO_2 was used as a carbon donor source, reduced species such as acetone, formate, methanol, or carbon monoxide are obtained as products. These compounds could act as interfering substances since they can compete for the active sites of the photocatalyst, decreasing the nitrate ion photocatalyzed reduction reaction. In the cases where the electron donor species 2–propanol or oxalic acid was used as a carbon donor, only urea was produced and also reduced species of nitrate ions such as NH₃ or NO₂⁻, demonstrating once again that this reduction is the most critical step for urea formation.

Although it has been possible to increase the specialization for urea formation in the various photocatalyzed reactions and different experimental set–ups proposed, there are still considerable challenges and opportunities to generate a system that allows scalability using renewable energy sources such as solar energy.

						Amount of Products, mM									
Photocatalyst	Time, h	C Source	N Source	Electron Donor	Solvent	Urea	NH ₃	$\mathrm{NH_4}^+$	NO ₂ -	(CH ₃) ₂ CO	HCOO-	CH₃OH	СО	H_2	Ref
Q-TiO ₂ /PVPD	5 ^(f)	CO ₂ sat.	LiNO3 0.020 M	2–propanol 1.0 M	PC	1.87 ^(a)	_	0.90 ^(a)	_	20.34 (a)	_	0.40 ^(a)	_	0.06 ^(a)	[41]
Q-TiO ₂ colloid	5 ^(f)	CO ₂ sat.	LiNO3 0.020 M	2-propanol 1.0 M	PC	0.07 ^(a)	-	_	-	0.83 ^(a)	_	0.04 ^(a)	-	-	[41]
P-25 TiO ₂ /PVPD	5 ^(f)	CO ₂ sat.	LiNO3 0.020 M	2-propanol 1.0 M	PC	0.77 ^(a)	-	0.40 ^(a)	-	10.03 ^(a)	-	0.01 ^(a)	-	0.03 ^(a)	[41]
P-25 colloid	5 ^(f)	CO ₂ sat.	LiNO3 0.020 M	2-propanol 1.0 M	PC	0.03 ^(a)	-	-	-	0.04 ^(a)	-	0.02 ^(a)	-	0.02 ^(a)	[41]
P-25 TiO ₂ /PVPD	5 ^(f)	CO ₂ sat.	LiNO3 0.020 M	2-propanol 1.0 M	H ₂ O	-	-	-	-	0.02 ^(a)	-	-	_	0.003 ^(a)	[41]
Q-TiO ₂ /PVPD	5 ^(f)	CO sat.	LiNO3 0.020 M	2-propanol 1.0 M	PC	0.77 ^(a)	-	1.4 ^(a)	-	14.70 ^(a)	-	0.97 ^(a)	_	0.04 ^(a)	[41]
	= (f)	HCOOH		2	DC	1 0 (a)		0.00 (a)		10.02 (2)				0.07(a)	[41]
$Q=11O_2/PVPD$	5 (1)	0.16 M	LINO3 0.020 M	2-propanol 1.0 M	PC	1.9 (a)	-	0.90 ^(a)	-	19.03 (a)	-	-	-	0.07 (4)	[41]
Q-TiO ₂ /PVPD	0.5 ^(f)	CO ₂ sat.	NH2OH 0.020 M	2-propanol 1.0 M	PC	2.99 (a,c)	-	2.04 (a,c)	-	8.88 (a,c)	-	0.47 ^(a,c)	-	-	[41]
Q-TiO ₂ /PVPD	2 ^(f)	CO ₂ sat.	NO (gas)	2-propanol 1.0 M	PC	4.56 (a,c)	-	0.41 (a,c)	-	28.40 (a,c)	-	0.34 ^(a)	-	-	[41]
$Q-TiO_2/SiO_2$	7 ^(f)	CO ₂ sat.	LiNO3 0.020 M	2-propanol 1.0 M	Ac	1.52 ^(b)	0.24 ^(b)	-	-	13.30 ^(b)	0.84 ^(b)	-	0.32 ^(b)	0.004 (a,b)	[42]
Q-TiO ₂ /SiO ₂	5 ^(f)	CO ₂ sat.	LiNO3 0.020 M	2-propanol 1.0 M	Eg	1.00 ^(b)	0.20 ^(b)	-	-	-	0.80 ^(b)	-	0.50 ^(b)	-	[42]
$Q-TiO_2/SiO_2$	5 ^(f)	CO ₂ sat.	LiNO3 0.020 M	2–propanol 1.0 M	Ac	1.15 ^(b)	0.15 ^(b)	-	-	-	0.70 ^(b)	-	0.20 ^(b)	-	[42]
O-TiO ₂ /SiO ₂	5 ^(f)	CO_2 sat.	LiNO ₃ 0.020 M	2–propanol 1.0 M	Sf	1.0 ^(b)	0.20 ^(b)	_	_	-	0.40 ^(b)	-	0.25 ^(b)	_	[42]
O-TiO ₂ /SiO ₂	5 ^(f)	CO_2 sat.	LiNO ₃ 0.020 M	2-propanol 1.0 M	PC	0.85 ^(b)	0.25 ^(b)	_	_	_	0.10 ^(b)	_	0.05 ^(b)	_	[42]
\tilde{O} -TiO ₂ /SiO ₂	5 (f)	CO ₂ sat.	LiNO3 0.020 M	2-propanol 1.0 M	H2O	2.75 ^(b)	0.75 ^(b)	_	_	_	0.10 ^(b)	_	0.05 ^(b)	_	[42]
TiO ₂	5 (g)	CO_2 sat.	NaNO ₃ 0.1 M	PVA	PVA	0.31 ^(c)	_	$0.04^{(c)}$	_	_	0.13 ^(c)	_	_	_	[44]
TiO ₂ -PVA-		2						0.0.2			0.20				
PAH/PSS	5 (g)	CO ₂ sat.	NaNO3 0.1 M	PVA	PVA	0.43 ^(c)	-	0.08 ^(c)	-	-	0.11 ^(c)	-	_	-	[44]
(8.1 μm capsule) TiO ₂ -PVA-	= (g)	CO, cot	NaNO, 0.1 M	DVA	DVA	0 (E (C)		0.15 (6)			0.00 (6)				[44]
(4.2 μm capsule) TiO2-PVA-	3 (8)	CO_2 sat.	INAINO ₃ 0.1 M	ГVА	ΓVΑ	0.65	-	0.15	-	-	0.09	_	-	_	[44]
PAH/PSS (2.2 µm cansule)	5 ^(g)	CO ₂ sat.	NaNO3 0.1 M	PVA	PVA	1.12 ^(c)	-	0.38 ^(c)	-	-	0.04 ^(c)	-	-	-	[44]
TiO ₂ /Cu	5 ^(g)	CO ₂ sat.	NaNO3 0.1 M	PVA	PVA	0.49 ^(c)	-	0.09 ^(c)	-	-	0.21 ^(c)	-	-	-	[44]
TiO ₂ /Cu–PVA–	= (-)			777.1		a a (r)		0.1.(1)			2 1 2 (2)				
PAH/PSS	5 (g)	CO_2 sat.	NaNO ₃ 0.1 M	PVA	PVA	0.70 (c)	-	0.16 ^(c)	-	-	0.19 (0)	-	-	-	[44]
(8.1 μm capsule) TiO ₂ /Cu–PVA–															
PAH/PSS	5 ^(g)	CO_2 sat.	NaNO3 0.1 M	PVA	PVA	1.05 ^(c)	-	0.32 ^(c)	-	-	0.23 ^(c)	-	-	-	[44]
(4.2 μ m capsule)															
TiO ₂ /Cu–PVA–	= (a)	<u> </u>		DI 74	D1 / 4	1 = 2(c)		a (= (a)			a a (c)				
PAH/PSS	5 ^(g)	CO_2 sat.	NaNO ₃ 0.1 M	PVA	PVA	1.72(0)	-	0.67 (c)	-	-	0.21 (c)	-	-	-	[44]
(2.2 µm capsule)	1 (b)	CO1	N-NO 10M	2		o o (c d)					0.1 (cd)				[45]
	1 ^(h)	CO_2 sat.	$NaNO_3 1.0 M$	2-propanol 1.0 M	PFD-H ₂ O	0.3 (c,d)	-	-	-		0.1 (c,d)	-		-	[45]
IIO ₂ /Cu	1 ^(h)	CO_2 sat.	NaNO ₃ 1.0 M	2-propanol 1.0 M	PFD-H ₂ O	$0.4^{(c,d)}$	-	-	-		0.1 (c,d)	-		-	[45]
PFD:1iO ₂	1 ^(h)	CO_2 sat.	NaNO ₃ 1.0 M	2–propanol 1.0 M	PFD-H ₂ O	$0.6^{(c,d)}$	-	-	-	-	$0.2^{(c,a)}$	-		-	[45]
PFD:11O ₂ /Cu	1 (ii)	CO_2 sat.	NaNO ₃ 1.0 M	2-propanol 1.0 M	$PFD-H_2O$	1.1 (c,u)	-	-	-	-	0.03 (c,u)	-		-	[45]
11O ₂	6 ⁽ⁱ⁾	Oxalic acid $1\% w/v$	KNO3 0.016 M	Oxalic acid $1\% w/v$	H ₂ O	0.18 (e)	0.12 (e)	-	-	-	-	-	-	-	[21]
T1O ₂	6 ⁽¹⁾	Oxalic acid $1\% w/v$	KNO ₃ 0.016 M	2–propanol 1% v/v	H ₂ O	0.20 ^(e)	0.15 ^(e)	-	_	-	-	-	-	-	[21]
TiO ₂	6 ⁽¹⁾	-	KNO ₃ 0.016 M	-	H ₂ O	-	0.05 ^(e)	-	Trace	-	-	-	-	-	[21]
TiO ₂ (5% wt)–Zeolite	6 ⁽¹⁾	2–propanol 1% v/v	KNO ₃ 0.016 M	2–propanol 1% v/v	H ₂ O	0.07 ^(e)	0.21 ^(e)	-	0.1 ^(e)	-	-	-	-	-	[21]

 Table 5. Distribution of reaction products for photochemical urea synthesis.

Table 5. Cont.

					Amount of Products, mM										
Photocatalyst	Time, h	C Source	N Source	Electron Donor	Solvent	Urea	NH ₃	$\mathrm{NH_4}^+$	NO_2^-	(CH ₃) ₂ CO	HCOO-	СН₃ОН	СО	H ₂	Ref
TiO ₂ (10% wt)–Zeolite	6 ⁽ⁱ⁾	2–propanol 1% v/v	KNO ₃ 0.016 M	2–propanol 1% v/v	H ₂ O	0.10 ^(e)	0.11 ^(e)	-	0.14 ^(e)	-	-	-	-	-	[21]
TiO ₂ (15% wt)–Zeolite	6 ⁽ⁱ⁾	2–propanol 1% v/v	KNO3 0.016 M	2–propanol 1% v/v	H ₂ O	0.05 ^(e)	0.05 ^(e)	-	0.08 ^(e)	-	-	-	-	-	[21]
Fe ₂ TiO ₅ Fe ₂ Ti ₂ O ₇	6 ⁽ⁱ⁾ 6 ⁽ⁱ⁾	2–propanol 1% v/v 2–propanol 1% v/v	KNO3 0.016 M KNO3 0.016 M	2–propanol 1% v/v 2–propanol 1% v/v	H ₂ O H ₂ O	0.20 ^(e) 0.09 ^(e)	0.05 ^(e) 0.12 ^(e)	-	0.002 ^(e) 0.01 ^(e)		-	-	-		[21] [21]
Fe ₂ TiO ₅ (10%wt)/HZSM–5	6 ⁽ⁱ⁾	2–propanol 1% v/v	KNO3 0.016 M	2–propanol 1% v/v	H_2O	0.31 ^(e)	0.15 ^(e)	-	0.22 ^(e)	-	-	-	-	-	[21]
Fe ₂ TiO ₅ (10%wt)/HZSM-5	6 ⁽ⁱ⁾	2–propanol 1% v/v	KNO3 0.016 M	Oxalic acid 1% w/v	H ₂ O	0.15 ^(e)	0.09 ^(e)	-	0.20 ^(e)	-	-	-	-	-	[21]
Fe ₂ Ti ₂ O ₇ (10%wt)/HZSM-5	6 ⁽ⁱ⁾	2–propanol 1% v/v	KNO3 0.016 M	2–propanol 1% v/v	H ₂ O	0.12 ^(e)	0.01 ^(e)	-	0.03 ^(e)	-	-	-	-	-	[21]
Ti ³⁺ –TiO ₂ (200 °C)	4	-	N_2 100 mL min ⁻¹	CO ₂ 100 mL min ⁻¹	H ₂ O	0.0152 ^(j)	0.0176 ^(j)	-	-	_	-	_	-	-	[47]
Ti ³⁺ -TiO ₂ (300 °C)	4	-	N_2 100 mL min ⁻¹	CO_2 100 mL min ⁻¹	H_2O	0.0298 ^(j)	0.027 ^(j)	-	-	-	-	-	-	-	[47]
Ti ³⁺ -TiO ₂ (400 °C)	4	-	N_2 100 mL min ⁻¹	CO_2 100 mL min ⁻¹	H ₂ O	0.1543 ^(j)	0.0778 ^(j)	-	-	_	-	_	-	-	[47]
Ti^{3+} - TiO_2 (500 °C)	4	-	N_2 100 mL min ⁻¹	CO_2 100 mL min ⁻¹	H_2O	0.0836 ^(j)	0.2227 ^(j)	-	-	-	-	-	-	-	[47]
Ti ³⁺ −TiO ₂ (600 °C)	4	-	N_2 100 mL min ⁻¹	CO_2 100 mL min ⁻¹	H ₂ O	0.0631 ^(j)	0.4529 ^(j)	-	-	-	-	-	-	-	[47]
70%–Ti ³⁺ – TiO ₂ /CNTs (400 °C)	4	-	$\begin{array}{c} N_2 \\ 100 \text{ mL min}^{-1} \end{array}$	CO ₂ 100 mL min ⁻¹	H ₂ O	0.3332 ^(j)	0.0704 ^(j)	-	-	-	-	-	-	-	[47]
75%–Ti ³⁺ – TiO ₂ /CNTs (400 °C)	4	-	N ₂ 100 mL min ⁻¹	CO ₂ 100 mL min ⁻¹	H ₂ O	0.4079 ^(j)	0.064.5 ^(j)	-	_	-	-	_	-	-	[47]
80%-Ti ³⁺ - TiO ₂ /CNTs (400 °C)	4	-	$ m N_2$ 100 mL min ⁻¹	CO ₂ 100 mL min ⁻¹	H ₂ O	0.7101 ^(j)	0.0727 ^(j)	_	-	-	-	-	-	_	[47]
85%-Ti ³⁺ - TiO ₂ /CNTs (400 °C)	4	-	N_2 100 mL min ⁻¹	CO ₂ 100 mL min ⁻¹	H ₂ O	0.414 ^(j)	0.01621 (j)	_	-	_	-	-	-	-	[47]
$90\%-Ti^{3+}-$ TiO ₂ /CNTs (400 °C)	4	-	N_2 100 mL min ⁻¹	CO ₂ 100 mL min ⁻¹	H ₂ O	0.1142 ^(j)	0.03663 (j)	-	-	-	-	_	-	-	[47]

^(a) Calculated from 3 cm³ volume of propylene carbonate solution used in the cell. ^(b) Calculated from data reported in charts and considering 5 cm³ as the solution volume used in the cell. ^(c) Estimated value from data reported in charts. ^(d) Reported value in mmol L⁻¹ h⁻¹, the normalized value per hour of radiation is presented. ^(e) Converted from ppm to mmol L⁻¹. Light source: ^(f) 500 W High–Pressure Hg arc lamp, ^(g) Hg–Xe Lamp, ^(h) 120 W High–pressure Hg lamp, ⁽ⁱ⁾ 250 W High–pressure Hg lamp. ^(j) Converted from μ mol L⁻¹ g⁻¹ and considered 1 g of catalyst.

7. Energy Consumption and Technology Scaling

B Srinivas et al. [21] scaled their experimental set–up five times, which allowed them to work in a 500 mL batch reactor and study the progress of product formation during 12 h of lighting, using 8.3 mM KNO₃ as a nitrogen source and 2–propanol 5% v/v as a source of CO₂, which, in turn, acts as an electron donor. This experiment reports a conversion of nitrate to products of 90% and a urea formation yield of 18%, approximately.

Given the difficulty of directly comparing the different technologies or experimental configurations addressed in this review, evaluating the scaling based on the energy consumption required to obtain urea was proposed. Developing this energy evaluation was considered the most significant amount of urea according to the experimental set–up presented by each author. The data was reported as MWh ton⁻¹ allowing its comparison with the industrial process of obtaining urea. Table 6 compares the calculated energy consumption required to produce one ton of urea according to the data reported. The considerations made for Table 6 are described according to superscript letters.

Table 6. Energy consumption comparison required for urea production by data reported.

Authors	Catalyst	Wattage Light Source, W	Irradiance, W cm ⁻²	Irradiated Effective Area, cm ² (a)	Illumination Time, h	Amount of Urea Produced, mg ^(e)	Energy Consumption, MWh cm ⁻² ton ⁻¹	Energy Consumption, MWh ton ⁻¹
S. Kuwabata et al. [41]	Q-TiO2/PVPD	500	0.36	2.5 (b)	1	1.03 (f)	350	876
BJ. Liu et al. [42]	Q-TiO ₂ /SiO ₂	500	1.00	2.0 (c)	5	1.49 (g)	6.05×10^{3}	1.21×10^{4}
D.G. Shchukin et al. [44]	Cu/TiO ₂ -PVA-PAH/PSS (2.2 µm diametre)	120	0.02	0.79 (d)	5	0.52 (g)	194	152
E.A. Ustinovich et al. [45]	Cu/TiO2:PFD	120	20	ND	1	1.06 (h)	1.89×10^4	-
B. Srinivas et al. [21]	Fe2TiO5(10wt%)/HZSM-5	250	ND	ND	6	1.86 (i)	-	-
H. Maimaiti et al. [47]	80%-Ti ³⁺ -TiO ₂	300	ND	ND	4	0.7101	-	-

^(a) Area reported under light source: ^(b) Pt mesh supported for Q–TiO2/PVPD film, ^(c) Quartz sheet support for QTiO₂/SiO₂ film, ^(d) 1 cm² diameter quartz window in the cell used. ^(e) Data calculated from Table 4 and volume solution used in the cell used by the author: ^(f) 3 cm³, ^(g) 5 cm³, ^(h) A volume of 16 cm³ prepared emulsion, and ⁽ⁱ⁾ 100 cm³ of volume batch capacity was estimated. ND: No data available.

It is estimated globally that the energy consumption for industrial urea production is in the range of 3.2-5.5 GJ ton⁻¹ [107,108], equivalent to ~0.8–1.5 MWh ton⁻¹. According to Table 6, the energy required to produce one ton of urea from each experimental set–up exceeds the energy value needed for an industrial urea production plant due to considering the lamp irradiation as an energy source. Another factor to consider in this analysis is the active area that captures the energy radiated on the photocatalytic systems. In this last case, the least amount of energy required corresponds to the method proposed by D.G. Shchukin et al. [44], which uses a cell with a quartz window of 1 cm in diameter, in which there is a solution with suspended microcapsules, and Cu/TiO₂ is used as a catalyst inside.

However, more efficient energy sources and lower costs should be considered for an industrial scaling of a photocatalyst system, such as light–emitting diodes (LEDs). Traditional lamps used for photocatalysis, such as fluorescent or mercury arc lamps, have a regular use of 500–2000 h and can reach temperatures above 600 °C in their operation, requiring constant cooling. Meanwhile, an LED is mercury-free, has an average life of use of 25,000 to 100,000 h, has higher energy and electrical efficiency, and is smaller than a traditional lamp, allowing for optimizing experimental designs, among other characteristics [109–112]. Undoubtedly, the best available radiant energy is solar energy, considered an inexhaustible energy source. It is estimated that around 5×10^4 exajoules of solar energy reach the earth annually. An effective global solar irradiance is between 60 and 250 W m^{-2} (equivalent to 70% of the total available irradiance) [113]. The most irradiated places on the planet are the southwest of North America, west of South America, southwest of Africa, northwest of the Arabian Peninsula, the Tibetan Plateau, and Australia, with values higher than 2.5 MWh m^{-2} annually, making these places especially suitable for the installation of photovoltaic plants [114]. Therefore, a promising future is expected for developing photocatalytic systems based on solar energy. However, there are still many challenges and opportunities, especially in optimizing the energy absorbed and utilized by photocatalyst materials.

8. Conclusions and Perspectives

According to the most outstanding publications, the photocatalyzed synthesis of urea using TiO_2 -based materials has been reviewed. Urea production has taken great interest not only for being the most widely used fertilizer worldwide but also for its potential use as a clean fuel that can be safely stored and transported. The use of TiO_2 for the photocatalytic conversion of CO_2 and nitrogen compounds to obtain urea, as an alternative proposal to industrial production, remains a promising future prospect since it is possible to activate these systems using solar energy.

Despite the progress made in photocatalyzed urea synthesis using modified and supported TiO_2 nanoparticles, improvements are still needed to optimize radiant energy absorption, shifting from UV light to visible light via doping with metals, non–metals, semiconductors, or sensitized dyes. Increasing the ability to absorb visible light would allow sunlight to be used more efficiently as photoactivation energy to TiO_2 –based materials.

Although it has been possible to determine that the photocatalyzed reaction of urea formation from CO_2 and nitrogen compounds is a simultaneous reaction reduction, the mechanism has not been determined yet. Studies in the area are still required, such as an analysis of DFT to evaluate the free energy of intermediary conformations or steps to propose a photocatalyzed urea synthesis pathway, which will allow for more efficient engineering of TiO₂–based catalyst designs.

Given the difficulty of directly comparing the different photocatalysis experimental set–ups, it is necessary to report efficiency parameters that allow a comparative analysis of the developed technologies, such as reactor design parameters, light intensity, quantum yield, reaction temperature, catalyst load, the effect of matrices, and surface defects, among others.

Energy consumption analysis demonstrated that photocatalytic systems, dependent on conventional lamps for obtaining energy, have low energy efficiency, increasing their consumption in several units to reach an industrial process. However, one way to improve this energy efficiency is using new, more efficient, and lower–cost energy sources such as lighting systems based on light–emitting diodes or LEDs. Furthermore, new ways to optimize the TiO₂–based photocatalysts should be proposed to scale photocatalytic technology, using doping elements, forming composites, or using sensitizers to optimize light–harvesting, especially when solar energy is considered for the development of photovoltaic plants.

One alternative route to reach the world demand for urea is photo–electrocatalysis, which complements the photocatalysis syntheses with the electrocatalysis processes. The latter alternative has been shown to achieve higher urea concentrations, so it is one step closer to becoming a real alternative to industrial synthesis.

We hope that this review generates interest in developing alternative photocatalytic TiO_2 -based technologies that are friendly to the environment and sustainable for producing products of worldwide demand, especially in those highly polluting or energy-demanding industries.

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