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# **Photocatalytic Synthesis of Hydrogen Peroxide from Molecular Oxygen and Water**

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## **Keywords**

Hydrogen peroxide synthesis ; photocatalyst ; titania ; graphitic carbon nitride ; water  
treatment ; reaction mechanism

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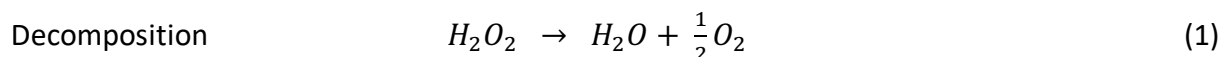
## Abstract

Hydrogen peroxide is a powerful and green oxidant that allows for the oxidation of a wide span of organic and inorganic substrates in liquid media under mild reaction conditions, and forms only molecular water and oxygen as end-products. Hydrogen peroxide is therefore used in a wide range of applications, for which the well-documented and established anthraquinone autoxidation process is by far the dominating production way at the industrial scale. That method being highly energy-consuming and environmentally-costly, the search for more sustainable synthesis methods is of high interest. To this end, the article reviews the basis and the recent development of the photocatalytic synthesis of hydrogen peroxide. Different oxygen reduction and water oxidation mechanisms are discussed, as well as several kinetic models, and the influence of the main key reaction parameters is itemized. A large range of photocatalytic materials is reviewed, with emphasis on titania-based photocatalysts and on high-prospect graphitic carbon nitride based systems that take advantage of advanced bulk and surface synthetic approaches. Strategies for enhancing the performances of solar-driven photocatalysts are reported, and the search for new, alternative, photocatalytic materials is detailed. Finally, the promise of *in-situ* photocatalytic synthesis of hydrogen peroxide for water treatment and organic synthesis is described, as well as its coupling with enzymes and the direct *in-situ* synthesis of other technical peroxides.

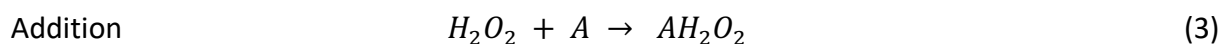
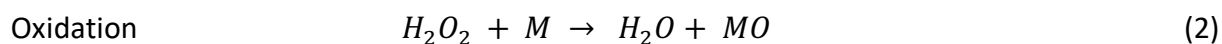
## 1. Hydrogen peroxide: from chemistry to applications

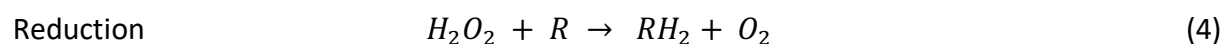
### 1.1. Chemistry of hydrogen peroxide

Hydrogen peroxide ( $H_2O_2$ ) is an odorless, colorless, and versatile liquid oxidant that shows high oxidation potential over the whole pH range, with  $E_0 = 1.763$  V and 0.878 V at pH 0 and 14, respectively. It is an environmentally friendly oxidant under mild conditions, as it generates only oxygen and water as decomposition products according to reaction (1). The decomposition of  $H_2O_2$  requires careful control as it forms gaseous oxygen with the release of heat at  $100 \text{ kJ.mol}^{-1}$ . Many compounds are able to catalyze the decomposition of  $H_2O_2$ , such as most of the transition metals and some organic substances.



$H_2O_2$  is a powerful oxidant allowing the oxidation of a wide span of organic and inorganic substrates in liquid media (2). Also,  $H_2O_2$  allows addition reactions in liquid phase, and molecularly binds to compounds such as metal peroxides with alkaline-earth or alkali metals, percarbonates or oxoacid salts among others (3). Further, the strong reducing power of  $H_2O_2$  allows the reduction of strong oxidants like  $KMnO_4$  or  $Ce(SO_4)_2$ , which is the basis for some volumetric methods for determining the  $H_2O_2$  concentration (4). Last, substitution reactions with organic reactants can take place, with the formation of peroxido molecules in particular extensively used in organic synthesis (5).





As oxidant,  $H_2O_2$  differentiates from stoichiometric oxidants like nitrous oxide ( $N_2O$ ), tert-butyl hydroperoxide (tBuOOH) or permanganates that produce wastes in large amounts, and make mandatory the implementation of additional separation steps.  $H_2O_2$  also benefits from its low molecular weight, and in consequence from its high active oxygen content, in comparison to other popular oxidants such  $HNO_3$  or NaClO (Table 1) [1].

**Table 1.** Classical industrial oxidants. Reproduced with permission from Ref. [1]. Copyright 2006 Wiley-VCH Verlag GmbH.

| Oxidant                   | By-product              | Active oxygen (% w/w) |
|---------------------------|-------------------------|-----------------------|
| $H_2O_2$                  | $H_2O$                  | 47.1                  |
| $N_2O$                    | $N_2$                   | 36.4                  |
| NaClO                     | NaCl                    | 35.6                  |
| $NaIO_4$                  | NaI                     | 29.9 <sup>[b]</sup>   |
| $HNO_3$                   | $NO_x$ , $N_2O$ , $N_2$ | 25.0                  |
| NaClO                     | NaCl                    | 21.6                  |
| tBuOOH                    | tBuOH                   | 17.8                  |
| NaBrO                     | NaBr                    | 13.4                  |
| « $KHSO_5$ » <sup>a</sup> | $KHSO_4$                | 10.5 -                |

<sup>a</sup> stabilized and marketed as the “triple salt”  $2 KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$  (oxone), <sup>b</sup> considering that all four oxygen atoms are used.

## 1.2. Applications of hydrogen peroxide

Figure 1 depicts the main fields of applications of  $H_2O_2$ . Pulp and paper bleaching is one of the most important applications of  $H_2O_2$ , that is used as an alternative to classical chlorine-

based bleaches and allows the release of halogenated byproducts in wastewater to be hindered. In alkaline media,  $\text{H}_2\text{O}_2$  operates as a bleaching agent through the presence of the  $\text{HO}_2^-$  anion, as it can eliminate many chromophores from the lignin polymer, notably by its nucleophilic attack on the carbonyl functions of the lignin.  $\text{H}_2\text{O}_2$  is also used as a bleach for the recycled paper, where the printing dyes are removed by a combined action of  $\text{H}_2\text{O}_2$  and of sodium dithionite used as reductive bleach.

$\text{H}_2\text{O}_2$  is also extensively used as a bleaching alternative to sodium hydrosulfite or hypochlorite in the textile industry, which requires the implementation of color-safe laundry bleaches. For this application, stable precursors like sodium perborate or percarbonate are used. They release  $\text{H}_2\text{O}_2$  during dissolution in water, percarbonates being preferred to perborates owing to a lower dissolution temperature.

Driven by more and more stringent environmental regulations, wastewater treatment is the most significant application of  $\text{H}_2\text{O}_2$  in the environmental field. It can supersede chlorine-based oxidants for the destruction of toxic chemicals such as thiocyanate, cyanide, chloride, hypochlorite, nitrite, cyanide or organic compounds in industrial wastewater, or hydrogen sulfide in the sewer pipes of municipal wastewater treatment networks [2]. One major advantage of  $\text{H}_2\text{O}_2$  is the absence of halogenated by-products such as the carcinogenic trihalomethanes that require the downstream implementation of granular adsorbents.

Chemical synthesis is also a driving force for the  $\text{H}_2\text{O}_2$  demand, with applications in the ammoximation of cyclohexanone to the corresponding oxime that is a key-intermediate in the Nylon-6 production [3], as well as in the HPPO (hydrogen peroxide propylene oxide) process, that integrates a unit generating  $\text{H}_2\text{O}_2$  by direct reaction of  $\text{H}_2$  and  $\text{O}_2$  for a more efficient propylene oxide production [4-6]. Other reactions consist notably in alkene epoxidation, aromatic hydroxylation, alkane oxidation or oxo-halogenation reactions.

Last,  $\text{H}_2\text{O}_2$  is used in several niche applications such as the mining and metal processing [7-8], with applications like the extraction and post-treatment of uranium and of many transition metals, but also metal finishing.  $\text{H}_2\text{O}_2$  is further used for cleaning wafers of silicon and germanium semiconductors and etching printed circuit boards.



**Figure 1.** Main fields of applications of hydrogen peroxide. Adapted and reproduced with permission from Ref. [9]. Copyright 2019 American Chemical Society.

The annual world production of  $\text{H}_2\text{O}_2$  demand was approximately 5.1 million metric tons in 2021. The sectoral distribution of the  $\text{H}_2\text{O}_2$  demand depends clearly on the geographical location, but the paper and pulp bleaching is by far the dominating sector irrespectively of the

location, followed by decreasing order of importance, first by the chemical synthesis and the textile bleaching, and further among other sectors, by cosmetics and healthcare, wastewater treatment, food and beverage, electronics and semiconductors.

### **1.3. Key highlights into the global hydrogen peroxide market**

Estimates are obviously subjected to variability depending on the projection models used, on intrinsic factors lying to the H<sub>2</sub>O<sub>2</sub> market and on external regional and world conjunctural factors. The global hydrogen peroxide market is expected to reach a revenue of US\$6.6 bn in 2026, compared to its 2020 level of US\$3.9 bn, and is estimated to exhibit a compounded annual growth rate (CAGR) of 7.3% between 2022 and 2026, with a 1.9 fold expansion [10]. High-purity grades are projected to remain the most sought-after grades for the different end-users, and the 35-70% grade should amount for over 74% share in the market volume. Remarkable contribution to the market growth will likely result from the growth of specialty application areas like electronics and semiconductor manufacturing (expected to be the fastest-developing end-user), food and beverage, cosmetics, water treatment, and aquaculture, due to the growing environmental awareness and to the soaring availability of sustainable alternatives. This growing demand for high-purity H<sub>2</sub>O<sub>2</sub> should provide new lucrative opportunities for key-manufacturers, and the main end-users that need high-purity H<sub>2</sub>O<sub>2</sub> will form newer niche markets for H<sub>2</sub>O<sub>2</sub> suppliers.

Asia Pacific is projected to keep its leadership in the market by contributing to over half of the revenues, while China should spearhead as the larger consumer and producer. However, the Middle East and Africa are all set to emerge as the most lucrative regional market for H<sub>2</sub>O<sub>2</sub>. The market is dominated by European players, and the top-five key-actors (namely Solvay S.A., Arkema S.A., Evonik Industries AG, Mitsubishi Gas Chemical Company and



Nouryon Holding B.V.) accounted in 2021 for a collective share of over 75% in the global hydrogen peroxide market space.

## 2. Synthesis routes of H<sub>2</sub>O<sub>2</sub>

### 2.1. An historical perspective of the industrial H<sub>2</sub>O<sub>2</sub> manufacture

The first isolation of the H<sub>2</sub>O<sub>2</sub> synthesis takes us back to the original works of L.J. Thenard in 1818 reporting that H<sub>2</sub>O<sub>2</sub> is obtained as a byproduct of the reaction between barium peroxide and acids [11]. Table 2 lists the chronological developments achieved in the field of the industrial production of H<sub>2</sub>O<sub>2</sub>, itemized as chemical and electrochemical processes [12]. Reaction schemes and descriptions can be found in Jones [13], Goor et al. [14-15] and Ranganathan and Sieber [12].

**Table 2.** Historical development in the industrial manufacture of H<sub>2</sub>O<sub>2</sub>. Reproduced with permission from Ref. [12]. Copyright 2018 MDPI.

| Year | Inventor     | Catalysis type  | Details                                                                                                                                                                                                                                                                                 |
|------|--------------|-----------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1818 | L.J. Thenard | Chemical        | Barium peroxide reacts with nitric acid and forms H <sub>2</sub> O <sub>2</sub> as a by-product. Barium peroxide reacts with hydrochloric acid to form barium chloride and H <sub>2</sub> O <sub>2</sub> . Yield of 3% H <sub>2</sub> O <sub>2</sub> was 2000 tons/annum (t/a) [11, 16] |
| 1853 | H. Meidinger | Electrochemical | Electrolysis of sulphuric acid to yield H <sub>2</sub> O <sub>2</sub> [17]                                                                                                                                                                                                              |
| 1878 | M. Berthelot | Electrochemical | Elucidated the mechanism of sulphuric acid electrolysis. Reported the formation of peroxodisulphuric acid as an intermediate [18]                                                                                                                                                       |
| 1901 | W. Manchot   | Chemical        | Autoxidation of hydroquinones and hydrazobenzenes under alkaline                                                                                                                                                                                                                        |

|           |                                                    |                       |                                                                                                                                                                                  |
|-----------|----------------------------------------------------|-----------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|           |                                                    |                       | conditions in the presence of molecular oxygen to yield $\text{H}_2\text{O}_2$ [19-21]                                                                                           |
| 1908      | Degussa-Weissenstein Process                       | Electrochemical       | First production plant set up in Weissenstein, Austria [22-23]                                                                                                                   |
| 1910      | Münchener Process or the Pietzsch-Adolph Process   | Electrochemical       | Developed by Pietzsch and Adolph at the Elektrochemische Werke, Munich. Used potassium peroxodisulphate instead of sulphuric acid to produce $\text{H}_2\text{O}_2$ [22-23]      |
| 1914      | Hugo Henkel and Walter Weber                       | Chemical              | First account of direct synthesis of $\text{H}_2\text{O}_2$ using its constituent gases [24]                                                                                     |
| 1924      | Riedl-Löwenstein Process                           | Electrochemical       | Similar to the Pietzsch-Adolph Process; used ammonium peroxodisulphate to produce $\text{H}_2\text{O}_2$ by electrolysis. Yield of 100% $\text{H}_2\text{O}_2$ was 35 kt [22-23] |
| 1932      | Walton and Filson                                  | Chemical autoxidation | Published their work on the alternate oxidation and reduction of hydrazobenzenes to produce $\text{H}_2\text{O}_2$ [25]                                                          |
| 1935      | Pfleiderer, Baden, Aniline and Soda Factory (BASF) | Chemical autoxidation | Alkaline autoxidation of hydrazobenzenes to form sodium peroxide, later hydrolysed to form $\text{H}_2\text{O}_2$ [26]                                                           |
| 1935–1945 | Riedl and Pfleiderer                               | Chemical autoxidation | Anthraquinone autoxidation process (AO) set up in two different cities each with 2000 t capacity [22, 27]                                                                        |
| 1953      | E.I. du Pont de Nemours                            | Chemical autoxidation | Commercial plant setup with based on the Riedl and Pfleiderer process [13-15]                                                                                                    |
| 1957–1980 | Shell process                                      | Chemical autoxidation | Oxidation of 2-propanol to yield $\text{H}_2\text{O}_2$ at a capacity of 15 kt [28]                                                                                              |

## 2.2. The anthraquinone process

The production of  $\text{H}_2\text{O}_2$  is currently realized at the industrial scale via electrolysis, partial oxidation of isopropanol, and mainly through the anthraquinone (AQ) autoxidation process, that accounts for more than 95% of the worldwide production of  $\text{H}_2\text{O}_2$  [1]. The first commercial development of the AQ autoxidation process with a production level of 1 ton/year was implemented in Germany by IG-Farbenindustrie AG following the so-called Riedl-Pfleiderer process pioneered at BASF in 1939 [27]. Although the original process has been improved, it is still based on a multi-step sequence consisting in hydrogenation, oxidation,

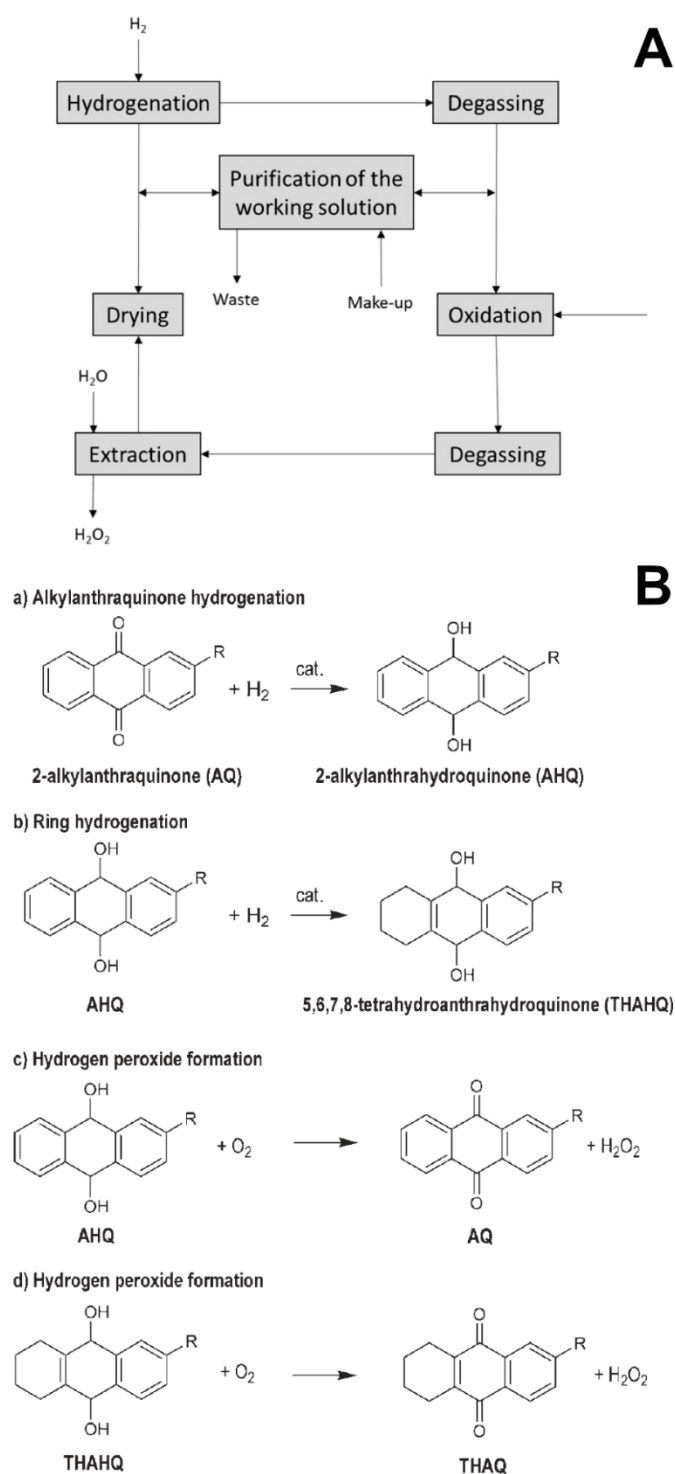
H<sub>2</sub>O<sub>2</sub> extraction and treatment of the working solution. A simplified block diagram of the multi-step AQ autoxidation process is shown in Figure 2A.

2-alkylanthraquinone (AQ), mostly 2-ethyl anthraquinone, is first hydrogenated into the corresponding anthrahydroquinone (AHQ) over a Pd or Ni catalyst in an organic solvent (Figure 2B). After separation of the catalyst from the solution, AHQ is oxidized back into AQ with the equimolar formation of H<sub>2</sub>O<sub>2</sub>. H<sub>2</sub>O<sub>2</sub> is recovered from the working organic solution by liquid-liquid countercurrent extraction with demineralized water. Further distillation allows for the purification of the aqueous H<sub>2</sub>O<sub>2</sub> and the increase of its concentration up to *ca.* 70% while the AQ-containing solvent is recycled. In both hydrogenation and oxidation steps, side reactions such as the hydrogenation of the unsubstituted aromatic ring in AHQ to form 5,6,7,8-tetrahydroanthrahydroquinone (THAHQ), and its further oxidation into tetra hydroquinone (THAQ), are lowering the yields to H<sub>2</sub>O<sub>2</sub> and result in a net consumption of AQ.

The great advantage of the AQ process remains the capacity to operate and to produce H<sub>2</sub>O<sub>2</sub> in a continuous way at relatively mild temperature, and without any contact between H<sub>2</sub> and O<sub>2</sub>. However, mass transfer limitations in both oxidation and hydrogenation reactors are lowering the performances, and the difficult control of both AQ residence time and AQ/H<sub>2</sub> ratio in the hydrogenation reactor favors the formation of byproducts. Cross-contamination between phases is observed, while organic contamination can also be introduced during the extraction step. Therefore, in addition to a significant energy input, the AQ process suffers globally from the generation of wastes in large amounts, namely wastewater containing *e.g.* 2-ethylanthraquinone, tri-octyl phosphate, tert-butyl urea or potassium carbonate, solid wastes (activated alumina) or exhaust gases (mesitylene isomers) [29].

Despite its relatively high E-factor (defined as the ratio between the amount of waste generated and that of the desired product) and its low atom efficiency, the AQ oxidation

process remains *de facto* the process operated at the industrial scale, as it is reported to be economically viable for yearly production volumes above  $10^5$  tons at  $\text{H}_2\text{O}_2$  high concentrations.

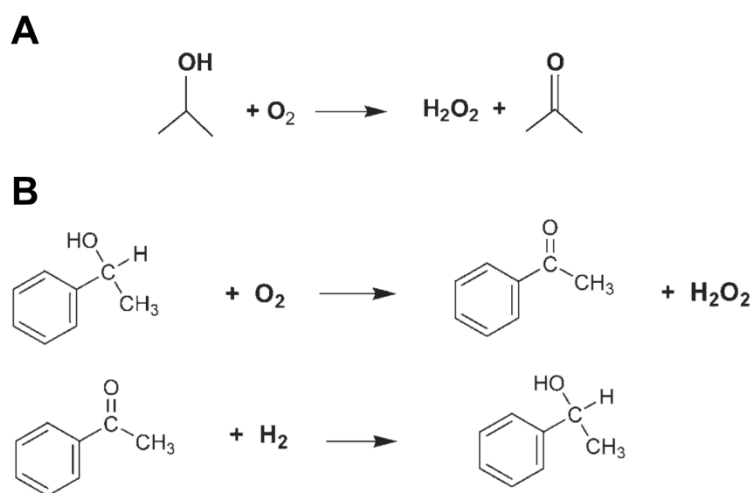


**Figure 2. (A)** Simplified block diagram of the multi-step AQ autoxidation process. Reproduced with permission from Ref. [12]. Copyright 2018 MDPI; **(B)** AQ autoxidation reaction process. Reproduced with permission from Ref. [1]. Copyright 2006 Wiley-VCH Verlag GmbH.

### 2.3. Industrial competitors to the anthraquinone process

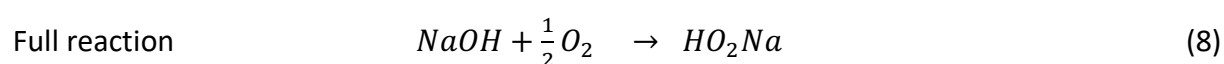
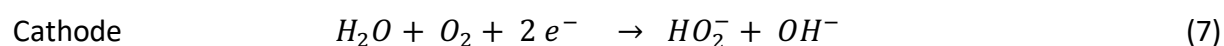
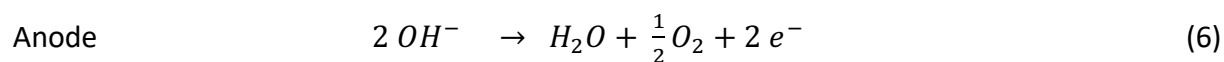
As shown in Figure 3,  $\text{H}_2\text{O}_2$  can be alternatively produced by the partial oxidation of primary or secondary alcohols, with the formation of aldehyde or ketone, respectively, as byproduct [30-31]. This process was implemented by Shell Chemical over the period 1957-1980, and relies on the autoxidation by an oxygen-rich gaseous stream of the 2-propanol reagent in an azeotrope mixture with water at moderate pressure and temperature (10-20 bar, 90-140°C).

The synthesis of  $\text{H}_2\text{O}_2$  through the oxidation of methylbenzylalcohol was developed separately by Repsol Quimica and Lyondell Chemical (Arco Chemical). At 120-180°C and under pressures of 3-10 bar, the production of methylbenzylalcohol and of  $\text{H}_2\text{O}_2$  as byproduct can occur without the help of any catalyst [32-33], although Ni-based complexes can be used as homogeneous catalysts [34].



**Figure 3.** Large scale processes alternative to the main AQ oxidation, based on the oxidation of alcohols. **(A)** Autoxidation of a secondary alcohol; **(B)** oxidation of methylbenzylalcohol, with the subsequent recycling of the acetophenone into methylbenzylalcohol after the extraction/distillation step. Methylbenzylalcohol is a byproduct of the propylene-oxide-styrene process. Reproduced with permission from Ref. [1]. Copyright 2006 Wiley-VCH Verlag GmbH.

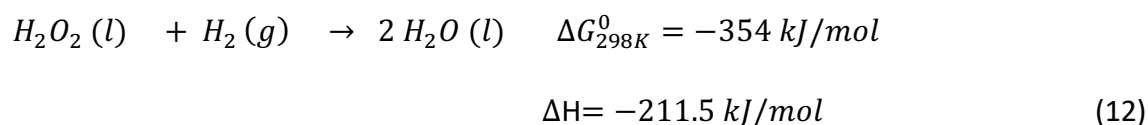
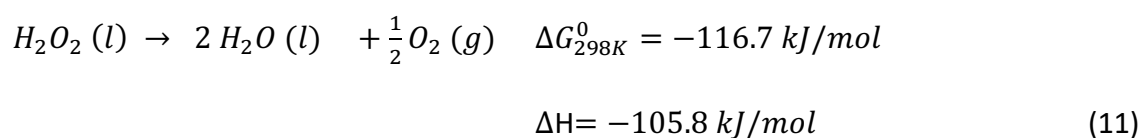
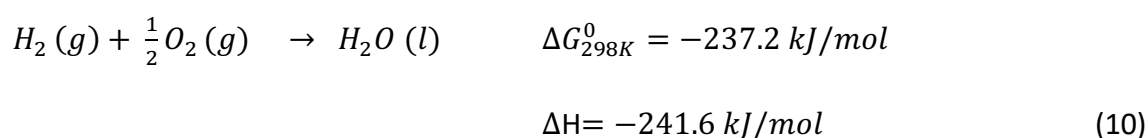
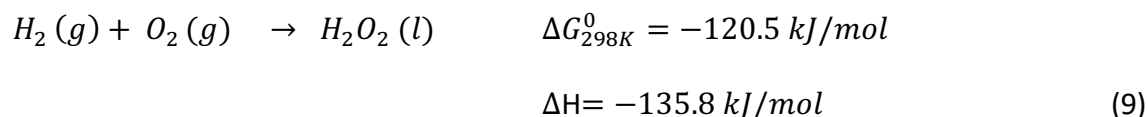
Last, the Dow process consists in conducting the electrochemical synthesis of  $H_2O_2$  in a diluted solution of NaOH, with the following half and overall reactions (6-8). This technology can mostly be used when the application does not require the separation of  $H_2O_2$  from the NaOH aqueous solution (*e.g.* pulp bleaching).



#### 2.4. Direct synthesis of $H_2O_2$ from molecular $O_2$ and $H_2$

The direct synthesis of  $H_2O_2$  from molecular  $O_2$  and  $H_2$  reactants appears as a greener and more atom-efficient route than the dominant, energy-intensive and low-sustainability industrial AQ process. Being in principle the simplest method, it might offer a valuable alternative in particular for decentralized production. Apart from the safety concerns related to the management of  $H_2/O_2$  mixtures known as explosive over a wide range of

concentrations, the main challenge of the process lies in selectivity issues, given that the formation of H<sub>2</sub>O from molecular O<sub>2</sub> and H<sub>2</sub> (10) is thermodynamically more favorable than that of H<sub>2</sub>O<sub>2</sub> (9). In addition, the process selectivity is also affected by both H<sub>2</sub>O<sub>2</sub> decomposition (11) and hydrogenation (12), which lead to the unwanted formation of H<sub>2</sub>O.



Pd catalysts are known to be very active for the direct synthesis of H<sub>2</sub>O<sub>2</sub> from molecular O<sub>2</sub> and H<sub>2</sub> since more than a century [24]. However, a proper and careful balance has to be found between activity and selectivity. Also, the degradation of H<sub>2</sub>O<sub>2</sub> needs a clear and strict control of the experimental conditions for being minimized, in particular by using a low temperature of reaction.

It is proposed that the synthesis of H<sub>2</sub>O<sub>2</sub> occurs by addition of hydrogen to the O<sub>2</sub>\* surface intermediate, and that the irreversible O-O cleavage in molecular O<sub>2</sub> leads to the formation of H<sub>2</sub>O and prevents that of H<sub>2</sub>O<sub>2</sub> [35-36]. A clear challenge relies on the ability of finely-tuned catalysts to unfavor the formation of both O\* and OH\* surface intermediates, known to lead to the formation of the unwanted H<sub>2</sub>O molecule [37].

Pd-based catalysts are reported to be highly active for the direct synthesis of  $\text{H}_2\text{O}_2$ . However the evidence whether metallic or oxidized Pd phases are needed, still remains a matter of debate, as well as the nature of the Pd active site favoring the irreversible cleavage of the O-O with consequent formation of  $\text{H}_2\text{O}$  [38]. The use of additives, either as promotor to the catalyst itself or to the reaction media, was reported as a worthy strategy for enhancing the selectivity, and in particular for inhibiting the reaction pathways leading to the  $\text{H}_2\text{O}_2$  degradation. They comprise mostly inorganic acids such as sulfuric or phosphoric acids, or halogen acids such as hydrochloric acid [39]. Solid acids as well as halides have also been used as additives to the catalyst. Wilson and Flaherty interestingly highlighted the crucial role of the protons in the formation of  $\text{H}_2\text{O}_2$ , in particular by aiding the key-reduction of  $\text{O}_2$ , while they suggested that the counteranions can play an important role towards the  $\text{H}_2\text{O}_2$  selectivity [40].

While intensive works have been conducted on Pd systems, Au catalysts dispersed on a large range of supports were more recently reported to be promising for synthesizing  $\text{H}_2\text{O}_2$  without addition of any halide promoters [41-42]. A wide range of noble (Pt, Ru, Au, Ir, Ag) and non-noble (Co, In, Ga, Zn, Ni, Sn, W, Sb, Te) secondary metals has been investigated, the use of cost-effective, abundant metals being of prime importance. Huge works remain to be performed to unravel the synergistic effect observed with finely-tuned bimetallic systems, that will require the association of both experimental and computational tools.

Further, as usually in heterogeneous catalysis, the support nature is a key-factor strongly impacting on the activity of the metal-based catalysts and on the selectivity pattern of the reaction. Among others, most of the supports studied comprise many transition metal oxides, mesoporous silica, zeolites, heteropolyacids or carbons under various forms [38].



An approach for preventing the detrimental decomposition of  $\text{H}_2\text{O}_2$  into  $\text{H}_2\text{O}$  and  $\text{O}_2$  lies in the use of a suited solvent, which strongly complexifies the process, in particular owing to mass transfer barrier limitations between the solvent and the gas phase. The solvent acts for enhancing the hydrogen solubility in the liquid phase but also can play additional roles. For instance, acetonitrile and ethanol were reported to inhibit the formation of  $\text{H}_2\text{O}$  by coordinating with the Pd surface [43]. Water as solvent provides the largest safety to the process, also with very good miscibility with  $\text{H}_2\text{O}_2$ . Unfortunately, it shows a low solubility with both  $\text{O}_2$  and  $\text{H}_2$ , which in consequence lowers the production of  $\text{H}_2\text{O}_2$ . Organic solvents can be used, but they are usually introducing problems of contamination for the aqueous phase.  $\text{CO}_2$  can be used as solvent in both supercritical and liquid phase conditions, the miscibility of  $\text{H}_2$  and  $\text{O}_2$  being by far higher than in aqueous or organic solvents. Nevertheless, mass transfer limitations between both liquid and gas phases are in favor of operating in supercritical conditions.

Additionally, membranes can be used as an elegant strategy to avoid the direct contact between molecular  $\text{H}_2$  and  $\text{O}_2$  [44]. They can in particular be used for supplying atomic hydrogen to the catalyst located in the porous network where it can interact with oxygen.

### **3. Experimental methodology for the quantification of $\text{H}_2\text{O}_2$ in water**

The measurement of the  $\text{H}_2\text{O}_2$  concentration is an indispensable first step to evaluate the catalyst performance, selectivity, and stability and, ultimately, to get the most suitable reaction conditions for developing new two-electron water oxidation reaction and two-electron oxygen reduction reaction (ORR) photo-, electro-, or photoelectro-catalysts able to pave for a more sustainable path in the synthesis of  $\text{H}_2\text{O}_2$ . Thus, analytic methods such as UV-

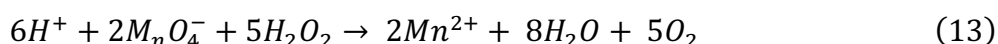
Vis spectroscopy [45], chemical titration [46], fluorometry [47], chemiluminescence [48], and colorimetric test strips [49] have been used to accurately quantify  $\text{H}_2\text{O}_2$ . Each method offers a unique advantage depending on the nature of the solvent or electrolyte, the accuracy requirement, or the concentration of *in-situ* produced  $\text{H}_2\text{O}_2$ . Although these methods are generally well established, accurate quantification sometimes poses a challenge since the complexity of the detection environments further complicates the  $\text{H}_2\text{O}_2$  measurement. Here, we will briefly discuss the working principle, the pros and cons of each method, and the interferences that may affect the measurements.

### **3.1. Methods for $\text{H}_2\text{O}_2$ quantification**

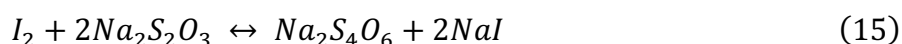
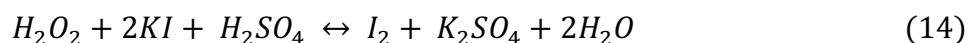
Among the different methods, the use of colorimetric test strips is the most convenient and straightforward means to estimate the unknown amounts of  $\text{H}_2\text{O}_2$ . When the strip is immersed in the sample solution,  $\text{H}_2\text{O}_2$  reacts with the peroxidase and the organic redox indicator, forming a colored oxidation compound (Figure 4A) [50]. By visually comparing the strip with the fields of the color scale, the  $\text{H}_2\text{O}_2$  concentration can be measured semi-quantitatively. Depending on the manufacturer, the paper strips can detect  $\text{H}_2\text{O}_2$  within the concentration range of 0.5 ppm to 1000 ppm with an accuracy of  $\pm 20\%$  (Quantofix®). However, factors such as exposure time, compatibility with different solvents, electrolytes, and pH generally affect the precision of the test strips. For instance, the difference in air exposure time by 5 seconds before reading in a strip reader leads to an overestimated concentration of  $\sim 50\%$  using 100 ppm test strips [51].

Methods such as spectrophotometry [45], chemical titration [52], and fluorimetry [47] are widely employed for more reliable quantification. In many reports, the concentration of  $\text{H}_2\text{O}_2$  generated photocatalytically is in the micromolar and millimolar range after a few hours.

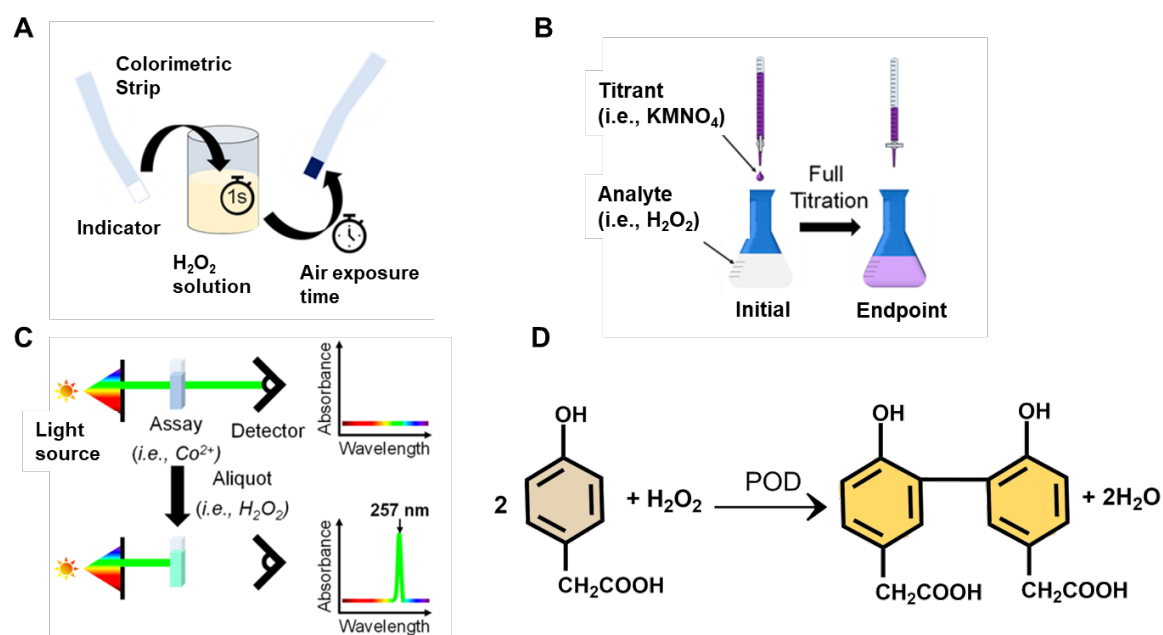
Therefore, the detection method must be sensitive and with a low detection limit. The most traditional measurement method is by permanganate (KMnO<sub>4</sub>) titration (Figure 4B) [52]. It is based on the reduction of MnO<sub>4</sub><sup>-</sup> by H<sub>2</sub>O<sub>2</sub> to produce colorless Mn<sup>+2</sup> (MnSO<sub>4</sub>) under acidic conditions (13). A change in the color of H<sub>2</sub>O<sub>2</sub> to faint pink indicates the reaction's endpoint. Based on the amount of KMnO<sub>4</sub> consumed during titration, and the reaction stoichiometry, the amount of H<sub>2</sub>O<sub>2</sub> can be calculated. Although the strongest advantage of the KMnO<sub>4</sub> titration method is its accuracy, the limit of detection is high (200-1000 ppm), so it is only useful for medium to high H<sub>2</sub>O<sub>2</sub> concentrations, and a large sample volume is usually necessary [52-53].



In contrast to the permanganate method, the iodometric titration method utilizes the oxidizing properties of H<sub>2</sub>O<sub>2</sub>. With this method, H<sub>2</sub>O<sub>2</sub> oxidizes I<sup>-</sup> (coming from KI) to form triiodide (I<sub>3</sub><sup>-</sup>) (14), then titrated with thiosulfate (15). Titration with thiosulfate results in a pale yellow-colored solution turning to deep blue with the addition of starch as the indicator [54].



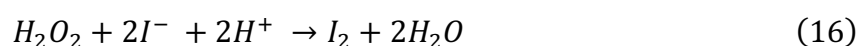
Overall, the titrimetric method's advantage compared to any other method is that it does not require the determination of a calibration curve or the use of any specific equipment before analysis, however, the concentration of H<sub>2</sub>O<sub>2</sub> being measured should be taken into consideration due to the high detection limit of quantification of this method.



**Figure 4.** Schematic representation of different  $\text{H}_2\text{O}_2$  quantification methods. **A)** Colorimetric test strips, **B)** titration by  $\text{KMnO}_4$ , **C)** UV-Vis spectroscopy, **D)** POHPAA fluorescence method. Reproduced with permission from [51]. Copyright 2020 American Chemical Society.

Direct detection of  $\text{H}_2\text{O}_2$  in solution through optical absorption is possible, although it is challenging for low concentrations since its absorption coefficient is small ( $0.01 \text{ M}^{-1} \text{ cm}^{-1}$  at 360 nm and  $13 \text{ M}^{-1} \text{ cm}^{-1}$  at 260 nm) [55]. Also, this method may have many interferences and should be only recommended in controlled reaction media. Therefore, colorimetric method is the most widely adopted for  $\text{H}_2\text{O}_2$  detection of low concentration. Here,  $\text{H}_2\text{O}_2$  can reduce or oxidize a reagent resulting in a color change, and measured using a UV-Vis spectrophotometer (Figure 4C). The absorption is usually proportional to the amount of  $\text{H}_2\text{O}_2$ , which can be accurately quantified by constructing a calibration curve. One example is the N, N-diethyl-p-phenylenediamine (DPD) method, which is based on the oxidation N, N- DPD by  $\text{H}_2\text{O}_2$  catalyzed with peroxidase (POD).

The radical  $\text{DPD}^+$  exhibits a stable pink color with strong absorption at 551 nm and 510 nm with a large absorption coefficient of  $2.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  [56] where the intensity at 551 nm can be directly correlated with the amount of  $\text{H}_2\text{O}_2$ . This method is linear for a concentration range of 0-100  $\mu\text{M}$ . Therefore, with this method, dilution is always necessary for samples with high  $\text{H}_2\text{O}_2$  concentration [57]. Parallel to DPD, the iodometric method using potassium iodide (KI) relies on the oxidation of excess  $\text{I}^-$  by  $\text{H}_2\text{O}_2$  to produce a yellow-colored  $\text{I}_3^-$ , which can be observed at 350 nm (16).



This procedure is similar to iodometric titration, except the iodine is not titrated with thiosulfate, and the  $\text{I}_3^-$ , which is in equilibrium with  $\text{I}_2$  and  $\text{I}^-$  is being measured. Since the reaction with KI and  $\text{H}_2\text{O}_2$  is slow, a small amount of ammonium molybdate is usually added as a catalyst and potassium hydrogen phthalate (KHP) as the buffer [58]. The large value of molar absorption coefficient of  $\text{I}_3^-$  ( $2.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $\lambda = 350 \text{ nm}$ ) makes it very suitable to measure even at less than 10  $\mu\text{M}$   $\text{H}_2\text{O}_2$  (17). Compared to  $\text{KMnO}_4$  titration, the KI method is less sensitive in the presence of organic impurities [52]. Other colorimetric methods are also reported:

- Oxidation of  $\text{Fe}^{+2}$  to  $\text{Fe}^{+3}$  [59].
- Cerium sulfate method, where  $\text{H}_2\text{O}_2$  reduces yellow-colored  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ , and is measured by the decrease in absorbance of  $\text{Ce}^{4+}$  at 316 nm [49].
- Cobalt-carbonate assay ( $\text{Co}/\text{CO}_3$ ), which forms a greenish ( $[\text{Co}(\text{CO}_3)_3]\text{Co}$ ) complex after  $\text{Co}^{2+}$  oxidation, where the formed complex can be measured at 260 nm [51].

- Reduction of vanadate ( $\text{VO}_3^-$ ) under acidic conditions to produce a red-orange peroxo-vanadium cation ( $\lambda = 450 \text{ nm}$ ) [60].
- Reduction of  $\text{Cu}^{+2}$  by  $\text{H}_2\text{O}_2$  in the presence of excess 2,9-dimethyl-1,10-phenanthroline (DMP) to form  $\text{Cu}^{+1}$ -DMP ( $\lambda = 454 \text{ nm}$ ) [61].
- Reaction of titanium sulfate reagent with  $\text{H}_2\text{O}_2$  to produce a yellow-colored complex of pertitanic acid ( $\text{H}_2\text{TiO}_4$ ), which absorbs at  $410 \text{ nm}$  [62].
- $\text{H}_2\text{O}_2$  oxidation of oxo [5,10,15,20-tetra(4-pyridyl)porphyrinato] titanium(IV) ( $\text{TiO}(\text{tpypH}_4)^{+4}$ ) to  $\text{TiO}_2(\text{tpypH}_4)^{+4}$  ( $\lambda=450 \text{ nm}$ ) [63].

The minimum detection limits for these methods range from 0.01-50 ppm, significantly lower than the titrimetric method [64]. Despite the numerous techniques mentioned here, new analytical methods are being developed to achieve a more robust, cheaper, and accurate  $\text{H}_2\text{O}_2$  quantification. For instance, the presence of dyes in water, such as rhodamine B and acid orange 7, causes the same absorption with  $\text{DPD}^+$  at  $551 \text{ nm}$ , leading to increased measured absorbance leading to inaccurate  $\text{H}_2\text{O}_2$  measurements. To improve the traditional DPD-POD method, the POD-KI method was recently established to improve the measurement in the presence of dyes. Moreover, it shows high tolerance to counter ions such as  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^-$ , and humic acids [65]. The accuracy of the measurement using the spectrophotometric method hugely relies on the accuracy of the known  $\text{H}_2\text{O}_2$  concentration of the standards. If done correctly, spectrophotometric methods are preferable to titration-based techniques due to their simplicity, low detection limits, low execution cost, and being completely quantitative.

The fluorometric method is also used to quantify  $\text{H}_2\text{O}_2$  accurately. This method relies on the horseradish peroxidase (HRP)-catalyzed dimerization of p-hydroxyphenyl acetic acid (POHPAA) by  $\text{H}_2\text{O}_2$  (Figure 4D). As proposed by Miller & Kester [66],  $\text{H}_2\text{O}_2$  oxidizes the

peroxidases from the +3 to +5 state. Subsequently, the oxidized peroxidase is reduced by the POHPAA to form POHPAA radicals through two related pathways. The two POHPAA radicals will form the fluorescent product, 2,2'-dihydroxybiphenyl, with excitation and emission wavelengths peaking at 320 nm and 400 nm, respectively. The formation of the dimer directly correlates to the concentration of  $\text{H}_2\text{O}_2$  with the detection limit of  $0.2 \mu\text{g L}^{-1}$  [67]. This assay is very sensitive towards impurities in the reagent POHPAA, so it should be freshly recrystallized before use. Table 3 provides more information about the analytical methods discussed above, as reviewed previously by Brandhuber & Korshin [64].

**Table 3.** Different analytical methods for H<sub>2</sub>O<sub>2</sub> quantification. Reprinted with permission from Ref. [64]. Copyright The Water Research Foundation.

| Type              | Method                          | H <sub>2</sub> O <sub>2</sub> range | Reaction mechanism and detection conditions                                                                                            | Performance assessment/interference                                                                                     |
|-------------------|---------------------------------|-------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------|
| Titration         | Iodometric                      | 0.1-6 wt%                           | Oxidize iodide to iodine, titrated with thiosulfate and starch.                                                                        | Not accurate at low concentration; subject to interference.                                                             |
|                   | Permanganate                    | 0.25-70 wt%                         | Reduce permanganate to manganous ion.                                                                                                  | Not accurate at low concentration.                                                                                      |
|                   | Ceric sulfate                   | 1-13 wt%                            | With a ferroin indicator, titrate to a pale blue.                                                                                      | Not accurate at low concentration.                                                                                      |
| Spectrophotometry | Cobalt carbonate                | up to 0.1 mg/L                      | Formation of a UV-absorbing complex between Co <sup>+3</sup> and carbonate, detection at 260 nm.                                       | Reducing and complexing agents; combined and free chlorine effects not known.                                           |
|                   | Iodometric                      | 0.05-10 mg/L                        | Oxidize iodide to iodine with molybdate catalyst at pH 5; detection at 351 nm.                                                         | Evidence of interference from oxidants; transition metals.                                                              |
|                   | Titanium oxalate                | 0.1-50 mg/L                         | In the presence of sulfuric acid, formation of colored peroxotitanium complex; detection at 400 nm.                                    | Some UV absorbing species, turbidity, color; combined and free chlorine effects not known.                              |
|                   | Peroxidase enzyme-leuco crystal | 0.1-10 mg/L                         | Oxidation of leuco-crystal violet dye by H <sub>2</sub> O <sub>2</sub> in presence of peroxidase enzyme catalyst; detection at 551 nm. | Usually interference-free; slow color development; sensitive to sunlight; combined and free chlorine effects not known. |



|                     |                          |                             |                                                                                                                   |                                                                      |
|---------------------|--------------------------|-----------------------------|-------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------|
|                     | Peroxidase enzyme-DPD    | 0.02-10 mg/L                | Oxidation of DPD by H <sub>2</sub> O <sub>2</sub> in presence of peroxidase enzyme catalyst, detection at 551 nm. | Likely interference from combined and free chlorine, color unstable. |
|                     | Copper-DMP               | 0.03-10 mg/L                | Reduction of Cu(II) and formation of copper-DMP complex, detection at 454 nm.                                     | Reported to be effective in presence of chlorine stable color.       |
|                     | Peroxovanadium           | 4-10 mg/L                   | Reduction of V(V) and formation of peroxovanadium cation; detection at 450 nm.                                    | High detection limit; interference not known                         |
| <b>Fluorescence</b> | Peroxidase enzyme-POHPAA | $> 1.0 \times 10^{-3}$ mg/L | Peroxidase catalyzed oxidation of POHPAA by H <sub>2</sub> O <sub>2</sub> ; fluoresces at 400 nm.                 | Known positive interference with chlorine.                           |

### 3.2. Factors affecting H<sub>2</sub>O<sub>2</sub> quantification

In a simple system, the accuracy of different H<sub>2</sub>O<sub>2</sub> quantification methods is widely established. Indeed, each reported literature uses different methods because of the complexity of the catalytic reactions where the electrolytes, anions, and organic compounds acting as sacrificial agents can possibly interfere and may lead to overestimation and underestimation of H<sub>2</sub>O<sub>2</sub> concentration. Recently, Zheng's group reported a systematic study of the effect of the complexation time, interferences such as the presence of alcohol, the pH, and the type of electrolytes on H<sub>2</sub>O<sub>2</sub> quantification using different methods (*e.g.*, UV-Vis measurements using Co/CO<sub>3</sub> assay, titration with KMnO<sub>4</sub>, Quantofix colorimetric test strips) [51]. For the detailed comparison of these effects, readers are directed to the reference [51].

In the photocatalytic process, organic compounds such as alcohols (*e.g.*, t-butanol, methanol, isopropanol) or organic acids (*e.g.*, oxalic acid, acetic acid, formic acid) are usually employed as electron donors or radical scavengers, which improves the rate of reaction. Overall, UV-Vis measurement is the most accurate method and less susceptible to species interference, contrary to the titration with KMnO<sub>4</sub>. Hence, careful consideration must be implemented. In the presence of alcohol (such as ethanol or acetaldehyde), KMnO<sub>4</sub> titration overestimates H<sub>2</sub>O<sub>2</sub> concentration [60]. For instance, the highest relative error of measurement was obtained when isopropanol was used, followed by ethanol and then methanol [51]. The overestimation in the presence of methanol is very important, especially at low H<sub>2</sub>O<sub>2</sub> concentrations, as MnO<sub>4</sub><sup>-</sup> is a strong oxidizing agent. Therefore, the MnO<sub>4</sub><sup>-</sup> can easily oxidize the alcohol, increasing the consumption of MnO<sub>4</sub><sup>-</sup> and leading to an overestimation of H<sub>2</sub>O<sub>2</sub> concentration. In

contrast, iodometry, cerium sulfate, vanadate, and DPD methods are less affected by the presence of alcohol [60, 68].

Another parameter that impacts  $\text{H}_2\text{O}_2$  quantification is the solution pH. The pH values of the solution or electrolyte play an essential role in the photo, electro, and photoelectro-catalytic processes, and many reports have shown the dependence of the  $\text{H}_2\text{O}_2$  formation, including the selectivity and activity of  $\text{H}_2\text{O}_2$  production on pH [69-70]. Changes in pH may interact with the reagents used in  $\text{H}_2\text{O}_2$  measurements, which can introduce bias in the quantification. For instance, Zhang's group [51] has also shown that  $\text{Co}/\text{CO}_3$  assay and  $\text{KMnO}_4$  titration is fairly robust in the pH ranging from 0-14. On the other hand, the test strip obtained large deviations in the detected  $\text{H}_2\text{O}_2$  at strongly acidic (pH 1) and alkaline solutions (pH 13), while a good reproducibility of the results was obtained over pH 2-12. Results imply that test strips can be a quick means to "semi-quantitatively" determine the  $\text{H}_2\text{O}_2$  concentration, which can be followed by the UV-Vis or titration method for more accuracy.

Although the iodometry is less affected by the presence of alcohols [60, 68], the pH value is a critical issue for this method. In general, iodometry titration works well in slightly acidic solutions to prevent the dismutation of  $\text{I}_2$  to  $\text{I}^-$  and  $\text{IO}_3^-$ , and avoid the dismutation of  $\text{H}_2\text{O}_2$  to  $\text{H}_2\text{O}$  and  $\text{O}_2$  at  $\text{pH} > 7$ . The optimal pH range identified for iodometry is pH 4.0 - 7.0 [65, 71]. In the presence of methanol, iodometric provides an underestimated amount of  $\text{H}_2\text{O}_2$ , especially at strongly acidic solutions (5 M  $\text{H}_2\text{SO}_4$ ) and low  $\text{H}_2\text{O}_2$  concentration ( $< 2$  mM). Provided that  $\text{H}_2\text{O}_2$  concentration is relatively high, iodometry and permanganate titration measurements in acidic alcoholic solutions are accurate [68].

Long and co-workers [60] studied the effect of organic compounds on the reliability of DPD,  $\text{KMnO}_4$ , and  $\text{NH}_4\text{VO}_3$  methods. Organic compounds such as phenol, bisphenol-A, and *p*-benzoquinone can be easily oxidized by  $\text{KMnO}_4$ , increasing the measured  $\text{H}_2\text{O}_2$  concentration. In the case of the DPD method, *p*-benzoquinone, rhodamine B, acid orange, and phenolic compounds can directly interact with DPD leading to an erroneous determination of  $\text{H}_2\text{O}_2$ , while  $\text{NH}_4\text{VO}_3$  method is relatively accurate when  $< 1 \text{ mM}$  benzoquinone is present [60].

Care should be taken when working in solutions with significant quantities of compounds which may form secondary peroxides from a reaction with  $\text{H}_2\text{O}_2$ . In particular, many acids are in equilibrium with their peracids in the presence of  $\text{H}_2\text{O}_2$ , resulting in the formation of compounds such as peracetic acid or peroxomonocarbonate. These are typically much more reactive than  $\text{H}_2\text{O}_2$  itself and may therefore invoke a disproportionate response from the quantification methods [72]. These problems can be avoided by calibrating the method in a solution of exactly the same composition (buffer, additives) and allowing sufficient time for equilibration.

## **4. Photocatalytic synthesis of $\text{H}_2\text{O}_2$ from molecular $\text{O}_2$ and $\text{H}_2\text{O}$**

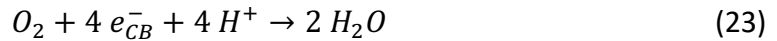
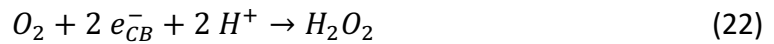
### **4.1. Mechanism of peroxide formation**

#### **4.1.1. Oxygen reduction reaction mechanisms**

Theoretically,  $\text{H}_2\text{O}_2$  can be formed both reductively from molecular oxygen and oxidatively from water. By far the most studied of the two mechanisms is the reductive one. Generally, molecular oxygen can be reduced in a one-, two- or four-electron transfer mechanism. The primary product of the one-electron process (18) is the

superoxide anion radical ( $O_2^{\bullet-}$ ) or, after protonation (19), a hydroperoxyl radical ( $HO_2^{\bullet}$ ) [47]. These intermediates are usually further reduced to hydrogen peroxide in another one-electron transfer with subsequent protonation (20-21). Alternatively, the direct two-electron reduction mechanism leads directly from molecular oxygen to hydrogen peroxide (22).

Further reduction of the peroxide is also possible and eventually leads to water. On some very efficient oxygen reduction catalysts such as Platinum, the reduction of molecular oxygen may also directly proceed to water in a concerted four-electron reduction mechanism (23). However, in the context of  $H_2O_2$  production and utilization, it is desirable to stop the reduction at the peroxide step and to avoid the pathway to water by over-reduction.



Studies on  $TiO_2$  have shown that superoxide is formed with a similar rate as hydrogen peroxide, strongly indicating that the majority of peroxide is formed in consecutive one-electron transfers *via* superoxide/hydroperoxide radicals as intermediate [73]. This is not surprising as on un-modified photocatalysts, charge

carriers are strongly gated and only have limited local availability which impedes multi-electron transfers [74].

The one-electron reduction requires a significantly higher reduction potential ( $-0.05$  V/RHE) than the two-electron reduction ( $+0.68$  V/RHE) and is therefore not accessible by some single oxide photocatalytic materials such as  $\text{WO}_3$  or  $\text{Fe}_2\text{O}_3$ . These are instead fully reliant on the direct two-electron transfer mechanism which may require the use of co-catalyst materials to promote this pathway. For example, it has been shown that grafting  $\text{Cu(II)}$  ions onto  $\text{WO}_3$  dramatically improves its  $\text{H}_2\text{O}_2$  generation rate while it only has a slight effect on  $\text{TiO}_2$  [75]. Presumably, this is the case because contrary to  $\text{WO}_3$ ,  $\text{TiO}_2$  can already reduce  $\text{O}_2$  through the one-electron pathway so unlocking the two-electron pathway with  $\text{Cu(II)}$  ion co-catalysts is not a game-changer.

Another possible strategy is to employ anthraquinones which are already well-known from the namesake AQ process for their excellent activity in forming  $\text{H}_2\text{O}_2$  from  $\text{O}_2$ . Here, it is believed that the photocatalyst reduces AQ to its hydroquinone which then reacts with oxygen to form the peroxide. This strategy has been successfully applied to graphitic carbon nitride, where the addition of AQ carboxylic acid increased the  $\text{H}_2\text{O}_2$  formation rate constant by more than 4-fold (see section 5.2.2) [76]. However, it should be noted that anthraquinones are photocatalysts themselves so it is difficult to only assign them co-catalytic properties [77].

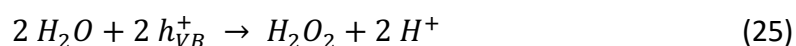
Some photocatalysts such as graphitic carbon nitride also have an intrinsic catalytic activity for the two-electron pathway and are therefore very efficient for  $\text{H}_2\text{O}_2$  production even without a co-catalyst [46]. The mechanism here is thought to proceed via a very fast formation of an 1,4-endoperoxide intermediate which suppresses the release of any possible superoxide intermediates (see section 5.2.2). Consequently,

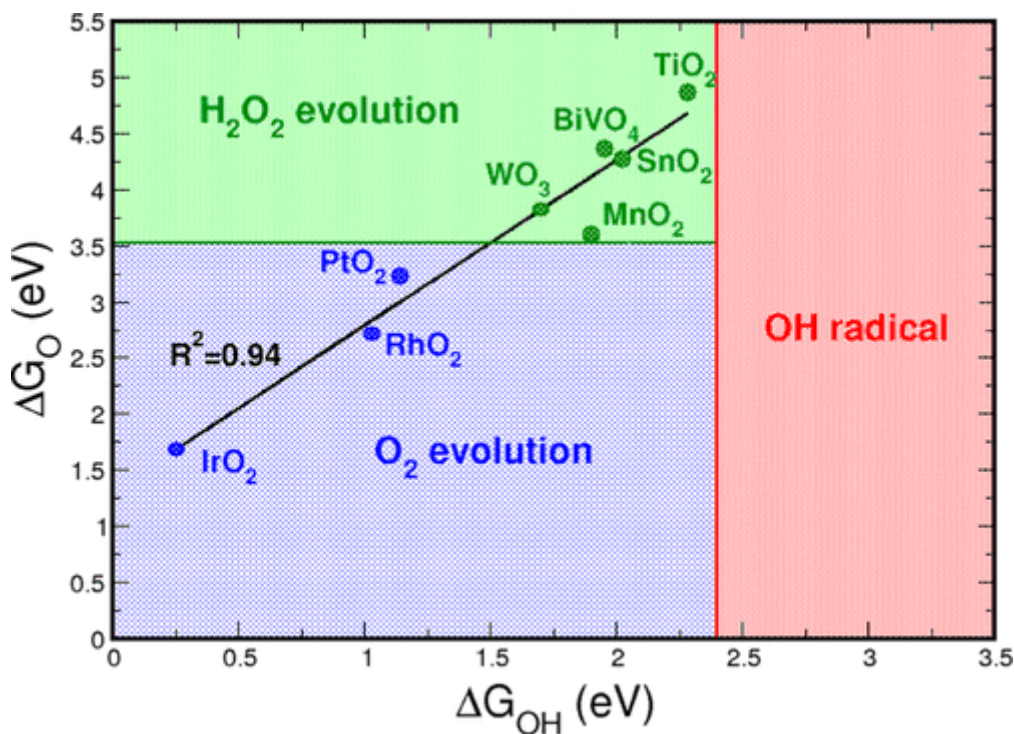
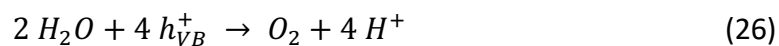
Electron Paramagnetic Resonance (EPR) spectroscopy analysis yielded no detectable amounts of superoxide as intermediates [46].

If high reaction rates are achieved, *e.g.*, by employing powerful lamps in combination with efficient photocatalysts, it should be kept in mind that the oxygen availability in an aqueous reaction medium may present a limiting factor [78]. The solubility of oxygen in water is rather poor and even further reduced in the buffer systems (*e.g.*, phosphate or borate) which are popular for H<sub>2</sub>O<sub>2</sub> generation [79]. A possible method to overcome this is to employ the photocatalyst directly on the gas-liquid interface, so the photocatalytic reaction may proceed on the three-phase-boundary akin to a gas-diffusion electrode [80].

#### 4.1.2. Anodic H<sub>2</sub>O<sub>2</sub> synthesis by water oxidation mechanism

In addition to the reductive process, hydrogen peroxide can also be formed by partial oxidation of water. This is a two-electron transfer process (25) which competes with both the one-electron oxidation to hydroxyl radicals (24) and the full four-electron oxidation to dioxygen (26). However, the former may also eventually lead to hydrogen peroxide formation *via* dimerization of hydroxyl radicals (27). Which one of these processes dominates is dependent on the relative binding energies of O\* and OH\* as surface species [81]. Among the more commonly studied materials, TiO<sub>2</sub>, WO<sub>3</sub>, SnO<sub>2</sub>, BiVO<sub>4</sub> and MnO<sub>2</sub> lie within the range predicting hydrogen peroxide formation, as displayed in Figure 5 [81].





**Figure 5.** Phase diagram in terms of the binding energies of O\* versus OH\*. The black solid line displays the scaling line between O\* and OH\* surface species on different metal oxides. Blue, green, and red highlighted colors indicate regions in which O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, or OH radical are expected to be the major water oxidation product, respectively, in terms of purely thermodynamic constraints. Reproduced with permission from Ref. [81]. Copyright 2017 American Chemical Society.

The simultaneous production of peroxide from both the reductive and oxidative pathways opens up very efficient processes with potentially up to 200% efficiency. In photocatalytic experiments, it is difficult to investigate the oxidative H<sub>2</sub>O<sub>2</sub> production



directly, as even in an oxygen-free medium, oxygen may be formed *in-situ* by water oxidation and subsequently reduced to  $\text{H}_2\text{O}_2$ . So, the observation of  $\text{H}_2\text{O}_2$  formation alone is no definite proof for the direct oxidative pathway. However, this becomes possible in photo-electrochemical or electrochemical experiments where the half-reactions are spatially separated.

Using these techniques, experimental evidence for oxidative (anodic)  $\text{H}_2\text{O}_2$  production has been reported for a variety of materials, most prominently  $\text{TiO}_2$  [82],  $\text{SnO}_2$  [82],  $\text{WO}_3$  [83],  $\text{BiVO}_4$  [83],  $\text{ZnO}$  [84] and  $\text{CaSnO}_3$  [85]. Nørskov et al. showed that  $\text{TiO}_2$ ,  $\text{SnO}_2$ ,  $\text{WO}_3$  and  $\text{BiVO}_4$  were able to anodically generate  $\text{H}_2\text{O}_2$  in sodium hydrogen carbonate electrolyte [86]. They observed that every metal oxide studied has its own optimal potential for the production of  $\text{H}_2\text{O}_2$ . For  $\text{WO}_3$ , a low potential of 2.25 vs. RHE is sufficient to generate  $\text{H}_2\text{O}_2$  with a maximum faradaic efficiency (FE) of 47%.  $\text{TiO}_2$ ,  $\text{SnO}_2$  and  $\text{BiVO}_4$ , on the other hand, require a higher potential of over 3 V vs. RHE for optimal performance.  $\text{BiVO}_4$  achieves an FE of 70% at 3.1 V vs. RHE,  $\text{SnO}_2$  50% at 3.1 V and  $\text{TiO}_2$  19% at 3.25 V vs. RHE [86]. It could also be shown that the required potential is significantly lowered when the electrodes are illuminated, indicating that this reaction can also be triggered under bias-free photo-electrochemical or photocatalytic conditions [86]. Generally, the efficiency appears to be higher in photo-electrochemical than in electrochemical systems [86], possibly due to the limited availability of holes which will impede the four-electron oxidation of water [74].

Even larger FE's have even been documented for  $\text{ZnO}$  and  $\text{CaSnO}_3$ . In aqueous 2M potassium hydrogen carbonate solution,  $\text{ZnO}$  (enriched in  $(10\bar{1}0)$  facets) could achieve an FE of 81% at 2.6 V vs. RHE and  $\text{CaSnO}_3$  at 3.2 V vs. RHE an FE of 76% [84-85]. In the last few years, the materials already mentioned have been further modified.  $\text{BiVO}_4/\text{WO}_3$

was coated with a thin layer of  $\text{Al}_2\text{O}_3$  in order to slow down the decomposition of  $\text{H}_2\text{O}_2$  and thereby achieve higher concentrations and efficiency [87]. By doping  $\text{BiVO}_4$  with gadolinium, a high stability and efficiency of the electrodes could be achieved [88]. In more recent works more promising materials were discovered. Porphyrins are able to oxidize water to hydrogen peroxide [89]. There is also work with PTFE-doped carbon [90], boron doped diamond [91] or other metal oxides such as  $\text{InSbO}_x/\text{CuSb}_2\text{O}_x$  [92] or  $\text{LaAlO}_3$  [93].

The reaction is reported to be strongly dependent on the electrolyte or buffer system [59]. The best results have been obtained using a 2 M  $\text{KHCO}_3$  solution (pH 8.3) or even higher concentrated more alkaline carbonate systems [94-95]. Here, the working hypothesis is that in the concentrated bicarbonate solution, peroxomonocarbonate ( $\text{HCO}_4^-$ ) is the primary oxidation product which is subsequently hydrolyzed to  $\text{H}_2\text{O}_2$  [94, 96]. However, we note that there is an equilibrium between  $\text{H}_2\text{O}_2$  and  $\text{HCO}_4^-$ , and in 2 M  $\text{KHCO}_3$  there will be no complete hydrolysis, but also significant (stable) concentrations of the latter [72,97].

#### **4.2. Kinetics of $\text{H}_2\text{O}_2$ formation (and degradation)**

The first kinetic model for the photocatalytic formation and degradation of  $\text{H}_2\text{O}_2$  was described by Kormann et al. in 1988 [98]. They studied the illumination of aqueous dispersions of  $\text{ZnO}$ ,  $\text{TiO}_2$  and a specifically prepared sample of desert sand from the Death Valley in presence of  $\text{O}_2$  and organic electron donors. They described three possible pathways for the hydrogen peroxide formation:

- The first and most important one is the reduction of O<sub>2</sub> by conduction band electrons, whose yield can be enhanced by adding electron donors as sacrificial reagents for the valence band holes.
- The second pathway is the oxidation of water, which is only likely to occur in the absence of electron donors.
- The last pathway is the generation of H<sub>2</sub>O<sub>2</sub> by secondary reactions of oxidized organic electron donors such as the dimerization and decomposition of methylperoxy- or α-peroxy-acetic acid radicals [99-100]. These reactions are important at high concentration of organic molecules and long illumination times.

If pathway 2 can be neglected [99] and pathway 3 is negligible in the initial phase, only the first pathway is relevant. With an excess concentration of electron donors and a constant oxygen concentration to accept conduction band electrons, the reaction order for the formation is zero. Equation (28) describes the formation rate  $r_F$  where  $\phi_0$  is the quantum yield of the formation and  $I_{abs}$  the absorbed photon flux, the product of which can also be termed as the formation rate constant  $k_F$ :

$$r_F = \phi_0 \cdot I_{abs} = k_F \quad (28)$$

The degradation can occur to water by reduction and to oxygen by oxidation. Both processes are first order reactions when the H<sub>2</sub>O<sub>2</sub> concentration is low. Eq. (29) describes the degradation rate  $r_D$  where  $\phi_1$  is the quantum yield and the  $k_D$  rate constant for the degradation:

$$r_D = \phi_1 \cdot [H_2O_2] \cdot I_{abs} = k_D \cdot [H_2O_2] \quad (29)$$

The combination of the formation and degradation results in a steady-state concentration of hydrogen peroxide during continuous irradiation. The overall concentration change of  $H_2O_2$  is given by combining eqs. (28-29) into eq. (30):

$$\frac{d[H_2O_2]}{dt} = r_F - r_D = (k_F - k_D[H_2O_2]) \cdot I_{abs} \quad (30)$$

Integration of this rate law with  $[H_2O_2] = [H_2O_2]_0$  at  $t = 0$  leads to the explicit Eq. (31) which can be used to model the concentration-time profiles of photocatalytic  $H_2O_2$  formation:

$$[H_2O_2] = \frac{k_F}{k_D} (1 - e^{-k_D t}) + [H_2O_2]_0 \cdot e^{-k_D t} \quad (31)$$

Under these conditions and assumptions, the steady-state concentration (at  $t \rightarrow \infty$ ) of hydrogen peroxide  $[H_2O_2]_{ss}$  should be independent of the photon-flux during the experiment (32).

$$[H_2O_2]_{ss} = \frac{k_F}{k_D} \quad (32)$$

Further illumination may lead to higher total peroxide concentration due to the formation of peroxides from organic radicals. These are formed during the oxidation of the organic hole scavengers if present [98]. Therefore, this simple model is only valid in

the initial phase if organic components are involved in the reaction. It also does not take into account many reaction parameters such as the catalyst loading and assumes a completely linear relationship between light intensity and reaction rate, which is usually not observed [47].

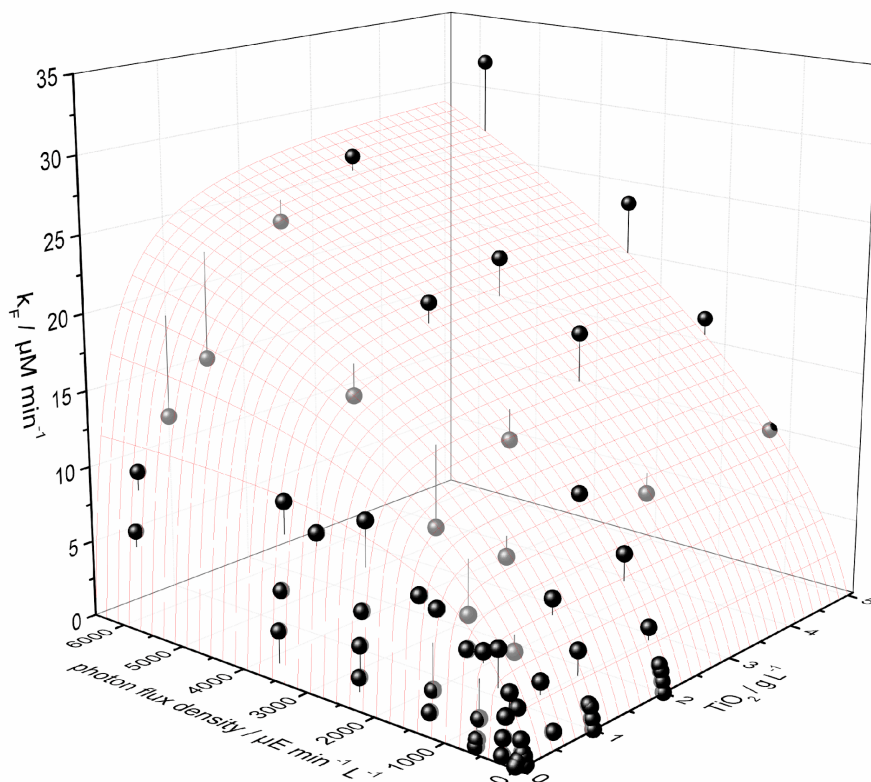
Understanding the influence of the light intensity in photocatalysis is particularly important. Many authors describe a linear increase in the reaction rate with the light intensity at low light intensities, while at higher light intensities a square root function can be assumed [101]. The nonlinearity is assumed to be a result of the increased charge carrier recombination. Others describe an exponential increase at high light intensities due to multiple electron transfers [102]. Burek et al. varied both the light intensity and the amount of  $\text{TiO}_2$  over 4 orders of magnitude to fill gaps in the literature values [47]. As expected, the formation rate initially increased linearly, while a diminished response was observed at a higher light intensity. However, an increase in the catalyst concentration extended the range of the linear regime towards higher light intensities, revealing an interdependence of both parameters. The degradation rate of  $\text{H}_2\text{O}_2$  is nearly constant over the complete investigated range of catalyst concentration and light intensity when 2-propanol is used as an electron donor. Therefore, contrary to the abovementioned model (30-32), the steady state concentration changes with the light intensity [47].

To account for this, a new holistic model for photocatalytic reactions was developed and applied to the case of the hydrogen peroxide formation [47, 103]. This new model is based on the three elementary reaction steps that are excitation, reaction and recombination, and employs a quasi-steady state approach. In certain geometries

featuring collimated unidirectional illumination, the integration of the resulting local rate law yields the explicit equation (33) for the overall observed reaction rate [47].

$$r_F = k_F = \frac{\beta}{\alpha} \cdot \ln \left( \frac{\phi \cdot \alpha \cdot c_{pc} \cdot I_{avg}}{\beta \cdot c_{pc} + k_{recom}} + 1 \right) \quad (33)$$

This equation has three reaction- and catalyst-specific parameters with direct physical meaning, namely the intrinsic quantum yield  $\phi$ , the maximum reaction rate per catalyst mass  $\beta$  and the recombination rate constant  $k_{recom}$ . Additionally, the reactor geometry plays a role via the effective optical density  $\alpha$  as well as the reaction parameters that are the catalyst concentration  $c_{pc}$  and the average incident photon flux  $I_{avg}$ . This rate equation was subsequently applied to the observed data points and the resulting plot is shown in Figure 6 [47].



**Figure 6.** Interdependence of the amount of catalyst and the photon flux density shown as black and dark gray dots, on the measured  $\text{H}_2\text{O}_2$  formation rate constant  $k_F$ . Also shown is the calculated best fit to the proposed model (32) as a surface plot. Reproduced with permission from Ref. [47]. Copyright 2019 American Chemical Society.

As can be seen from the data, the reaction rate initially increases linearly with the light intensity but shows a pronounced non-linear behavior at a higher light intensity, even leveling off completely to a plateau in case of low catalyst concentration [47]. This is a symptom of photon saturation, in this case the photocatalyst is unable to transfer the photo-generated charges to oxygen fast enough to make use of additional photons (kinetic limitation) [77, 103]. However, as it is apparent in Figure 6, this can partly be counteracted by employing a higher catalyst concentration. This both increases the

maximum attainable reaction rate and also shifts to higher light intensity the tipping point at which non-linear effects appear [47]. So essentially, efficiency losses at higher light intensity can be at least partially counteracted by employing higher catalyst concentrations. Tuning other reaction parameters (see section 4.3.) which increase the photocatalysts' surface kinetics has a similar effect [77].

Likewise, increasing the catalyst concentration initially increases the reaction rate, both by increasing the amount of absorbed light but also by increasing the overall available active sites. However, once a sufficiently-high concentration is reached, no further gain in reaction rate is observed upon further addition. Nonetheless, a high light intensity demands a higher catalyst concentration to reach the plateau because the amount of photogenerated charge carriers is higher and therefore needs more active sites [47, 77]. Another approach to alleviate kinetic bottlenecks is to improve the light distribution in the reactor, *i.e.*, reduce the degree of inhomogeneity, for example using delocalized internal illumination [104].

It should be noted that currently all kinetic models of the photocatalytic  $\text{H}_2\text{O}_2$  production in particulate systems only account for the reductive formation *via* the reduction of molecular oxygen. The possible oxidative formation from water is usually deemed insignificant and neglected. This is because in particulate systems, there has not been any experimental evidence suggesting a significant contribution of this pathway in the studied materials. Also, the common use of sacrificial electron donors strongly suppresses the water oxidation reaction and thereby the oxidative  $\text{H}_2\text{O}_2$  pathway. However, this assumption should be carefully revisited for materials and conditions which may more strongly favor this pathway (see section 4.1).



### 4.3. Influence of reaction conditions

In addition to the influence of both the light intensity and the catalyst concentration, numerous other parameters also influence the hydrogen peroxide formation rate. First of all, the employed electrolyte has a significant effect on both the formation and degradation rate of  $\text{H}_2\text{O}_2$ . The use of phosphate buffer as a solvent instead of water has the advantage of a higher formation rate and lower degradation rate due to the stabilization of  $\text{H}_2\text{O}_2$  [105]. Moon et al. systematically investigated the effect of different electrolytes on the  $\text{H}_2\text{O}_2$  formation rate over carbon nitride photocatalysts [106]. Generally, phosphate systems performed best, particularly those based on high fractions of  $\text{KH}_2\text{PO}_4$ . In a similar fashion to phosphate, bisulfate or bicarbonate electrolytes also showed beneficial effects, although not as pronounced. Among the cations, potassium salts showed higher formation rates than the sodium, lithium or ammonium variants.

Burek et al. investigated the influence of pH, oxygen partial pressure and temperature on the  $\text{H}_2\text{O}_2$  formation over illuminated  $\text{TiO}_2$  [47]. When the pH value of the phosphate buffer solution was varied between pH 2 and pH 10, the degradation rate increases exponentially between pH 2 and 9 and decreases slightly at higher pHs values [107].  $\text{H}_2\text{O}_2$  is stabilized in acidic phosphate solutions; in presence of hydroxyl ions, hydrogen peroxide disproportionates to  $\text{H}_2\text{O}$  and  $\text{O}_2$ . The formation rate, on the other hand, stays constant between pH 2 and 7 but increases exponentially above pH 8, emphasizing the critical role of hydroxyl ions also in the formation reaction. However, this may be different if a sacrificial electron donor such as an alcohol is employed [47].

The oxygen content in solution has also a significant effect as it is the required reagent. Due to its poor solubility in aqueous systems, limitation of oxygen availability

may already occur at mild reaction rates. It is therefore important to achieve a high oxygen transfer rate into the system, *e.g.*, by using a sparger or by using pure oxygen gas instead of air. The effect of the oxygen partial pressure in the supplied gas was already observed in the early studies by Kormann et al. [98]. Up to 20 % oxygen content, the reaction rate increased before reaching saturation, indicating that the oxygen availability was no longer a limiting factor. However, in the study of Burek et al., 50 % oxygen partial pressure was necessary for reaching saturation, indicating that this is dependent on the mode of aeration and also the reaction rate [47]. When the formation rate is lower, a lower gradient between liquid and gas phase oxygen is needed to maintain saturation at the catalyst surface and thus less oxygen is required in the atmosphere. The same study also shows that the oxygen concentration can be accounted for in the proposed kinetic model, *e.g.*, by integrating a Langmuirian adsorption term, and this fits well with the observed behavior [47]. Simple oxygen bubbling may not be enough at high light intensities to ensure oxygen saturation, as more oxygen is needed at high formation rates. Possible solutions include for example the use of a photocatalytic membrane, similar in function to a gas-diffusion electrode in electrochemistry [79].

Temperature is often treated as an insignificant parameter in photocatalysis as the majority of the energy for the reaction comes from the photons. However, in some cases, pronounced temperature effects are observed, particularly at high light intensity [47]. This is due to the fact that the increase in the rate of charge transfer on the photocatalysts' surface with increasing the temperature only translates into an observable reaction rate increase if the reaction is conducted in the kinetically-limited regime (and not in a photon-limited regime at low light intensity) [77]. An attempt to

determine the activation energy of the reaction ( $E_A$ ) led to a value of  $31.6 \text{ kJ mol}^{-1}$  when using 2-propanol as a sacrificial electron donor [47]. However, the overall temperature effect is much more complex as it also affects other parameters such as the oxygen solubility and peroxide decomposition and can therefore have more complex interactions with the reaction rate.

The reaction kinetics are strongly influenced by the electron donor, *i.e.*, the corresponding oxidation reaction. While theoretically, water can fill this role and even increase the peroxide formation rate by concomitant oxidative production, it is a kinetically-demanding reaction. So in practice, this approach often leads to poor quantum yield with the oxidation reaction being rate-limiting. Therefore, alternative, easily oxidizable electron donors, often termed *sacrificial reagents*, are very popular. These are often simple alcohols such as methanol, 2-propanol or triethanolamine. Side-effects of the use of alcohols are autoxidation with molecular oxygen or superoxide radicals, which can lead to imperfect electron balance and the so-called current-doubling effect, which may double the number of reducing equivalents per photon [108-109]. The addition of alcohols also increases the oxygen solubility in the solution, which may in turn increase the reaction rate.

The effect of the concentration of 2-propanol in the solution was studied between 0 and 30 % [47]. The formation rate rises with increased 2-propanol up to 10 % volume and declines at higher amounts. This can be explained by a better availability at higher concentrations due to better mass transfer, but too much alcohol blocks the oxygen from the catalyst surface. Also, the solubility of oxygen in the solution is higher with alcohol present. The degradation rate gets smaller with higher 2-propanol concentrations because of the preferred oxidation of the alcohol and therefore less

oxidation of hydrogen peroxide. The degradation is already suppressed down to a quarter at 1 % volume of 2-propanol in the solution because it is easier to oxidize the alcohol compared to water.

When working with sacrificial reagents, it should be considered that their oxidation also yields secondary compounds which may induce unexpected side-effects. Aldehydes such as formaldehyde often react readily with other compounds, acidic intermediates (*e.g.* formic or acetic acid) can influence the pH value. With this in mind, methanol, ethanol, 2-propanol and *tert*-butanol were studied and evaluated for their use as sacrificial reagents [110]. Methanol is oxidized to CO<sub>2</sub> *via* formaldehyde and formic acid, the subsequent reaction steps are faster so that no significant build-up of intermediates is observed. Ethanol is oxidized *via* acetaldehyde to acetic acid, which is relatively stable and accumulates to significant concentrations before being broken down *via* a photo-Kolbe reaction and subsequently the above-mentioned C<sub>1</sub>-pathway. 2-propanol is oxidized to acetone, which is resistant to further oxidation and accumulates. Eventually, this can be broken down to acetaldehyde and formaldehyde which can be oxidized to CO<sub>2</sub> as described. In the case of *tert*-butanol, several pathways are possible which lead to a plethora of intermediates, many of them accumulating [110].

The comparison of the H<sub>2</sub>O<sub>2</sub> generation rates with the different alcohols showed similar rates for the primary and secondary alcohols but a significantly lower rate for *tert*-butanol. Overall, methanol proved to be the most suitable candidate for use as a sacrificial reagent because it both yields a high H<sub>2</sub>O<sub>2</sub> formation rate, and the intermediates react quickly and cannot accumulate [110].

## 5. Photocatalytic materials for H<sub>2</sub>O<sub>2</sub> synthesis from molecular O<sub>2</sub> and H<sub>2</sub>O

### 5.1. TiO<sub>2</sub>-based photocatalysts

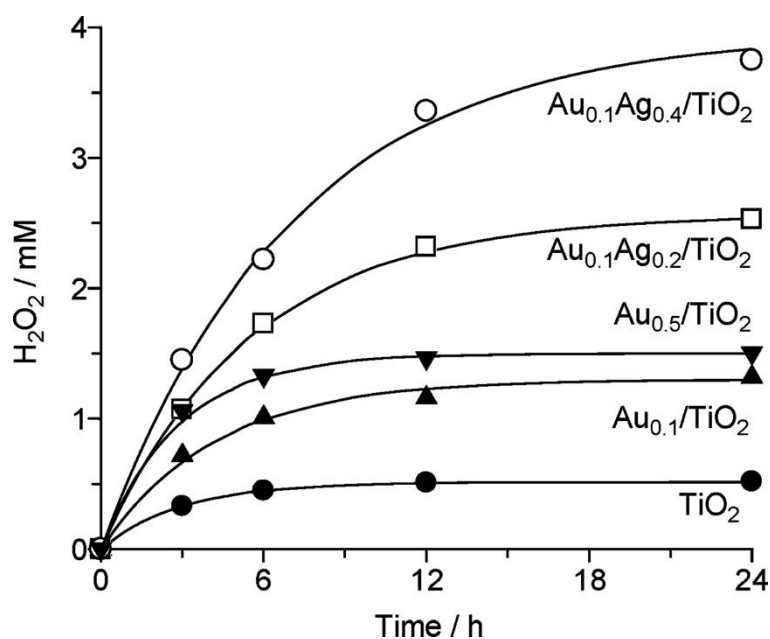
In 2013, Shirashi et al. described one of the first H<sub>2</sub>O<sub>2</sub> photocatalytic syntheses by using the TiO<sub>2</sub> Aeroxide P25 Degussa catalyst [111]. In this work, they studied the effect of different organics in efficiency and selectivity. Figure 7 shows the mechanism that this group proposed regarding the main steps involved in the photocatalysis synthesis of H<sub>2</sub>O<sub>2</sub> from molecular O<sub>2</sub> in aqueous solution. Titania (TiO<sub>2</sub>) systems were logically the first family of semiconductor photocatalysts being of interest for the synthesis of H<sub>2</sub>O<sub>2</sub> [110-117], due to good stability and biocompatibility as well as suited optical and electronic properties. Indeed, the CB of titania (-0.19 V vs. NHE) favors the reduction of oxygen into hydrogen peroxide (0.68 V).

Nevertheless, TiO<sub>2</sub> requires UV light to be excited, making use of only 3.3% of the solar spectrum in terms of irradiance. Furthermore, the scarce production of hydrogen peroxide obtained so far can be attributed to its surface decomposition due to further reaction at the titania surface, giving rise to complexes which are further decomposed into OH<sup>-</sup> or H<sub>2</sub>O.

In this regard, several strategies have been followed in order to inhibit the decomposition of H<sub>2</sub>O<sub>2</sub>. Some studies affirm that the decomposition can be avoided if the surface -OH sites are blocked by complexation with cations like Zn<sup>2+</sup> [118], or substituted by anions like F<sup>-</sup> [119]. However, in those works, in addition to the needed use of UV light, an organic sacrificial agent (alcohol, organic acid, etc.) was employed as hole scavenger (easier to oxidize compared to water).

Also, noble metals like Au, Ag or Pt nanoparticles have been interfaced with the  $\text{TiO}_2$  photocatalyst for this reaction. In most of cases, UV light was employed as a source of energy and also by using an organic hole scavenger. Loading with noble metals has demonstrated that the electrons in the CB of  $\text{TiO}_2$  can be trapped by the metal particle, leading to a more efficient charge separation [113, 120-121]. Besides, it decreases the decomposition of  $\text{H}_2\text{O}_2$  by Ti-OOH species as required and in some cases it can also absorb visible light due to the surface plasmon resonance effect [29]. Nevertheless, in some cases, like Au-decorated  $\text{TiO}_2$ , the metal particle strongly interacts with  $\text{H}_2\text{O}_2$  promoting its depletion through reduction reactions [122]. This confirms that there are some controversial statements about how  $\text{H}_2\text{O}_2$  is photocatalytically produced. The maximum rate achieved was 6 mM in 24 h of irradiation in presence of ethanol for Au- $\text{TiO}_2$ . In the case of combined materials, the highest  $\text{H}_2\text{O}_2$  production rate achieved so far is 26 mM in 20 h under UV-A light with an Au- $\text{TiO}_2$ /carbon catalyst by using ethanol and oxygen at acidic pH [79].

In Figure 8, Tsukamoto et al. [120] shows the change in  $\text{H}_2\text{O}_2$  concentration over time with the employment of the bimetallic-titania base catalyst and titania for the sake of comparison. The rate for  $\text{H}_2\text{O}_2$  production becomes lower as the time proceeds due to the simultaneous peroxide decomposition.



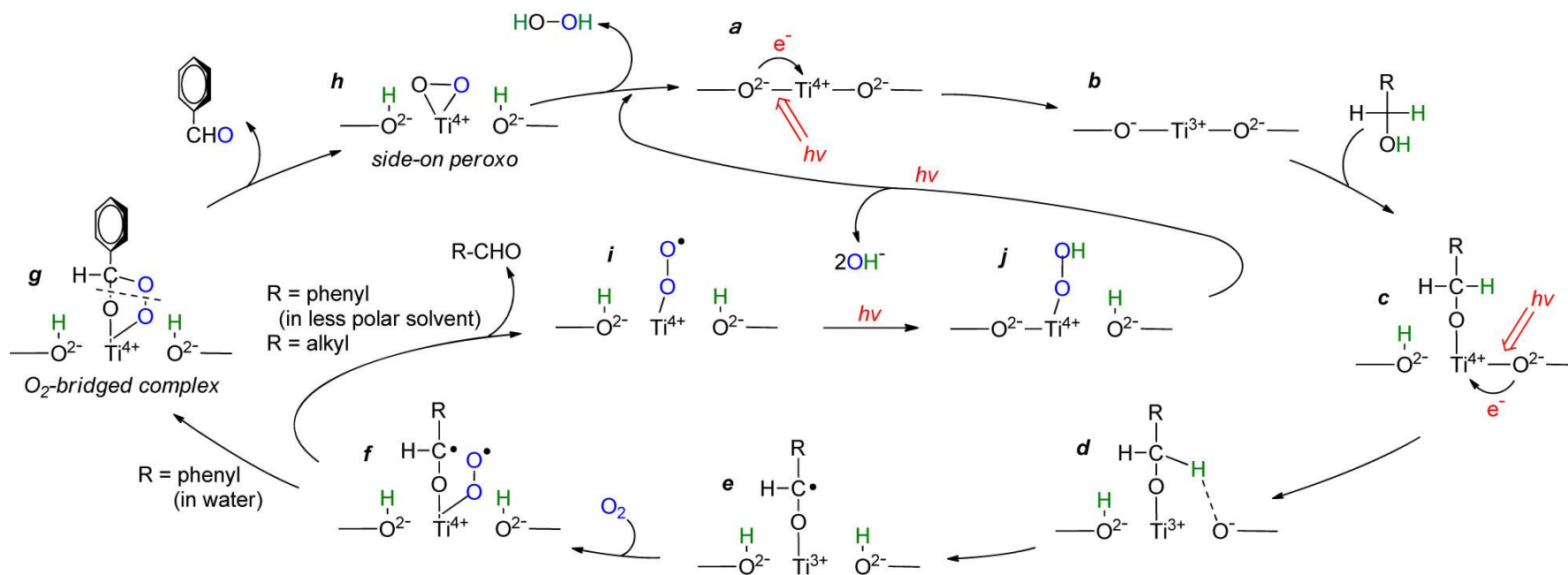
**Figure 8.** Time-dependent change in  $\text{H}_2\text{O}_2$  concentration during photoreaction with respective catalysts. The reaction conditions are identical to those in Table 4. The lines are the calculated results using the equation;  $[\text{H}_2\text{O}_2] = (k_f/k_d)\{1 - \exp(1 - k_d t)\}$ . Reproduced with permission from Ref. [120]. Copyright 2012 American Chemical Society.

Others propose the employment of heterojunction to promote the charge separation for higher yield achievements (*e.g.*,  $\text{CoPi/T-GO/TiO}_2$ ,  $\text{C-dots/r-GO/TiO}_2$ ) [105, 123]. However, the amount of  $\text{H}_2\text{O}_2$  obtained in the range 0.08-1.3 mM was far from those of pure  $\text{TiO}_2$  ( $\approx 40$  mM).

The last strategy followed with titania is the combination with reduced graphene oxide (rGO). The interest of that resides in that rGO helps to transfer electrons to  $\text{O}_2$  due to the fact that the Fermi level of rGO is lower than the CB of titania. In an early study, Moon et al. obtained much higher activity with  $\text{rGO/TiO}_2$  than with bare titania [105]. Then, this composite was incorporated in a ternary heterojunction giving rise to

TiO<sub>2</sub>/rGO/WO<sub>3</sub> [123]. The role of the rGO was to act as electron mediator between the two other photocatalytic phases. Nevertheless, this ternary material also employed a hole scavenger and reached relatively low yields: a final concentration of 270 μM after 1 h, without photonic yield reported.





**Figure 7.** Proposed Mechanism for Photocatalytic Oxidation of Alcohols with  $\text{O}_2$  on the  $\text{TiO}_2$  surface. Reproduced with permission from Ref. [111].

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**Table 4.** Titania-based photocatalysts for the photocatalytic production of H<sub>2</sub>O<sub>2</sub>.

| Catalyst                               | Conditions                                                                                                  | H <sub>2</sub> O <sub>2</sub> measurements                                                   | Amount produced                                       | Reference |
|----------------------------------------|-------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------|-------------------------------------------------------|-----------|
| TiO <sub>2</sub>                       | Benzyl alcohol, Hg lamp UV-Vis, O <sub>2</sub> saturation                                                   | redox titration with KMnO <sub>4</sub>                                                       | 40 mM                                                 | [111]     |
| Co@TiO <sub>2</sub>                    | Methanol reduces H <sub>2</sub> O <sub>2</sub> production (competition with H <sub>2</sub> O <sub>2</sub> ) | Scavengers                                                                                   | 1.71 mmol/L in 60 min                                 | [112]     |
| Au-TiO <sub>2</sub>                    | UV                                                                                                          | horseradish peroxide-catalyzed oxidation of N,N-diethyl-pphenylenediamine                    | 0.3 mM                                                | [113]     |
| Au-Ag/TiO <sub>2</sub>                 | Ethanol/water, O <sub>2</sub> saturated solution, UV radiation                                              | redox titration with KMnO <sub>4</sub> (detection limit: 0.05 mM).                           | 4 mM (24h)                                            | [120]     |
| F-TiO <sub>2</sub>                     | O <sub>2</sub> /hole scavenger (formic acid)                                                                |                                                                                              | 1.3 mM                                                | [119]     |
| CoPi/r-GO/TiO <sub>2</sub>             | O <sub>2</sub> and UV (wavelength>320 nm)                                                                   | DPD method                                                                                   | 80 µM                                                 | [105]     |
| C-dots/r-GO/TiO <sub>2</sub>           | Disinfection/ UV/2-propanol/pH=7                                                                            | colorimetric method using copper (II) ions and DMP at 454 nm                                 | 300 µM (1h)                                           | [123]     |
| Pt/TiO <sub>2</sub> (anatase)          | No sacrificial agent. Water splitting with H <sub>2</sub> production too.                                   | o-tolidine method                                                                            | 5096 µmol g <sup>-1</sup> h <sup>-1</sup> (first 1 h) | [121]     |
| Carbon/Au-TiO <sub>2</sub>             | Ethanol, oxygen, pH=3                                                                                       | iodometric titration using the UV-Vis spectroscopy                                           | 26 mM (20h)                                           | [79]      |
| Carbon dots/ TiO <sub>2</sub> nanotube | Ethanol, UV light                                                                                           | redox titration using standard Ce(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O solution | 3.4 mM (3h)                                           | [124]     |

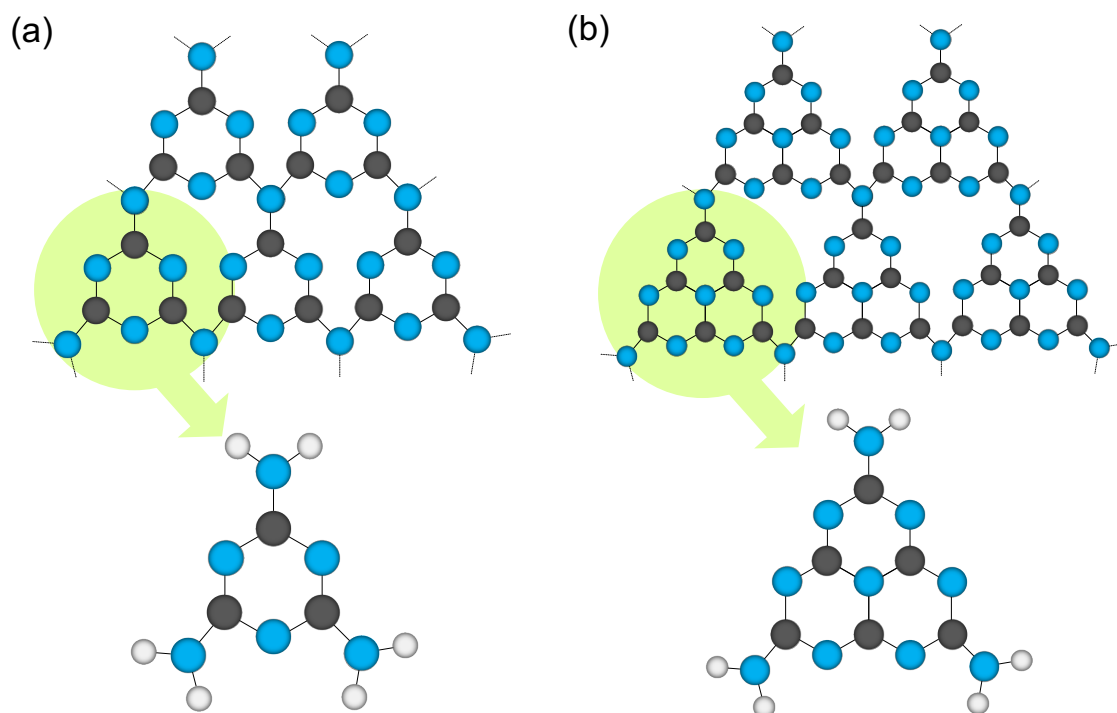
|                                                                                           |                                                                                                    |                                                                      |              |       |
|-------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|----------------------------------------------------------------------|--------------|-------|
| WO <sub>3</sub> /TiO <sub>2</sub> /GO                                                     | 2-propanol as hole scavenger,<br>Xenon lamp with 1.5 AM filter                                     | colorimetric method using copper(II)<br>ions and DMP at 454 nm       | 270 µM       | [123] |
| Au/SnO <sub>2</sub> /TiO <sub>2</sub>                                                     | Alcohol, UV light                                                                                  | ESR spectra                                                          | 15 mM (25 h) | [125] |
| Nafion Coatings on S,N-<br>Codoped Graphene-<br>Quantum-Dots-Modified<br>TiO <sub>2</sub> | Solar and visible light, neutral pH,<br>2-propanol as hole scavenger, O <sub>2</sub><br>saturation | DPD–POD method                                                       | 373 µM/h     | [126] |
| Zn-TiO <sub>2</sub>                                                                       | Formate as scavenger, O <sub>2</sub> , varied<br>pH values                                         | spectrophotometric method based on<br>the catalysed iodide oxidation | 0.22 mM      | [118] |

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## 5.2. Graphitic carbon nitride based photocatalysts

### 5.2.1. Introduction to graphitic carbon nitride materials

g-C<sub>3</sub>N<sub>4</sub> is a metal-free n-type polymeric semiconductor regarded as a promising candidate for a wide span of energy and environmental applications, as it can be activated by visible light irradiation, is produced from Earth-abundant elements by facile synthesis methods, and possesses high physicochemical stability and unique electronic band structure [127-129]. Since its first report in 2009 by Wang et al. for the photocatalytic production of hydrogen from water [130], g-C<sub>3</sub>N<sub>4</sub> has been extensively employed in photocatalytic CO<sub>2</sub> reduction, organic pollutant degradation, organic synthesis, H<sub>2</sub> evolution, water splitting, nitrogen fixation, and H<sub>2</sub>O<sub>2</sub> production [130-136]. g-C<sub>3</sub>N<sub>4</sub> is composed by stacked 2D layered polymeric s-triazine or tri-s-triazine units interconnected through tertiary amines forming  $\pi$ -conjugated graphitic planes of sp<sup>2</sup> hybridized carbon and nitrogen with a stoichiometric C/N ratio of 0.75 (Figure 9) [128, 130, 138]. The band gap of g-C<sub>3</sub>N<sub>4</sub> is approximately 2.7 eV (~460 nm), providing a wide visible-light absorption range, and the position of the conduction band is appropriate for various reduction reactions, such as H<sub>2</sub> evolution, CO<sub>2</sub> reduction and O<sub>2</sub> reduction [139-141]. g-C<sub>3</sub>N<sub>4</sub> is thermally stable up to 600°C due to the aromatic C-N heterocycles, with complete decomposition occurring beyond 700°C. It exhibits high chemical resistance to acidic and basic media, as well as commonly used solvents (*e.g.*, water, alcohols, dimethylformamide, tetrahydrofuran, toluene and diethyl ether), owing to the Van der Waals interactions between the stacked graphitic layers [129, 142-143].



**Figure 9. (a) Triazine and (b) tri-s-triazine (heptazine) structures of g-C<sub>3</sub>N<sub>4</sub>** (H, white; C, grey; N, blue).

g-C<sub>3</sub>N<sub>4</sub> materials are generally synthesized by simple and cost-effective thermal polycondensation at 450-650°C of nitrogen-rich precursors, such as dicyanamide, cyanamide, melamine, urea and thiourea [46, 144-147]. The reaction pathway mainly involves three temperature-dependent processes: (i) polymerization of precursors to melamine by addition and condensation reactions, (ii) condensation of melamine releasing ammonia, and (iii) g-C<sub>3</sub>N<sub>4</sub> formation *via* polymerization [128, 130, 148-150]. The precursor type, as well as the reaction conditions (temperature, duration and atmosphere), have demonstrated to influence the g-C<sub>3</sub>N<sub>4</sub> physicochemical features (*i.e.*, morphology, specific surface area, porosity, C/N ratio, electronic band structure,

presence of defects and carbon/nitrogen vacancies, etc.) and, in consequence, the photocatalytic activity [151-152].

Despite the remarkable properties mentioned above, bulk g-C<sub>3</sub>N<sub>4</sub> faces a few redhibitory shortcomings that hinder its practical applications, such as a low specific surface area (<10 m<sup>2</sup> g<sup>-1</sup>), a high recombination rate of photogenerated charge carriers, an inefficient visible light utilization at wavelengths above 460 nm, and a relatively poor electrical conductivity, that are globally responsible of the achievement of low photocatalytic performances [153-156]. In addition, pristine g-C<sub>3</sub>N<sub>4</sub> exhibits a relatively low oxidation potential of holes from VB, relative to water oxidation potential, compared to other semiconductors (*e.g.*, TiO<sub>2</sub> or ZnO) and a limited ability to adsorb target reactants, such as O<sub>2</sub> and NO [157-160]. To overcome these limitations, multiple approaches have been developed, including the exfoliation of g-C<sub>3</sub>N<sub>4</sub> into nanosheets, defect engineering, nanoarchitecture engineering (*e.g.*, nanospheres, nanorods, nanoribbons, nanobelts, nanowires, etc.), hard and soft-templating, metal and non-metal doping, copolymerization, and coupling with carbon materials and/or other semiconductors, which have been discussed in the literature [128, 138, 148-149, 161-163]. Among them, thermal exfoliation into 2D nanosheets stands out for its simplicity, and allows for a significant increase in the specific surface area (it should be noted that the theoretical specific surface area of an ideal monolayer of C<sub>3</sub>N<sub>4</sub> is about 2500 m<sup>2</sup> g<sup>-1</sup>), facilitates the separation of charge carriers and improves the diffusion of reactants and products [149, 164].

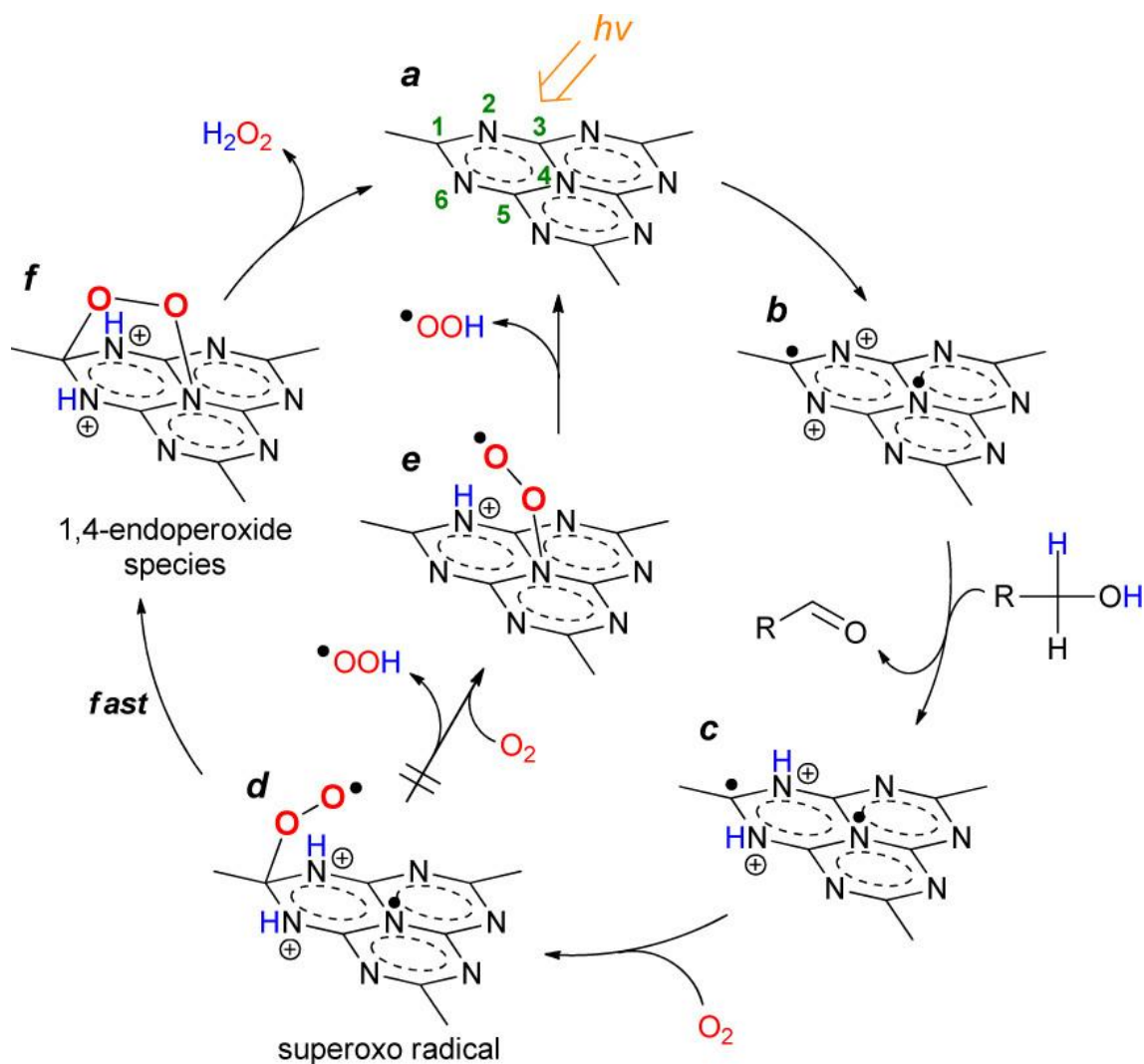
### 5.2.2. Photocatalytic H<sub>2</sub>O<sub>2</sub> production on g-C<sub>3</sub>N<sub>4</sub> materials

g-C<sub>3</sub>N<sub>4</sub> photocatalyst can selectively generate H<sub>2</sub>O<sub>2</sub> under visible light irradiation and mild conditions (neutral pH, room temperature) in the presence of dissolved oxygen owing to its electronic properties and the formation of 1,4-endoperoxide species [46, 145, 165]. The conduction band of g-C<sub>3</sub>N<sub>4</sub>, with an energy level of approximately -1.12 eV, is properly located to promote O<sub>2</sub> reduction to H<sub>2</sub>O<sub>2</sub>, as the standard redox potential of O<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> is less negative (-0.33 V vs. SHE; pH = 7) [166-167]. In comparison to the water oxidation route, O<sub>2</sub> reduction is the only pathway observed for photocatalytically generating H<sub>2</sub>O<sub>2</sub> on g-C<sub>3</sub>N<sub>4</sub>, as demonstrated by experiments performed under anoxic conditions (in absence of oxygen) where no formation of H<sub>2</sub>O<sub>2</sub> was observed [144-145, 168]. Compared to other semiconductors such as TiO<sub>2</sub>, g-C<sub>3</sub>N<sub>4</sub> displays higher selectivity (> 90%) for H<sub>2</sub>O<sub>2</sub> production when activated by visible light irradiation (> 400 nm), since subsequent decomposition of the formed H<sub>2</sub>O<sub>2</sub> by UV light is suppressed [46, 167]. The addition of a sacrificial agent (aliphatic or aromatic alcohols) to the g-C<sub>3</sub>N<sub>4</sub> system under visible light irradiation has been reported to yield higher concentrations of H<sub>2</sub>O<sub>2</sub> than in pure water, the H<sub>2</sub>O<sub>2</sub> selectivity increasing as the proton-donating capacity of the organic sacrificial agent increases [46, 144-145]. In this regard, it is worth mentioning that the photocatalytic generation of H<sub>2</sub>O<sub>2</sub> and the degradation of pollutants acting as proton donors can be conducted simultaneously (see section 6.1) [137, 145].

Table 5 displays a selection of recent works on H<sub>2</sub>O<sub>2</sub> synthesis using g-C<sub>3</sub>N<sub>4</sub>-based photocatalysts including details on the reaction conditions, the H<sub>2</sub>O<sub>2</sub> quantification method, and the H<sub>2</sub>O<sub>2</sub> production performance. Following their pioneering works on TiO<sub>2</sub>, Shiraishi et al. first reported the high selectivity of g-C<sub>3</sub>N<sub>4</sub> for H<sub>2</sub>O<sub>2</sub> production through the two-electron reduction of O<sub>2</sub> and proposed a mechanism involving the formation of the 1,4-endoperoxide intermediate on the catalyst surface under visible

light irradiation (Figure 10) [46]. According to this mechanism, the process takes place as follows: (a) visible light triggers electron-holes pairs generation, (b) photoexcited electrons are located at the C1 and N4 positions of the triazine ring, while holes are positioned on the N2 and N6 positions, (c) holes take  $\alpha$ - and  $\beta$ -hydrogens of alcohol (sacrificial agent) producing aldehyde, (d)  $O_2$  is reduced by photoexcited electrons forming superoxo radical, (f) superoxo radical is further reduced by another electron at the *para* position of the triazine ring to the 1,4-endoperoxide species, suppressing one-electron  $O_2$  reduction (e), and finally the 1,4-endoperoxide species are converted to  $H_2O_2$  by protonation [46, 165, 169]. The inhibition of the one-electron  $O_2$  reduction to the superoxide and the formation of 1,4-endoperoxide species were confirmed by electron spin resonance (ESR) analysis and Raman spectroscopy, respectively [46].





**Figure 10.** Two-electron  $\text{O}_2$  reduction-based mechanism involving the surface 1,4-endoperoxide intermediate proposed by Shiraishi for the selective formation of  $\text{H}_2\text{O}_2$  on the surface of photoactivated  $\text{g-C}_3\text{N}_4$ . Reproduced with permission from Ref. [46]. Copyright 2014 American Chemical Society.

### ***Nanoarchitecture and defect engineering of $\text{g-C}_3\text{N}_4$***

Subsequently, the same authors prepared  $\text{g-C}_3\text{N}_4$  catalysts with larger surface areas by silica-templated thermal polymerization of cyanamide with the aim of improving the photocatalytic activity for  $\text{H}_2\text{O}_2$  production [170]. Noteworthy, they

found that the selectivity for the two-electron reduction of  $O_2$  decreased as the surface area of the catalysts increased (92% for  $10\text{ m}^2\text{ g}^{-1}$  > 72% for  $56\text{ m}^2\text{ g}^{-1}$  > 58% for  $160\text{ m}^2\text{ g}^{-1}$  > 42% for  $228\text{ m}^2\text{ g}^{-1}$ ), which was explained by the formation of a large number of primary amine moieties on the surface of mesopores [170]. They proposed that these defects promoted the four-electron reduction of  $O_2$  to  $H_2O$ , as confirmed by ESR analysis, as well as the rapid photocatalytic decomposition of the formed  $H_2O_2$  due to the attraction between the basic primary amine sites and acidic  $H_2O_2$  [170-171]. Liu et al. transformed amino groups ( $-NH_2$ ) on the  $g\text{-C}_3\text{N}_4$  surface into stable *N*-hydroxymethyl groups ( $-NH\text{-CH}_2\text{-OH}$ ) by reaction with formaldehyde ( $g\text{-C}_3\text{N}_4\text{-NH}_2 + \text{HCHO} \rightarrow g\text{-C}_3\text{N}_4\text{-NH-CH}_2\text{-OH}$ ), while maintaining the morphological features, light absorption capacity, electronic structure, and charge separation and transfer ability of the photocatalyst [172]. Interestingly,  $g\text{-C}_3\text{N}_4$  with surface  $-NH\text{-CH}_2\text{-OH}$  functions showed more energetically favorable kinetics for photocatalytic  $O_2$  reduction to  $H_2O_2$  in water compared to pristine  $g\text{-C}_3\text{N}_4$ , owing to enhanced  $O_2$  adsorption and  $H_2O$  dehydrogenation properties.

In order to increase the photocatalytic activity for  $H_2O_2$  production, Liu et al. synthesized ultra-thin  $g\text{-C}_3\text{N}_4$  nanoplates (1-3 nm thickness) through a glucose-assisted mechanical exfoliation process, which exhibited an increased surface area ( $89.5\text{ m}^2\text{ g}^{-1}$ ), a higher charge separation efficiency, and a lower charge transfer resistance compared to the a bulk  $g\text{-C}_3\text{N}_4$  counterpart at  $10.6\text{ m}^2\text{ g}^{-1}$  [173]. In addition, the exfoliation treatment was shown to improve the redox capacity of  $g\text{-C}_3\text{N}_4$  by raising the CB potential and changed the reaction pathway from a sequential two-step one-electron route to a one-step two-electron reduction of  $O_2$  to  $H_2O_2$ , as determined by Mott-Schottky and ESR analyses, respectively.  $g\text{-C}_3\text{N}_4$  microrods with the simultaneous presence of C, N dual

vacancies and a nearly stoichiometric C/N ratio were obtained through thermal polymerization of melamine-cyanuric acid supramolecular precursors under  $H_2$  [174]. The C and N vacancies were reported to enhance visible light absorption, suppress charge carrier recombination by trapping/donating electrons and serve as active sites for  $O_2$  adsorption, facilitating its reduction to  $H_2O_2$  by a sequential two-step one-electron pathway.

#### ***Non-metal doping of g-C<sub>3</sub>N<sub>4</sub>***

Non-metal doping (C, O, P, S, B) is a strategy that has been extensively explored to improve the performance of  $H_2O_2$  photocatalytic synthesis by g-C<sub>3</sub>N<sub>4</sub>. Carbon modified g-C<sub>3</sub>N<sub>4</sub> photocatalysts with tunable energy levels were prepared by adjusting the concentration of glucose additive during a hydrothermal synthesis [175]. The authors found that C atoms partially replaced N atoms in the g-C<sub>3</sub>N<sub>4</sub> framework, leading to an increased light absorption capacity and a positive shift of the conduction and valence bands, which improved the selectivity for the reduction of  $O_2$  to  $H_2O_2$  and favored the water oxidation reaction, respectively. g-C<sub>3</sub>N<sub>4</sub> with oxygen-enriched structures (C-O-C and -OH), obtained using dicyandiamide and ammonium paratungstate, was demonstrated to promote the formation of the 1,4-endoperoxide species and, in consequence, the reduction of  $O_2$  to  $H_2O_2$  *versus* the generation of the superoxide radical [176]. According to DFT calculations, the C-O-C group (rather than the -OH group) was responsible for the increased activity, leading to an efficient charge carrier separation and favoring, especially, the final release of  $H_2O_2$ .

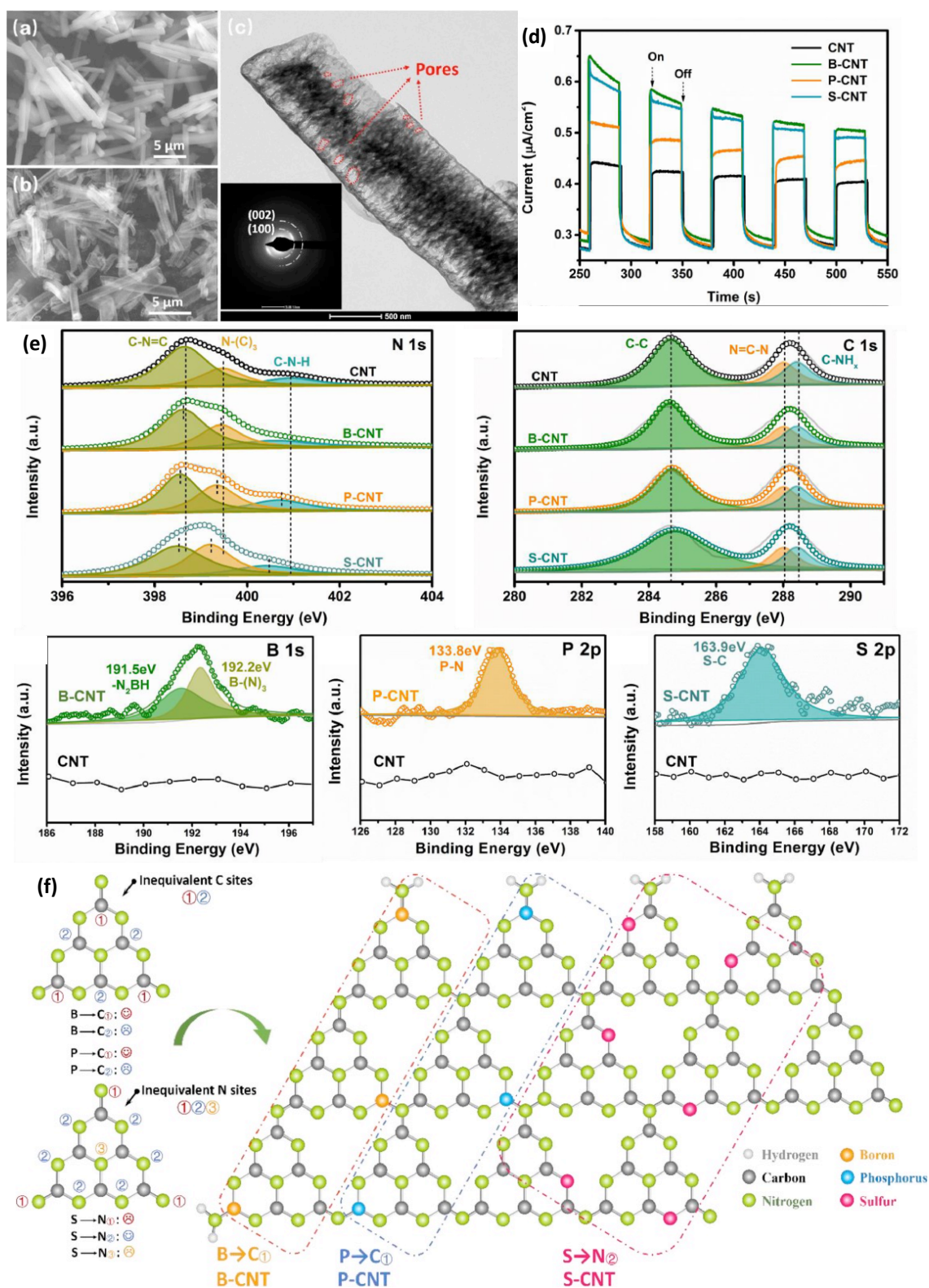
Phosphate modification of g-C<sub>3</sub>N<sub>4</sub> by acid-hydrothermal method (22.2%  $H_3PO_4$  solution) resulted in an increase in the surface area, a better separation of the

photogenerated electron-hole pairs, as well as an improved ability for both adsorption and reduction of  $O_2$  [177]. As determined by  $O_2$  temperature-programmed desorption ( $O_2$ -TPD) experiments, more  $O_2$  molecules could be adsorbed due to the presence of phosphate on the g- $C_3N_4$  surface that can trap the photoexcited electrons, what is therefore enhancing the charge carrier separation. In addition, Moon et al. reported that the incorporation of phosphate species to g- $C_3N_4$  by solid-state thermal polymerization of melamine in the presence of dibasic potassium phosphate (~25 wt.%) facilitated the proton transfer process and suppressed the decomposition of *in-situ* generated  $H_2O_2$  [106]. Thereby,  $H_2O_2$  production in water was enhanced by the presence of phosphate species and less dependent on the pH of the medium (or the proton concentration). On the other hand, g- $C_3N_4$  was co-doped with K, P, O, and S (0.1, 1, 3, 5 and 10 wt.%  $K_2HPO_4$ , and 50 wt.% urea/thiourea as precursors), achieving higher visible light absorption and hindering the recombination of photogenerated electron-hole pairs due to the presence of heteroatoms and of N defects after doping [178]. In particular, S-doping was reported to increase the  $H_2O_2$  synthesis performance, which was explained by a favored charge transfer through the heptazine ring [178-179].

In this context, the introduction of S atoms into the heptazine units of g- $C_3N_4$  nanosheets (in replacement of N atoms) has been reported to result in improved light absorption ability and charge transfer efficiency due to the reduction of the band gap and the increase of the local electronic density, respectively [180]. Although thermal exfoliation mostly leads to a wider band gap with a positive shift of CB and VB compared to the bulk g- $C_3N_4$ , when the treatment was performed simultaneously with S-doping, a smaller shift of the VB was observed, overcoming this constraint. Furthermore, S-doped g- $C_3N_4$  nanosheets exhibited a highly selective two-electron reduction of  $O_2$  to  $H_2O_2$ ,

enhancing the performance of pristine g-C<sub>3</sub>N<sub>4</sub> nanosheets, on which the simultaneous two-electron and one-electron reduction pathways occurred, but only a part of the superoxide radical intermediate gave rise to H<sub>2</sub>O<sub>2</sub>. Liu et al. synthesized non-metal (B, P, S) doped g-C<sub>3</sub>N<sub>4</sub> tubes by a hydrothermal method with a subsequent thermal polymerization from a melamine-cyanuric acid supramolecular precursor (Figure 11a) [181]. The obtained tube structure (~1 μm diameter, 30-80 nm wall thickness), displayed in Figure 11b-c, was proposed to increase the light absorption capacity by multiple reflection-effect, while the dopants would promote the separation of photogenerated electron-hole pairs, as confirmed by transient photocurrent response experiments (Figure 11d), and tune the electronic structure of g-C<sub>3</sub>N<sub>4</sub> [181]. XPS results (Figure 11e) indicated that B and P atoms replaced the C atoms, while N atoms were replaced by S atoms, as depicted in Figure 11f. Interestingly, in this case, H<sub>2</sub>O<sub>2</sub> was mainly generated through the two-steps one-electron O<sub>2</sub> reduction pathway by B, P, and S- doped g-C<sub>3</sub>N<sub>4</sub> tubes.

B-doped g-C<sub>3</sub>N<sub>4</sub> nanoplatelets (~2.5 nm thickness) and nanosheets with a highly porous structure and a large surface area have been obtained *via* thermal polymerization followed by an ultrasound-assisted exfoliation process [182-183]. The oxidative ultrasonic exfoliation process was informed to improve both the hydrophilicity and the surface area, while B doping led to a decrease in the band gap and to an increase in the electron density at the B site, promoting charge separation and transfer [182]. It was found that the electron-deficient B-N units served as active sites for O<sub>2</sub> adsorption and the subsequent two-step one-electron O<sub>2</sub> reduction route yielded H<sub>2</sub>O<sub>2</sub> [183].



**Figure 11.** SEM image of melamine-cyanuric acid supramolecular precursor (a); SEM (b) and TEM (c) images of g-C<sub>3</sub>N<sub>4</sub> tubes (CNT); Transient photocurrent response (d) and XPS

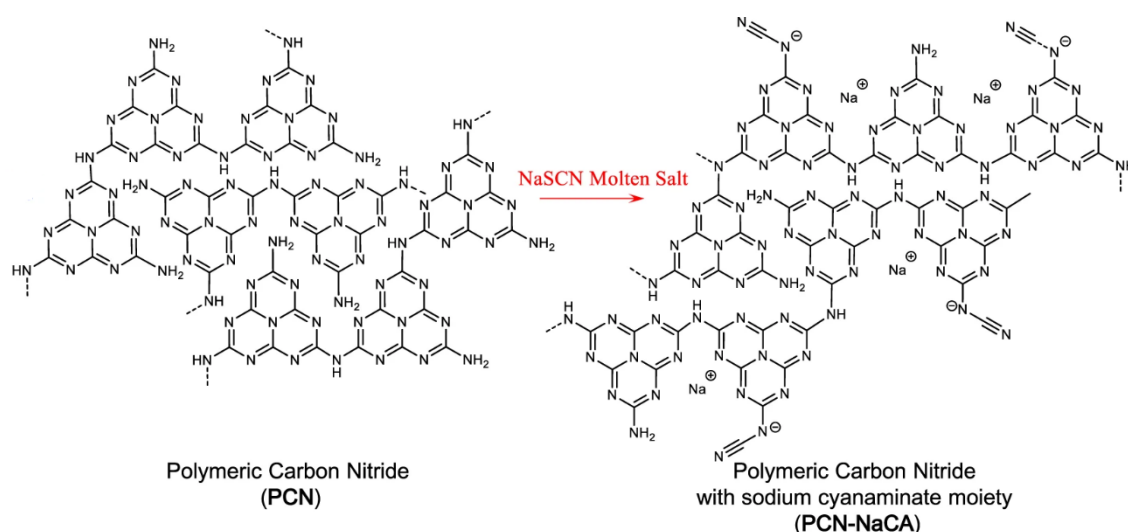
spectra **(e)** of CNT and B-, P-, and S -doped CNT; Schematic diagram of B, P, and S atoms doping sites in the g-C<sub>3</sub>N<sub>4</sub> framework **(f)**. Reproduced with permission from Ref. [181]. Copyright 2021 Elsevier.

### ***Metal doping of g-C<sub>3</sub>N<sub>4</sub>***

The doping of the g-C<sub>3</sub>N<sub>4</sub> framework by alkali and transition metals has been also investigated and demonstrated to promote the photocatalytic synthesis of H<sub>2</sub>O<sub>2</sub>. Alkali metal (K<sup>+</sup> and Na<sup>+</sup>) modified g-C<sub>3</sub>N<sub>4</sub> with tunable band gap was obtained by adjusting the weight ratio of eutectic salts to the melamine precursor using the molten salt method [184]. Molten salt synthesis involves incorporating salts to the constituent precursors and carrying out the reaction at temperatures above the melting point of the salts, which act as a solvent enhancing solid-state reaction rates by increasing the contact area and mobility [185]. K<sup>+</sup> and Na<sup>+</sup> coordinated into the C-N rings and provided g-C<sub>3</sub>N<sub>4</sub> with enhanced visible light absorption, larger specific surface area and reduced recombination of electron-hole pairs. K<sup>+</sup> and Na<sup>+</sup> co-doped g-C<sub>3</sub>N<sub>4</sub> with a weight ratio of 20:1 for eutectic salts to melamine (1.3 wt.% and 0.7 wt.% of K<sup>+</sup> and Na<sup>+</sup> contents, respectively) was able to produce H<sub>2</sub>O<sub>2</sub> in the absence of O<sub>2</sub> and in the presence of an electron scavenger, suggesting that H<sub>2</sub>O<sub>2</sub> was not only synthesized by the O<sub>2</sub> reduction pathway but also by the oxidation of OH<sup>-</sup> to HO<sup>•</sup> with subsequent reaction between two HO<sup>•</sup> forming H<sub>2</sub>O<sub>2</sub> due to a more positive VB potential [184, 186].

Likewise, Zhao et al. introduced sodium cyanamate moiety into g-C<sub>3</sub>N<sub>4</sub> (sodium content of 6.9 wt.%) [187]. For that purpose, sodium thiocyanate (NaSCN) molten salt method was used, which resulted in a coordinative interaction between sodium and pyridinic nitrogen, as shown in Figure 12, and, together with cyanamino groups,

promoted photon absorption, charge carrier separation efficiency, O<sub>2</sub> adsorption and selective two-electron O<sub>2</sub> reduction to H<sub>2</sub>O<sub>2</sub>. However, reusability experiments showed that the catalyst lost both cyanamino groups and Na<sup>+</sup> when subjected to long-term reactions. On the other hand, potassium intercalated into the g-C<sub>3</sub>N<sub>4</sub> structure by a KHCO<sub>3</sub>-mediated synthesis (*ca.* 6.49 wt.%), with the simultaneous introduction of cyano groups (–C≡N) into the framework, was reported to increase the number of active sites and favor a highly selective two-electron O<sub>2</sub> reduction route to H<sub>2</sub>O<sub>2</sub> [188].



**Figure 12.** Schematic diagram of g-C<sub>3</sub>N<sub>4</sub> with cyanamate moiety (PCN-NaCA) synthesized from g-C<sub>3</sub>N<sub>4</sub> (PCN) by the molten-salt method. Reproduced with permission from Ref. [187]. Copyright 2021 Nature Publishing Group.

Cu-doped g-C<sub>3</sub>N<sub>4</sub> hollow microspheres (~100 nm diameter and 0.23 wt.% Cu content) were prepared using a SiO<sub>2</sub> template, where Cu<sup>+</sup> was inserted at the interstitial position through coordinative Cu(I)-N bonds [157]. These Cu(I)-N active sites significantly improved the O<sub>2</sub> adsorption capacity, while acting as a transfer bridge for



the photogenerated electrons from the catalyst to the adsorbed  $O_2$  molecules, generating  $H_2O_2$  by a selective one-step two-electron reduction pathway. Metal-ion incorporated single atom g- $C_3N_4$  photocatalyst (< 0.7 wt.% of metals species) were prepared by isolating three transition metals (Fe, Co, Ni) and two main group metals (In, Sn) sites with pyridinic N atoms [189]. It was observed that the introduction of  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Co^{2+}$  and  $Ni^{2+}$  favored the charge carrier recombination, leading to a decrease in the photocatalytic performance compared to bare g- $C_3N_4$ . In contrast,  $In^{3+}$  and  $Sn^{4+}$  sites accumulated electrons during excitation, inhibiting the recombination of electron-hole pairs and promoting the adsorption of the electrophilic  $O_2$  and its subsequent reduction.

### ***Metal/g- $C_3N_4$ heterostructures***

Metals and metal oxides have also been incorporated as nanoparticles into g- $C_3N_4$  with the purpose of improving its photocatalytic activity. In this regard, Chang et al. anchored Au nanoparticles in a  $C_3N_4$  matrix (1.05 wt.% Au loading) through a carbon-layer-stabilized method, achieving a reduction of charge carrier recombination, which was explained by the robust metal-support interaction and the small size of the nanoparticles (~5 nm) and led to a good photocatalytic performance for  $H_2O_2$  production [190]. Hollow tubular g- $C_3N_4$  was substitutionally doped with oxygen (replacing N atoms) and loaded with highly dispersed Ni nanoparticles in the size range of 20-60 nm by a photodeposition process [144]. The authors found that oxygen doping and the presence of Ni increased the visible light absorption and charge separation efficiency, while the Ni loading (2%, 4%, 6% and 8%) changed the reaction pathway from a two-step one-electron to a single-step two-electron  $O_2$  reduction to  $H_2O_2$ , with an increase in the selectivity from 60.8% to 88.9%. Nevertheless, an excess of Ni ( $\geq 6\%$  Ni loading) lowered

the performance for  $\text{H}_2\text{O}_2$  synthesis, which was attributed to the aggregation of metal particles blocking light absorption.

Dysprosium oxide ( $\text{Dy}_2\text{O}_3$ ) particles were dispersed on N-deficient g- $\text{C}_3\text{N}_4$  nanosheets by a simple thermal condensation route, with an observed interlayer stacking of the g- $\text{C}_3\text{N}_4$  structure, and a reduction of both the band gap and the photogenerated charge carrier recombination [191].  $\text{H}_2\text{O}_2$  formation was proposed to occur in  $\text{Dy}_2\text{O}_3/\text{g-C}_3\text{N}_4$  systems *via* a mixed two-step one-electron and one-step two-electron  $\text{O}_2$  reduction route. Chu et al. prepared a cyano and  $\text{SnO}_2$  co-modified g- $\text{C}_3\text{N}_4$  *via* one-step pyrolysis of melamine with  $\text{Na}_2\text{SnO}_3$  (mass ratio of 1%, 2.5%, 5% and 10% to melamine), which exhibited an enhanced photocatalytic performance for  $\text{H}_2\text{O}_2$  production [192]. In addition to increasing the utilization of visible light and inhibiting charge carrier recombination, the introduction of cyano groups and  $\text{SnO}_2$  nanocrystals favored the adsorption of  $\text{O}_2$  and  $\text{H}^+$  due to the negatively charged catalyst surface. Briefly, photoexcited electrons in g- $\text{C}_3\text{N}_4$  were suggested to be accepted by the cyano groups and subsequently transferred to  $\text{SnO}_2$ , where the adsorbed  $\text{O}_2$  was reduced to  $\text{H}_2\text{O}_2$  through a two-step single-electron pathway.

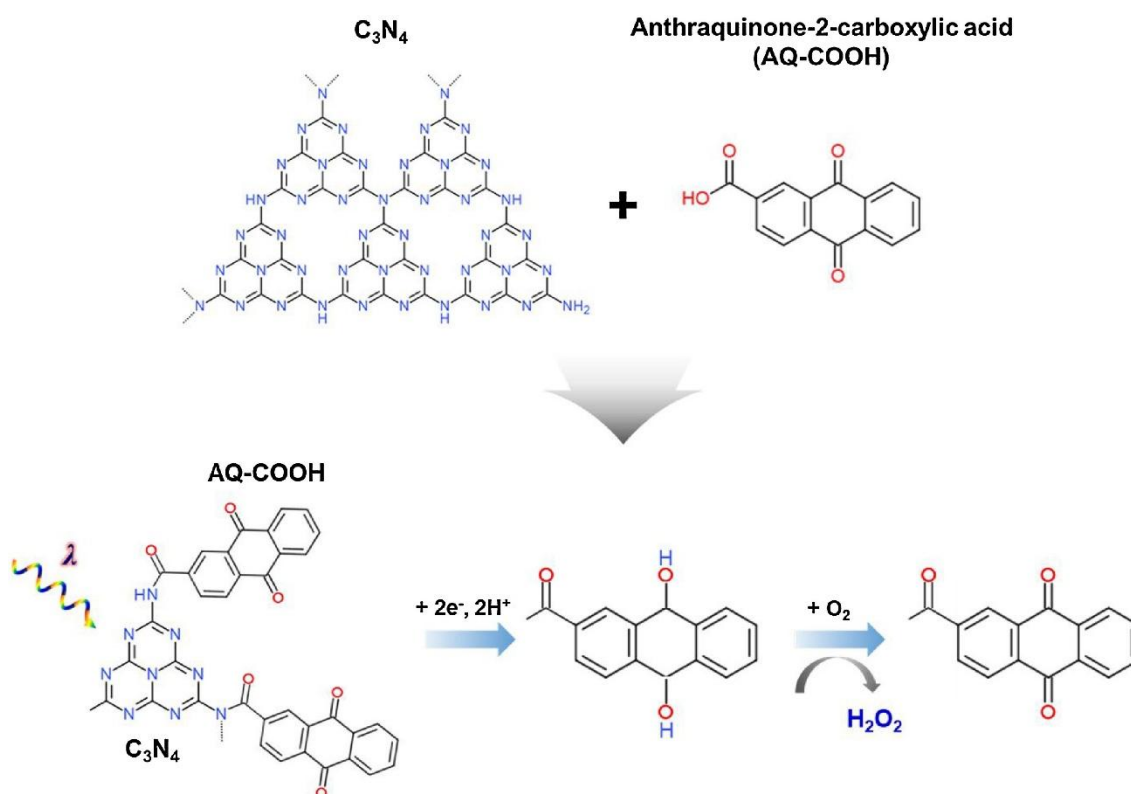
### ***Molecular engineering of g- $\text{C}_3\text{N}_4$***

Molecular engineering has proven to be a simple and effective approach to significantly improve the photocatalytic performance by extending the  $\pi$ -conjugated system or by incorporating proton donors into the g- $\text{C}_3\text{N}_4$  structure. In this context, Yang et al. synthesized a 2-hydroxy-4,6-dimethylpyrimidine (HDMP) grafted g- $\text{C}_3\text{N}_4$  through an *in-situ* keto-enol cyclization of urea and acetylacetone that improved the photocatalytic activity for  $\text{H}_2\text{O}_2$  production [193]. The incorporation of the HDMP moiety

into the g-C<sub>3</sub>N<sub>4</sub> framework enhanced the visible light absorption, as delocalized  $\pi$ -electrons increased, and promoted charge carrier separation and transfer. This efficient charge separation and transfer was ascribed to the electronegativity of HDMP, which accepted the photoexcited electrons while the holes remained in the heptazine moiety. 1,3,5-Trihydroxybenzene (TB)-substituted g-C<sub>3</sub>N<sub>4</sub>, compared to pristine g-C<sub>3</sub>N<sub>4</sub>, displayed larger specific surface area, improved visible light absorption capacity, and reduced charge carrier recombination, what resulted in superior photocatalytic activity for H<sub>2</sub>O<sub>2</sub> synthesis [194]. In addition, as the free -NH<sub>2</sub> groups of the urea were partially replaced by TB (rich in -OH groups), the catalyst hydrophilicity increased. Zhang et al., reported the use of hydroxyethyl cellulose (HEC) as proton donor for modifying g-C<sub>3</sub>N<sub>4</sub> *via* hydrogen bonds (0.01-0.2 mass ratio of HEC to g-C<sub>3</sub>N<sub>4</sub>) [195]. HEC modification was shown to promote not only proton-coupled electron transfer, but also charge carrier separation through electron transfer from HEC to g-C<sub>3</sub>N<sub>4</sub>, thus enhancing H<sub>2</sub>O<sub>2</sub> production performance.

Proton-coupled electron transfer also occurred when AQ was anchored onto C<sub>3</sub>N<sub>4</sub> (10 wt.% of AQ-COOH) by heat-induced hybridization method without altering its structure, with in consequence the favored formation of H<sub>2</sub>O<sub>2</sub> and the reduction of its decomposition [76]. As shown in Figure 13, AQ molecules are suggested to accept photoexcited electrons from C<sub>3</sub>N<sub>4</sub>, and to transfer them to initiate the hydrogenation reaction of AQ to anthrahydroquinone (AQH<sub>2</sub>), H<sub>2</sub>O<sub>2</sub> being formed as side-product of the dehydrogenation of AQH<sub>2</sub> back to AQ with the reduction of O<sub>2</sub>. Torres-Pinto et al. also obtained an enhanced photocatalytic performance for H<sub>2</sub>O<sub>2</sub> production using an AQ-functionalized g-C<sub>3</sub>N<sub>4</sub> catalyst (10 wt. % of AQ) prepared by a simple hydrothermal method [196]. The increased H<sub>2</sub>O<sub>2</sub> formation was explained by the replacement of some

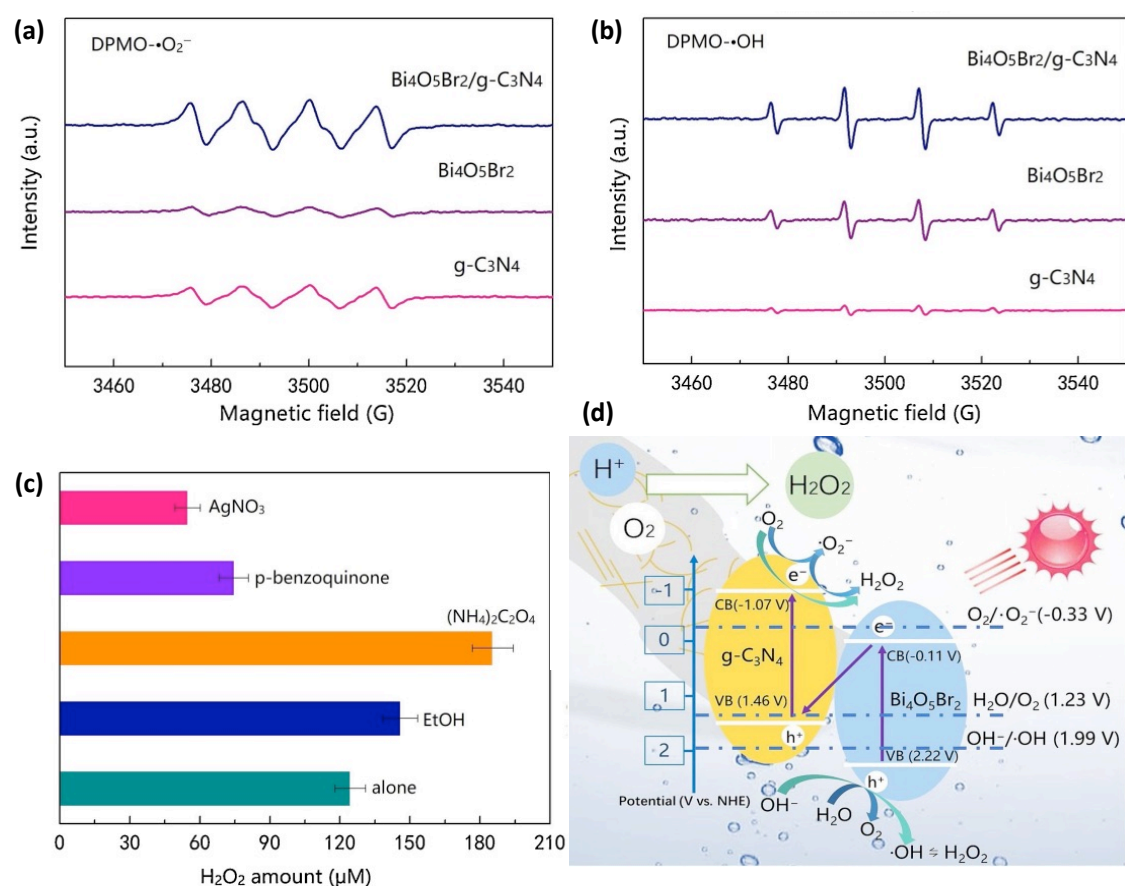
functional groups in g-C<sub>3</sub>N<sub>4</sub> with C-O, C=O bonds and quinone groups. Specifically, the C-O bond has proton-donating capacity, and the C=O and quinone groups would trap electrons due to their high electronegativity, thus suppressing charge carrier recombination and favoring the formation of intermediate radicals (e.g., hydroperoxyl radicals).



**Figure 13.** Schematic diagram of the coupling process of C<sub>3</sub>N<sub>4</sub> with AQ and the photocatalytic synthesis of H<sub>2</sub>O<sub>2</sub> by AQ/C<sub>3</sub>N<sub>4</sub> under solar light irradiation. Reproduced with permission from Ref. [76]. Copyright 2018 Elsevier.

### ***Semiconductor/g-C<sub>3</sub>N<sub>4</sub> heterojunctions***

Heterojunction construction is a strategy that has been shown to favor charge carrier separation and transfer, and in consequence to lead to an improved photocatalytic activity for  $\text{H}_2\text{O}_2$  production. The growth of  $\text{NiIn}_2\text{S}_4$  on  $\text{C}_3\text{N}_4$  with lamellar structure resulted in a highly efficient  $\text{C}_3\text{N}_4/\text{NiIn}_2\text{S}_4$  heterostructure with a larger number of catalytic sites, higher visible light absorption and better separation of the photogenerated charge carriers [197]. Additionally, the authors found that the Ni atoms from the  $\text{C}_3\text{N}_4/\text{NiIn}_2\text{S}_4$  heterojunction possessed mixed valence states ( $\text{Ni}^{3+}$  and  $\text{Ni}^{2+}$ ), giving the composite a low electrical resistance. Farzin et al. elaborated a Z-scheme heterojunction system by decorating oxygen-doped  $\text{g-C}_3\text{N}_4$  nanosheets with  $\text{NaBiS}_2$  nanoribbons that achieved an effective charge separation, as electrons and holes accumulate in the CB of  $\text{NaBiS}_2$  and the VB of oxygen-doped  $\text{g-C}_3\text{N}_4$ , respectively, and generated  $\text{H}_2\text{O}_2$  following the one-step two-electron  $\text{O}_2$  reduction pathway [198].  $\text{Bi}_4\text{O}_5\text{Br}_2$  nanorods ( $\sim 3.8$  nm diameter, 25-30 nm length) decorating on  $\text{g-C}_3\text{N}_4$  nanosheets (25, 50 and 75 wt.% of  $\text{Bi}_4\text{O}_5\text{Br}_2$  to  $\text{g-C}_3\text{N}_4$ ) were also proposed to form a highly efficient Z-scheme system [199]. In this case, photoinduced electrons accumulated in the CB of  $\text{g-C}_3\text{N}_4$  would be responsible for the reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}_2$  *via* simultaneous one-step two-electrons and two-steps one-electron pathways, while electrons in the CB of  $\text{Bi}_4\text{O}_5\text{Br}_2$  would combine with the holes in the VB of  $\text{g-C}_3\text{N}_4$  (Figure 14). Furthermore, it was found that the holes in the VB of  $\text{Bi}_4\text{O}_5\text{Br}_2$  had the potential to oxidize  $\text{H}_2\text{O}$  molecules to  $\text{O}_2$  and  $\text{HO}^\bullet$ , which subsequently combined with each other to form  $\text{H}_2\text{O}_2$ .



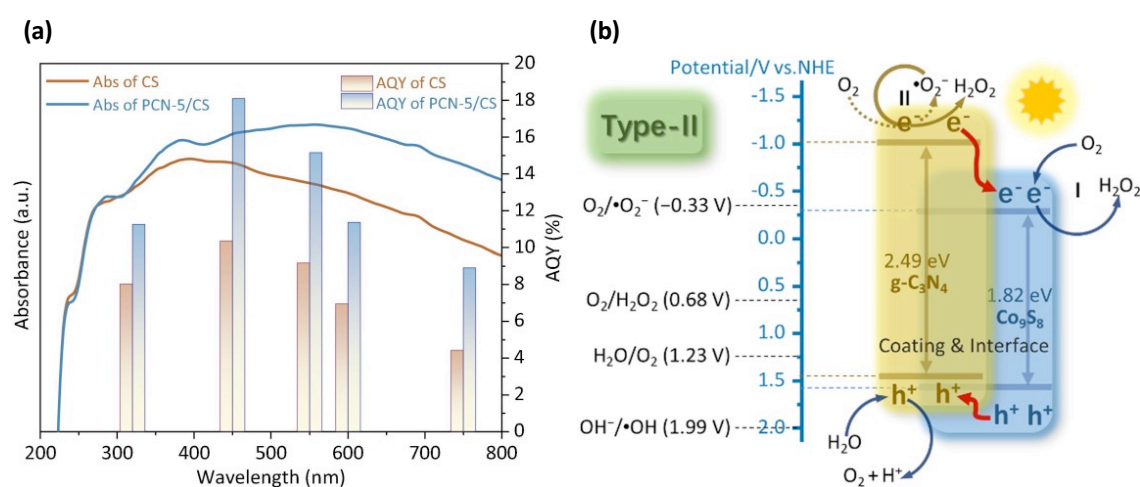
**Figure 14.** EPR spectra of  $\text{DMPO-O}_2^{\bullet-}$  (a) and  $\text{DMPO-}\bullet\text{HO}$  (b) for  $\text{g-C}_3\text{N}_4$ ,  $\text{Bi}_4\text{O}_5\text{Br}_2$  and  $\text{Bi}_4\text{O}_5\text{Br}_2/\text{g-C}_3\text{N}_4$ . Photocatalytic production of  $\text{H}_2\text{O}_2$  on  $\text{Bi}_4\text{O}_5\text{Br}_2/\text{g-C}_3\text{N}_4$  in the presence of  $\text{AgNO}_3$ ,  $p$ -benzoquinone,  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and ethanol (EtOH) as scavenger species for electrons, superoxide radicals, holes and hydroxyl radicals, respectively (c). Proposed mechanisms for the photocatalytic synthesis of  $\text{H}_2\text{O}_2$  by a Z-scheme mechanism on  $\text{Bi}_4\text{O}_5\text{Br}_2/\text{g-C}_3\text{N}_4$  (d). Reproduced with permission from Ref. [199]. Copyright 2020 Elsevier.

An interfacial Schottky junction constructed by an electrostatic self-assembly process from  $\text{Ti}_3\text{C}_2$  nanosheets and porous  $\text{g-C}_3\text{N}_4$  nanosheets (1, 2 and 5 wt.% of  $\text{Ti}_3\text{C}_2$  to  $\text{g-C}_3\text{N}_4$ ) was reported to enhance visible light absorption, photogenerated electron-

hole pairs separation and thus the performance for  $O_2$  reduction to  $H_2O_2$  *via* a two-step single-electron pathway [200]. Photogenerated electrons were proposed to migrate from g- $C_3N_4$  to  $Ti_3C_2$  with the formation of a Schottky barrier, which prevented electrons from back-transfer to the g- $C_3N_4$  semiconductor, and lowered charge carrier recombination. Yang et al. reported the simultaneous formation of a Schottky barrier-type junction and a Z-scheme mechanism by decorating the surface of g- $C_3N_4$  with  $Ti_2C_3$  and BiOCl, which synergistically promoted the photocatalytic synthesis of  $H_2O_2$  [201]. In such a mechanism involving the photogeneration of electrons and holes in both g- $C_3N_4$  and BiOCl semiconductors of the  $Ti_2C_3$ /g- $C_3N_4$ /BiOCl composite upon the sunlight irradiation, the photoexcited electrons in the CB of BiOCl could combine with the holes in the VB of g- $C_3N_4$ , favoring the oxidation reaction in the VB of BiOCl. Meanwhile, the electrons in the CB of g- $C_3N_4$  were transferred to  $Ti_2C_3$  taking part in the reduction of  $O_2$  to  $H_2O_2$ .

The formation of a g- $C_3N_4$ /Co $_9$ S $_8$  heterojunction by coating the surface of Co $_9$ S $_8$  nanosheets with ultrathin protonated g- $C_3N_4$  (2, 5 and 10 wt.% of g- $C_3N_4$  to Co $_9$ S $_8$ ) was proposed to favor visible light absorption and both separation and transfer of photogenerated electron-hole pairs, resulting in a higher photocatalytic activity for  $H_2O_2$  production (Figure 15a) [202]. In the g- $C_3N_4$ /Co $_9$ S $_8$  composite, the photoexcited electrons migrated from the CB of g- $C_3N_4$  to the CB of Co $_9$ S $_8$ , participating in the one-step two-electron reduction of  $O_2$  to  $H_2O_2$  pathway, and the holes were transferred from the VB of Co $_9$ S $_8$  to that of g- $C_3N_4$  (type-II heterojunction), as displayed in Figure 15b. Moreover, the remaining electrons in the CB of g- $C_3N_4$  can form  $H_2O_2$  *via* a *two-step* single-electron  $O_2$  reduction route, thus allowing both pathways to simultaneously occur in the composite. Finally, an isotype heterojunction consisting of g- $C_3N_4$  doped with

benzene-rings, which partially replaced the heterocyclic rings in the g-C<sub>3</sub>N<sub>4</sub> network, and P-doped g-C<sub>3</sub>N<sub>4</sub> was constructed and demonstrated efficient charge carrier separation and enhanced visible light absorption [203]. The electronic structure of the composite resulted in the promotion of photoinduced electrons from the benzene-ring doped g-C<sub>3</sub>N<sub>4</sub> to the P-modified g-C<sub>3</sub>N<sub>4</sub>, and vice versa in the case of holes (type-II heterojunction).



**Figure 15.** UV–vis absorption spectra and wavelength-dependent apparent quantum yield (AQY) of photocatalytic H<sub>2</sub>O<sub>2</sub> production on Co<sub>9</sub>S<sub>8</sub> (CS) and g-C<sub>3</sub>N<sub>4</sub>/Co<sub>9</sub>S<sub>8</sub> (PCN-5/CS) **(a)**. Proposed mechanism for the photocatalytic synthesis of H<sub>2</sub>O<sub>2</sub> by a type-II heterojunction on g-C<sub>3</sub>N<sub>4</sub>/Co<sub>9</sub>S<sub>8</sub> **(b)**. Reproduced with permission from Ref. [202]. Copyright 2022 Elsevier.

### ***Stability of g-C<sub>3</sub>N<sub>4</sub> photocatalysts***

The stability of photocatalytic materials under reaction conditions is a key-factor for practical application and, therefore, has been also extensively studied for H<sub>2</sub>O<sub>2</sub>



synthesis using g-C<sub>3</sub>N<sub>4</sub> based catalysts. Reusability tests and physico-chemical characterization have shown that g-C<sub>3</sub>N<sub>4</sub> photocatalysts are stable and recyclable for H<sub>2</sub>O<sub>2</sub> production [144, 157, 172-175, 177-178, 182, 184, 194, 199-203]. It must be stressed that the negligible reduction in photocatalytic performance observed in some cases corresponds typically to the inevitable catalyst loss that occurs during the test cycling of the powdery catalysts in slurry reactors when submitted to multiple recovery steps. For instance, ultra-thin g-C<sub>3</sub>N<sub>4</sub> nanoplates maintained a yield of more than 75% for H<sub>2</sub>O<sub>2</sub> synthesis, while no changes were observed by FTIR, XRD and XPS characterization after ten test cycles [173]. The activity and crystal structure of K-, P-, O-, and S-doped g-C<sub>3</sub>N<sub>4</sub> did not change significantly after four reaction cycles [178]. SEM and XRD analyses proved that both the morphology and the crystal structure of Ni-loaded oxygen-doped g-C<sub>3</sub>N<sub>4</sub> nanotubes were stable under the photocatalytic reaction conditions upon five 4 h-long cycles, keeping over 81% activity for H<sub>2</sub>O<sub>2</sub> generation [144]. The catalytic stability of metal-doped g-C<sub>3</sub>N<sub>4</sub> systems has been also confirmed by measuring metal concentrations after reaction using ICP [157]. Elemental analysis by ICP was also used to demonstrate that the C/N ratio did not change after five cycles using carbon-doped C<sub>3</sub>N<sub>4</sub> catalysts [175].

**Table 5.** g-C<sub>3</sub>N<sub>4</sub>-based photocatalysts for H<sub>2</sub>O<sub>2</sub> production.

| Catalyst                                                            | Conditions                                                                                                                             | H <sub>2</sub> O <sub>2</sub> measurements | Amount produced                                                                      | Reference |
|---------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------|--------------------------------------------------------------------------------------|-----------|
| g-C <sub>3</sub> N <sub>4</sub>                                     | 2 kW Xe lamp ( $\lambda > 420$ nm, 26.9 W m <sup>-2</sup> ), 90% ethanol, O <sub>2</sub> saturation                                    | KMnO <sub>4</sub> titration                | 30 $\mu$ mol (12 h)                                                                  | [46]      |
| Mesoporous g-C <sub>3</sub> N <sub>4</sub>                          | 2 kW Xe lamp ( $\lambda > 420$ nm, 26.9 W m <sup>-2</sup> ), 90% ethanol, O <sub>2</sub> saturation                                    | KMnO <sub>4</sub> titration                | 90 $\mu$ mol (24 h)                                                                  | [170]     |
| g-C <sub>3</sub> N <sub>4</sub> with -NH-CH <sub>2</sub> -OH groups | 5 W LED lamp ( $\lambda > 420$ nm, 30 mW cm <sup>-2</sup> ), no scavenger, air bubbling                                                | Iodometry                                  | 179 $\mu$ mol L <sup>-1</sup> (7 h)                                                  | [172]     |
| Ultra-thin g-C <sub>3</sub> N <sub>4</sub> nanoplates               | Visible light (400 nm $\leq \lambda \leq$ 700 nm), 10% isopropanol, dry air purging                                                    | DPD-POD method <sup>a</sup>                | 43.07 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup>                                      | [173]     |
| g-C <sub>3</sub> N <sub>4</sub> microrods with C, N dual vacancies  | 300 W xenon lamp ( $\lambda > 420$ nm), 10% isopropanol, O <sub>2</sub> bubbling                                                       | Iodometry                                  | ~718.36 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup>                                    | [174]     |
| Carbon-content C <sub>3</sub> N <sub>4</sub>                        | 300 W Xe lamp (100 mW cm <sup>-2</sup> ), 5% isopropanol, O <sub>2</sub> saturated, acidic pH                                          | DPD-POD method                             | 1271 $\mu$ mol L <sup>-1</sup> (4 h)                                                 | [175]     |
| Oxygen-enriched g-C <sub>3</sub> N <sub>4</sub>                     | 500 W Xe lamp ( $\lambda > 420$ nm), O <sub>2</sub> saturation, pure water or supplemented with 10% isopropanol                        | Iodometry                                  | 53 $\mu$ mol (10 h) in water, 300 $\mu$ mol (5 h) when supplemented with isopropanol | [176]     |
| Phosphate-modified g-C <sub>3</sub> N <sub>4</sub>                  | 250 W high-pressure sodium lamp with NaNO <sub>2</sub> solution filter (400-800 nm), EDTA scavenger (7.5 wt%), O <sub>2</sub> bubbling | Iodometry                                  | 5.4 mM (18 h)                                                                        | [177]     |

|                                                                             |                                                                                                                                      |                  |                                                  |       |
|-----------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------|------------------|--------------------------------------------------|-------|
| C <sub>3</sub> N <sub>4</sub> with heteroelements (K, P and O)              | 300 W Xe arc lamp ( $\lambda \geq 420$ or $\geq 320$ nm; 726.8 and 833 mW cm <sup>-2</sup> ), 10% ethanol, O <sub>2</sub> saturation | DPD-POD method   | ~2mM (12 h)                                      | [106] |
| K-, P-, O-, and S-co-doped g-C <sub>3</sub> N <sub>4</sub>                  | 300 W Xe lamp ( $\lambda \geq 420$ nm), 10% vol isopropanol, O <sub>2</sub> saturated, pH = 3                                        | Iodine titration | 6.231 mM (180 min)                               | [178] |
| Sulfur-doped g-C <sub>3</sub> N <sub>4</sub>                                | 300 W Xe lamp ( $\lambda > 420$ nm), 10% isopropanol, O <sub>2</sub> saturated                                                       | Iodometry        | 566.69 $\mu\text{mol g}^{-1} \text{h}^{-1}$      | [180] |
| B-, P-, S -doped g-C <sub>3</sub> N <sub>4</sub> tubes                      | Simulated solar light, 10% isopropanol, O <sub>2</sub> bubbling                                                                      | Iodometry        | 1830.98, 1677.75 and 1189.56 $\mu\text{M}$ (2 h) | [181] |
| B-doped g-C <sub>3</sub> N <sub>4</sub> nanoplatelets                       | 6 neon lamps (20 W, 400-800 nm), 5% vol isopropanol, O <sub>2</sub> saturated                                                        | Iodometry        | 4240.3 $\mu\text{M g}^{-1} \text{h}^{-1}$        | [182] |
| B-doped g-C <sub>3</sub> N <sub>4</sub> nanosheets                          | LED 365 nm (100 mW cm <sup>-2</sup> ), 10% isopropanol, O <sub>2</sub> bubbling                                                      | Iodometry        | 1.16 mmol L <sup>-1</sup> h <sup>-1</sup>        | [183] |
| K <sup>+</sup> , Na <sup>+</sup> - modified g-C <sub>3</sub> N <sub>4</sub> | 250 W high-pressure sodium lamp with NaNO <sub>2</sub> solution filter (400-800 nm), no scavenger, O <sub>2</sub> bubbling           | Iodometry        | 4.6 mM (18 h)                                    | [184] |
| g-C <sub>3</sub> N <sub>4</sub> with sodium cyanamate moiety                | Solar simulator (100mW cm <sup>-2</sup> ), 3.5 wt% glycerol, O <sub>2</sub> bubbling                                                 | DPD-POD method   | 18.7 $\mu\text{mol mg}^{-1} \text{h}^{-1}$       | [187] |
| g-C <sub>3</sub> N <sub>4</sub> decorated with K and cyano groups           | 300 W Xenon lamp ( $\lambda > 420$ nm, 69.5 mW cm <sup>-2</sup> ), 10% isopropanol, O <sub>2</sub> saturated                         | Iodometry        | 278.9 $\mu\text{mol L}^{-1} \text{h}^{-1}$       | [188] |
| Cu-doped g-C <sub>3</sub> N <sub>4</sub>                                    | 250 W high-pressure sodium lamp with NaNO <sub>2</sub> solution filter (400-800 nm), no scavenger, O <sub>2</sub> saturated          | Iodometry        | 4.8 mM (18 h)                                    | [157] |

|                                                                                               |                                                                                                                    |                                                        |                                                |       |
|-----------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------|------------------------------------------------|-------|
| Fe, Co, Ni, In, Sn - C <sub>3</sub> N <sub>4</sub> (single atomic catalyst)                   | 500 W Xe lamp ( $\lambda > 420$ nm), 10% ethanol, O <sub>2</sub> bubbling                                          | Colorimetric method using PACKTEST (4-Aminoantipyrine) | 0.1-7.5 mg L <sup>-1</sup>                     | [189] |
| Au-C <sub>3</sub> N <sub>4</sub>                                                              | 300 W Xe lamp (100 mW cm <sup>-2</sup> ), 5% isopropanol, O <sub>2</sub> bubbling, acidic pH                       | DPD-POD method                                         | 1320 $\mu$ M (4 h)                             | [190] |
| Ni-loaded oxygen-doped g-C <sub>3</sub> N <sub>4</sub> nanotubes                              | 300 W Xe lamp ( $\lambda \geq 420$ nm, 100 mW cm <sup>-2</sup> ), 10% vol ethanol                                  | Iodometry                                              | 2464 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup> | [144] |
| Dy-oxide (Dy <sub>2</sub> O <sub>3</sub> )/nitrogen-deficient g-C <sub>3</sub> N <sub>4</sub> | Simulated solar light (25°C), 10 % ethanol, O <sub>2</sub> purging                                                 | Iodometry                                              | 48.36 mM g <sup>-1</sup> h <sup>-1</sup>       | [191] |
| Cyano and SnO <sub>2</sub> co-modified g-C <sub>3</sub> N <sub>4</sub>                        | 300 W Xe lamp ( $\lambda > 420$ nm), O <sub>2</sub> bubbling, 10 % vol isopropanol as sacrificial agent, acidic pH | Iodometry                                              | 703.4 $\mu$ M g <sup>-1</sup> h <sup>-1</sup>  | [192] |
| 2-hydroxy-4,6-dimethylpyrimidine / C <sub>3</sub> N <sub>4</sub>                              | 300 W xenon lamp ( $\lambda > 420$ nm), 10% isopropanol, O <sub>2</sub> bubbling                                   | Iodometry                                              | 174 $\mu$ mol L <sup>-1</sup> (60 min)         | [193] |
| 1,3,5-Trihydroxybenzene substituted g-C <sub>3</sub> N <sub>4</sub>                           | 300 W xenon lamp ( $\lambda > 400$ nm, 100 mW cm <sup>-2</sup> ), 10% isopropanol, O <sub>2</sub> bubbling         | Iodometry                                              | 257 $\mu$ M h <sup>-1</sup>                    | [194] |
| Hydroxyethyl cellulose-modified g-C <sub>3</sub> N <sub>4</sub>                               | PLS-SXE300D xenon lamp ( $\lambda \geq 420$ nm), no scavenger, O <sub>2</sub> saturated                            | DPD-POD method                                         | 65.76 $\mu$ mol L <sup>-1</sup> (60 min)       | [195] |

|                                                                                                      |                                                                                                  |                                            |                                                                               |       |
|------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|--------------------------------------------|-------------------------------------------------------------------------------|-------|
| Anthraquinone (AQ)/<br>C <sub>3</sub> N <sub>4</sub>                                                 | Simulated solar light (100 mW cm <sup>-2</sup> ), 10% 2-propanol, O <sub>2</sub> bubbling        | Titanium (IV) oxysulfate<br>DPD-POD method | 361 μmol g <sup>-1</sup> h <sup>-1</sup>                                      | [76]  |
| Glucose, perylene and anthraquinone functionalized g-C <sub>3</sub> N <sub>4</sub>                   | 4 LEDs (417 nm, 450 W m <sup>-2</sup> ), 90% isopropanol, O <sub>2</sub> saturated               | Titanium (IV) oxysulfate                   | 11.1 (glucose), 14.2 (perylene) and 25.0 mmol g <sup>-1</sup> h <sup>-1</sup> | [196] |
| C <sub>3</sub> N <sub>4</sub> /NiIn <sub>2</sub> S <sub>4</sub>                                      | 300 W xenon lamp (λ > 420 nm, 100 mW cm <sup>-2</sup> ), 10% ethanol, O <sub>2</sub> saturated   | Iodometry                                  | 1080 μmol L <sup>-1</sup> h <sup>-1</sup>                                     | [197] |
| Oxygen-doped g-C <sub>3</sub> N <sub>4</sub> nanosheet/NaBiS <sub>2</sub> nanoribbon                 | Xe lamp (25 °C), 10% isopropanol, O <sub>2</sub> bubbling                                        | Iodometry                                  | 8.92 mmol L <sup>-1</sup> (180 min)                                           | [198] |
| Bi <sub>4</sub> O <sub>5</sub> Br <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>                      | 300W Xenon (λ > 420 nm), no scavenger, O <sub>2</sub> saturated                                  | KMnO <sub>4</sub> titration                | 124 μM (60 min)                                                               | [199] |
| Ti <sub>3</sub> C <sub>2</sub> /C <sub>3</sub> N <sub>4</sub>                                        | 200 W xenon lamp (λ > 420 nm), 10% isopropanol O <sub>2</sub> bubbling                           | Iodometry                                  | 131.71 μmol L <sup>-1</sup> (60 min)                                          | [200] |
| Ti <sub>2</sub> C <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub> /BiOCl                               | 300 W Xenon lamp, 5% isopropanol, O <sub>2</sub> saturated, pH = 2-3                             | Indirect UV-vis spectrometry               | 1275 μM (60 min) and 2277 μM (120 min)                                        | [201] |
| Protonated g-C <sub>3</sub> N <sub>4</sub> coated Co <sub>9</sub> S <sub>8</sub>                     | 300W Xe lamp with cut-off filter, no scavenger, no O <sub>2</sub> supply, alkaline medium        | KMnO <sub>4</sub> titration                | 2.17 mM (5 h)                                                                 | [202] |
| g-C <sub>3</sub> N <sub>4</sub> doped with benzene-ring / P-modified g-C <sub>3</sub> N <sub>4</sub> | 9 W LED blue lamp (450 ± 5 nm, 43.6 mW cm <sup>-2</sup> ), no scavenger, O <sub>2</sub> bubbling | Iodometry                                  | 41.02 μmol L <sup>-1</sup> (60 min)                                           | [203] |

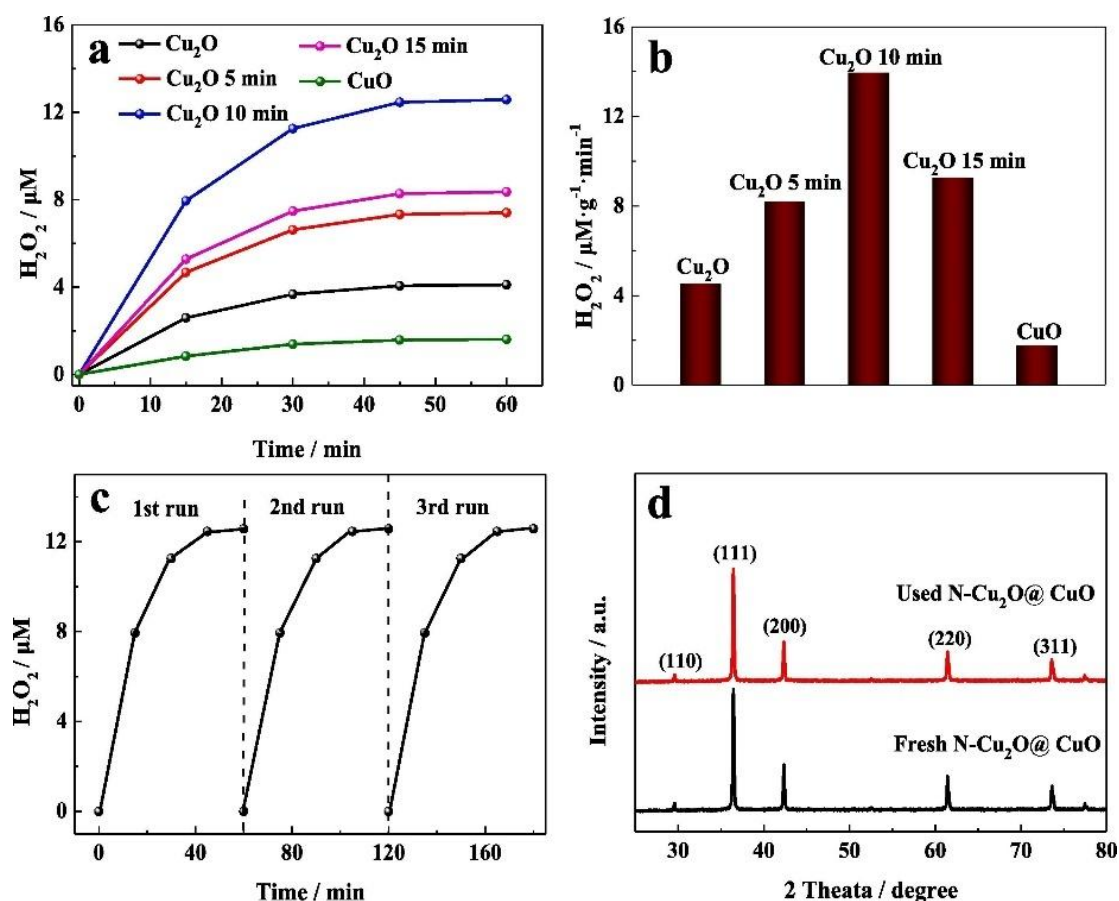
<sup>a</sup> DPD-POD method: N,N-diethyl-1,4-phenylene-diamine sulfate (DPD), peroxidase (POD) horseradish.

### 5.3. Other photocatalytic systems

Aside from carbon nitrides and common inorganic semiconductor photocatalysts such as ZnO [204], TiO<sub>2</sub>, or noble metal (Au, Pt, Au-Ag) modified TiO<sub>2</sub> [205], other semiconductors have also been applied for this process. The employment of some oxides and sulphides must be remarked, including MoS<sub>2</sub>, CuO, and Ag<sub>2</sub>O, most of them doped either with metals or with other semiconductors, like in Au-MoS<sub>2</sub>, Cu<sub>2</sub>O-CuO and WO<sub>3</sub>-Ag-Ag<sub>2</sub>O, for boosting the separation and the transfer of carriers while promoting the molecular O<sub>2</sub> activation [206-208]. The example of Cu<sub>2</sub>O-CuO nanocomposite systems is highlighted in Figure 16.

Also, polymeric materials emerged as promising low-cost and easily processable materials for solar-driven H<sub>2</sub>O<sub>2</sub> production, such as linear conjugated polymers [209], polymer networks [210-211] (*e.g.*, covalent organic frameworks (COFs), covalent triazine frameworks (CTF), resins [212-213], and pigments/dyes [214-215] in the form of thin films or powders.

The search for new systems is driven by the need to overcome the main drawbacks of most of the reference catalysts, namely the necessity to use a sacrificial agent and to extend the usable wavelengths towards the visible fraction of the solar light spectra. This section reports on a wide span of photocatalytic systems, either briefly itemized in Table 6 or more detailed in specific paragraphs.



**Figure 16.** (a) Time-dependent photocatalytic  $\text{H}_2\text{O}_2$  yields and (b) rates of  $\text{Cu}_2\text{O}$  octahedrons and N-doped  $\text{Cu}_2\text{O}@\text{CuO}$  after the nitrogen plasma treatments for different time of 5.0–15 min, taking pristine  $\text{CuO}$  as the control. (c) Recycling experimental results of N-doped  $\text{Cu}_2\text{O}@\text{CuO}$  nanocomposites in the photocatalytic  $\text{H}_2\text{O}_2$  generation reactions, and (d) XRD patterns of the nanocomposites before and after being used for three runs of photocatalytic reactions, where the nanocomposites were yielded by the 10-min  $\text{N}_2$  plasma treatment for  $\text{Cu}_2\text{O}$  octahedrons. Reproduced with permission from Ref. [208]. Copyright 2022 Elsevier.

**Table 6.** Selected semiconductor photocatalysts.

| Catalyst                                                      | Conditions                                           | H <sub>2</sub> O <sub>2</sub> measurements                                         | Amount produced                                 | Reference |
|---------------------------------------------------------------|------------------------------------------------------|------------------------------------------------------------------------------------|-------------------------------------------------|-----------|
| CN <sub>QDs</sub> @MA-Ag                                      | 300 W Xenon lamp; 420 cut-off filter                 | Fluorescence (products of H <sub>2</sub> O <sub>2</sub> -HPAA)                     | ≈5 μmol/L                                       | [216]     |
| WO <sub>3</sub> /Ag@Ag <sub>2</sub> O                         | 300 W Xenon lamp; 420 cut-off filter<br>norfloxacin  | Different scavengers                                                               | -                                               | [206]     |
| Pd-BiVO <sub>4</sub>                                          | CH <sub>3</sub> OH (hole scavenger)<br>Visible light | Colorimetric based on the change of colour of Fe <sup>2+</sup> to Fe <sup>3+</sup> | >300 μM in 2h<br>> 600 μM with phosphate buffer | [217]     |
| La <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub> /rGO           | Visible light, tetracycline oxidation                | Scavengers (catalase)                                                              | Non measured                                    | [218]     |
| C <sub>3</sub> N <sub>4</sub> biphenil Diimide (e-defficient) | Visible light                                        |                                                                                    | Milimollars levels                              | [219]     |
| Au-MoS <sub>2</sub>                                           | sunlight                                             |                                                                                    | 600 μM                                          | [207]     |
| Bi/Bi <sub>2</sub> O <sub>2-x</sub> CO <sub>3</sub>           | NO <sub>x</sub> removal                              | ESR spectroscopy                                                                   | 1.2 mM                                          | [220]     |
| CN/rGO@BPQDs                                                  | Visible light                                        | Iodine titration                                                                   | 1 μmol/Lmin                                     | [221]     |
| SN-GQDs                                                       | Water/propanol, acidic pH                            | DPD–POD method (peroxidase)                                                        | 420 μmol /L in 60 min                           | [117]     |
| Graphene, quantum-dots                                        | Saturated with O <sub>2</sub> and visible light      |                                                                                    |                                                 |           |
| ZIF                                                           | Xenon lamp, water, O <sub>2</sub> continuous flow    | GC-FID (GC-2014, Shimadzu, Japan) and titration method                             | 0.15 mmolL/L in 2h                              | [222]     |
| Nitrogen (N)-doped Cu <sub>2</sub> O@CuO                      | Visible light; Xe lamp cut-off visible light         | PHPAA-based analysis method                                                        |                                                 | [208]     |

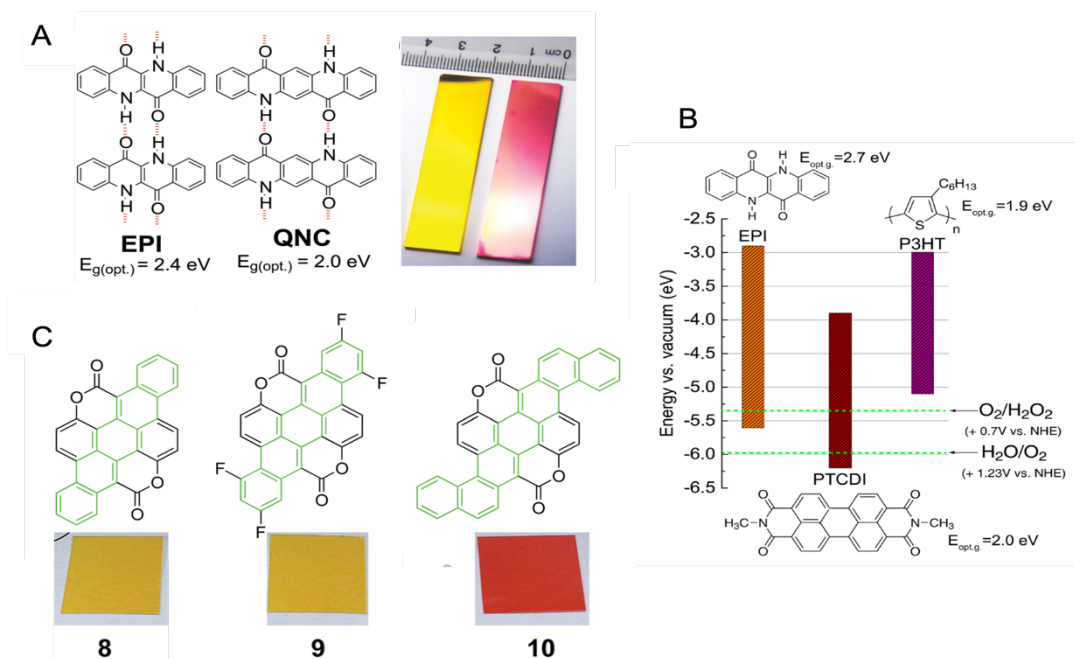


|                              |                                                                   |                                      |                 |       |
|------------------------------|-------------------------------------------------------------------|--------------------------------------|-----------------|-------|
| Ni <sub>2</sub> P/carbon dot | O <sub>2</sub> saturation, visible light, no<br>sacrificial agent | potassium permanganate<br>titration. | 1281.4 μmol/h/g | [223] |
|------------------------------|-------------------------------------------------------------------|--------------------------------------|-----------------|-------|

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### 5.3.1. Organic dyes

In a search for low-cost and robust semiconductors, Głowacki and group [215] have pioneered the use of dyes and pigments as promising ORR photo-electrocatalysts. In 2016, carbonyl-based organic pigments, epindolidione (EPI), and quinacridone (QNC) coated photoelectrodes have been reported to catalyze the two-electron oxygen reduction to  $\text{H}_2\text{O}_2$  in low pH environments (Figure 17A) [215]. Of these two, EPI showed a more efficient two-electron ORR activity. The EPI pigment produced 3 mM of  $\text{H}_2\text{O}_2$  within 48 h in  $\text{O}_2$  purged system and 0.1 M HCl as the electrolyte, surpassing the g- $\text{C}_3\text{N}_4$  system reported in 2014 [46]. To improve  $\text{H}_2\text{O}_2$  generation, organic heterojunction photocathodes with varying thicknesses of donor-acceptor layers based on phthalocyanine ( $\text{H}_2\text{Pc}$ ) and perylene tetracarboxylic diimide (PTCDI) and EPI or PTCDI as the catalyst layer were constructed by the same group. To limit electron-hole recombination, a layer of Au was incorporated. The heterojunction photocathode, PN/Au/PTCDI and PN/Au/EPI, attained continuous  $\text{H}_2\text{O}_2$  generation with a faradaic yield of 86-62% within 6 h of photoelectrolysis [224].

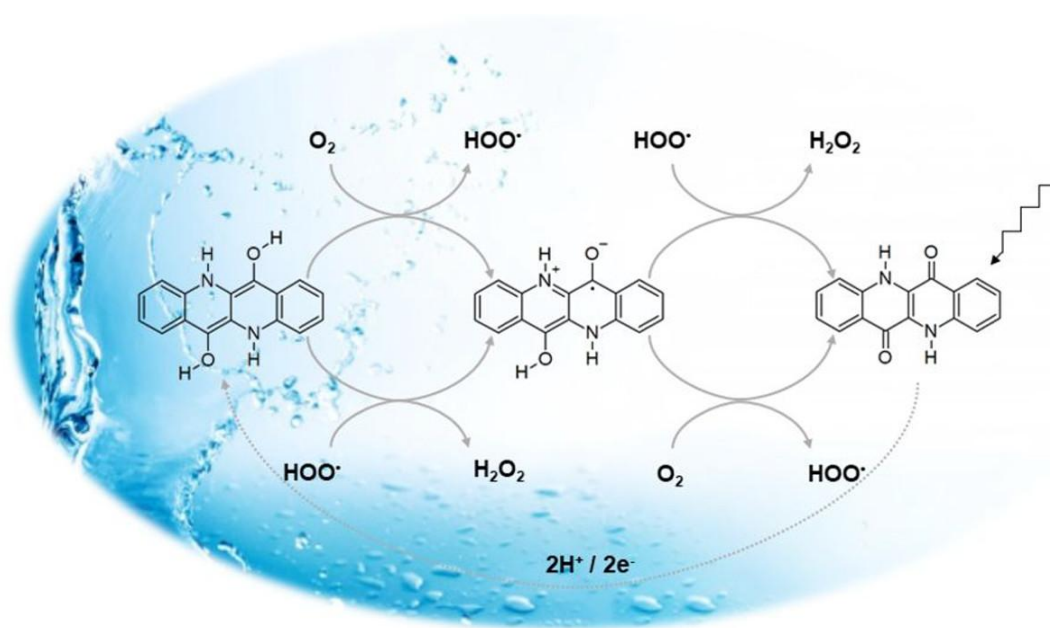


**Figure 17.** Dye-based organic semiconductor photocatalysts for  $\text{H}_2\text{O}_2$  production. **A)** Molecular structures of EPI and QNC and its corresponding thin films coated on Au-coated glass slide. Reprinted with permission from Ref. [215]. Copyright 2016 Wiley-VCH. **B)** Energy diagram and molecular structures of EPI, PTCDI, and P3HT. Reprinted with permission from Ref. [225]. Copyright 2018 America Chemical Society. **C)** Molecular structures of biscoumarin-based pigments. Reprinted from Ref. [226]. Copyright 2017 Royal Society of Chemistry.

This work was further extended by depositing the organic semiconductors, EPI, PTCDI, and poly(3-hexylthiophene) (P3HT), in a TPU screen protector foil to examine the photocatalytic activity of the dyes in different electron donors (Figure 17B). Oxalate and phenol at pH 2 or 7 were shown to be the best electron donors for EPI and PTCDI with a possible turnover number for  $\text{H}_2\text{O}_2$  production of 10-800. Further analysis shows that although PTCDI is capable of water oxidation to form  $\text{H}_2\text{O}_2$ , the  $\text{H}_2\text{O}_2$  formation with PTCDI *via* oxygen reduction predominates. Compared to thin films, colloidal crystals of EPI showed faster  $\text{H}_2\text{O}_2$

evolution rates due to an increase in the catalytic surface area. The mechanism of H<sub>2</sub>O<sub>2</sub> production with EPI was recently studied by DFT and identified to be similar to the AQ method [227]. Based on the theoretical calculations, the hydrogen atoms in EPI-2H (reduced form of EPI after photoinduced 2 H<sup>+</sup>/2 e<sup>-</sup> process) are capable of abstracting triplet oxygen, <sup>3</sup>O<sub>2</sub>, forming an intermediate complex of HOO• and EPI-H•. The HOO• after released, will abstract another hydrogen atom from EPI-H•, forming H<sub>2</sub>O<sub>2</sub>, and thereby regenerating EPI in the process (Figure 18). Another pathway being considered was the abstraction of hydrogen from neighboring EPI-2H, forming EPI-H•. Although it can be perceived that the hydrogen in N-H could also participate in the hydrogen atom transfer (HAT) (Figure 17A), their DFT calculations also showed negligible participation of hydrogen from N-H, which coincides with their earlier experiment [215, 227].

Inspired by the performance of EPI and QNC, they evaluated three types of biscoumarin-containing molecules (Figure 17C, compounds 8-10). Visible light irradiation of the compounds in pure water and ambient air conditions showed an evolution rate of 1-3 μg<sub>H<sub>2</sub>O<sub>2</sub></sub> mg<sup>-1</sup> h<sup>-1</sup>. The biscoumarins did not show any degradation and were stable in the pH range of 2-13. Similar to the structure of the previous molecules EPI and QNC, the carbonyl functionalities in biscoumarin compounds were identified as the key factor for their observed catalytic activities [226].



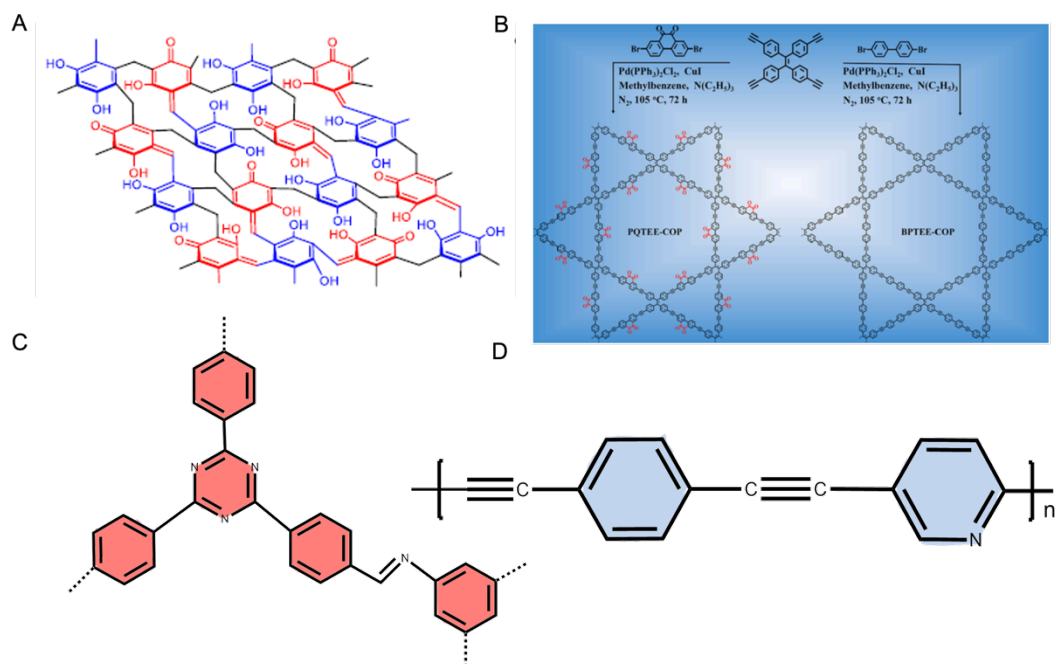
**Figure 18.** Proposed mechanism for  $\text{H}_2\text{O}_2$  formation *via* two-electron ORR of EPI. Reprinted with permission from Ref. [227]. Copyright 2020 American Chemical Society.

### 5.3.2. Conjugated polymers

Aside from the utilization of organic semiconductors, many efforts have been dedicated to synthesizing  $\pi$ -conjugated polymers with attractive functionalities to drive kinetically-challenging redox reactions [228]. Well-known semiconducting polymers such as polyaniline (PANI), polypyrrole (PPy), and polythiophene (PTh), poly(3,4-ethylenedioxythiophene) (PEDOT) are known to possess catalytic activity towards oxygen reduction based on the early electrocatalytic studies [229-231]. However, in the past years, designing conjugated polymers, especially with donor and acceptor moieties, has become a popular approach to tune photocatalytic  $\text{H}_2\text{O}_2$  generation from two-electron ORR [232]. Shiraishi and co-workers reported that resorcinol-formaldehyde (RF) resin (Figure 19A) prepared by the simple hydrothermal treatment could catalyze the overall photosynthesis of  $\text{H}_2\text{O}_2$  production. These

RF powders have a broad light absorption of up to 700 nm and a low band gap of 1.7 eV. The polymeric system composed of  $\pi$ -conjugated and  $\pi$ -stacked benzenoid-quinoid donor-acceptor (D-A) units, serving as the sites of redox reactions, achieved a solar-to-chemical conversion (SCC) efficiency of  $\sim 0.7\%$  for  $\text{H}_2\text{O}_2$  production under  $\text{O}_2$  and simulated solar conditions [212]. However, the D-A units were linked by non- $\pi$ -conjugated methylene, producing a discontinuous band that interferes with the charge transport. The same group achieved an improvement in  $\text{H}_2\text{O}_2$  amount and SCC efficiency to  $\sim 1\%$  under solar irradiation when these RF powders were doped with poly(3-hexylthiophene-2,5-diyl (P3HT)). P3HT enhances the charge transport of the photogenerated electrons by acting as a conducting linker between the quinoid and benzenoid units [213].

Inspired by the utilization of AQ in  $\text{H}_2\text{O}_2$  production, phenanthrenequinone (PQ) (which possesses two adjacent carbonyl functionalities in cyclohexane linking two phenyl groups) was utilized as a redox-active site for the same purpose. Cross-coupling of 2,7-dibromophenanthrenequinone (PQ) and 1,1,2,2-tetrakis(4-ethynylphenyl)ethene with phenanthrenequinone moieties as redox centers were reported as a photocatalyst for  $\text{H}_2\text{O}_2$  production. Within the polymeric chain, tetraphenylene and phenanthrenequinone serve as the electron-donating and electron-withdrawing groups. The improved photocatalytic activity is attributed to the push-pull effect of these substituents, which improves the light-harvesting and separation of the photo-induced charges. As the redox-active site, phenanthrenequinone accepts the photogenerated electrons and transfers them to adsorbed  $\text{O}_2$  through an electron-coupled hydrogenation reaction (PQ to  $\text{PQH}_2$ ). The  $\text{H}_2\text{O}_2$  production rate of BPTEE-COP and PQTEE-COP reached 982 and 3009  $\mu\text{mol g}^{-1} \text{h}^{-1}$  respectively from  $\text{H}_2\text{O}$  and  $\text{O}_2$  under visible light irradiation ( $> 400 \text{ nm}$ ) without any sacrificial agent (Figure 19B) [233].



**Figure 19.** Molecular structures of **A)** resorcinol-formaldehyde resin. Reprinted with permission from Ref. [212]. Copyright 2020 Nature Publishing Group. **B)** PQTEE-COP and BPTEE-COP. **C)** sonoCOF-F2 **D)** DE7. Reprinted with permission from Ref. [233]. Copyright 2023 Elsevier.

Pushing the utilization of conjugated polymers as two-electron ORR catalysts, high throughput experiments were recently conducted to screen many conjugated linear polymers and covalent organic frameworks (COFs) as potential photocatalytic systems [209, 234]. COFs are emerging photocatalysts for solar-to-fuel conversion. It is a porous crystalline organic material made up of covalently linked organic moieties. They are highly tunable polymers such that one can change the charge transfer kinetics and charge separation just by incorporating molecules such as triazine, porphyrin, benzothiadizole, or even alternating donor-acceptor moieties into the covalent framework [235]. Linear conjugated polymer poly(3-4-ethynylphenyl)ethynylpyridine (DE7) (Figure 19D) showed efficient activity towards

photocatalytic two-electron ORR to  $\text{H}_2\text{O}_2$ . At short reaction times, DE7 was more active than the reported RF resins with an apparent quantum yield of 8.7% at 420 nm. However, this polymer decomposed after 50 hours of reaction [209]. The same group performed high-throughput sonochemical synthesis and explored 76 conjugated organic polymers for  $\text{H}_2\text{O}_2$  production. Imine-based COF coined as sonoCOF-F2 showed the highest photocatalytic  $\text{H}_2\text{O}_2$  production among all the tested polymers (Figure 19C). Without any sacrificial agents, sonoCOF-F2 produced  $> 300 \mu\text{mol H}_2\text{O}_2$  within 90 h of visible light irradiation, which was further improved using benzyl alcohol as electron donor [234]. Diarylamine moiety, a strong reducing agent, has been used to design a (diaryl amino) benzene-based COF for  $\text{H}_2\text{O}_2$  production [236]. The highest  $\text{H}_2\text{O}_2$  production rate was obtained with TAPD-(Me)<sub>2</sub> COF ( $97 \mu\text{mol g}^{-1} \text{ h}^{-1}$ ) under visible light with ethanol as an electron donor. In another study, triphenylbenzene-dimethoxyterephthaldehyde-COF (TPB-DMTP-COF) was rationally designed. DFT calculations show that  $\text{O}_2$  molecules were being activated and reduced in the TBP region. Moreover, by immobilizing the TPB-DMTP-COF in carbon paper, a triphase system (gas-liquid-solid) was realized, which facilitated high  $\text{O}_2$  transfer rate leading to the enhancement in the photocatalytic activity [237]. From using organic semiconductors to novel conjugated polymers, studies have suggested that rationally designing materials with organic moieties acting as the activation center is a useful approach toward  $\text{H}_2\text{O}_2$  photosynthesis.

### 5.3.3. Miscellaneous catalysts

Similar to the reports on EPI, QNC, and biscoumarins, the presence or incorporation of oxygen functional groups is very beneficial for oxygen reduction reaction to  $\text{H}_2\text{O}_2$ . Hou and Wang first reported the potential of pure graphene oxide (GO) to catalyze  $\text{H}_2\text{O}_2$  photoproduction without any electron donors [205]. Metal-free GO reached a millimolar



concentration of  $\text{H}_2\text{O}_2$  after 6 hours of solar irradiation at pH 7. The addition of oxalate as an electron donor enhanced the photoproduction at low pH. The authors proposed a similar two-electron ORR pathway identified for  $\text{g-C}_3\text{N}_4$ , although further studies are necessary [205]. Carbon dots incorporated in a polymer formed by dye-crosslinked molecule procyanidine and 4-methoxybenzaldehyde (PM-CDs) have also been shown to be very efficient photocatalysts for  $\text{H}_2\text{O}_2$  production. While the polymer alone also generated  $\text{H}_2\text{O}_2$  at a rate of  $771 \mu\text{mol g}^{-1} \text{h}^{-1}$ , the incorporation of carbon dots (CDs) has significantly improved the photoproduction ( $1776 \mu\text{mol g}^{-1} \text{h}^{-1}$ ), especially in a seawater medium. According to the authors, the functional groups -OH, C=O, -COOH of the carbon dots efficiently traps electrons, thereby increasing the time of electron-hole separation, while the ions in seawater ionize the functional groups on the surface of CDs, which increases the “electron sink effect” inducing a higher photocatalytic activity in seawater [238]. Recently, enhanced selectivity and activity of  $\text{H}_2\text{O}_2$  production were obtained with oxidized carbon nanotubes (O-CNTs) [49]. The increase in the oxygen content (C=O, C-O) by simple surface oxidation treatment enhances the oxygen reduction performance, further substantiating the importance of oxygen functional groups. Based on DFT calculations, carbon atoms adjacent to oxygen functional groups, COOH and C-O-C, were the active sites of two-electron ORR.

## 6. *In-situ* photocatalytic synthesis of $\text{H}_2\text{O}_2$

As hydrogen peroxide is often used as a reagent in chemical reactions, there is also the option of integrating the photocatalytic peroxide synthesis directly into these reactions. This way, the peroxide is generated *in-situ*, skipping the otherwise required process steps of separation, purification and concentration as well as storage and transportation. The resulting

integrated processes may therefore be more efficient, less expensive, and also safer, as no concentrated peroxide solutions need to be handled. This section reports on the interest of the *in-situ* photocatalytic synthesis of  $\text{H}_2\text{O}_2$  for Fenton-type advanced oxidation processes for water treatment and for organic synthesis. The coupling of *in-situ*  $\text{H}_2\text{O}_2$  synthesis with enzymes as well as the direct in-situ generation of other technical peroxides are also discussed.

### 6.1. *In-situ* synthesis for water treatment

In water treatment, the *in-situ* synthesis of  $\text{H}_2\text{O}_2$  is usually associated to a catalytic Fenton-type process that operates in homogeneous or heterogeneous phase through the catalytic decomposition of  $\text{H}_2\text{O}_2$  in the dark or under light by Fe cations via the  $\text{Fe}^{\text{III/II}}$  redox cycle (34-35).

$\text{H}_2\text{O}_2$ -mediated Fenton-type catalysis is a family of Advanced Oxidation Processes (AOPs) promising for the removal in water of a large panel of (bio)recalcitrant (refractory) compounds that are not degraded by classical treatments, or at least for their degradation into readily biodegradable compounds [239]. As part of AOPs, this catalysis is based on the generation of highly active  $\text{HO}_x\bullet$  ( $\text{HO}\bullet$  and  $\text{HOO}\bullet$ ) oxidative radicals that react with the pollutant and further with the reaction intermediates to yield full mineralization of the pollutant. Are concerned, the homogeneous catalytic Fenton process, or its heterogeneous counterpart, Catalytic Wet Peroxide Oxidation (CWPO) for which Fe is incorporated as cation in a catalytic solid [240]. Photo-CWPO (also called heterogeneous photo-Fenton) consists in performing the CWPO process under light, as a strategy to enhance the catalyst reactivity by further boosting the rate-limiting  $\text{Fe}^{\text{III}} \rightarrow \text{Fe}^{\text{II}}$  conversion in the  $\text{Fe}^{\text{III/II}}$  redox cycle (Eqs. 34-35). In a typical Fenton-

type catalysis, the Fe-catalyzed H<sub>2</sub>O<sub>2</sub>-mediated generation of HO<sub>x</sub>• leads to initial reaction rates far higher than those achieved in photocatalysis on semiconductors [239].



Albeit very active, and although H<sub>2</sub>O<sub>2</sub> is a green oxidant, producing only H<sub>2</sub>O and O<sub>2</sub> as end-products, H<sub>2</sub>O<sub>2</sub>-mediated Fenton-type catalysis still faces a limited perspective for technological deployment. This results from the external use of costly H<sub>2</sub>O<sub>2</sub> instead of O<sub>2</sub> as oxidant, its non-sustainable production *via* the AQ process, and the moderate H<sub>2</sub>O<sub>2</sub> efficiency value of the catalytic reaction, owing to a high rate of useless recombinations of radicals. Also, commercial H<sub>2</sub>O<sub>2</sub> solutions are stabilized with inhibitors that act as poisons for the catalyst.

In a typical reaction, the concentration of external H<sub>2</sub>O<sub>2</sub> oxidant is usually exceeding that of stoichiometry, and a very high proportion of H<sub>2</sub>O<sub>2</sub> is wasted inefficiently in side-reactions. For instance, Li et al. have calculated that *ca.* 25% of the amount of externally-added H<sub>2</sub>O<sub>2</sub> was used for the degradation of an organic pollutant in a homogeneous system, the efficiency dropped down to 0.4% in a heterogeneous H<sub>2</sub>O<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> system in dark conditions [241].

In consequence, there is a need for the development of new processes and/or of novel materials combining two catalysts working in synergy, the first one producing and providing H<sub>2</sub>O<sub>2</sub> *in-situ* to the second one for degrading the pollutants. For instance, formic acid, hydrazine and hydroxylamine were used as substitutes to molecular H<sub>2</sub> to generate H<sub>2</sub>O<sub>2</sub> for performing the degradation of phenol by Fenton reaction using *in-situ* generated hydrogen peroxide. The combined process operated at ambient conditions in a semi-heterogeneous mode using a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst (for the production of H<sub>2</sub>O<sub>2</sub>) and soluble Fe<sup>2+</sup> as homogeneous

catalyst (for the decomposition of  $\text{H}_2\text{O}_2$  into active radicals), as well as in a fully heterogeneous mode with  $\text{FePd}/\text{Al}_2\text{O}_3$  catalysts [242]. It must be said that the catalysts were more stable in the presence of formic acid than hydrazine or hydroxylamine. Using the degradation of phenol in aqueous phase, Hutchings et al. attributed to the absence of any stabilizing additives such as acetanilide or phosphoric acid, the superiority of generating *in-situ*  $\text{H}_2\text{O}_2$  from molecular  $\text{O}_2$  and  $\text{H}_2$  on Fenton-type Pd-Fe bimetallic catalysts supported on  $\text{TiO}_2$  and  $\text{SiO}_2$  in comparison to the addition of commercial  $\text{H}_2\text{O}_2$  as oxidant [243]. Very recently, Sable et al. combined adsorption and catalytic properties for the Fenton-like oxidation of phenol over Pd/Fe-ZSM-5 catalysts allowing the *in-situ* formation of  $\text{H}_2\text{O}_2$  using formic acid as H-source and externally-supplied oxygen [244].

In the search for efficient and sustainable heterogeneous solutions, an elegant and high-prospect approach relies on the use of  $\text{H}_2\text{O}$  as hydrogen provider instead of external molecular hydrogen. In that case, two main strategies are investigated. The first one consists in operating with two different heterogeneous catalysts working in tandem for the synthesis of  $\text{H}_2\text{O}_2$  from  $\text{H}_2\text{O}$  and molecular oxygen, and further its use as oxidant over a heterogenized photoFenton catalyst. Usually close proximity of both active sites strongly enhances the overall process yield. The second one consists in using the dual ability of some catalysts to oxidize water and to be used as a photocatalyst for degrading organic pollutants in water, and diffusion limitations of the  $\text{H}_2\text{O}$  generated should be avoided.

Finally, as the sacrificial agent used to enhance the  $\text{H}_2\text{O}_2$  production needs usually to be present in the aqueous media in by-far higher concentrations than the pollutants to degrade for playing a significant role, the necessity to design photocatalysts able to operate in the absence of any sacrificial agents is highly important. Also the degradation of the sacrificial

agent forms various reaction intermediates and consequently complexifies the aqueous mixture and alter the impact of the sacrificial organic substrate(s).

The approach of *in-situ* synthesis of  $\text{H}_2\text{O}_2$  is only in its infancy, but we have to stress that the objective is not to compete with the industrial anthraquinone process in terms of kinetics or production level. The strategy aims at delivering  $\text{H}_2\text{O}_2$  only from water and molecular  $\text{O}_2$  as reagents in the closest vicinity of the surface active site of the Fenton-type catalysts. While the maintain of the Fe-catalyzed decomposition kinetics in the absence of any costly external  $\text{H}_2\text{O}_2$  supply would be seen as a holy grail, *a priori*, even moderate production of  $\text{H}_2\text{O}_2$  should be beneficial and allow the external supply of  $\text{H}_2\text{O}_2$  to be significantly lowered.

## 6.2. $\text{H}_2\text{O}_2$ -mediated organic synthesis

Beside degradation and mineralization of pollutants in water, it must be said that synthetic chemistry is also an area of interest for the one-pot combination of the *in-situ* generation and use of  $\text{H}_2\text{O}_2$ . Indeed, the use of  $\text{H}_2\text{O}_2$  as an *in-situ* oxidant is a promising research field that finds applications in catalysis also beyond the specific area of light-mediated catalytic water treatment. One can cite for instance the propylene oxidation to propylene oxide, the valorization of methane into methanol, or the cyclohexane oxidation into cyclohexanone and cyclohexanol (mixture known as KA oil) [38].

Already approximately 30% of the global peroxide production is utilized for chemical synthesis [245]. This market is also expected to grow steadily as more and more oxidation processes are converted to utilize greener oxidants. One example is the oxidation of propylene to propylene oxide, where using hydrogen peroxide (HPPO process) has been established as a green alternative to the waste-intensive chlorohydrin-process [246]. There are some early

attempts to also realize this reaction directly with oxygen as oxidant using photocatalysis to activate it *in-situ* to superoxide or hydrogen peroxide [247-248].

In addition to the already industrially implemented propylene oxidation, there is also extensive research into other H<sub>2</sub>O<sub>2</sub>-mediated oxidation reactions, which could all potentially be coupled with photocatalytic *in-situ* production. A noteworthy example is the production of adipic acid from cyclohexanol/one. This is industrially realized by oxidation with highly concentrated nitric acid which is associated with notable NO<sub>x</sub> and N<sub>2</sub>O emissions. So H<sub>2</sub>O<sub>2</sub> is explored as a greener alternative which can also be envisioned to be produced *in-situ* by a photocatalytic process [249-251].

### **6.3. Coupling of *in-situ* H<sub>2</sub>O<sub>2</sub> synthesis with enzymes**

The use of enzymes as biocatalysts has many advantages such as excellent selectivity and the typically mild reaction conditions [252]. The oxyfunctionalization of non-activated C–H, C–C or C=C bonds using enzymes has not yet been fully embraced by industry [253]. The main problems are the catalyst availability and the cofactor dependency of most oxidoreductases [254]. The so-called *Oxygen Dilemma* describes the disruption of electron transfer from the cofactor nicotinamide adenine dinucleotides (phosphate) (NAD (P) H) *via* a mediator to the active site of monooxygenase through oxygen [255]. The use of H<sub>2</sub>O<sub>2</sub> as a cofactor comes with the advantages of using a green reagent and contains oxygen which is already reduced for catalysis with oxygenases. For example, the usage of the unspecific Peroxygenase from *Agrocybe aegerita* (*AaeUPO*) can hydroxylate a substrate with reduction of hydrogen peroxide to water and produces only water as the byproduct.

Different enzymes can use H<sub>2</sub>O<sub>2</sub> as cofactor for example Peroxidases, Peroxygenases, Hydrolases and Haloperoxidases. The active center of peroxidases forms a heme center and a

coordinated ligand which can be cysteine (*AaeUPO*, P450) or histidine (HRP) [256]. An oxygen from the hydrogen peroxide can coordinate on the heme-Fe<sup>III</sup>. Vanadium-dependent haloperoxidases form a peroxo-complex with the vanadate group in presence of H<sub>2</sub>O<sub>2</sub> and are more robust against H<sub>2</sub>O<sub>2</sub> than heme-dependent enzymes [257]. Hydrolases are capable of oxidizing carboxylic acid to their corresponding peracids [258]. The *AaeUPO* is known for many different oxidations like aromatic and aliphatic hydroxylations, alkene epoxidations, heteroatom oxidations, ether cleavage, halogenations and one-electron oxidations [259].

A major disadvantage of using peroxidases and peroxygenases is the relative instability to H<sub>2</sub>O<sub>2</sub> even in the millimolar range. H<sub>2</sub>O<sub>2</sub> as a strong oxidant can oxidize labile amino acids [259]. Amino acid oxidations affect enzyme stability when these undergo polymerization reactions or when an amino acid close to the active site is oxidized. Another instance of inactivation occurs when the hydrolyzed heme center reacts with another molecule of H<sub>2</sub>O<sub>2</sub>. Further reactions with oxygen and hydrogen peroxide leads to the generation of biliverdin under release of the iron [260]. The solution to the inactivation problem is to synthesize H<sub>2</sub>O<sub>2</sub> *in-situ* to avoid hot spots in concentration, such as those caused by stoichiometric addition. Amongst others, the photocatalytic production of hydrogen peroxide offers a promising solution to this challenge [261-262].

The combination of enzyme catalysis with heterogeneous photocatalysis has the advantage that the utilized light is the only energy source and the photocatalyst can be easily removed from the product [72]. With the usage of water as electron donor, there is no waste left, but the hydrogen production rate is low and so is the turnover rate of the enzyme. With methanol or other alcohols as electron donors the production rate is significantly increased with only CO<sub>2</sub> as waste. The oxidation of water generates hydroxyl radicals, which quickly inactivates the enzyme so the usage of methanol also stabilizes the enzyme in solution [263].

The UV light used, which is required to stimulate  $\text{TiO}_2$ , for example, also inactivates the enzyme. Nevertheless, turnover numbers of 220,000 and an apparent quantum yield of 13.6% could be achieved. By enzyme immobilization a spatial separation of enzyme and inactivating radicals can be achieved, in addition, UV light can be avoided by using photocatalysts with a smaller band gap and therefore the efficiency further optimized. All three methods described have the disadvantage that they work with peroxide to a limited extent, so that the enzyme works below its  $K_m$  value and the turnover rate is reduced. The turnover numbers achieved are nevertheless high, due to the reaction conditions optimized for stability [264].

#### 6.4. Direct *in-situ* generation of other technical peroxides

In addition to hydrogen peroxide a number of other peroxides are relevant in many applications. This is mostly due to the fact that  $\text{H}_2\text{O}_2$  is inherently unstable, making its transport and storage problematic. Peroxides of acids such as percarbonate, peracetate, persulfate or perborate are therefore interesting alternatives, as they form precipitable salts which are easier to handle than solutions. They also typically show faster reaction kinetics than  $\text{H}_2\text{O}_2$  under many conditions. One reason for this is that the peroxide anions are more reactive and peracids are much easier to deprotonate than  $\text{H}_2\text{O}_2$ .

These peracids are typically produced by reacting the acid with concentrated  $\text{H}_2\text{O}_2$  solutions. However, there is also evidence for their formation *via* direct oxidation or *via* hydroxyl radicals. An example of this is percarbonate, which occurs as peroxydicarbonate ( $\text{C}_2\text{O}_6^{2-}$ ) and as peroxymonocarbonate ( $\text{HCO}_4^-$ ). The generation of the peroxymonocarbonate should take place in hydrogen carbonate solutions via an  $\text{OH}\cdot$  activated  $\text{HCO}_3^-$ , which reacts with a  $\text{CO}_2$  dimer  $(\text{CO}_2)_2^*$  and the  $\text{HOO}^-$  formed by  $\text{H}_2\text{O}_2$  to build  $\text{HCO}_4^-$  [265]. The



peroxydicarbonate can be synthesized electrochemically by BDD's in concentrated sodium carbonate solution [266]. In addition to percarbonate, it is also possible to generate electrochemically other peroxo-species such as peracetic acid [267], perphosphate [268] or persulfate [269]. Due to the similar mechanism and the presence of hydroxyl radicals in photocatalytic systems, it is highly likely those species may be formed *via* photocatalysis as well.

## 7. Conclusion

H<sub>2</sub>O<sub>2</sub> is a green and powerful oxidant able to oxidize in mild conditions a large range of organic and inorganic substrates in liquid media, that differentiates from stoichiometric oxidants by its high active oxygen content and by the release of H<sub>2</sub>O and O<sub>2</sub> as only end-products. However, the scientific literature dealing with the photocatalytic synthesis of H<sub>2</sub>O<sub>2</sub> from water and molecular oxygen is still lower compared to other key-reactions and applications in photocatalysis such as water treatment, artificial photosynthesis of solar fuels, water splitting or photoreforming. The pioneering, albeit recent, works on TiO<sub>2</sub> under UV-A light and further on g-C<sub>3</sub>N<sub>4</sub> under solar light paved the way for cutting-edge research and stimulating key-challenges that drive the actual research in the high-prospect field of the artificial photosynthesis of H<sub>2</sub>O<sub>2</sub>. As we have tried to point out here, some recent works have reported interesting results in respect of the fundamental mechanistic understanding of the reaction and of the advanced engineering of solar-light driven heterogeneous photocatalysts.

The artificial photosynthesis of H<sub>2</sub>O<sub>2</sub> offers prospects to boost sustainability of the production of H<sub>2</sub>O<sub>2</sub>, albeit being in its infancy, and in consequence must face significant challenges, namely related to the necessity to work in the absence of sacrificial reagents, to

extend the usable wavelengths towards the visible fraction of the solar light spectra, and to increase the photonic efficiency of the photogenerated electron and hole charge carriers.

Advances should be the result of joint input of advanced operando/*in-situ* characterization and modeling/computational tools. Time-resolved techniques should be further applied for unraveling the surface mechanisms and getting full understanding of the key physico-chemical properties of the photocatalysts driving the performances in H<sub>2</sub>O<sub>2</sub> synthesis.

By gathering a wide span of photocatalytic materials and of synthetic strategies, we hope that this article can inspire interdisciplinary research for designing the next generation of single- or multi-component photocatalytic materials with enhanced photonic efficiency towards selective artificial photosynthesis H<sub>2</sub>O<sub>2</sub> and an optimized use of the solar spectra.

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Authors declare no competing interests.

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