Prophyrin Composites in Variety of Photocatalytic Processes

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Abstract

In recent years, prophyrin composites have received a great deal of interest owing to their remarkable photocatalytic characteristics. Applications for these composites, which include water purification, air pollution management, and energy conversion, have been found for a wide range of materials, including porphyrins and metals, metal oxides, and carbon-based compounds. Recent advances in porphyrin composites for photocatalysts are summarised in this chapter. This chapter discusses how these composites are made, what properties they exhibit, and how effective they are as photocatalysts. We also talk about the difficulties and potential of porphyrin composites in photocatalytic activity.

Key words

porphyrins, photocatalytic properties, metal oxides, water purification, air pollution control, energy conversion.

1. Introduction

The macrocyclic compounds known as porphyrins have a central metal ion and a cyclic structure having four nitrogen atoms that may be utilised to interact with some other molecules and facilitate electron transport. Just 18 of the 22 electrons present in the porphyrin cores are involved in conjugation (refer Figure 1, bold). These compounds are given stability, planarity, and unique electrical properties by the porphyrins' aromatic system.It has been referred to as the "pigments of life" because it's crucial role in many biological activities, including oxygen transport (haemoglobin), reduction-oxidation reactions for the detox of substances like cytochrome P450, and photosynthesis such as chlorophylls and bacteriochlorophylls [1,2]. Porphyrins stand out among this large collection of molecules because of both its physicochemical and electrical characteristics.The central metal ion, connecting different groups, and geometry may all be used to tune these features. When the porphyrin characteristics are tuned properly, they can absorb light in nearly the whole UV-visible range. Apart from having a high molar absorptivity (ca 105 L. mol^{-1}. cm^{-1}), porphyrins also have the right electronic states for both transfer of energy as well as single transfer of electrons in a number of photoprocesses [3-5].

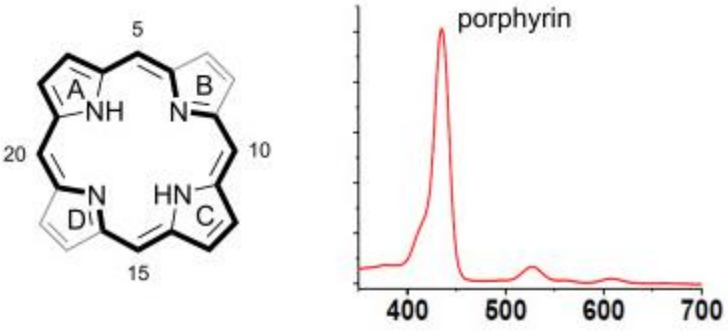


Figure1: Prophyrin ring and its UV spectrum

Solar energy conversion is one of the core areas in which porphyrin photocatalysts are used [6-8]. They have a wide range of wavelengths that they can absorb, and when stimulated, they have the ability to transmit energy or electrons to acceptor molecules, like water, to produce hydrogen and other hydrocarbons [9]. As sensitizers that enable the conversion of light into electrical energy, porphyrins are also employed in the construction of dye-sensitized solar cells [10]. They have also been used to degrade pollutants in the environment and water, such as dyes, pesticides, and medications [11–12].The creation of oxygen species that are reactive, which may oxidise or degrade contaminants, is facilitated by their ability to serve as electron donors as well as acceptors [13]. These chemical compounds have a significant amount of documented photocatalytic performance. The stability and sensitivity to deterioration of porphyrin photocatalysts are among their drawbacks. By changing porphyrins' constitution and chemical makeup, researchers hope to increase their stability and effectiveness. Porphyrin or other opto-electronic compounds can be combined to create novel hybrid structures (composites), which appear to be perfect for satisfying augmented light-harvesting and charge-transfer features. This results in an increase in the effectiveness of photocatalysis with better stability and customised characteristics.

2. Porphyrin Composites

As contrasted with porphyrins, porphyrin composites, which are compounds in which porphyrins are combined with some other chemicals, exhibit increased photocatalytic properties. Coupling porphyrins to semi - conductive substances like polymeric materials,oxides of metals, nanomaterials, carbon-based compounds, or graphene oxide is one method for making porphyrin composites. These substances may function as electron acceptors as well as donors, making the photocatalysts process more effective by promoting electron transfers.

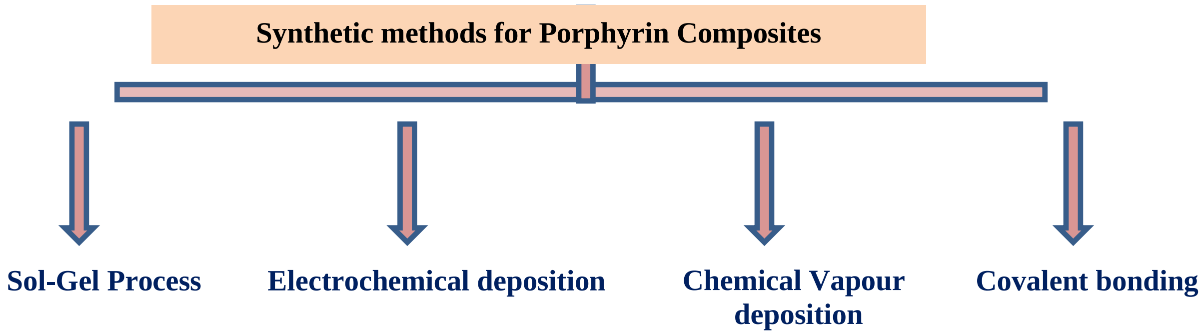
Some illustrations of porphyrin composites are listed below:

1. Metal-organic frameworks (MOFs) based on porphyrin: MOFs also are porous materials made of metal ions linked together by organic linkers. Because porphyrins can pair up with metal ions, they were employed as basic components in the making of MOFs [14].
2. Carbon nanotubes (CNTs) with encapsulated porphyrin are cylinder-shaped carbon constructs with distinct mechanical and electrical characteristics. CNTs may include porphyrins to create hybrid substances that have better properties. The possibility for using porphyrin-CNT composites in electrical and sensing applications has also been explored [15].
3. Porphyrin-silica composites Because of its outstanding stability and bio-compatibility, silica is a substance that is utilised extensively [16].
4. Porphyrin-polymers: To create composite materials with improved qualities, porphyrins may be covalently joined to polymers. For instance, porphyrin-featuring polymers have already been examined for their possible application in biosensing and solar cells [17].
5. Composites fabricated of porphyrin and graphene: Graphene is a two-dimensional type of material with superior electrical and mechanical characteristics. Graphene can together with porphyrins to create composite materials with improved characteristics. Composites made of porphyrin and graphene can be employed in modern electronics, sensors, and power storage [18].

2.1. Synthesis of Porphyrin Composites

In order to form a functionalized composite, the porphyrin molecule is often added to a matrix phase or onto a surface during the fabrication of porphyrin composites.

Porphyrin composites may be made in a variety of ways, including:



1. **Sol-Gel Process:** The porphyrin molecule is combined with a sol-gel precursor mixture via the sol-gel process, which then results in the gel's production. The resultant gel may undergo further processing to create a composite [19].

2. **Electrochemical deposition:** In this method, the porphyrin molecule is deposited onto a material surface by using an electrode. An electrical potential is supplied while the electrode is submerged in a solution which contains the porphyrin molecule to aid with in deposition procedure [20].

3. **Chemical vapour deposition:** Using a gas-phase process, the porphyrin molecule is deposited onto a surface under this process. The porphyrin molecule is released onto the substrate as a vapour, where it performs a chemical process to create the composites [21].

4. **Covalent bonding:** The porphyrin molecule is covalently joined to a functionalized area or matrices material. This may be accomplished through a number of chemical methods, such as esterification processes or amide formation [22].

2.2. Photocatalytic Applications of Porphyrin Composites

Due to their distinctive electrical and optical characteristics, porphyrin composites have demonstrated high photocatalytic activity. The porphyrin molecule possesses a significant conjugated-system that enables effective absorbance in the UV-Vis spectrums [23]. The porphyrin molecule may function as a photosensitizer when it is included into composites, transferring excitation energy to the adjacent matrix material so that it can engage in redox processes. Porphyrin composite's photocatalytic activity may be further increased by modifying the molecular makeup of the composite to maximise charge transfer and reduce photoexcited hole and electron recombination. For instance, a hybrid composit with enhanced photocatalytic activity may be made by covalently attaching porphyrin molecules to a semiconductor nanostructure, like Titanium dioxide [24]. Although the semiconductor nanoparticle offers a surface for separation of charge and their transfer, the porphyrin serves as a sensitizer. The breakdown of organic contaminants [25], the creation of hydrogen by water breakdown [26], as well as the conversion of atmospheric CO_2 to fuels [27] are only a few of the photocatalytic uses for porphyrin composites (Figure 2). Techniques including UV-vis and fluorescence spectroscopy along with electrochemical tests may be used to analyse their photocatalytic activity.

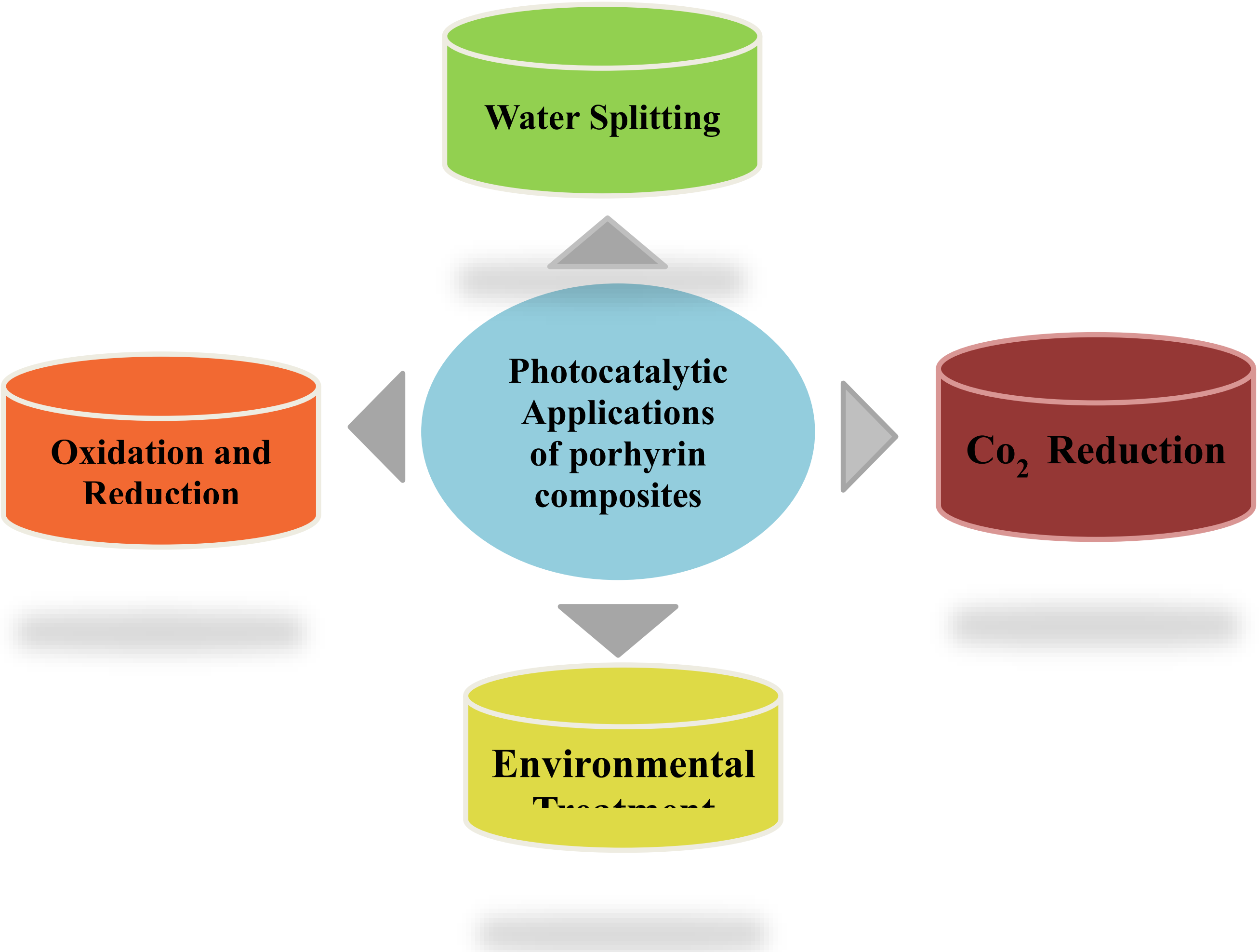


Figure 2: Some Important photocatalytic applications of porphyrin composites.

Porphyrin composites are a noteworthy family of photocatalytic materials that have a significant amount of potential for use in the environment and in the production of energy. This chapter covers all significant photocatalytic uses of porphyrin composites, including the photocatalytic breakdown of dyes and organic contaminants, water splitting, and more importantly the conversion of atmospheric carbon dioxide into compounds with environmental benefit.

2.2.1. Photocatalytic production of hydrogen fuel by water splitting

The reckless use of fossil energy over the past two centuries has brought us to a junction where we must urgently seek for new, more sustainable forms of energy and growth. Hydrogen is getting a lot of attention because of its potential as a renewable energy source having zero carbon emission along with high energy density, although the conversion of solar energy is still the most viable option. It has great promise as a futuristic energy source because to its ability for production from plentiful sustainable materials like water and even biomass and its ease of storage and transmission. Hydrogen is produced by a process called water splitting, which relies on the photo-induced formation of charge carriers, specifically electron-hole pairs, as its foundational mechanism. Charge passes to the surface, and as a result, photogenerated electrons may reduce water to make H_2, whereas holes can oxidise water to produce O_2 in a 2:1 [28] (Figure 3).

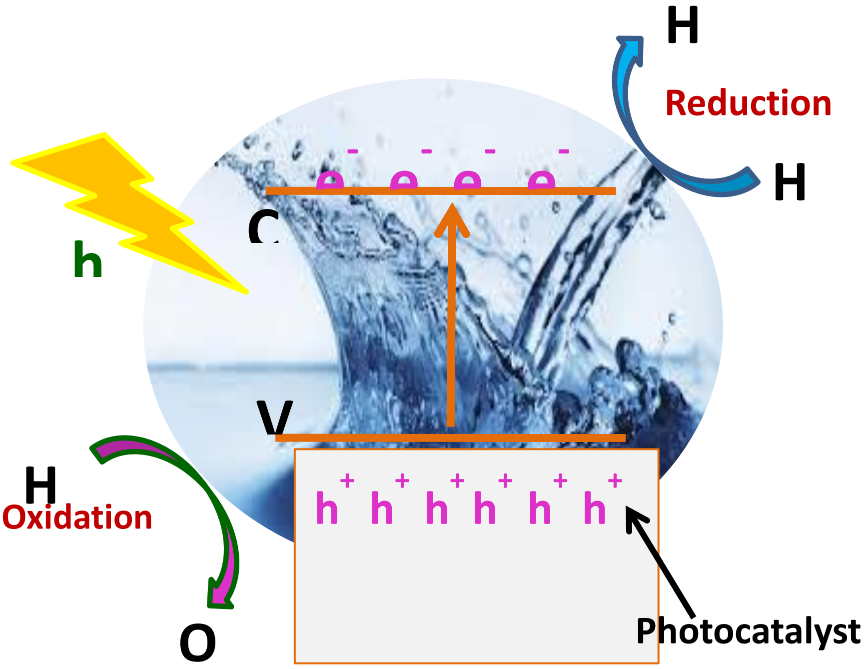


Figure 3: Plausible mechanism for photocataytic Production of H_2 by water splitting.

Due to their potent and effective panchromatic light absorption, strong S and Q-band, ability to transfer electrons, high fluorescence, chemical and thermal stability, and suitable energy levels for photosensitizing various semiconductors, porphyrin as well as their metallic derivative products with conjugate structures have drawn more attention. Moreover, studies emphasising the use of porphyrin moieties as molecular or supramolecular light collecting systems have been stimulated by their central role in natural photosynthesis. It is discovered that the central metal ion, connecting groups, and attachment geometry all have a significant impact on how effectively porphyrin functions as a sensitizer. It has been discovered that electron withdrawing moieties at the meso position are beneficial for hydrogen evolution. High - performing hydrogen evolution catalyst may be easily created by the formation of hybrid materials (composites). For effective photocatalytic H_2 generation, porphyrin has been functionalized on a large number of dye-sensitive metal oxides. Upon irradiation, photoexcited porphyrin electrons are injected into the metal oxide's conduction band and eventually transferred, causing the reduction of H2O at the cathode and the production of hydrogen. Porphyrin composites have been used successfully in a number of investigations to split water photocatalytically. These are a few examples of various porphyrin hybrid materials in use.

2.2.1.a. Metal oxides-porphyrin composites

Liu et al. [29] investigated the Hydrogen evolution abilities of a variety of Sn-porphyrins with various functional groups using Pt nanostructures being a sensitizer for Pt/TiO_2. The synergistically effect between the sensitised TiO_2 and the Q-band of Tin-porphyrins was attributed to the increased photocatalytic activity of Pt/TiO_2 sensitised Tin-porphyrins. A set of metalated and base free trifluoromethylated porphyrin sensitised tinoxide and TiO2 was utilized to study the mechanism of interfacial electron transport [30]. By changing the meso substituents on the porphyrin ring, redox potential may be fine-tuned. Both of these porphyrins on SnO2 showed similar electron injection rates, according to time-resolved spectroscopic observations, transient absorption, and computational estimates, but Zn-porphyrin on TiO_2 howed effective electron injection.While SnO_2 was effectively bombarded with electrons, the free base porphyrin complexes displayed a quick recombination. In order to create the cathode for something like a tandem photoelectrochemical cell, platinum-coated $CuFe_2O_4$ sensitised by MnTPP served as an effective hybrid material and developed both Hydrogen and oxygen at a low voltage bias [31]. The Mott-Schottky plot and high cathodic current relative to dark current proved the copper ferrite's p type property.The intense and prolonged optical absorption of the porphyrin moiety in addition to the efficient photo-excited transfer of electrons from the dye molecule to $CuFe_2O_4$ were both considered to be the causes of the increased photocurrent densities in porphyrin connected samples. The Electrochemical impedance spectrum also showed reduced resistance and improved charge transport at the contact. Hagiwara et al. [32] investigated the porphyrin/GaN:ZnO composite's photocatalytic performance. As a first step in the production of superior performance porphyrin sensitised composites, the effect of nitridation parameters on the crystalline structure and photoabsorption characteristics was thoroughly analysed. The atomic composition of the GaN:ZnO composite was discovered to be primarily responsible for determining the photocatalytic performance, despite the fact that the composition had no impact on absorption spectra. As a co-catalyst for the production of oxygen, IrO_2 packed on galliume zinc oxynitride was used. The efficacy of photocatalysis seems to be enhanced by high nitrogen surface concentration.

2.2.1.b. Carbon material-Porphyrin composites

Graphene, CNT, and C_3N_4 are examples of -conjugated carbon structures that provide an excellent platform for promoting charge transport and electron transfer from porphyrins moeity to carbon surfaces. Hasobe et al. have provided a thorough discussion of supramolecular composite designs for light harvesting and electronics that combine porphyrin functionalities with fullerenes, CNT, carbon nanohorns, and graphene. [33] Tetra(4-carboxyphenyl)porphyrin (TCPP) was tested for photocatalytic hydrogen evolution in the presence of a sacrificial donor after being simply adsorbed onto the surface of platinum-loaded g-C3N4 [34]. The hetero configuration with overlapping band gap, which promotes electron transport and prevents electron-hole recombination, was primarily responsible for the heterogeneous double enhancement of the H2evolution capacity of Pt/g-C3N4 following porphyrin sensitization. Because to the greater negative LUMO of TCPP compared to C3N4 conduction band, photogenerated electrons are transported to C_3N_4 before being eventually collected by Pt nanoparticles. Simultaneously, the holes of C3N4 from the valence band move to the TCPP HOMO, resulting in efficient and quick charge separation. Catalytic efficiency was significantly influenced by the kind of electron donor, with triethanolamine having the best results. The maximum activity was attained at pH = 9, and triethanolamine's protonation may be to responsible for the activity decline at acidic pH levels. With its outstanding electron-accepting and electron-transport characteristics, graphene oxide (GO) may provide a fantastic matrices for immobilising porphyrin. In this regard, GO has been functionalized both covalently and non-covalently. Here are a few recent examples:

It was suggested that an effective hybridized material for the visible light-driven hydrogen evolution in the presence of ethanolamine as a sacrificial donor was methylpyridyl substituted Zinc porphyrin stimulated MoS_2/RGO [35]. By measuring emission quenching, it was determined that RGO efficiently transferred electrons from the sensitizer to the MoS_2, and an oxidative quenching mechanism was postulated. With a rise in GO content in the composite, emission quenching increased.

The electrostatic as well as co-ordination contact between the pyridyl group of the porphyrin moiety and the Co ion preimplanted on the graphene oxide surface, which was used to create porphyrin pillared graphene oxide, was shown to be conducive to hydrogen evolution [36]. According to reports, Co^{2+} functions as an interface linker across GO and porphyrin, enhancing the efficiency of charge transport and segregation as shown by fluorescence spectra. Due to the weak contact between GO and the porphyrin moiety in the absence of $Co^{2+,}$ porphyrin molecules accumulate as J aggregates on the surface of GO. A nanohybrid with strong photocatalytic activity was produced by noncovalently anchoring 5,10,15,20-tetrakis-(4-hydroxyphenyl)porphyrin (THPP) and 1-pyrene sulphonic acid (PSA) on GO [37]. It was hypothesised that THPP and PSA were joined to GO via a hydrogen bond and a stacking interaction. Efficient charge segregation and activity were ascribed to a broader light responsiveness and multichannel electron transfer.

2.2.2. Photocatalytic degradation of dyes and organic pollutants

Due to rising industrial and agricultural activity, the environment suffers from water contamination, which poses major issues for aquatic life [38,39]. Large quantities of dangerous nitro and amino pollutants along with dyes, pesticides and herbicides, etc are released into water bodies on an annual basis, degrading the water's quality for human consumption.This is why there are more and more scientific efforts being made to eliminate these hazardous chemicals from wastewater [40, 41]. Again for adsorption and destruction of these organic contaminants, many techniques including have been used like electro-catalytic degradation, precipitation, ultra-filtration. The removal of these contaminants from water using photocatalytic degradation has shown to be an efficient use of energy and money. Several catalysts were employed in order to examine how organic contaminants in water are degraded. Visible light is significantly absorbed by porphyrinoids, which makes them useful as photocatalysts that are triggered by visible light [42]. Nevertheless, porphyrinoids' agglomeration in solution, limited surface area, low reuse, and difficulty in postseparating the catalysts from the reaction medium restrict their utility in homogeneous catalysis [43]. New photocatalysts must also be created in order to address major problems such the narrowed bandgap, high solar absorbance, quick electron-hole recombination, and seamless recuperation from of the reaction medium. To this purpose, porphyrin-based hybrids composite materials have received a lot of interest in the applied chemical industry over the last several decades [44–46]. They are potential photocatalysts for the breakdown of organic contaminants in water. There are typically five phases involved in the photocatalytic breakdown of organic pollutants (OP) (Figure 4). A photocatalyst absorbs visible light and an organic dye in the first stage. As a consequence, after bridging the band gap, the valence electrons go into the conduction band. The photocatalyst's surface gains electron-hole (e-/h+) pairs as a consequence of this promotion. Next, in a series of subsequent reactions, these photogenerated holes (h+) combine with H_2O to produce an extremely reactive hydroxyl radical (•OH), and electrons combine with dissolved oxygen to create fenton reaction superoxide radical anions (O_2•). OP is eventually broken down into tiny molecules and CO_2 and H_2O by these photos- generated, extremely reactive superoxide radical anions and OH radicals.

This porphyrin-based porous framework P has a five-step mechanism.

$$\mathbf{P} + hv \rightarrow \mathbf{P}\,(\,e^- + h^+) \quad (1)$$

$$H_2O + h^+ \rightarrow \bullet OH + H^+ \quad (2)$$

$$O_2 + 2e^- \rightarrow O_2^{-}\bullet \quad (3)$$

$$\bullet OH + OP \rightarrow \text{degraded products} \quad (4)$$

$$O_2^{-}\bullet + OP \rightarrow \text{degraded products} \quad (5)$$

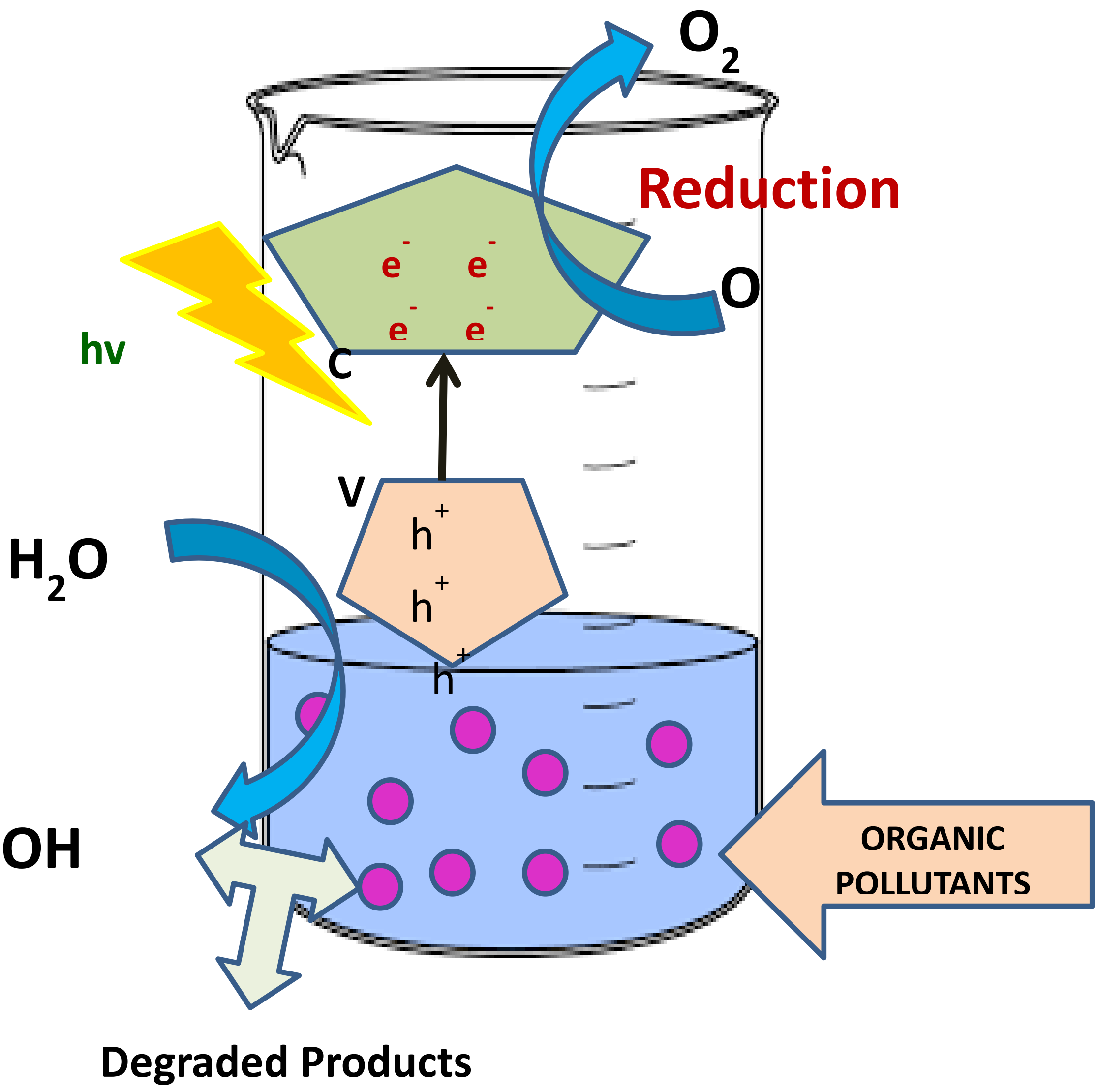


Figure 4: General mechanism for photocatalytic degradation of Organic Pollutants.

The capacity of porphyrin composites to photodegrade organic contaminants has gained much attention. Examples of organic contaminants that have been broken down by porphyrin composites include as follows:

By allowing the porphyrin subunits to self-assemble in the medium of graphene and Fe2O3-TiO_2 nanoparticles, D.D. La *et al.* have created the graphene@Fe_2O_3-TiO_2@porphyrin composite. This hybrid mix surpasses existing photocatalytic methods in the breakdown of Rhodamine B dye, with degradation rate constants up to 1.12×10^{-2} min^{-1}[47]. The other porphyrin composites that were employed to break down the colour Rhodamine B were created by chemically attaching (trans-dihydroxo) (5,10,15,20-tetraphenylporphyrinato)tin(IV) (SnP) to the mesoporous structure of MCM No. 41 (MCM-41) and SiO_2 nanoparticles. The photocatalytic destruction of anionic erioglaucine and cationic dye (rhodamine B), and neutral m-cresol purple dyes in an aqueous phase is supported by the incorporation of SnP into MCM–41 and SiO_2. As compared to SnP@SiO_2, SnP@MCM41 has a larger pseudo-first-order breakdown rate constant (0.013 min-1 vs. 0.011 min^{-1}) and a stronger degrading power (0.013 min^{-1}) [48]. In another instance, porphrin linked graphene composite was utilised to degrade several kinds of contaminants, including the dye methylene blue (MB), the herbicide 2,4-D, and polyethylene glycol (PEG), a component in personal care and household items. Methylene blue (MB) and polyethylene glycol (PEG) had the best photocatalytic degradation results [49].I n order to enhance the photodegradation of methylene blue (MB) in visible light, Wan *et al.* in 2016 created a Ternary combination of TiO_2 nanotubes containing less graphene oxide (rGO) along with meso-tetra (4-carboxyphenyl) porphyrin. It was found that the 92% purity of the MB waste water handled by this composite product. As a result, it demonstrated 4.3 times greater photocatalytic activity than pure TNT [50].Mele et al. used porphyrin(Pp)/Fe co-loaded TiO2 hybrids to study the photocatalytic degradation of para-nitrophenol while subjecting them to UV light and H_2O_2. After examination, it was discovered that this complex composite's photocatalytic activity was more effective than that of simple bare TiO_2 or Fe-TiO_2[51]

2.2.3. Conversion of CO_2 to value-added chemicals

Due to rising worldwide output and population, human civilization has faced difficult challenges in recent decades, including an increase in global temperature and a need for energy from clean, renewable sources [52–53]. Despite the fact that carbon dioxide is crucial for maintaining the earth's habitable temperature and radiative balance, a significant rise in CO_2 levels is also to blame for rising temperatures, rising sea levels, and a rise in ocean acidity. Due to the buildup and dissolving of CO_2 in ocean water, the atmospheric CO_2 concentration has grown from 310 parts per million to around 390 parts per million in the previous 50 years alone [54]. This might cause the pH of the ocean to decrease between 8.2 to 7.8 by 2095. As a result, research in the fields of environmental and energy has focused heavily on the process of transforming carbon dioxide into high-value compounds [55–57]. Modern technology has successfully converted CO_2 into tiny C1 structure chemicals like CO, CH_4, formaldehyde, and formic acid, as well as highly energetic high - density liquid fuels like methanol (MeOH), ethylene (CH_2CH_2), ethanol, petrochemical polymers, hydrogels, and CO[58], CH4[59], and formic acid [61–62].Due to their high catalytic properties, stability, and selectivity, porphyrin compounds have been demonstrated as efficient catalysts for this reaction. Porphyrin composites are also simple to synthesis utilising a number of techniques, making them a desirable alternative for mass manufacturing. Using sunshine or other sources of light energy to activate the porphyrin composites and start a chemical process with CO_2 molecules is the process of photocatalytic carbon dioxide conversion. After that, the stimulated porphyrin composite may reduce CO_2 to the required fuel product by transferring electrons to it (Figure 5).

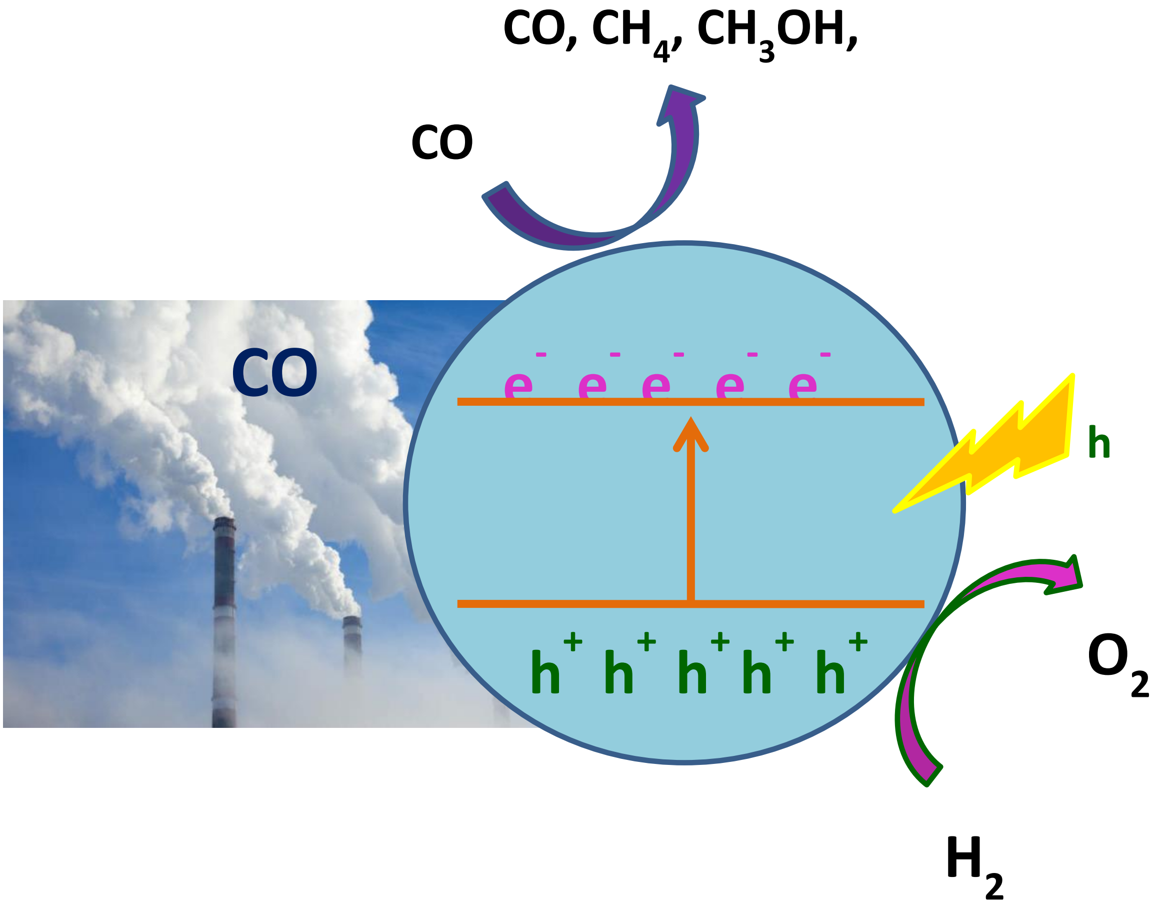


Figure 5: General mechanism for photocatalytic Conversion of CO_2.

There have been multiple investigations on the photocatalytic processing of carbon dioxide into value-added fuels using porphyrin composites. Here are some noteworthy examples:

Metal-organic framework (MOF) hybrids with embedded porphyrin have been utilised to photocatalyze the conversion of CO2into useful fuel. In one experiment, carbon dioxide was converted into carbon monoxide and a hydrogen molecule using an iron-MOF composite with porphyrin incorporated in it. Pyrene was employed as the linker. A self-contained photocatalyst is created when the pyrene conduits in the MOF capture photons and transport electrons to the porphyrin catalyst. With a flip over number for CO of 22 in 2 hours, the developed heterogeneous photocatalyst demonstrates activity for CO2 photoreduction under irradiation at 390 nm [68].

In another work, CO2 was photocatalytically converted to methane and carbon monoxide using a metal-semiconductor hybrid composite with embedded porphyrins. During visible light irradiation, the composite, which was made of tetra (4-carboxyphenyl) porphyrin-featured TiO2 nanoflakes, generated carbon monoxide at a rate of 141.74 μmol g−1 h−1, which is much greater than that of the majority of reported catalysts [69].

Another example makes composites of various TiO2-covalent porphyrin polymers using the in-situ hydrothermal method (COP-Ps). The COP-Ps/TiO2 composites showed increased photocatalytic properties for the carbon dioxide transformation into CO owing to the strong contact between the two moieties. The greatest outcomes are obtained when TiO2 is more equally mixed with the sulfonated porous COP-P (sh-COP-P). In this case, a CO production rate of 5.70 mol g-1 h-1 was found, which is around 20.4 times more than that of pure TiO2 having 2.3 times greater than sh-COP-P polymer [70].

For the photocatalytic conversion of CO2to formic acid, Sobral's team employed a graphene oxide enhanced using cobalt metallated aminoporphyrin material. Under visible light irradiation, the composite produced 96.49 mol of formic acid in 2 hours while displaying strong formic acid selectivity [71].

Co-porphyrin (Co-TCPP) was placed on the surface of MgAl coated double hydroxide to create a wonderful metal free nano-composite (LDH). Comparing the final composite material (Co-TCPP@LDH) to pure MgAl LDH, it was discovered that it had higher photocatalytic activity. According to the findings of the experiments, 20% Co-TCPP@LDH has the highest photocatalytic activity, with a CO production rate of 0.40 mol gcat-1, a value that is 4.1 times and 3.3 times greater compared to MgAl LDH or Co-TCPP, respectively [72].

Conclusion

To recap, porphyrins that are class of organic compounds with exceptional light-absorbing properties that may be utilised to catalyse processes by transferring electrons from an excited porphyrin to its reactant molecules. The photocatalytic activity of porphyrins may be increased by combining them with a composite material like a semiconductor/ metal oxide, which can then be used to degrade pollutants at a higher rate.H2O splitting, atmospheric purification through Carbon dioxide reduction, especially organic pollutant destruction are just a few of the photocatalytic uses of porphyrin-based composites that we've examined in this chapter. High catalytic performance and persistence across a wide range of environmental conditions have been shown for porphyrin composites in this research. In addition, porphyrin composites are desirable both for commercial and ecological applications due to their cheap cost, simplicity of manufacture, and biocompatibility. In sum, existing data suggests that porphyrin composites have promising future applications as effective photocatalysts, and further study in this field is warranted.

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