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Porphyrins and ZnO hybrid semiconductor materials: A review

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ABSTRACT

The use of materials based on semiconducting oxides is taking an important place in modern chemistry. The application of such materials to catalysis, photocatalysis, and other fields is producing more and more scientific and technological advances every year. Because of its catalytic, electrical, optoelectronic, and photochemical capabilities, zinc oxide (ZnO) is a widely utilized substance in a variety of industries, including sensors, field emission devices, biological and biomedical printing, and security printing. On the other side, porphyrins are versatile biomimetic molecules with multiple functions that are created by condensing pyrrole with aromatic aldehydes. By introducing various peripheral functional groups or metal atoms into the core of the porphyrin, it is possible to modify the structure of the porphyrin synthetically. Consequently, numerous porphyrin derivatives can be synthesized with remarkable optoelectronic properties. The combination of porphyrins and ZnO can also lead to the development of a new class of hybrid materials due to the interaction of their optical, electronic, and chemical properties. In addition, it is possible to control the morphology as well as the reactivity of the hybrid material during the synthesis process, aside from the individual properties of porphyrins and ZnO. This review intends to present the evolution of those ZnO/porphyrin hybrid compounds and point to future research trends in this vital field.

1. Introduction

1.1. Semiconductors

Despite having a long and complicated history, semiconductors have revolutionized several fields beyond what could be imagined. Alessandro Volta conceived the term “semiconducting” back in 1782, as outlined by G Busch [1]. Two significant characteristics of semiconductors are their ability to rectify metal–semiconductor junctions and photosensitivity. In the year 1833, Michael Faraday observed the

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Abbreviations: aPDT, Antimicrobial Photodynamic Therapy; DFT, Density Functional Theory; ET, Electron Transfer; DOS, Density Of States; DSSCs, Dye-Sensitized Solar Cells; HOMO, Highest Occupied Molecular Orbital; LUMO, Lowest Unoccupied Molecular Orbital; NWs, Nanowires; P3HT, Poly(3-hexylthiophene); POMs, Polyoxometalates; TPP, *meso*-tetraphenylporphyrin; UPS, Ultraviolet Photoemission Spectroscopy; VBM, Valence Band Maximum.

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characteristics that define a semiconductor for the first time [2]. He found that the silver sulfide resistance changes with temperature, unlike that of metals, as the temperature increases. Braun in 1874 discovered and documented the first rectifying properties of a metal sulfide-metal point contact, and Schuster in 1885 observed similar properties of copper oxide [3]. Although Braun's discovery, originally overlooked, made an important contribution to the development of the radio during World War II and later indirectly to the detection of microwave radiation as well [4]. In 1929, Walter Schottky conducted a series of experiments demonstrating the existence of an internal barrier in metal–semiconductor junctions [5].

There has been a growing interest in semiconductor nanomaterials as a result of their advantages over their traditional counterparts. Consequently, nanorods, nanowires, nanoparticles, and nanotubes are among the nanoscale and nanostructured materials which are currently available. In recent years, nanostructured materials, particularly semiconductor nano photocatalysts, have experienced rapid growth as a result of advances in synthesis techniques and novel applications for solar energy and environmental remediation. The photocatalyst is typically a solid semiconductor that absorbs both visible and UV light, is chemically and physiologically inactive, is photostable, is low in cost, and is environmentally friendly. There are more than a thousand papers published worldwide every year using the terms "photocatalysis" and "oxide/semiconductor" in the ISI online database, which indicates the importance of this field to the scientific community. Hence, current research mainly focuses on altering semiconductor oxide's physical and chemical properties by various approaches like doping with metals/nonmetals, co-doping, coupling semiconductors, metal doping, etc. [6–15].

1.2. *Zinc oxide*

The word "zinc" gained widespread recognition in the seventeenth century after zinc re-emerged as a metal. Scientists were able to condense the vapors and use them for smelting without exposing them to the air [16], and later listed in the periodic table [17]. Generally, zinc is not found in its pure form in nature, but is always bonded to another element, like oxygen or sulfur. In particular, zinc oxide (ZnO) has outstanding physical and chemical properties, making it a highly functional material. A very important functional material, it is characterized by its excellent chemical stability, superior electrochemical coupling coefficients, excellent radiation absorption, and excellent photostability. In the 1920′s, the semiconducting characteristic of ZnO was initially used in radio signal rectifiers for make-your-own radio sets. Since then, ZnO research has expanded tremendously in the last two decades and it was one of the most thoroughly studied materials. The first ZnO electron diffraction pattern was described in 1935 [18], and a scanning transmission electron microscope was utilized to obtain the first scan three years later [19]. ZnO was first demonstrated to exhibit n-type properties by temperature-dependent Hall measurements in 1954 [20]. After initial studies in Germany [21], light emission from ZnO gained considerable interest during the 1940 s and 1950 s.

As a white powder, zinc oxide hardly dissolves in water but binds to acids and alkalis when they come into contact with it. As a naturally occurring substance, it can also be found in zincite, which exhibits three distinct crystal structures: wurtzite, zinc blende, and rock salt. At room temperature and atmospheric pressure, zinc oxide crystallizes as hexagonal wurtzite (Fig. 1) with tetrahedrally coordinated zinc cations and oxygen atoms; the crystal lattice parameters are 3.25 A° and 5.20 A°. The detailed structure of ZnO is described elsewhere [22–24].

Since ZnO can be used as an alternative to TiO_2, semiconductor oxides play a significant role in energy and environmental applications. It has a band gap energy that is nearly identical to that of TiO_2 [13,25], the most widely used and standard photocatalytic material. Similar photocatalytic performance has been demonstrated for ZnO, suggesting that it could be a viable alternative to TiO_2 [25–27].

A semiconductor's electronic structure (ZnO), which is made up of an empty conduction band and a filled valence band, is responsible for the separation of its charges under light irradiation. By irradiating a semiconductor with the light of greater energy than its band gap energy (E_g) with an electric field greater than its band gap energy (E_g) [6], a semiconductor is activated.

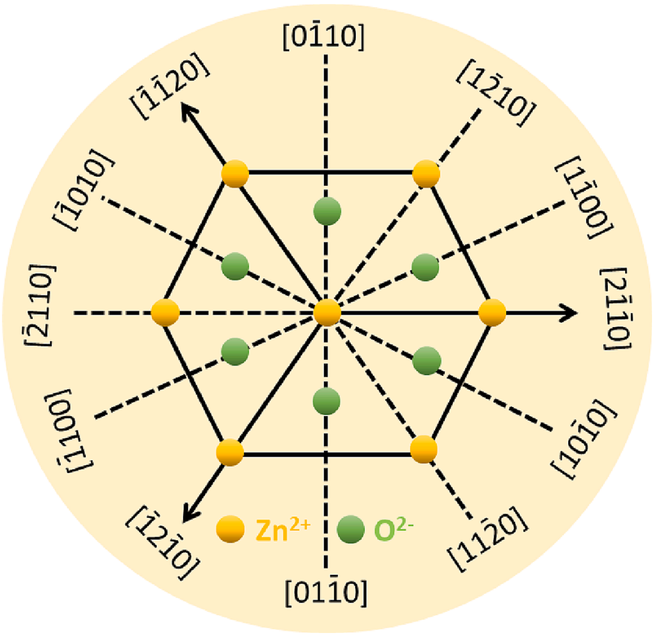


Fig. 1. Different crystal planes of the ZnO Wurtzite structure.

$ZnO + h\gamma \rightarrow ZnO\ (e^-_{CB} + h^+_{VB})$ …..(1)

In either case, they recombine and are transferred as heat or, as a result of their reaction with oxygen or water molecules, they produce powerful oxidizing radicals such as superoxide radicals and hydroxyl radicals (Eqs. (2) and (3)). Both species are powerful oxidizing agents [6].

$e^-_{CB} + O_2 \rightarrow O_2^{\bullet -}$ ….(2)

$h^+_{VB} + H_2O \rightarrow H^+ + HO^\bullet$ ….(3)

Generally, the formed electrons and holes will naturally recombine in the case of unmodified ZnO, decrease the formation of both species in the degradation process (superoxide radical anion and hydroxyl radical), and decrease the charge separation. In order to avoid this, the surface of ZnO is suitably modified by differing materials.

1.3. *Porphyrins and porphyrinoids*

Porphyrins, including haem and chlorophyll, are heterocyclic macrocyclic organic compounds with four modified pyrrole subunits that are connected by methine bridges (=CH). Porphyrins and chlorophyll comprise most of the natural biosphere. Porphyrins have several essential roles in biological systems, including oxygen transport, enzyme active sites, and light harvesting. Biosystems using porphyrin-based functional nanodevices provide excellent tremendous for developing biomimetic functional materials. Further, porphyrins have several distinctive photophysical and electrochemical properties mainly due to the extended π-conjugation [28–35]. A variety of metal ions can be integrated into the porphyrin core. Consequently, metal coordination allows porphyrins to be fine-tuned in their chemical and physical properties. Because of their symmetric skeleton, porphyrins are often employed as components in supramolecular architectures for their functional properties. It has also been shown that porphyrin derivatives can be used in photodynamic treatment and diagnostic procedures to treat and diagnose diseases. Typically, porphyrin is generated by the condensation and oxidation of pyrrole and an aldehyde in Rothemund reactions. Formic acid, acetic acid, or propionic acid are commonly used as solvents for solution-phase reactions [36], while Lewis acid and p-toluenesulfonic acid can be dissolved in nonacid solvents.

1.4. Organic/inorganic hybrid compounds

As a result of their chemical and structural properties, inorganic–organic hybrid materials make excellent choices for next-generation solid-state materials because they may be used for a variety of applications, including catalysis, gas storage, molecular separation, and molecular identification [37–41]. Further, materials science research plays a significant role in studying the interface properties of organic molecules and inorganic semiconductors. It has become increasingly popular in these fields as a result of its potential applications in energy conversion [42], optoelectronics [43], and gas- and liquid-operated chemical sensors [44]. The interface characteristics are determined by the interaction between the Fermi level of the semiconductor and the energy levels of the molecular orbitals of the organic molecule. Electron transfer processes between these two systems have caused distortions in semiconductor energy bands near the surface in several interesting cases. Among the reported examples, porphyrins and ZnO nanostructures exhibit peculiar photo-conversion properties [45,46] and chemical sensing properties [46,47].

A wide range of organic dyes have been used to sensitize broad bandgap semiconductors to visible light [28–34]. As one of the reported organic dyes, porphyrin has the strongest Soret bands located between 400 and 450 nm and a moderate Q band located between 500 and 650 nm, which make them very promising candidates as a photosensitizer [28–35]. Many review articles have been published about titania-based photocatalysts [48–55]. However, not so many review articles are published related to ZnO. The degradation of organic dye-containing wastewater by zinc oxide-photocatalyzed has been reviewed in a recent article [22], in which recent ZnO photocatalytic research on organic dye degradation is summarized. Additionally, modified ZnO photocatalysis was discussed, with a focus on optimizing degradation efficiency and activity under visible light and solar illumination. The impact of essential operating parameters on the photocatalytic degradation and mineralization of dyes has been studied in depth. Further, this review emphasizes the importance of multivariate analysis in determining optimal operating parameters for improving photodegradation efficiency and system performance [22]. The identification of reaction intermediates created during dye degradation, as well as the methods for analyzing them, were briefly discussed. There was another excellent review regarding the surface chemistry of porphyrins and phthalocyanines reported by Michael Gottfried [56], and one more review article was published related to Porphyrins in bio-inspired transformations: Light-harvesting to solar cell [57].In our present review, ZnO (inorganic)/Porphyrin (organic) based hybrid materials, synthesis, characterization, and their applications toward catalytic and photocatalytic are described in detail. We also highlighted the application and potential synthesis method of porphyrins/ZnO nanocomposites, along with optimum operating parameters for optimizing performance. A detailed discussion will also be given on the recent modifications to ZnO with porphyrins for photocatalytic/catalytic applications. We conclude by summarizing and discussing real-world process scenarios for their potential practical application.

2. Binding nature and charge transport characteristics of porphyrin/ZnO hybrids

2.1. Valence band structure of the hybrids

A combination of organic and inorganic semiconductors appears to be a promising strategy for the development of hybrid cell materials [58–72]. Several advantages can be gained from dye-sensitized solar cells (DSSCs) using these two types of materials due to their compatibility, including cheaper manufacturing costs and easier organic component manufacturing. A further benefit of these hybrid materials is that they are chemically and physically stable, can be adjusted in size, and can absorb complementary light, all of which are critical factors when it comes to photo and electrocatalytic applications. Besides, the transfer of energy from nanomaterials to organic molecules, which results in their luminescence, is of crucial importance for biomedical and photodynamic therapy applications. Many efforts are undertaken to achieve this luminescence.

Ichiro Hiromitsu *et al.,* [73] investigated the optical absorption and photoluminescence properties of dispersed (ZnO-LC)-porphyrin systems (NH_2) containing four types of tetraphenylporphyrins with and without p-aminophenyl groups (H_2TPP, $H_2TPP(NH_2)$, $H_2TPP(NH_2)_2$, and ZTPP). Although ZnO and TPP do not combine due to L-cysteine not being bonded to the ZnO particles, authors concluded that energy is transferred through collisions between ZnO particles and porphyrins in the dispersion. An innovative solar cell component was created by Taleatu *et al.,* [74] using tetraphenylporphyrin (TPP) and nanocrystalline zinc oxide (ZnO). Changing the alignment of the energy for the porphyrin macrocycles at the interface with the ZnO valence band maximum can make electron injection much faster. A UPS measurement was used to analyze how TPP layers were covering ZnO substrates and to determine how well they covered them. The surface of ZnO was found to be covalently attached to TPP molecules. From the valence band spectra in Fig. 2 (UPS-Ultraviolet photoemission spectroscopy), Porphyrin reduces Zn 3d peak intensity (peaks on ZnO substrates). According to the authors, traces of both clean ZnO and TPP of the hybrids cross at this intersection, indicating that the bands are aligned.

UPS spectra show the valence band structures of clean ZnO and TPP/ZnO hybrids (Fig. 2). The edge of the valence band was found by following the leading edge of each spectrum until it reached zero intensity on the axis of binding energy. The values (intercepts) at these binding energies are known as VBM (see insets in Fig. 2). A change in photoemission intensity above or near the VBM indicated the density of states (DOS) and alignment of the valence band. Traces from both clean and hybrid samples showed this characteristic. It is due to the organic molecules (TPP) covering the ZnO, and the photoemission from the valence band of the organic molecules.

In order to achieve strong binding of tetra-anionic *meso*-tetrakis(4-sulfonatophenyl)porphyrin to ZnO nanorods, a step-by-step surface functionalization technique was developed based on hybrid covalent and non-covalent approaches [75]. The carboxyalkylphosphonic acids can self-assemble monolayers when they are surface grafted with -PO_3H_2 headgroups. As a result of the exposed carboxylic functionalities, cationic poly-L-lysine can be effectively grafted on top, which drives the non-covalent anchoring of anionic porphyrin in water to its maximum extent. Using the suggested method, anionic porphyrin can be deposited on ZnO nanostructures. Due to its versatility and full reversibility, it combines covalent and non-covalent functionalizations.

2.2. Binding nature of the porphyrins with semiconductors

It was reported by Jonathan Rochford *et al.*, [76] that porphyrins bind to semiconductor surfaces and the location and length of the anchoring groups have an impact on this binding (Fig. 3). A series of tetra(carboxyphenyl) porphyrin derivatives were fabricated to determine how interfacial processes and the efficiency of solar cells are affected by the distance and attachment of sensitizing chromophores on colloidal TiO_2 and ZnO films (Fig. 3).

An analysis of four porphyrins with multiple anchoring groups (COOH and $COONHEt_3$) was performed, including Zn(II)-5,10,15,20-tetra(3-carboxyphenyl) porphyrin (m-ZnTCPP), Zn(II)-5,10,15,20-tetra (4-carboxyphenyl) porphyrin (p-ZnTCPP), as well as Zn(II)-5,10,15,20-tetra(3-ethynyl) (m-ZnTC(PEP)P). The properties of Zn(II)-5,10,15,20-

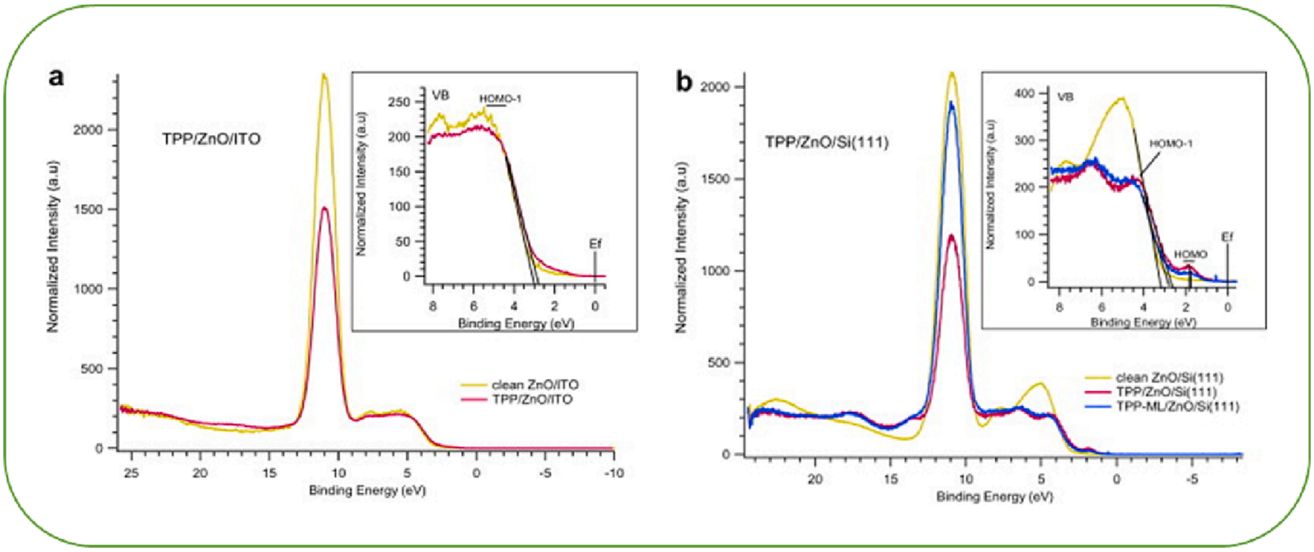
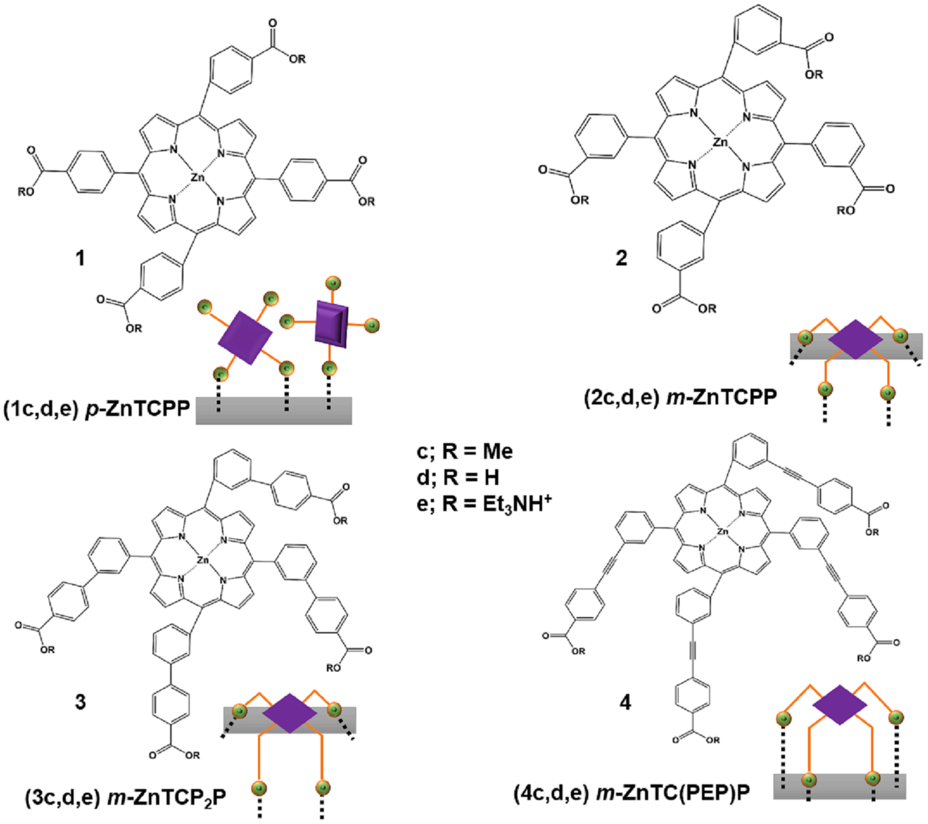


Fig. 2. (a, b) Valence band structures of clean ZnO substrates and TPP/ZnO hybrid specimens determined by UPS measurement. Insets show the valence band edges of the materials [74], copyright © 2012 Elsevier B.V.



(1c,d,e) *p*-ZnTCPP

(2c,d,e) *m*-ZnTCPP

c; R = Me
d; R = H
e; R = Et$_3$NH$^+$

(3c,d,e) *m*-ZnTCP$_2$P

(4c,d,e) *m*-ZnTC(PEP)P

Fig. 3. Structures of the tetra(carboxyphenyl) porphyrins derivatives. Also shown are the anticipated binding geometries of the COOH and COOEt$_3$NH derivatives on metal oxide surfaces [76].

tetra(3-(4-carboxyphenyl)-6 are also correlated. The four anchoring groups in the *meta*-position on the *meso*-phenyl rings of the porphyrin macrocycle of m-ZnTCPP, m-ZnTCP2P, and m-ZnTC(PEP) enable P to planarly bind to metal oxide surfaces. Porphyrin salts with *meta*-substituted phenyls, biphenyls (P), biphenyl (P2), and diphenylethynyls (PEP) have rigid spacer units between the macrocycles and the carboxyl anchoring bands, which raise the macrocycles from the metal oxide surface. Consequently, porphyrin salts with *meta*-substituted groups (phenyl (P) and diphenylethynyl (PEP)) raise the macrocycle from the surface of metal oxides, permitting it to interact with them. Porphyrins bound to ZnO exhibit a substantial quenching of fluorescence emission when electrons are introduced into the semiconductor's conduction band (CB).

At the interface between the adsorbate and the surface, electron transfer is significant in a variety of applications. There is, however, a lack of clarity regarding the steps that precede and accompany the transfer. An analysis of a model system involving 4-(porphyrin-5-yl) benzoic acid adsorbed as a corresponding benzoate on the surface of ZnO wurtzite has been carried out using density functional theory (DFT) and time-dependent DFT.

A significant contribution has been made in understanding how electron transfer (ET) can occur between molecular adsorbates (porphyrin) and semiconductor surfaces (ZnO). Based on their findings, the researchers concluded that the orientation of porphyrin molecules as well as their proximity to the ZnO surface affected the electron transfer, but at the same time, Porphyrin's orbital energies and ZnO bands were often unaffected by the twisting of porphyrin closer to the surface. However, there is an increase in coupling intensity between the bands when porphyrin is located adjacent to that surface. In particular, the bond strength between an excited porphyrin and a ZnO atom plays a critical role in charge transfer. The binding energy is calculated by comparing the ZnO conduction band with the porphyrin LUMO or LUMO + 1 band (Fig. 4). In twisted porphyrin models, the coupling is stronger than in untwisted porphyrin models, and this tendency increases with increasing surface tilt. Once a certain distance is attained from the surface of porphyrin, its coupling strength does not alter considerably. In addition, porphyrin-porphyrin interactions expand LUMO and LUMO + 1 of the porphyrins when they are twisted. Alternatively, electrons can migrate between porphyrins through the porphyrin-porphyrin interaction.

Calculations using TD-DFT suggest that when ET occurs, alterations in the coordination of porphyrin at the surface have no measurable impact on the excitation energies of porphyrin. It should be noted that porphyrin LUMO levels have an energy greater than the conduction band of ZnO minimums, which agrees with ET in related systems. As porphyrin approaches the surface, the coupling strength between the LUMO and ZnO conduction bands increases steadily; however, Porphyrin can be twisted so that the p-electrons face the surface of the surface, which can increase the coupling strength. A band coupling strength is a measure of how effectively porphyrin LUMOs transmit energy to the ZnO conduction band by determining the ET rate. The polarization effect of porphyrin on the ZnO surface is affected by its distance from the surface. The strongest coupling occurs when the porphyrin is aligned and closest to the surface of the molecule. The ET rate of dye molecules may be increased by adding a linker to the dye molecule that tilts the dye close to the ZnO surface. By examining the strength of the coupling between the porphyrin LUMO and the ZnO conduction band, it is possible to predict the ET rate between the porphyrin LUMO and the ZnO conduction band. The distance between porphyrin and the ZnO surface, as well as the direction in which the porphyrin is oriented relative to the surface, affect the porphyrin's ability to couple with ZnO. Their research shows that porphyrins stick together best when lined up and close to the surface. Using dyes with a special linker design that tilts the dye molecules near the surface might also accelerate ET transfer from the dye molecules to the ZnO surface.

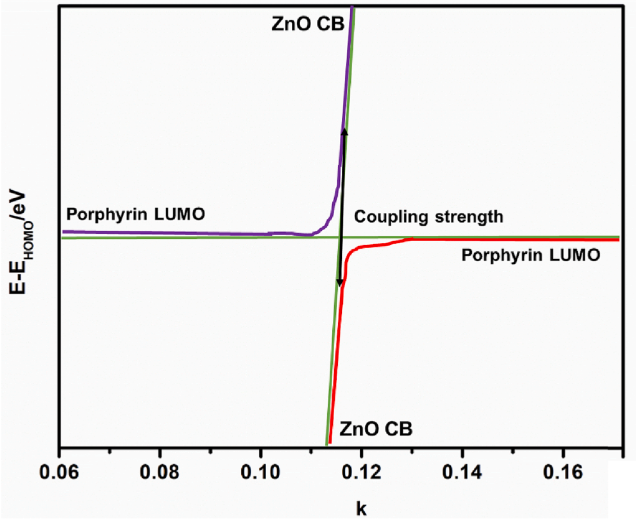


Fig. 4. Coupling strength between the porphyrin LUMO and the ZnO conduction [24].

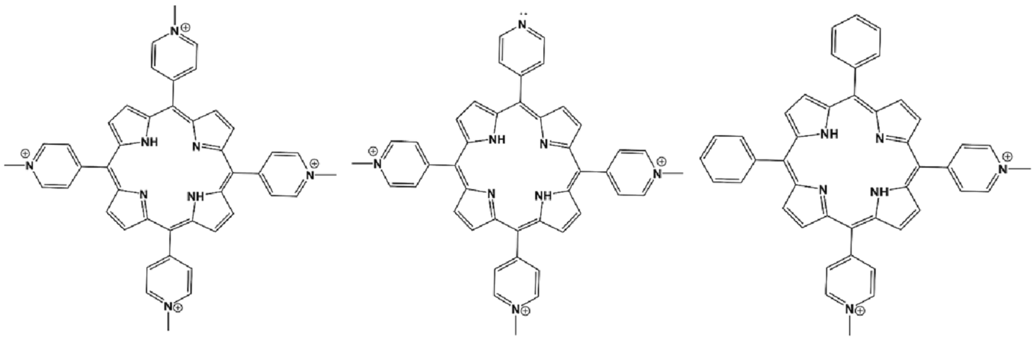
Using steady-state and time-resolved fluorescence spectroscopy in combination with transient absorption spectroscopy, Parida *et al.*, [77] investigated the electrostatic interactions between cationic porphyrins and zinc oxide nanoparticles. During this investigation, three different free-base cationic porphyrins were selected for investigation: mesotetrakis(N-methyl-4-pyridyl)porphine chloride (TMPyP), tri (Nmethyl-4-pyridyl)-20-(4-pyridyl) porphine chloride (Tri-MPyP), and *cis*-di(N-methyl-4-pyridyl)diphenyl porphine chloride (DMPyP) (see Fig. 5). They investigated both the ground and excited states of nano assemblies generated by porphyrins and ZnO NPs. Their results demonstrate that the intensity of fluorescence of porphyrin ZnO NP assemblies can be controlled by adjusting the number of cationic substituents on the porphyrin. The intensity of fluorescence of free porphyrin can be controlled from 3.4 to 1.3 times that of the NP assembly. Depending on the amount of cationic pyridiniums present, the localization and density of charges on the porphyrin macrocycle can be altered. This will alter the chemistry between porphyrin and zinc oxide nanoparticles.

A liquid phase preparation of stable ZnO nanoparticles was carried out by combining lithium hydroxide and zinc acetate in homogenous ethanolic solutions. Further, a catechol-anchoring group with dye molecules was incorporated into colloidal ZnO nanoparticles, namely, 5-(N-(3,4-dihydroxyphenethyl)-2-phenoxyacetamide)-10,15,20 -(p-*tert*-butyltriphenyl)porphyrinatozinc (DOPAZ) and 5-(3,4-dihydroxy-N-phenylbenzamide)-10,15,20-tris(4-*tert*-butyl)porphyrinatozinc (CAMIZ) (Fig. 6) and their photochemical properties were also studied [78]. In a thermogravimetric study, the catechol anchor groups were found to be stable. Furthermore, steady-state and time-resolved emission experiments, as well as steady-state absorption spectroscopy, have demonstrated steady-state electronic communication between two porphyrins and their excited nanoparticles. The catechol-functionalized zinc porphyrins could be employed to anchor the ZnO nanoparticles as support structures. These processes have been demonstrated by steady-state and time-resolved emission measurements, steady-state absorption spectroscopy, and dye molecules' interactions with ZnO [38–41]. The results presented in this study provide a roadmap toward designing ordered ZnO-based nanostructures that are effective at harvesting light energy. In a study published by Rangan *et al.,* [79], energy level alignment was demonstrated on Zn(II)-5-(3,5-dicarboxyphenyl)-10,15,20-triphenylporphyrin dye (ZnTPP-IPA) adsorbed on TiO_2 and ZnO. These results suggest that an experimental and theoretical approach is the most effective way to determine how the energy alignment of the molecular levels corresponds to the band edges on the oxide surface and to gain a fundamental understanding of the ZnTPP-Ipa electronic structure.

3. Various applications of porphyrin/ZnO hybrids

3.1. Dye-sensitized solar cells

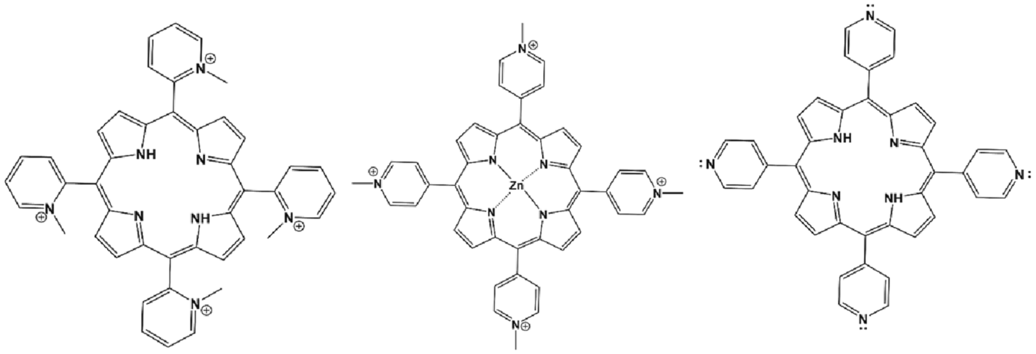
It has been shown that porphyrins as well as ZnO semiconductors nanostructures are both capable of acting as light sensitizers and photocatalysts both in academic research and industrial applications. A dye-sensitive solar cell containing porphyrins anchored by carboxylic acid shows high solar energy conversion efficiency. It has also been demonstrated that different ZnO nanostructures, including nanospheres, nanorods, and tetrapods, can be successfully grafted with them. This section presents selected examples of the effects of porphyrin grafting on the external quantum efficiency (EQE), carrier dynamics, and blend morphology of hybrid porphyrins / ZnO semiconductors.



Meso-tetrakis (N-methyl-4-pyridyl)porphine chloride
(TMPyP)

5,10,15-tri(N-methyl-4-pyridyl)-20-(4-pyridyl)porphine chloride
(Tri-MPyP)

Meso-cis-di(N-methyl-4-pyridyl)-Diphenyl porphine chloride
(DMPyP)



Meso-tetrakis (1-methylpyridinium-2-yl) porphine chloride
(2-TMPyP)

Zn(II)meso-tetra (N-methyl -4- pyridyl)porphine chloride
(Zn-TMPyP)

5,10,15,20-Tetra (4-pyridyl) porphine
(TPyP)

Fig. 5. Chemical structure of different cationic porphyrins [77].

A composite solar cell array has been developed by Abdul Almohsin and J. B. Cui [80] by combining poly(3-hexylthiophene) (G-P3HT) enriched with graphene and tetra(4-carboxyphenyl) porphyrin grafted on ZnO nanowires. The possibility of using porphyrin-enriched P3HT (GP3HT) in hybrid NW solar cells was examined using ZnO NW arrays as well as graphene-enhanced P3HT (GP3HT). Porphyrin modification of the ZnO surface is found to significantly improve the cell performance in terms of both open circuit voltage and short circuit current when both porphyrin and ZnO surfaces are modified. Due to improved hole conduction in the polymer material, G-P3HT also improves cell performance over pristine P3HT. ZnO NWs/P3HT solar cells with and without porphyrin grafting are shown in Fig. 7. Both the ZnO and porphyrin grafted NWs behave similarly in the dark in terms of their JV curves. However, ZnO NW surfaces grafted with porphyrin exhibit a better heterojunction property. A pure ZnO NWs/P3HT cell does not demonstrate an obvious photovoltaic effect when exposed to light. However, both forward and reverse biases of its current value are much higher. A similar observation was made by Lee *et al.,* [81].

In the presence of illumination, porpyrin-grafted ZnO NWs display conventional PV properties. The open-circuit voltage (Voc) was 0.44 V at a fill ratio of 0.499, while the short-circuit current density was 0.33 mA/cm^2 at a fill ratio of 0.499. Approximately 0.087% of the energy in this photovoltaic cell is converted to electricity. Compared to clean NWs, porphyrins provide improved photovoltaic effects when modified. It has been shown that the surface modification of G-P3HT, the p-type semiconductor, contributes to the increased efficiency of solar cells. As seen in Fig. 8, typical JV characteristics of hybrid structures based on G-P3HT and ZnO NW arrays are illustrated with and without porphyrin modification. Again, porphyrin-grafted ZnO NW arrays outperform bare NW arrays in terms of PV performance. Porphyrin-grafted ZnO NWs improved their Voc from 0.2 V to 0.475 V when treated with G-P3HT. A significant increase in the short-circuit current density occurred from 0.3 to 1.66 mA/cm^2. There was a significant improvement in the performance of ZnO NW arrays when G-P3HT was used instead of pure P3HT for the same solar cell design. It is believed that GP3HT's improved charge collection capabilities contributed significantly to the success of this experiment.

P3HT and porphyrin-modified ZnO nanorods were also used in a hybrid bulk heterojunction solar cell by Said *et al.,*[82]. ZnO nanorod and P3HT blend hybrid BHJ solar cells are investigated here to see whether dye grafting can improve spectral response. The role of dye grafting in spectrum response is examined in this study using a solution-processed, hybrid BHJ solar cell composed of ZnO nanorods and P3HT blends. To increase the blend's absorption spectrum, ZnO nanorods were dye-sensitized with TCPP dye, and then mixed with poly(3-hexylthiophene) (P3HT). It has been demonstrated that even at low dye concentrations, extra bands in the EQE spectra can be found at the ZnO surface, which corresponds to Soret and Q-band absorptions. When TCPP is directly grafted onto ZnO nanorods, its light absorption allows an electron injection process to happen. Yet, as the concentration of TCPP at the surface of the ZnO nanorod increases, the overall photocurrent of the devices decreases. TCPP grafting enhances P3HT ZnO nanorod aggregation significantly when viewed with high-resolution transmission electronic microscopy. Accordingly, the TCPP grafting increases the photocurrent generation in the P3HT: ZnO blend, but alters the shape of the blend and the dynamics of the charge carriers at the interface, thereby decreasing the generation of the photocurrent. A simplified energy diagram of dye-sensitized BHJs is shown in Fig. 9, which illustrates the possibility of charge injection from TCPP into ZnO and P3HT via TCPP. Based on the literature [83–85], it was determined

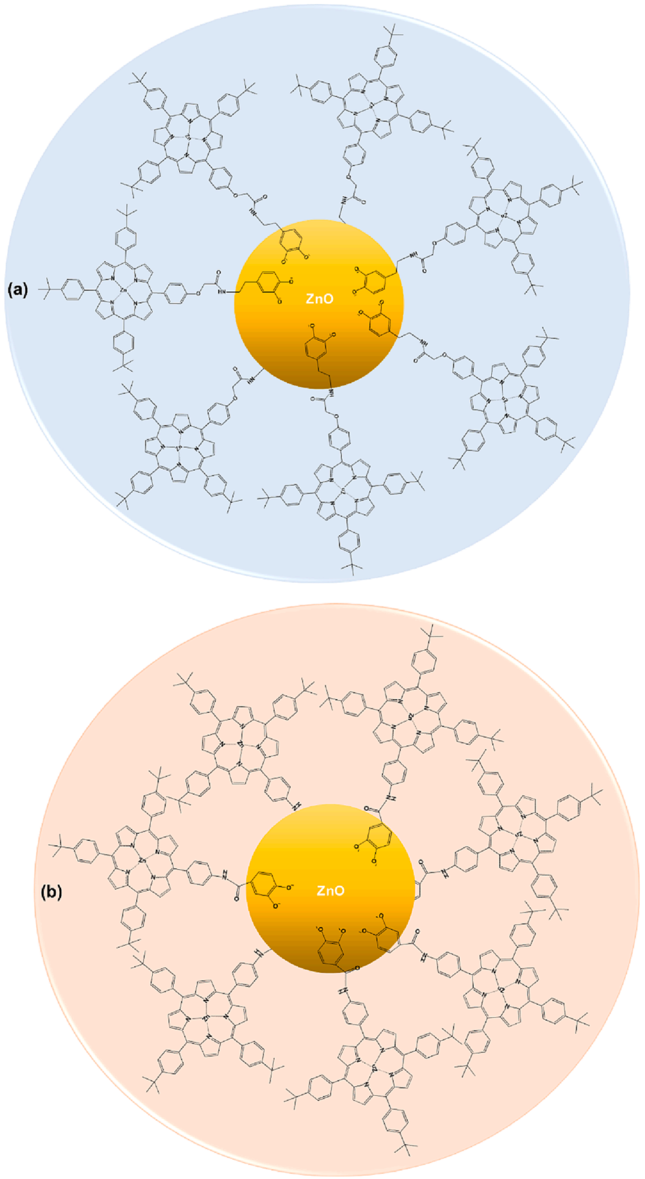


Fig. 6. (a) 5-(N-(3,4-Dihydroxyphenethyl)-2-phenoxyacetamide)-10,15,20-(p-*tert*-butyltriphenyl) porphyrinatozinc, DOPAZ, and (b) 5-(3,4-Dihydroxy-Nphenylbenzamide)-10,15,20-tris (4-tertbutylphenyl) porphyrinatozinc, CAMIZ, Molecules onto the ZnO Nanoparticle Surface [78].

what the energy levels are for ZnO, TCPP, and P3HT.

Recent work by Werner *et al.,* [86] demonstrated that porphyrin grafts to ZnO porphyrins could be accomplished (face-to-face/orthogonal through parallel routes) on DSSCs. Novel binding motives have been investigated in the context of sensitizing ZnO-based dye-sensitized solar cells with metalloporphyrins. A new class of metalloporphyrins was synthesized to study the effect of an orthogonal position versus a parallel position on ZnO, and compared with TiO_2-based dye-sensitized solar cells. By employing steady-state and time-resolved methods, this research provides a comprehensive understanding of the distinct electron-transfer processes occurring at the ZnO/metalloporphyrin interface, namely electron injection, recombination, and dye regeneration. Interestingly, this revolutionary ZnO/metalloporphyrin system exhibits a close-to-unity injection efficiency, despite its extended, nonconjugated anchoring groups. Specifically, they have examined how catecholate can be used as a powerful tool for binding porphyrins to nanostructured ZnO films and how they can be applied to photovoltaics by reviewing key aspects, including charge injection kinetics, charge recombination kinetics, and assess regeneration dynamics. To further explain the role of ZnO/porphyrin orientation, the functionalization of the porphyrin was changed from face-to-edge/orthogonal to face-to-face/parallel (see Fig. 10). Fig. 10 shows the anchoring groups of the first and second compounds. In contrast to the second molecule, which contains the translocated phenyl rings of the porphyrin, the first compound has anchoring groups at the *para*-position of the phenyl rings.

Cells were built on nanostructured ZnO films that were sensitized with **1** or **2** to evaluate the effectiveness of the device. The current–voltage characteristics (see Fig. 11) first appear similar to ZnP-sensitized solar cells [87]. This analysis reveals that under full one-sun illumination, the open circuit voltage and short circuit current are both approximately 0.4 V and 1.5 mA/cm^2, respectively. The nanostructured ZnO films sensitized with **1** or **2** exhibit only a few minor differences when examined more closely. This study shows that the short circuit current for **1**, which is 1.42 mA/cm^2, is somewhat higher than the short circuit current for **2**, which is 1.40 mA/cm^2 and this is similar to the short circuit currents obtained by sensitizing metal oxides with

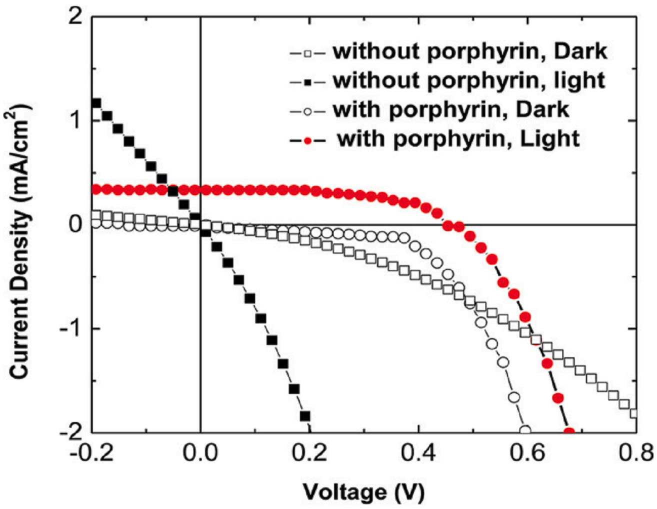


Fig.7. Current density–voltage curves measured on P3HT/ZnO nanowire arrays with and without porphyrin grafting [80], copyright © 2012, American Chemical Society.

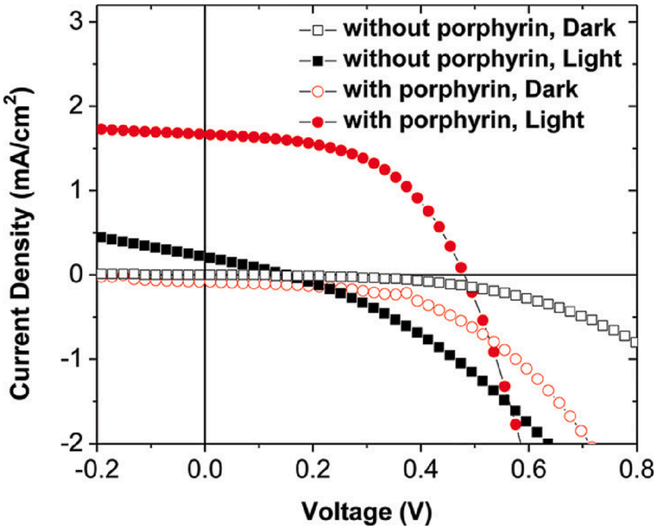


Fig. 8. Current density versus voltage measured on G-P3HT and ZnO nanowire arrays with and without porphyrin grafting [80], copyright © 2012, American Chemical Society.

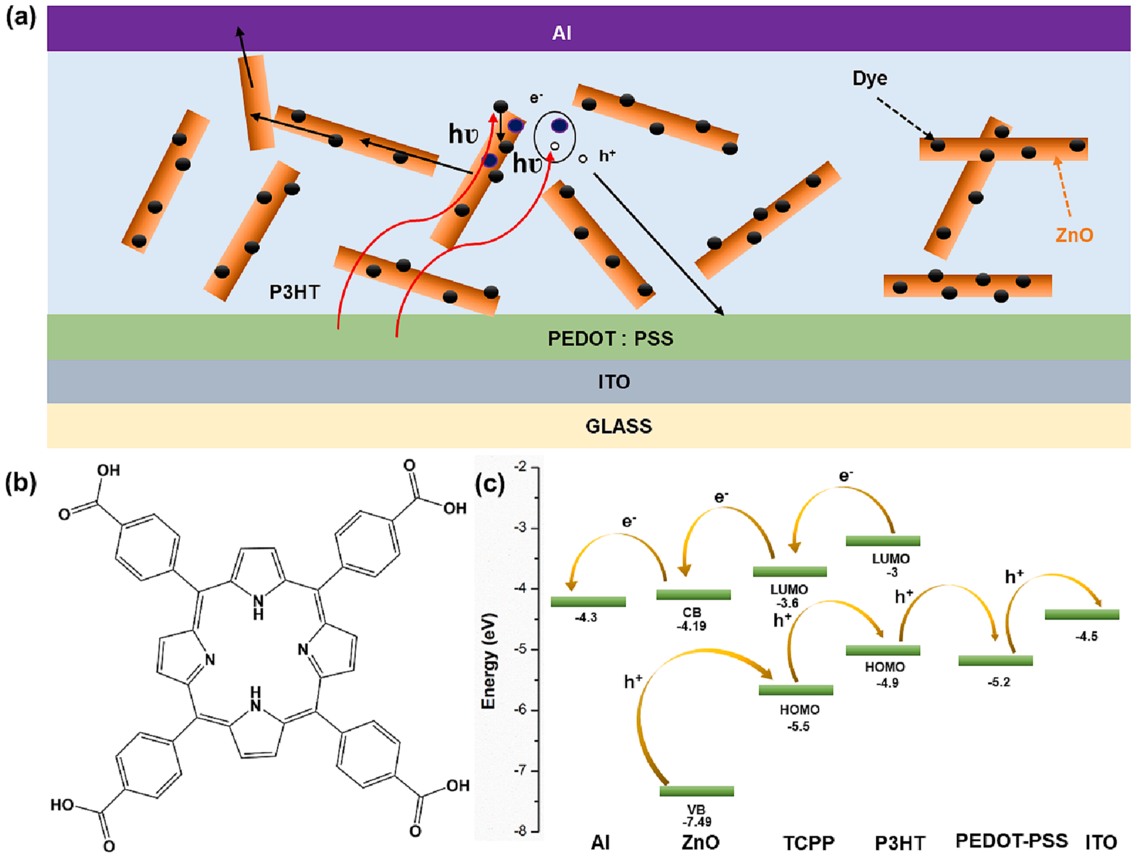


Fig. 9. (a) Solar Cell Structure Showing the Different Layers, (b) Molecular Structure of TCPP, and (c) Energy Diagram of the Dye-Sensitized Bulk Heterojunction Solar Cell Using TCPP as Dye [82].

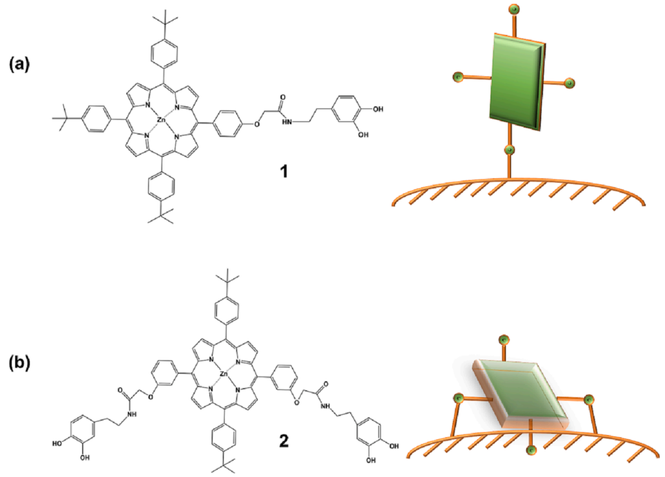


Fig.10. (a) Face-to-Edge/Orthogonal and (b) Face-to-Face/Parallel Orientations of Linking Porphyrins as Dyes/Sensitizers to Nanostructured Oxides [86].

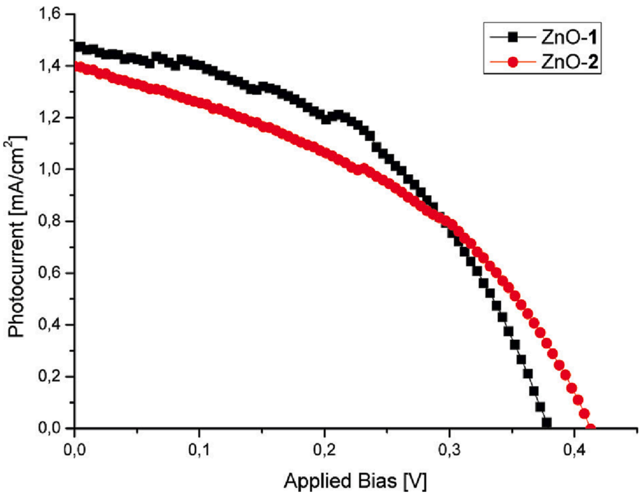


Fig.11. Current-voltage characteristics for ZnO films sensitized (with 1 and 2 porphyrins) devices under 100 mW/cm^2 of AM 1.5 illumination [86], copyright © 2010, American Chemical Society.

porphyrins [88]. An optical density of 0.68 and 0.55, respectively, has been observed for ZnO/**1** at 552 nm, which displays a higher optical absorption than ZnO/**2**. The short circuit current may be affected by a slight increase in ZnP uptake due to a lower spatial requirement. Despite this, there appears to be a higher open circuit voltage for two (i.e., 0.42 V, as opposed to 0.38 V). When ZnO and **2** are oriented parallel to each other, the electronic structure of ZnP will most likely be disrupted, making the oxidation of ZnP thermodynamically more difficult. A shifted ZnP oxidation will result in a larger energy gap between the radical cation ZnP and I^{3-}/I^{-} couples, which will result in a greater open circuit voltage in terms of the ZnP radical cation. This is also reflected in the power conversion efficiencies, which are 0.27% for **1** and 0.23% for **2**.

Based on the extensive characterization of the cell and a thorough investigation of the kinetics and output of the light-to-energy conversion, it has been determined that there are several issues that need to be addressed to make DSSCs work as effectively as possible. In the first place, it is very important to take note that the orientation of ZnP with respect to ZnO is critical as it affects how electrons transfer to and from both interfaces. A second consideration is to find the right pore size to optimize ZnP diffusion and charge diffusion through ZnO to electrodes for nanostructured ZnO films.

In order to increase the efficiency of electron injection into ZnO nanotubes, the type of anchoring group of the porphyrin dye has to be considered [89]. ZnO nanotubes corroded by acidic tethering groups show unexpected increases in electron injection efficiency and cell efficiency. There is a reduction in injection efficiency and cell efficiency due to deprotonated tethering groups. ZnO nanotube electrodes were tested with two porphyrin-based dyes with carboxylic acid tethers of different acidities. If tethering groups are deprotonated, injection efficiency is poor, as well as overall cell efficiency. Fig. 12 shows two porphyrin-based dyes that are protonated and deprotonated with carboxylic acid tethers of different acid systems studied on ZnO nanotube electrodes. In spite of this, it was found that only the added acidic dye corroded ZnO in its acid system; the dye injects electrons well but the surface coverage is not the same as that of ZnO. A control experiment on TiO_2 nanoparticle electrodes shows that the dyes infiltrate protonated and deprotonated forms. As a result of these findings, it seems that dye injection is highly dependent on partially corroding the ZnO surface before it can produce efficient results. Alternately, it may also be that electron injection is coupled to proton uptake and that the two processes are interconnected. The authors concluded that for efficient electron injection to occur, ZnO films must either (a) be somewhat corroded by the dye and/or (b) couple the injection with interfacial proton adsorption or intercalation.

Zinc can significantly alter the electronic properties of 5–1,1,3,4,5–0,10-tetrakis-(4-carboxyphenyl) porphyrin after incorporation into TiO_2, according to a report [90] (TCPP). A significant reduction in luminescence was observed in the emission spectra of TCPP-sensitized Ti(:Zn)O_2, suggesting that electrons may be more readily introduced from the molecular orbitals to the semiconductor conduction band. In another approach, using ZnO nanorods that are modified with hematoporphyrin (HP) for photocatalysis and DSSC applications, Soumik Sarkar *et al.,* [91] showed that they are capable of being used for both purposes. An excellent electron transfer is observed between photoexcited HP and ZnO nano roofs in HP-ZnO nanohybrids.

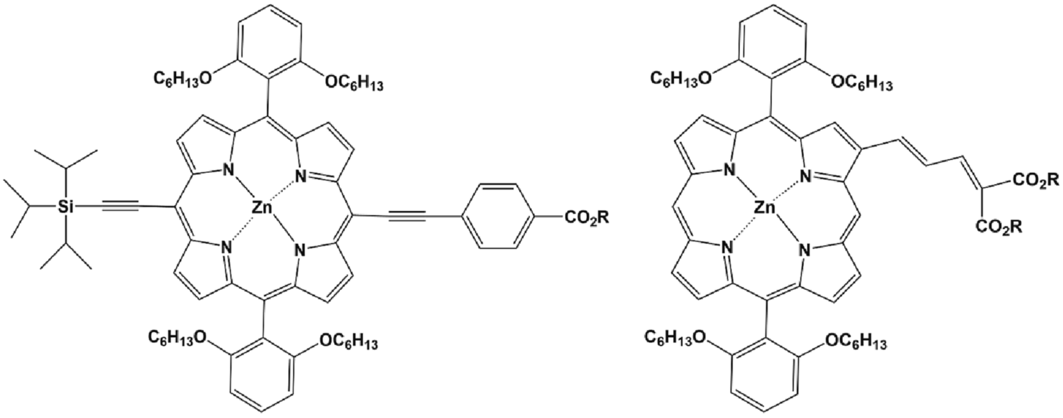
3.2. Dye degradation

Photoexcitation of porphyrins or metalloporphyrin derivatives generates an extremely high quantum yield of singlet oxygen thanks to their high extinction coefficient in visible light. As a result of this property, oxidation reactions are among the many applications of photocatalysis. However, homogeneous catalysis has the disadvantage of making it difficult to recover and reuse catalysts. It also has problems with intermolecular self-oxidation, dimerization, and decomposition during the reaction and high preparation costs. Porphyrin can easily be immobilized on a solid surface to overcome these problems. There are many reasons why ZnO is an excellent choice to be used as a support material, including its high surface area, excellent electrical properties, uniform dispersion in water, and photostability.

It has been demonstrated that a composite (ZnO/TAPPI-CoTPPS), composed of ZnO microrods and nano-hetero-aggregates consisting of tetrakis(4-trimethylaminophenyl) porphyrin (TAPPI) and tetrakis(4-sulfonatophenyl) porphyrin cobalt, can be prepared through a simple mixing procedure [92]. As demonstrated by the optical properties of the composite, ZnO and porphyrin hetero-aggregates have a strong interaction, which is responsible for electron transfer. The optical properties of the composite, which are responsible for the electron transfer from Por* to ZnO, indicate that ZnO is strongly bonded to porphyrin hetero-aggregates. In addition, RhB photodegradation was studied under visible light using a 1000 W halogen–tungsten lamp positioned parallel to the quartz tank and fitted with a 420 nm cut-off filter. The light source and the quartz vessel were separated by 18 cm. Compared with unmodified ZnO, porphyrin-modified ZnO is more active under visible light. As a result, electrons are injected into the CB of ZnO from the excited state of porphyrin, preventing electron-hole recombination.

A reflux method was successfully used to synthesize *meso*-tetrakis(4-carboxyphenyl) porphyrin TCPP/$ZnFe_2O_4$@ZnO nanocomposites with improved photocatalytic performance [93]. To accomplish this, mixtures of $ZnFe_2O_4$ and zinc salt were mixed to form a $ZnFe_2O_4$@ZnO core–shell, which was then immobilized with porphyrin in order to increase its photocatalytic activity. As can be seen in Fig. 13, TCPP plays a crucial role in the degradation mechanism. Since the CB level of $ZnFe_2O_4$ is lower (0.9 eV) than that of ZnO, the photogenerated electrons in the CB can move to that of ZnO within the CB of $ZnFe_2O_4$. At the same time, photo-generated holes are being transferred from the VB of $ZnFe_2O_4$ to that of ZnO by photo transfer. The probability of electron-hole recombination is reduced as a consequence. Furthermore, the TCPP generates electrons in visible light irradiation, which facilitates the process of photodegradation. ZnO reduces molecular oxygen via photoexcited electrons to produce hydroxyl radicals and superoxide radicals, both capable of degrading water. With the introduction of copper (II) porphyrin to the surface of ZnO, Wan-jun Sun and colleagues have demonstrated the enhanced photocatalytic degradation of Rhodamine B under UV–VIS and visible light conditions [94].

SnTCPP, a tin porphyrin, was used to functionalize ZnO nanorods as a photosensitizer, and methyl orange degradation was conducted to assess their catalytic activity [95]. Under visible light irradiation in



1 (a) R = H
(b) R = K

2 (a) R = H
(b) R = Li

Fig. 12. The structure of the meso- and beta-tethered porphyrin dyes [89].

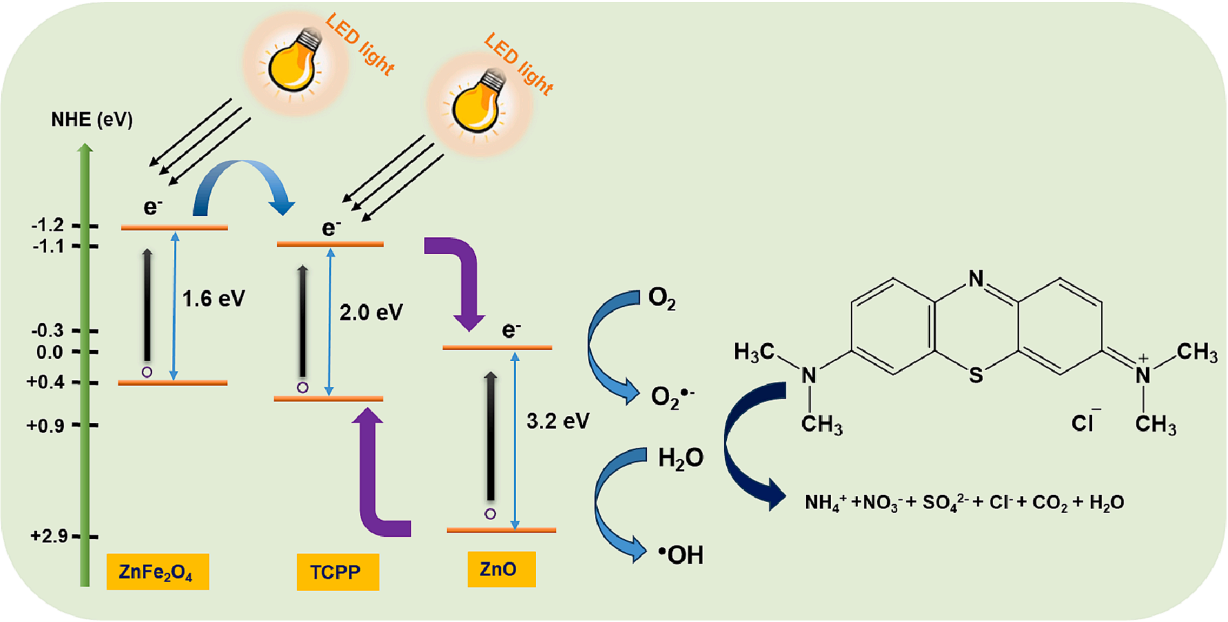


Fig. 13. The possible mechanism of MB and 4-NP photodegradation by TCPP/$ZnFe_2O_4$@ZnO Composite [93].

ethanolamine, which serves as a hole catcher, the photoreduction of graphene oxide to graphene was also conducted to determine the photoactivity of the SnTCPP/ZnO combination (Fig. 14). With light irradiation of SnTCPP/ ZnO, the VB electron is driven to the conduction band, leaving a hole in VB. Simultaneously, electron-hole pairs are formed in the SnTCPP complex. When SnTCPP photoexcites electrons, they migrate to the CB of ZnO, where the highly electron-affine GO sheets catch them. Photogenerated electrons diminish oxygen functional groups on GO sheets. In addition, the holes contribute to ethanolamine oxidation.

Krishnakumar *et al.,* [96] demonstrated the use of amino porphyrin and SiO_2 combined with ZnO to degrade naphthol blue black (NBB). Despite SiO_2 being an insulator, they combined 70% SiO_2 with 30% ZnO for photocatalytic applications such as azo dye degradation. It was shown that naphthol blue black (NBB) was degraded by using the produced SiO_2-ZnO coupled with 5,10,15,20-*meso*-tetra-(*para*-amino)-phenyl-porphyrin (TPAPP) in both direct sunlight and visible light. As a coupling agent, glycidoxypropyltrimethoxy silane (GPTMS) was used before the formation of the TPAPP/SiO_2-ZnO composite. There has been a proposed mechanism for NBB degradation in sunlight that involves TPAPP/SiO_2-ZnO (Fig. 15). Apparently, the catalyst can be reused.

In recent years, metallothioporphyrzine (MPz) has also gained increasing interest in photocatalysis research. MPz is a macrocyclic porphyrin compound with sulfur-containing groups at the periphery, which has distinct physical and electrical properties [9,10]. In a recent study, Lan Cao *et al.,* [97] reported that coupling ZnO with CoPz$(hmdtn)_4$ enhanced the photocatalytic performance of ZnO by combining their advantages. In combination with ZnO, CoPz$(hmdtn)_4$ and ZnO exhibit synergistic photocatalytic activity that is significantly higher than pure ZnO and pure CoPz$(hmdtn)_4$. In addition, the XPS study suggested that CoPz(hmtn)4 and ZnO may have strong contact. According to the results of the reusability test, ZnO/CoPz$(hmtn)_4$ can maintain a strong photocatalytic activity for five cycles with exceptional stability. In another study, Tan *et al.,* [98] utilized iron tetra(2,3-bis

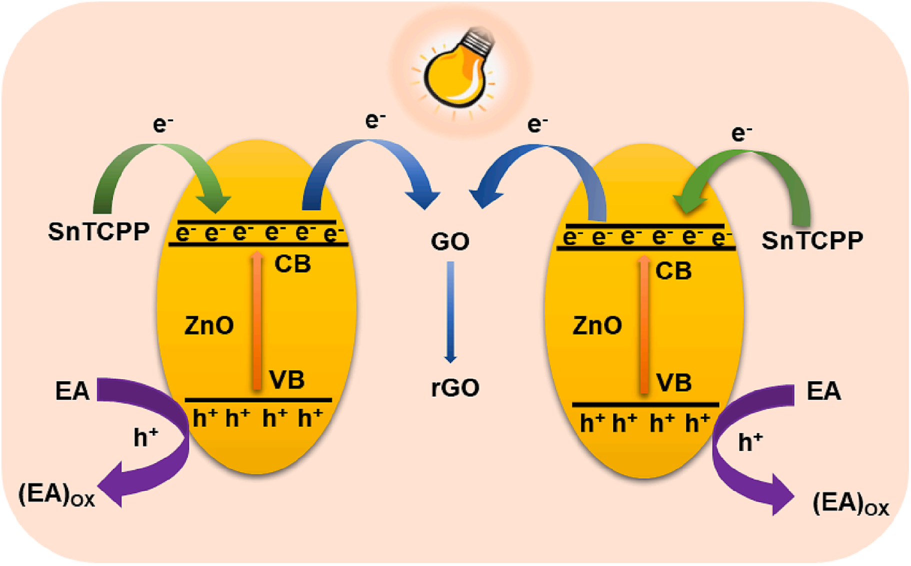


Fig.14. Schematic illustration of the photoreduction process of GO to rGO using SnTCPP/ZnO [95].

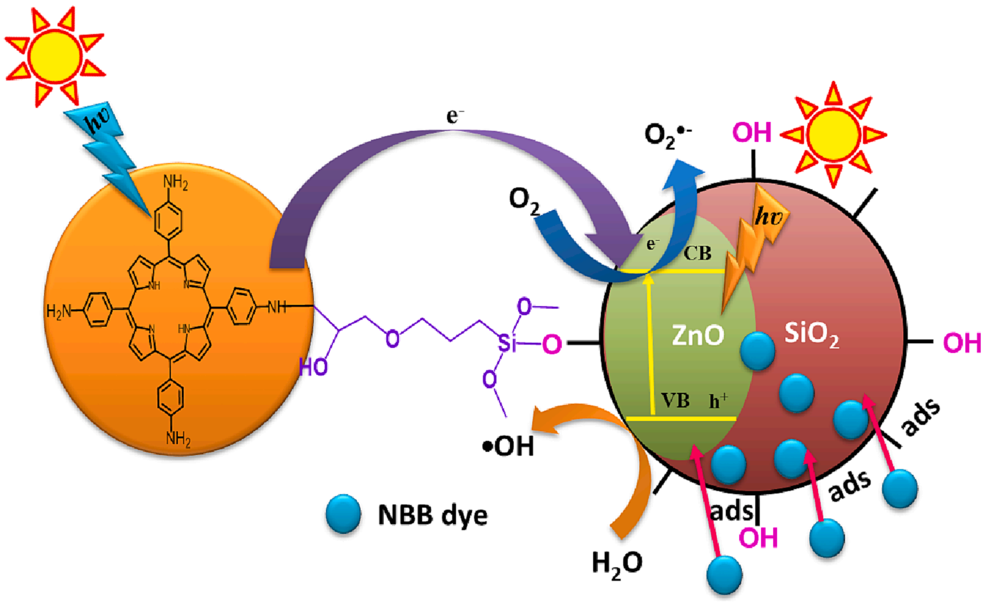


Fig. 15. Mechanism of degradation of NBB by TPAPP-Si/Zn [96].

(butylthio)maleonitrile)porphyrazine (FePz) (Fig. 16) in conjunction with ZnO in order to prepare a composite photocatalyst that selectively oxidized glycerol to oxygenated products including dihydroxyacetone and glyceraldehyde at mild reaction temperatures. With ESR tests, they determined that ZnO/FePz composite produced high OH, O_2, and $^1O_2$ signals during light irradiation, which was consistent with scavenger experiments.

Ying-Xin Feng *et al.,* [99] explored another method to assemble multiporphyrin arrays layer by layer on nano ZnO particles using coordinative bonds. Consequently, nano ZnO@(Pd-TPyP)n hybrids can be synthesized, which can be controlled on a molecular scale and have a thickness of several nanometers. Rhodamine B (Rh B) and phenol were degraded more effectively with these hybrid semiconductors when irradiated with ultraviolet and visible light, particularly under visible light conditions. It was demonstrated that excited porphyrin macrocycles transferred energy to the conduction band of nano ZnO by the nanohybrid's photophysical properties.

An innovative reprecipitation self-assembly process was developed, which uses ZnO nanoparticles and a monomeric tetrakis(4-carboxyphenyl) porphyrin (TCPP) precursor to produce ZnO/porphyrin nanofiber composites. Porphyrin aggregates and ZnO nanoparticles are shown to enhance charge separation, which boosts photocatalytic activity by capturing photons across the entire visible spectrum.

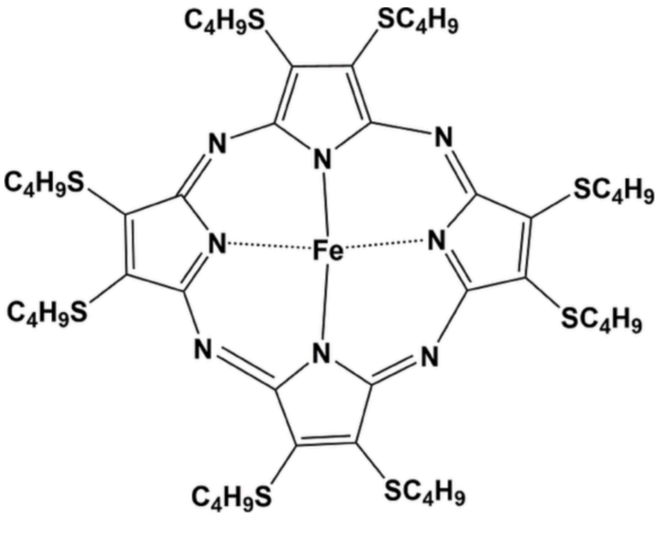


Fig. 16. Molecular structure of FePz [98].

3.3. Photo-electrocatalytic applications

The development of hybrid thin films of crystalline ZnO modified by 5,10,15,20-tetrakis(4-sulfonatophenyl) zinc (TSTPPZn) and 2,9,16,23-tetrasulfophthalocyaninatozinc(II) (TSPcZn) was achieved by electrochemical deposition from aqueous zinc salt solutions [100]. An acetonitrile-based solution with I^{3-}/I^{-} as the redox electrolyte was used to study the photoelectrochemical properties of the electrodes. Photocurrent spectra and time-resolved photocurrent measurements were used to examine the electrochemical properties of the electrodes. In the presence of both sensitizers, panchromatic sensitization could be achieved simultaneously.

Hayashi *et al.,* [101] demonstrate how organic/inorganic ternary composites can be used to transfer electrons between semiconducting electrodes without adversely affecting their respective donor–acceptor properties (porphyrin, ZnO NPs, rGO). With a photon-to-current conversion efficiency of up to 70%, the hierarchical electron transfer cascade system creates extraordinarily high photocurrents. It has been shown that a multistep electron transfer (ET) system can effectively generate photocurrents when porphyrin (ZnP), zinc oxide nanoparticles (ZnONP), and reduced graphene oxide (RGO) are used as donors and acceptors (Fig. 17). The electrophoretically deposited film of ZnP, ZnONP, and RGO on the FTO/SnO_2 electrode, compared to the reference device without RGO sheets and ZnONP, exhibited impressive photocurrent generation (IPCE = 70%). Similarly, in another study, Hironobu Hayashi *et al.,* [102] investigated the effect of fullerene monolayers formed between porphyrin-fullerene composite multilayers and ZnO nanorods on the efficiency of generating photocurrents in composite multilayers.

Using dye-sensitive solar cells as well as fundamental studies, Düring *et al.,* [103] examined how ZnO nanoparticles are associated with TCPP. In order to adjust the size of the network assembly that results, one parameter is the size of the ZnO nanoparticles. Other variables that influence the size of an assembly include the ratio of TCPP to ZnO as well as the growth duration. It was found that ZnO nanoparticles with sizes ranging from 2.6 to 4.0 nm can be interconnected using *meso*-tetra(4-

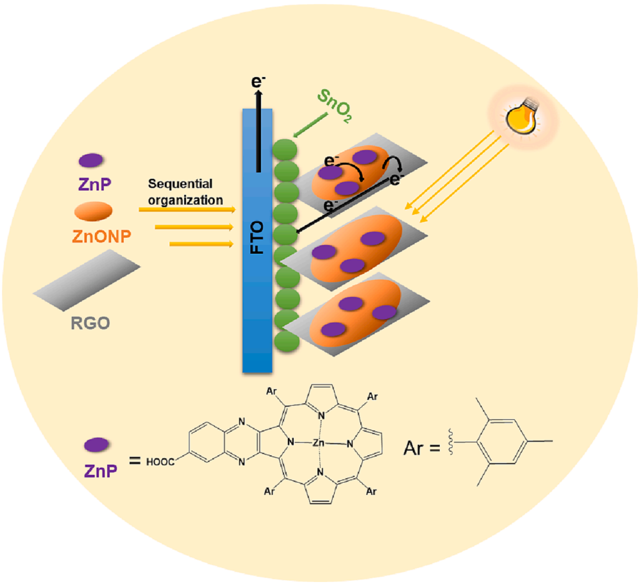


Fig.17. Hierarchical electron cascade system on an electrode [101].

carboxyphenyl)porphyrin (TCPP), which results in the formation of distinct ZnO-TCPP networks with lateral dimensions ranging from 50 to 800 nm. These ZnO-TCPP networks were examined as photoactive top layers in dye-sensitive solar cells (DSSC) constructed with TiO_2 and ZnO. ZnO-TCPP networks can improve the efficiency of TiO_2- and ZnO-based electrodes by 10% and 46%, respectively, when placed on top of semiconductor electrodes.

3.4. *Sensors*

As a result of the optical, electrical, and chemical characteristics of porphyrins and ZnO, new classes of materials are produced for chemical sensing [46,104–115]. Porphyrins and ZnO have specific properties that influence chemical sensitivity, which is influenced by their form as well as their specific characteristics. It is possible to control this at the synthesis level. Further, porphyrin-functionalized organic components have the potential to affect semiconductor conductivity even though they are not themselves conductive. When an electron donor molecule is absorbed, the same mechanism is activated in dye-sensitized solar cells. ZnO is enhanced in conductivity and band bending is decreased due to porphyrins transporting photoelectrons to it. Porphyrins are nearly depleted of electrons in their highest-occupied molecular orbital (HOMO) level under visible light, so electrons can be transferred more efficiently from the absorbed molecule. Most notably, the sensitivity rises in visible light and when electron donor species are present (e.g. amines).

In a study by Yuvaraj Sivalingam *et al.,* [105], copper and manganese porphyrins coated on ZnO nanorods were evaluated for their ability to detect a thiolated biomolecule like l-cysteine. A straightforward one-pot approach was used to form metalloporphyrin-coated ZnO nanostructures by adding porphyrins directly to the solution used to grow the ZnO nanostructures on the ITO substrate. The concentration of l-cysteine in water was measured using an amperometric measurement setup. An analysis of I/V curves obtained by scanning the potential range from 0 to + 1.1 V can be conducted by chemometrics in order to determine their entire characteristics. Sensor responses are highly reliable and efficient when analyzed from the standpoint of the first principal component. In both materials, visible light affects their first principal component. Electron density in the porphyrin layer is depleted during illumination, allowing l-cysteine molecules to interact.

Zinc oxide nanoparticles produced hydrothermally and subsequently hybridized with 5-(4-carboxyphenyl)-10,15,20-triphenylporphyrin (ZnTPP) have been reported to serve as carbon monoxide sensors [106]. It has been demonstrated that porphyrin-functionalized ZnO nanorods are useful in detecting volatile organic substances, including trimethylamine and ethanol [111]. The initial steps were to grow ZnO in the ITO substrate and then to hybridize it with 5-($4'$-Carboxyphenyl)-10,15,20-triphenylporphyrin (H2TPPCOOH). SEM images of porphyrin-coated and uncoated ZnO were analyzed to determine their morphology in Fig. 18. There are clusters of porphyrins tens of nanometers in size. In terms of appearance, the ZnO nanorod can be described as a wurtzite structure grown along the c-axis. According to the SEM image, these nanorods are 50–100 nm in diameter and 2–3 cm long. The photoconductivity of the porphyrin-coated ZnO nanorod is significantly higher than that of ethanol when it is exposed to triethylamine. Porphyrins, despite their low selectivity, can produce electric signals when particles are transferred from an adsorbed molecule to the porphyrin during these interactions. This opens a motivating opportunity to enhance porphyrin-based sensors' selectivity.

3.5. *Photodynamic therapy*

The development of phototherapy including photodynamic and/or photothermal treatments by porphyrin-inorganic hybrid materials has gained attractive research in the current scenario [116–118]. Senthilkumar *et al.,* [119] reported an antimicrobial photodynamic therapy (aPDT) could be delivered using zinc oxide nanomaterials loaded with *meso*-tetra (4-sulfonatophenyl) porphyrin (TSPP). The inactivation of *E. coli* over nanostructured ZnO, ZnO/TSPP, and TSPP following dark conditions and visible light illumination have been conducted. A significant difference has not been observed between nano ZnO, nano TSPP, and nano ZnO/TSPP in the absence of visible light when it comes to inactivating *E.coli*. In contrast, ZnO nanomaterials were not significantly effective in inactivating *E. coli* under visible light, and TSPP only showed 30% inactivation. It was observed, however, that nano ZnO–TSPP showed significantly greater antibacterial activity (i.e. 98%) under visible irradiation compared to ZnO nanomaterials and TSPP alone. This specifies that the synergistic effect of nano ZnO/TSPP performs a vital role in the enhancement of antibacterial activity. The irradiation of visible light could effectively induce the formation of singlet oxygen on nanosized ZnO particles and further attack their cell membrane, leading to their destruction, which allows TSPP molecules to enter cells and enhance photodynamic effects.

3.6. *H_2 production*

We have presented here all current findings concerning hydrogen production using porphyrin/ZnO hybrid photocatalytic systems, where one or more of the fundamental components is not in the same phase as the catalyst, electron donor, or electron acceptor. As reported by Yuan *et al.,* [120], zinc porphyrin-sensitized hydrogen production from the water was achieved by using MoS_2/ZnO treated under visible light, with triethanolamine acting as a sacrificial reductant. For the production of composites of ZnTCPP/MoS_2/ZnO, two steps had to be followed. As a first step, MoS_2/ZnO composites (with varying MoS_2 contents) were synthesized, and the second step involved treating them with an aqueous solution of ZnTCPP. The prepared materials have been characterized and used for H_2 production from water splitting. For comparison purposes, ZnTCPP/Pt/ZnO composites (with different Pt content) were prepared and used for the same applications (Fig. 19). At 2.0 wt%, ZnTCPP-Pt/ZnO photocatalysts can afford 67 mmol h^{-1} g^{-1} of water evolution, a lower rate than with ZnTCPP-MoS_2/ZnO at 0.50 wt% (75 mmol h^{-1} g^{-1}).

According to Xi *et al.,* [121], photo-generated electron transfer was more efficient in the ZnO NR nanocomposite implanted with Cu nanoparticles and anchored with sulfonyl groups for the porphyrin. Using copper-implanted ZnO nanorods and 4,10,15,20-tetrakis(4-sulfophenyl) porphyrins (TSPP), composite photocatalysts were prepared. Copper in

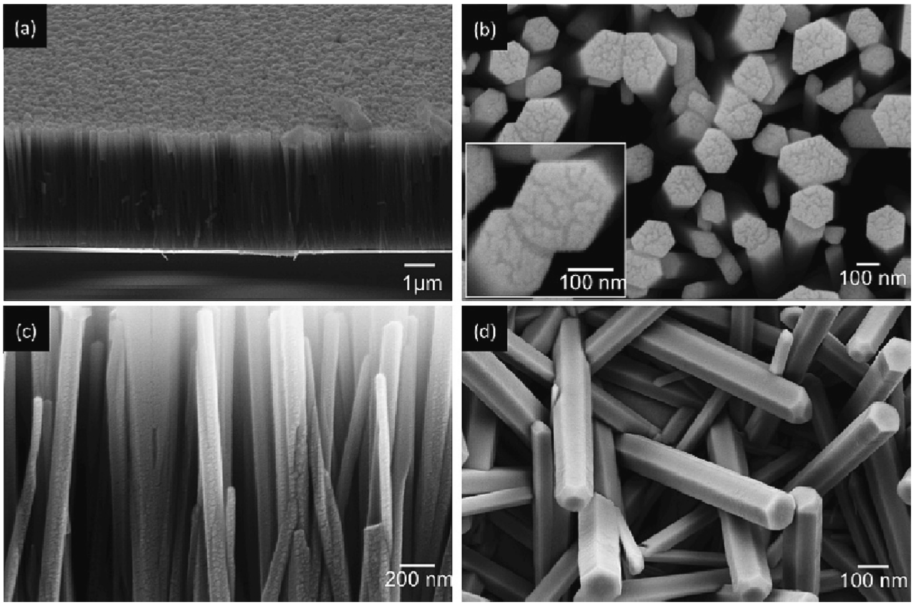


Fig.18. SEM images of the sensor surface, (a) 45° tilted view of uncoated ZnO nanorods grown on the flat ITO surface, (b) Top view of porphyrin-coated nanorods, (c) Lateral view of porphyrins-coated nanorods, and (d) Top view of coated ZnO nanorods in the gap region between the ITO electrodes [111], copyright © 2012, American Chemical Society.

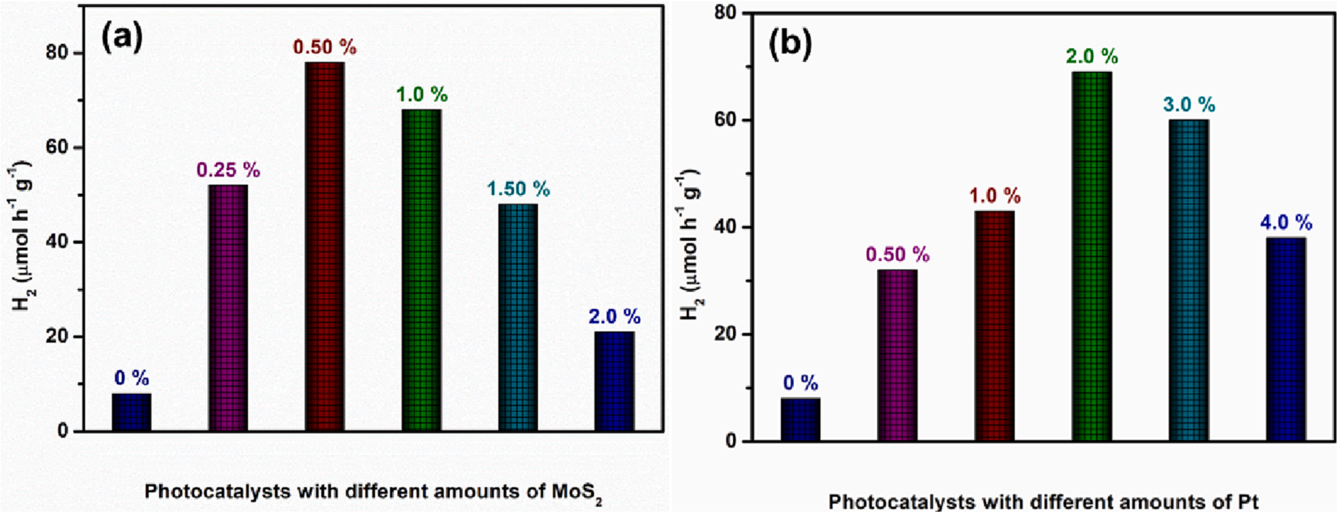


Fig.19. (a) Photocatalytic H_2 evolution over ZnTCPP-MoS_2/ZnO (b) Photocatalysts (ZnTCPP-Pt/ZnO) loaded with different amounts of cocatalyst in 0.2 M TEOA aqueous solution under visible light irradiation (λ > 420 nm) [120].

the nanocomposite can act as electron channels and active centers, and promote the separation of charges based on detailed studies of charge transport and photocatalytic mechanisms. Nanocomposite photocatalytic activity was significantly affected by the amount of TSPP present, with an optimal TSPP content of 6.67 wt%. Additionally, the composites proved to be stable when recycled.

As an investigation of the effects of nitridation conditions on gallium-zinc oxynitride solid solution (GaN:ZnO), Hagiwara *et al.,* [41] explored Cr-TPPCl porphyrin-modified photocatalysts (GaN:ZnO). The UV–visible absorption spectra of GaN:ZnO powders are identical. Nevertheless, dye-modified GaN:ZnO photocatalysts exhibit varying water-splitting activities based on their composition and gas generation rates. With a Zn content of approximately 15%, a formation rate of 21 to 42 Âμmol per hour was achieved.

4. Conclusions and future trends

Nanomaterials of new varieties have made it possible to develop organic–inorganic hybrid materials at a rapid pace. There are several areas of research in this field, which bridge different types of chemistry (organic, inorganic, and coordination chemistry) to materials science and allow for multiple possibilities of application. Nowadays, the design and synthesis of semiconductors hybrid materials containing a semiconductor (ZnO) and an organic molecule (porphyrins), synthesis, charge transport properties, and band alignment of porphyrin/ZnO hybrids and their various applications is an important scientific area. Due to its advantageous properties in terms of its broad band gap, as well as its excellent thermal, chemical, and structural properties, zinc oxide is one of the most popular materials for electrical, optical, and piezoelectric applications. Due to their superior properties as photo-sensitizers for semiconductors, porphyrin derivatives are excellent candidates for the synthesis of new organic–inorganic hybrid materials. A wide range of biomedical energy and environmental applications are seeking to utilize the optical properties of structures that combine inorganic nanoparticles with organic molecules, such as sensors, solar cells, photodegradation, and photodynamic therapy. In these applications, the transfer of energy between photoexcited nanoparticles and organic molecules is of utmost importance. The purpose of this review is to present a comprehensive overview of some fundamental issues related to porphyrin/ZnO hybrids, as well as highlight some of the advances made in the field of improving their surface and electronic structure.

CRediT authorship contribution statement

Krishnakumar Balu: Conceptualization, Visualization, Writing – original draft. **Selvam Kaliyamoorthy:** Writing – original draft, Investigation, Software, Validation. **Mani Durai:** Methodology, Investigation. **António Aguiar:** Writing – review & editing. **Margarida C.M. Sobral:** Investigation, Software. **I. Muthuvel:** Investigation. **Sakthivel Kumaravel:** Visualization, Investigation, Software. **Balakrishna Avula:** Writing – review & editing. **Abilio J.F.N. Sobral:** Validation, Supervision. **Young-Ho Ahn:** Validation, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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