Conducting polymers/zinc oxide-based photocatalysts for environmental remediation: a review

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Abstract

The accessibility to clean water is essential for humans, yet nearly 250 million people die yearly due to contamination by cholera, dysentery, arsenicosis, hepatitis A, polio, typhoid fever, schistosomiasis, malaria, and lead poisoning, according to the World Health Organization. Therefore, advanced materials and techniques are needed to remove contaminants. Here, we review nanohybrids combining conducting polymers and zinc oxide for the photocatalytic purification of waters, with focus on in situ polymerization, template synthesis, sol–gel method, and mixing of semiconductors. Advantages include less corrosion of zinc oxide, less charge recombination and more visible light absorption, up to 53%.

Keywords Conducting polymers · Zinc oxide · Photocatalysis · Environmental remediation · Polyaniline · Poly(o-phenylenediamine)

Abbreviations

AB25	Acid blue dye
AMP	Amino phenol
AOT	Diocetyl sodium sulfosuccinate
APS	Ammonium persulfate
AR	Alizarin red
AR249	Acid red 249

AV	Acid violet
BB	Bismarck brown
CBB	Coomassie brilliant blue
CDs	Carbon dots
CN	Carbon nitride
COVID	Coronavirus disease
CPs	Conducting polymers
CR	Congo red
CV	Crystal violet
DB	Direct black
DCF	Diclofenac
DMF	Dimethylformamide
DMSO	Dimethyl sulphoxide
DSC	Differential scanning calorimetry
17 β ED	17- β Estradiol
FAC	Fly ash cenosphere
FTIR	Fourier transform infrared spectroscopy
GA	Gemifloxacin antibiotic
GFM	Gemifloxacin
HQ	Hydroquinone
IM	Imidacloprid
HRP	Horseradish peroxidase
MB	Methylene blue
MG	Malachite green
MO	Methyl orange
MIP	Molecular imprinted polymer
MNZ	Metronidazole
NMP	N-methyl pyrrolidone

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NMR	Nuclear magnetic resonance
OLEDs	Organic light-emitting diodes
OAA	Ortho-anthranilic acid
OAP	Ortho-aminophenol
OPD	Ortho-phenylenediamine
OTD	Ortho-toluidine
PAM	Poly(azomethine)
PAN	Polyacrylonitrile
PANI	Polyaniline
PAP	Para-aminophenol
PAZ	Poly(azomethyne)
PEDOT	Poly (ethylene dioxythiophene)
PEG	Poly (ethylene glycol)
PNA	Polynaphthylamine
POPD	Poly(ortho-phenylenediamine)
PPD	Poly(phenylenediamine)
PPPD	Poly (para-phenylenediamine)
PPY	Polypyrrole
PTH	Polythiophene
RB	Rhodamine B
R6G	Rhodamine 6-G
RO	Reactive orange
RR	Reactive red
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscope
TC	Tetracycline
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
UV	Ultraviolet
WHO	World Health Organization
XRD	X-ray diffraction

Introduction

“It isn't pollution that's harming the environment, it's the impurities in our air and water that are doing it”, a well famous quote by Dan Quayle, Former US Vice President, best suits on today's situation where air and water get contaminated by several impurities due to anthropogenic activities. According to WHO (World Health Organization), the half population of the world will be forced to live in water-stressed areas by 2025. Contaminated water is directly associated with the cause of various disease transmissions such as cholera, hepatitis A, typhoid fever, diarrhea, lead poisoning, and COVID-19 (Organization 2020; Sharma et al. 2020; Ferreira et al. 2021; Huo et al. 2021; Lahrich et al. 2021). Nowadays, environmental remediation for polluted water due to organic pollutants, residual dyes from some industries and textiles, toxic metals incorporation in natural water resources is of great concern (Akpomie and Conradie 2020; Bhavya et al. 2021). Contaminated water

has thoughtful consequences for living organisms as well as for the ecosystem; hence, an alarm has been raised for the scientific community to work for the removal of the organic contaminants before their discharge into the environment (Durgalakshmi et al. 2020; Hussain et al. 2021).

A lot of review articles are given for materials and methods which have been cast-off for the degradation and adsorption of those organic contaminants (Crini 2021; Kumar et al. 2021; Ponnuchamy et al. 2021; Vishnu et al. 2021). During the last few decades, heterogenous photocatalysis has been expanded rapidly for environmental remediation due to its simple design, stability, low set-up cost, and whole mineralization of pollutants into safe by-products (Luo et al. 2019; Madima et al. 2020). Water and air purification, solar water splitting are the most widely investigated fields in photocatalysis (Ke et al. 2018). Photocatalysis is used for the rapid and efficient destruction of environmental pollutants by using non-toxic semiconductors. This is also known as artificial photosynthesis in which sustainable chemistry plays a major role in resolving environmental and energy issues. This is a five-step process: (i) transfer of the reactant to the surface in the fluid phase, (ii) adsorption of reactant at the surface of the semiconductor, (iii) reactions in the adsorbed phase, (iv) decomposition or desorption of the products and finally (v) removal of the by-products at the interface region. The process is almost similar in conventional catalysis and heterogenous photocatalysis but the only difference is step (iii) in which mode of activation is changed to photonic activation in the case of heterogeneous photocatalysis and thermal activation in the case of conventional catalysis (Herrmann 1999; Kanamarlapudi et al. 2018).

For photocatalysis, inorganic semiconductors such as zinc oxide (ZnO) (Miranda et al. 2016; Acuña et al. 2017; Suresh et al. 2018), TiO₂ (Nakata and Fujishima 2012; Pradenas et al. 2019), CdO (Amita et al. 2019), CdSe (Hiragond et al. 2018) and MoS₂ (Li et al. 2018) showed immense potential and revealed noteworthy physicochemical and electronic properties applicable in photochromism and photovoltaics (Miranda et al. 2016). These inorganic semiconductors possess an empty conduction band and filled valence band in their ground state, when these are excited by more energy than their bandgap, the formation of excitons (holes in valence band and electrons in conduction band) occurs in the photocatalysis process (Talaiekhazani et al. 2020; Subudhi et al. 2021).

Among inorganic oxides, ZnO is one of the most extensively investigated photocatalytic semiconductors because of its unique features such as abundance, low toxicity, eco-friendly and cost-effectiveness (Yashni et al. 2020; Albiter et al. 2021). It has 60 meV excitation binding energy and 3.37 eV of direct wide bandgap at room temperature (Sharma 2020). Although in terms of eco-friendly and relative less toxicity, ZnO is a much better photocatalyst

as compared to TiO_2 , CdO , CdSe , etc., however, on large scale, its practical applications are not that much appreciable because of reabsorption of photogenerated charge carriers at a high extent (Bera et al. 2019). These electron holes recombination favored the depleted quantum yield, and the absorption occurs only in the ultraviolet region due to the wide band gap of the semiconductor. The activation of ZnO nanoparticles occurs mainly in the ultraviolet region of the spectrum; hence, its use in sunlight irradiation is narrow. Therefore, shifting the absorption wavelength to the visible or near-infrared region is needed for improving its performance under solar irradiation. Also, ultraviolet radiations are harmful to the humans and environment (Bomila et al. 2019).

To overcome this problem, many efforts have been done in the field of modification of the surface of ZnO nanoparticles by numerous materials such as anionic and cationic doping, rare earth doping, co-doping, and couple semiconductor. In this regard, nanohybrids synthesized by conducting polymers and semiconductors have attracted a lot of attention from researchers (Sandoval et al. 2019). To achieve good charge separation efficiency along with good charge transfer, the nanohybrids of ZnO with conducting polymers such as polyaniline (Mozafari and Chauhan 2019; Deng et al. 2020), polyphenylendiamine (Khokhar

et al. 2020a, 2021), polypyrrole (Jadoun et al. 2018), poly(1-naphthylamine) (Jadoun et al. 2017b, c) having unique thermal, optical, electrical, mechanical, biomedical and catalytic properties which have been extensively employed in photocatalysis for degradation of organic contaminants, dyes, and reduction of toxic metals. Here, conducting polymers act as a sensitizer for ZnO nanoparticles. Energy levels of conducting polymers match with the ZnO and both can be excited by visible light to produce photogenerated carriers, Fig. 1 (Ghosh 2021). Consequently, they can absorb appropriately sunlight for solar photocatalysis to improve sustainability. Therefore, it is preferable and economical with the use of nanohybrid photocatalyst of conducting polymers and ZnO for rapid and efficient destruction of environmental pollutants (Riaz et al. 2015).

Here, we review the various nanohybrids comprising conducting polymers and ZnO which are specially synthesized for efficient photocatalysis to overcome the photo-corrosion tendency of ZnO and inactivation under ultraviolet light illumination occurred in hollow ZnO core/ ZnS shell structure (Yu et al. 2015), while this drawback was overcome by using polyaniline in form of nanohybrids of polyaniline/ ZnS/ZnO in which no reduction of photocurrent was achieved and photo-corrosion was inhibited by using polymer (Kim et al. 2020).

Fig. 1 Conducting polymers/zinc oxide-based photocatalysis for environmental remediation including the bandgap and transfer of electrons for complete photocatalysis by nanohybrids. Here, the conducting polymers possess low band gap of 2–2.5 eV, while ZnO has wide

band gap and shows synergistic relation to each other for transfer of electrons. CB: conduction band; VB: valence band; HOMO: highest occupied molecular orbital; LUMO: Lowest unoccupied molecular orbital; CPs: conducting polymers; ZnO : zinc oxide

Photocatalysis

The combination of photochemistry and catalysis is known as photocatalysis. Photocatalysis involves the light and catalyst simultaneously to boost any chemical reaction (Iervolino et al. 2020; Rueda-Marquez et al. 2020). The phenomena of photocatalysis were firstly discovered by *Fujishima* and *Honda* in 1972 on TiO_2 surface by water splitting under ultraviolet light and referred to as Honda–Fujishima Effect (Fujishima and Honda 1972; Hashimoto et al. 2005). However, electrochemists initially discarded this event due to their thought about the generation of oxygen is not possible at low voltage. They mentioned that electrolysis of water occurs at a minimum of 1.5–2 V. Afterthought, wide research was carried out by researchers in various fields and came to know that these studies were associated with renewal and storage of energy. With his discovery of such a photocatalyst, Prof. Fujishima said for the society “The primary objective of science and technology is to create a society where people can have healthy, comfortable, and long lives. The crucial thing in science and technology is to develop a new concept that can be applied to actual products and services, and these new products and services will eventually make people happy” (Fujishima et al. 2000). From that time photocatalysis was rapidly grown for the degradation of contaminants in wastewater (Fujishima et al. 2008).

Generally, photocatalysis is a light-induced redox reaction in which the surface of the catalyst is exposed to the light source to excite the valence band electrons and transferred to the conduction band, leaving a hole in the valence band. The hole in the valence band can oxidize the water molecules by creating hydroxyl radicals and excited electrons in the conduction band can reduce the absorbed oxygen on the surface of the photocatalyst. Additionally, the photogenerated holes can directly oxidize organic matter (Palominos et al. 2008).

The redox process occurred at the surface of the catalyst. The absorbed water remains on the photocatalyst surface, and it is oxidized by the holes (present in the valence band after excitation of the electron to conduction band) resulting in the hydroxyl radicals ($\cdot\text{OH}$). The hydroxyl radicals further come in contact for reaction with organic contaminates, and after radical chain reactions, the organic contaminants degrade in carbon dioxide and water. This whole process is known as the oxidation process. In the reduction process, the oxygen reacts with electrons present in the conduction band to produce superoxide anions which further attach to the intermediate products of oxidative reaction to produce peroxide or convert to hydrogen peroxide to water. In organic matter, the reduction is much easier than water, and hence, the number of positive holes

increased with the increment of concentration of organic matter which decreases the recombination of charges and increases the photocatalysis (Saravanan et al. 2017).

To overcome the recombination of charge carriers during photocatalysis, semiconductors are combined with conducting polymers possessing a low bandgap and absorb light in both ultraviolet and visible regions. The nanohybrids possessed two distinct energy levels to play a key role in charge separation. In nanohybrids of conducting polymers and ZnO, conducting polymers absorb a wide range of visible light and act as a photosensitizer due to having a lower bandgap of conducting polymers compared to the ZnO. The electrons which reached from HOMO (highest occupied molecular orbital) to LUMO (lowest unoccupied molecular orbital) of conducting polymers by excitation are finally transferred to conduction band of ZnO and react with the molecular oxygen to produce $\text{O}_2^{\cdot-}$, while the holes in HOMO (highest occupied molecular orbital) of conducting polymers react with water to produce $\cdot\text{OH}$ to increase the efficiency of photocatalysis. Therefore, photocatalysis using the nanohybrids with various combinations of conducting polymers and ZnO seems to be the best alternative to remove the water pollutants/dyes by inhibiting the possibility of recombination of charge carriers and enhancing the potential for redox reaction at the surface of photocatalyst.

Synthesis of conducting polymer/zinc oxides composites

There are various methods to synthesize conducting polymers/ZnO nanohybrids for active photocatalysis which are as follows.

In situ polymerization

In situ polymerization is one of the best and successful techniques for the preparation of nanohybrids, to attain great interfacial interactions between conducting polymers and ZnO and it means “in the polymerization mixture.” In this method, polymer nanohybrids are achieved via the mixing of semiconductor in a solution containing monomer followed by polymerization, and at the same time, semiconductor and matrix make the covalent linkage (Abinaya et al. 2019; Mittal et al. 2019). In situ polymerization starts with the initiation step followed by many polymerization steps resulting in the formation of nanohybrids. The addition of an initiator or oxidizing/reducing agent starts the polymerization reaction by this homogenous mixture when exposed to any heat, radiation, etc., followed by washing and drying of nanohybrids. On completion of the polymerization reaction, a polymer nanocomposite is fashioned consisting of the

bonding between polymer and nanoparticle (Abinaya et al. 2019; Mittal et al. 2019).

Several research articles included in situ polymerization method for synthesis of conducting polymers/ZnO as it is an easy method without any hurdles (Demir et al. 2006; Ameen et al. 2011; Ramesan et al. 2017; Ponnammam et al. 2019). Gilja and coworkers (Gilja et al. 2018) synthesized polyaniline/ZnO nanocomposites in various ratios by using the same method at room temperature with water and diethylene glycol mixture at neutral pH. ZnO nanoparticles were taken in solution, and aniline monomer was added in the same mixture followed by oxidizing agent ammonium persulphate. The concentration of diethylene glycol was taken 0.02, 0.024, and 0.04 M, while the molar ratio of aniline (monomer) and oxidant was taken 1:0.25, aniline, and ZnO was taken in a weight ratio of 15:85. Initially, a fixed amount of aniline, ZnO, and diethylene glycol was taken in a flask containing 25 ml of distilled water and allowed to react for 15 min at ultrasonicator to achieve stable suspension followed by the addition of ammonium persulphate to start polymerization, and the reaction was carried out for 2 h. Finally, these were washed several times by water and centrifuged then dried at 60 °C.

Olad et al. (OLAD et al. 2012) also used the in situ oxidative polymerization method to synthesize polyaniline/ZnO nanohybrids with the dispersion of 0.9313 g of ZnO nanoparticles in the presence of 0.01 mol of aniline monomer and 0.01 mol of hydrochloric acid with ammonium persulphate (0.01 mol) as an oxidant. The nanohybrids were able to degrade 82% of methylene blue dye in 60 min. The nanohybrids of poly(p-phenylenediamine) with ZnO were synthesized by Rostami and labmates by using ammonium persulphate as an oxidant. (Rostami et al. 2015). Some other researchers also adopted the same method for the synthesis of conducting polymers/ZnO nanohybrids (Eskizeybek et al. 2012; Haldorai et al. 2014; Sivakumar et al. 2014).

In situ polymerization method has many advantages such as cost-effective materials used in the reaction, easy to handle, and being compatible during various curing and heating methods. Also, strong covalent interaction between polymers and semiconductors occurs using this method.

Sol–gel synthesis

The sol–gel synthesis method can be adopted to change or to improve the properties of nanoparticles (Faisal et al. 2020). For the synthesis of conducting polymers/ZnO nanohybrids via sol–gel preparation method, zinc nitrate was mixed with citric acid to make a solution and stirred for 3 h at 80 °C and metal citrate was formed. The ammonia solution (pH 4.5) was added to the above reaction mixture and stirred continuously for 6 h. After completion of the reaction, a complex of citrate of zinc was formed in the spongy gel form which

was washed several times with acetone and distilled water, further heated for 1 h at 150 °C. The obtained material was ground and calcinated to remove the impurities. After that, the synthesis of polyaniline/ZnO was done by the oxidative polymerization method in which aniline monomer (0.1 M) was mixed with hydrochloric acid (1 M) to produce aniline hydrochloride. In this step, ZnO was added in a fixed amount and 0.1 M ammonium persulphate was added dropwise for polymerization and the temperature of the reaction was maintained at 4 °C using ice. The synthesized sample was washed several times and dried in a vacuum oven for 24 h (Ambalagi et al. 2016). The whole process is shown in form of a flowchart in Fig. 2.

Likewise, Patil and their lab mates adopted the sol–gel synthesis method. Firstly, they prepared polyaniline by using the chemical oxidative polymerization method with 2 ml of aniline monomer in 1.0 M hydrochloric acid. 5.393 g of zinc acetate was used in 40 ml of methanol and stirred continuously at 60 °C for the synthesis of ZnO nanoparticles in gel form. The heating was stopped after 1 h and the reaction was continuous until the white powder was formed. Further, the polyaniline powder previously synthesized was dissolved in *m*-cresol and stirred followed by the filtration of the solution with a few microns size Whatman filter paper. After that, the film of polyaniline was deposited on a glass substrate by spin coating method for 30 s at 2000 rpm and dried at 100 °C on a hot plate, while the filtered solution of polyaniline was allowed to react with various percent solutions of ZnO on stirrer for 11 h to form nanohybrids of polyaniline/ZnO (Patil et al. 2012). The sol–gel method for the synthesis of nanohybrids is simpler and cheaper than others but much time is needed to optimize the stability and durability of sol which is needed to be overcome.

Template synthesis

Numerous nanohybrids of conducting polymers/ZnO were fabricated by using some templates. To get the nanohybrids some post-synthetic procedures are needed to eliminate the template used in synthesis. In this regard, firstly, ZnO nanoparticles were synthesized using sodium dodecyl sulfate as a template via precipitation method in a bicontinuous micro-emulsion system. 40.5 wt % of surfactant and 32.5 wt % of 0.7 M zinc nitrate solution were allowed to react in toluene and water mixture on magnetic stirrer followed by addition of aqueous NaOH solution by dosing pump in 15 min. After 30 min of reaction, acetone was added to get precipitate of ZnO nanoparticles which was washed and dried. 250 mg of ZnO nanoparticles was taken in an aqueous solution having 0.8 g of sodium dodecyl sulfate followed by the addition of 0.4 g of pyrrole and allowed to react for 2 h.

To start the polymerization, ammonium persulphate (0.6 M) was added to the reaction mixture. Methanol was

Fig. 2 Synthesis of zinc oxide nanoparticles using zinc nitrate and citric acid followed by the synthesis of polyaniline/zinc oxide nanohybrids by sol-gel method by using aniline monomer and zinc oxide

in hydrochloric acid medium (Reprinted from Ambalagi et al. 2016 with permission from Elsevier). PANI: polyaniline; ZnO: zinc oxide

Fig. 3 Template synthesis of polypyrrole /zinc oxide nanohybrids using sodium dodecyl sulfate as template and ammonium persulfate as oxidant. Here, synthesis of zinc oxide nanoparticles was performed using zinc nitrate in the AOT/SDS template followed by nanohybrids

synthesis. Reprinted from Ovando-Medina et al. 2015 with permission from Springer). AOT: dioctyl sodium sulfosuccinate; NaOH: sodium hydroxide; ZnO: zinc oxide; PPy: polypyrrole; APS: ammonium persulfate; SDS: sodium dodecyl sulfate

used to separate the nanohybrids after 1 h of reaction, as shown in Fig. 3 (Ovando-Medina et al. 2015). Zhao and coworkers also synthesized polyaniline/ZnO nanohybrids via this method using the combination of wet-chemical technique in situ polymerization route (Zhao et al. 2011). Some other researchers have also adopted this route for

conducting polymers /ZnO nanohybrids synthesis (Mitra et al. 2017; Zoshki et al. 2019). Template synthesis is an efficient method for controlling the morphology and size but the only difficulty is to remove the template after synthesis which limits its use and needs to be worked on that in the future.

Mixing or blending of polymer and nanoparticles

Direct mixing of polymer and nanoparticles is another method for the fabrication of nanohybrids. This method includes the direct mixing of polymer with ZnO nanoparticles. Firstly, the synthesis of polymer and ZnO occurs separately, afterthought the mixing of both can be done via various techniques. For this, polyaniline was synthesized by its monomer using 0.5 M of hydrochloric acid and 0.05 M of ammonium persulphate. The reaction was carried out for 6 h, and the resultant precipitate was washed and dried at 70 °C for 30 h. The obtained polyaniline was in emeraldine salt form (doped) and was washed with ammonia solution to achieve polyaniline in emeraldine base form. For the synthesis of ZnO rods, the hydrothermal method was chosen. In this method, 0.2 M zinc sulphate (25 ml) solution and 4 g of sodium hydroxide (25 ml) were mixed with deionized water (50 ml). This mixture was stirred for 30 min and kept on stainless steel autoclave followed by keeping in an oven for 10 h at 80 °C. Later on, this precipitate was washed with ethanol and water several times and dried in an oven for 12 h at 80 °C. In the last step, 0.05 g of polyaniline was taken in 100 ml of THF (tetrahydrofuran), and the solution containing polyaniline was ultrasonicated for 30 min and stirred again. At this stage, ZnO was added to the mixture followed by stirring of mixture for 24 h. After completion of the reaction, precipitates were washed with deionized water and kept for drying at 60 °C (Sharma et al. 2016).

The blending of polymers and semiconductors is the most effortless way for the nanohybrid synthesis as only mechanical mixing of polymer and semiconductor is required in this technique, but the main disadvantage of this method is the lack of bonding and interactions between polymer and semiconductor compared to other above methods. To overcome this problem, some such techniques should be designed that can deeply blend for interaction between polymer and semiconductors or nanomaterials.

Photocatalysis by conducting polymer/zinc oxide nanohybrids

Conducting polymers are the class of conjugated polymers having the π -conjugated system in their backbone and have a wide area of applications in the field of optoelectronics (Khokhar et al. 2020b), biomedical (Jadoun et al. 2021c), photovoltaic devices (Jadoun and Riaz 2020), etc., due to their unique optical, electrical, and photoelectric properties (Jadoun et al. 2021b). Conducting polymers are extensively used as a photosensitizer to enhance the semiconductor's photocatalytic properties (Jangid et al. 2020b). Some conducting polymers combined with ZnO to form nanohybrids

for the photocatalytic degradation of pollutants from water are discussed here and summarized in Table 1 and Fig. 4.

Polyaniline/zinc oxide

Polyaniline is a mostly studied conducting polymer among all due to its outstanding properties and multiple applications (Chauhan et al. 2016; Jangid et al. 2020a). It is used widely used to tune the electrical, optical, and photocatalytic properties of composites with ZnO due to its narrow bandgap of 2.13 eV. The polyaniline/ZnO nanohybrids are the extensively explored class of all conducting polymers/ZnO. These were synthesized in various media and neutral is one of them studied by some researchers. They concluded that the synthesis in neutral media with DEG enhanced the solubility of aniline in water and forms dispersion which was more stable and have diminished bandgap. These photocatalysts were able to react under solar irradiation.

During photocatalysis, the corrosion dissolution of ZnO was also prevented by this method. These photocatalysts had shown high catalytic activity and stability for the removal of the acid blue dye from model wastewater. Upon light irradiation, electrons got excited from HOMO of polyaniline and transferred to LUMO and further easily transferred to the conduction band of ZnO due to well-matched energy levels of both. Hence, holes reacted with water and electrons reacted with oxygen to form reactive oxygen species such as $\cdot\text{OH}$, $\text{O}_2^{\cdot-}$, $\text{HO}_2^{\cdot}$, and the most active radical was $\cdot\text{OH}$ which was produced by the reaction between hydroxyl ions and holes. These were able to degrade organic pollutants and finally produce CO_2 and H_2O , Fig. 5 (Gilja et al. 2018).

The photocatalytic activity was found to enhance with the polyaniline and ZnO combination due to the synergic effect between polyaniline and ZnO. These nanohybrids were 2.5 times more photocatalytically active as compared to ZnO for the degradation of methyl orange dye under ultraviolet light (Pei et al. 2014). These nanohybrids were also capable to remove toxic and stable pollutants such as 4-chlorophenol. On ultraviolet irradiation, it removed organic carbon species up to 82% in 120 min. In natural sunlight, these nanohybrids degraded 97% and 99% of methylene blue and malachite green, respectively, in 5 h (Eskizeybek et al. 2012). Zhu and coworkers fabricated polyacrylonitrile/polyaniline nanofibers and later ZnO was immobilized by atomic layer deposition to enhance the photocatalytic degradation of MB under UV light. The photocatalyst was easily recycled with very less decrement of photocatalytic activity. (Zhu et al. 2018).

To resolve existing energy or environmental hitches, architecture and structural design also played a significant role in a nanohybrid photocatalyst to enhance photocatalytic efficiency. In this regard, a novel polyaniline /ZnO-CoMoO₄ Z-scheme photocatalyst was fabricated and applied to the degradation of imidacloprid pesticide under visible light

Table 1 Composition, method of synthesis, the degradation efficiency of nanohybrids fabricated using conducting polymers and zinc oxide nanoparticles for photocatalysis PANI: polyaniline; PPY: polypyrrole; PTH: polythiophene; PAM: Poly(azomethine); PEDOT: Poly (ethylene dioxithiophene); PAN: polyanisidine; PNA: polynaphthylamine; ANI: aniline; PPD: polyphenylenediamine; OAA: ortho-anthranilic acid; OTD: ortho-tolidine; OAP: ortho-aminophenol; CR: Congo red; MB: methylene blue; TC: tetracycline; IM: imidacloprid; MG: malachite green; AV-7: acid-violet-7; MNZ: metronidazole; BB: brilliant blue; RB: rhodamine blue; RO-16: reactive orange 16; CBB-R-250: coomassie brilliant blue; DCF: diclofenac; AB 25: acid blue 25; C.I. RR 45: C.I. reactive red 45; AR: alizarin red; MO: methyl orange; CV: crystal violet

Year	Photocatalyst	Method of synthesis	Size (nm) and morphology	Model Pollutants	Degradation efficiency and time	Reference
2021	PANI/Cu ₂ O/ZnO	facile one-pot solvothermal method and <i>in situ</i> polymerization	101; irregular shape	Degradation of CR	100% in less than 30 min	Mohammed et al. (2021)
2021	PANI/ZnO/MoS ₂	Facile hydrothermal route	5; sea urchin-like morphology	Degradation of MB and TC	99.6% of MB and 94.5% TC in 60 min	Sharma et al. (2021)
2021	PANI/ZnO-CoMoO ₄	In situ polymerization	–	Degradation of IM	97% in 180 min	Adabavazeh et al. (2021)
2021	PPY/ZnO	Ultrasonic assisted	–	Reduction of Cr ⁺⁶	99.2% after four cycles	Balakumar and Baishnisha (2021)
2020	PTH/ZnO	Facile sol–gel and oxidative polymerization	10	Degradation of MB and gemifloxacin antibiotic	95% of MB and 80% of gemifloxacin antibiotic in 180 min	Faisal et al. (2020)
2020	α -SiW11Cr/PANI/ZnO	Electrostatic self-assembly	Irregular and spherical,	Degradation of MG	94% in 180 min	Zhang et al. (2020)
2020	PPY/ZnO	In situ polymerization	–	Degradation of real textile wastewater containing azo dye Direct Black 22	99.8% in 60 min	Ceretta et al. (2020)
2019	PPY/ZnO	Template synthesis	500; needle-shaped particles	Degradation of AV- 7	66% in 360 min	González-Casamachin et al. (2019)
2019	PANI/ZnO	In situ polymerization	35	Degradation of metronidazole (MNZ)	97% in 150 min	Asgari et al. (2019)
2019	PAM/ZnO	In situ polymerization	35	Degradation of MB, MG and BB	97%, 96% and 95% in 300 min	Pradeeba and Sampath (2019)
2019	PPY/ZnO	In situ polymerization	50; uniform spherical particles	Degradation of RB	99% in 120 min	Podasca et al. (2019)
2019	PPY/Chitosan/ZnO	In situ polymerization	10–100	Degradation of the RO-16, CBB-R-250 and MB	87% of RO-16 and 92% of CBB R-250 and 85% of MB in 70 min	Ahmad et al. (2019)
2019	PPY/ZnO	In situ polymerization	–	Degradation of DCF	81% in 60 min	Silvestri et al. (2019)
2018	PANI/ZnO	In situ polymerization	100 – 200; spherical-granular particles and lamellas	Degradation of AB25	90% in 60 min	Gilja et al. (2018)
2018	PAN/PANI/ZnO	In situ polymerization and atomic layer deposition of ZnO	200–250	Degradation of MB	92% in 60 min	Zhu et al. (2018)
2017	PPY/ZnO	Electrodeposition	250	Degradation of MB	85.95% in 180 min	Yan et al. (2017)
2017	PEDOT/ZnO	In situ polymerization	–	Degradation of C.I. RR45	47% in 90 min	Katančić et al. (2017)
2016	PANI/ZnO	In situ polymerization	15; spherical aggregated	Degradation of MO and MB	98.3% MO and 99.2% MB in 180 min	Saravanan et al. (2016)

Table 1 (continued)

Year	Photocatalyst	Method of synthesis	Size (nm) and morphology	Model Pollutants	Degradation efficiency and time	Reference
2016	PANI/ ZnO	By mixing of polymer and nanoparticle	–	Degradation of MB	100% in 80 min	Sharma et al. (2016)
2016	PNA/ ZnO	In situ polymerization	25–40; core-shell	Degradation of AR dye	90% in 40 min	Riaz et al. (2016)
2016	PPY/I-D ZnO	In situ polymerization	30–50	Degradation of CV	97.13% in 120 min	PATIL et al. (2016)
2016	PEDOT/ZnO	In situ polymerization	9.19; nanorods	Degradation of MO	70% in 120 min	Dagar and Narula (2016)
2015	Poly AN-co-OTD)/ZnO	In situ polymerization	15–25; Spherical	Reduction of Cr (VI) and degradation of MB	65% conversion of Cr (VI) into Cr (III) and 92% degradation of MB in 180 min	Sivakumar et al. (2015)
2015	PPY/ZnO	Precipitation method	8–15 nm; acicular rod-like morphology	Degradation of MB	95.2% in 60 min	Ovando-Medina et al. (2015)
2015	PPY/ZnO	Electrochemical polymerization	–	Degradation of RB and R6G	80% of RB and 90% R6G in 270 min	Nascimento et al. (2015)
2014	PTH/ZnO	In situ polymerization	30	Degradation of MO	88% in 180 min	Khatamian et al. (2014)
2014	PEDOT/ZnO	Solid-state heating method	50; spherical shape	Degradation of MB	98.7% in 300 minutes	Abdiryim et al. (2014)
2014	Poly (ANI-co-OAP)/ZnO	In situ polymerization	15–25; Spherical	Degradation of MB	88% in 180 min	Sivakumar et al. (2014)
2014	Poly (AN-co-OAA)/ZnO	In situ polymerization	15–25; Spherical	Reduction of Cr (VI) and Ni (II) and degradation of MB	78% and 81% efficiency for Cr (VI) and Ni (II) reduction and 82% MB degradation in 180 min	Haldorai et al. (2014)
2013	PMPD/ZnO	In situ polymerization	25–35; aggregates	Degradation of C.I. acid red 249	81.7% in 120 min	Peng et al. (2014)
2012	PANI/ZnO	In situ polymerization	50–100; core-shell structure	Degradation of MB and MG	97% MB and 99% MG in 300 min	Eskizeybek et al. (2012)
2012	Poly (ANI-co-PPD)/ZnO	In situ polymerization	15–25; Spherical	Degradation of MB	80% in 180 min	Sivakumar et al. (2012)
2011	PANI/ZnO	In situ polymerization	1000 nm; irregular sheet like morphology	Degradation of MB	76% in 160 min	Ameen et al. (2011)
2011	PANI/ZnO	In situ polymerization	260; coreshell spherical	Degradation of MB	82% in 60 min	OLAD et al. (2012)
2010	PNA/ZnO	In situ polymerization	Irregular spherical particles	Degradation of MB	22% in 140 min	Ameen et al. (2010)

Photocatalytic properties, stability, reusability, and adsorption properties were enhanced by Cu₂O/ZnO/ polyaniline, a Z-scheme heterojunction properties ternary composite. The surface area of composites was increased up to 45.32 m²g⁻¹ which was high in comparison to pristine Cu₂O, ZnO, and polyaniline. These composites revealed excellent 100% degradation of Congo red dye in less than 30 min which was a milestone in photocatalysis and even for reusability these were still active after the fifth cycle with 92% efficiency. In Z scheme heterojunction, there is always a semiconductor with electron donor and acceptor moieties, and hence, upon light irradiation, the electrons and holes are transferred from one semiconductor to another semiconductor via electron donor and acceptor moieties. As result, generation of higher redox ability due to electrons and holes on the semiconductor occurs by which charge separation of carriers occurred effectively and caused retention of sturdy oxidation–reduction potential for a long time.

Fig. 5 Photocatalytic degradation mechanism of AB25 using polyaniline /zinc oxide composites. Here, polyaniline acts as a sensitizer and the transfer of electrons from LUMO of polyaniline to conduction band of zinc oxide, while holes are transferred from valence band of zinc oxide to HOMO diminished the electrons and holes recombination. Reprinted from Gilja et al. 2018 with permission from MDPI). CB: conduction band; VB: valence band; PANI: polyaniline; HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital; AB25: acid blue dye 25

Fig. 6 Charge transfer pathway of **a** double Z-scheme Cu₂O/ZnO/ polyaniline ternary composite (CZP) for oxidation and reduction under visible-light irradiation. **b** the rate constant of photocatalytic activity on Congo red dye by Cu₂O/ZnO/ polyaniline ternary composite (CZP) at different loadings, **c** effects of scavengers on the degradation of Congo red on to Cu₂O/ZnO/ polyaniline ternary compos-

ite (CZP) (Reprinted from Mohammed et al. 2021 with permission from Elsevier). HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital; PANI: polyaniline; ZnO: zinc oxide; Cu₂O: copper (I) oxide; CB: conduction band; VB: valence band; CZP: Cu₂O/ZnO/ polyaniline ternary composite

of photoluminescence also favored the decrease in recombination of charge carriers, Fig. 6a. For the comparison, Z scheme Cu₂O/ZnO/ polyaniline ternary composite was prepared in the various ratios of polyaniline, and the best results were shown by Cu₂O/ZnO/ polyaniline ternary composite (0.1) in terms of maximum rate constant (0.10 min^{-1}) and the least half-life (9.93 min), Fig. 6 (b), supported the highest photocatalytic activity of Cu₂O/ZnO/ polyaniline ternary composite (0.1). The active species involved in the degradation of CR such as hydroxyl radicals ($\cdot\text{OH}$), holes (h^+) and superoxide radicals ($\text{O}_2^{\cdot-}$) were captured by isopropyl alcohol (2 mL), benzoquinone (0.001 M), and ammonium oxalate (0.001 M) in radical scavenging experiment and revealed the degradation in order of no scavenger > isopropyl alcohol > benzoquinone > ammonium oxalate, Fig. 6c. The results showed that superoxide radicals ($\text{O}_2^{\cdot-}$) and holes (h^+) were the main active radicals during photocatalysis and hydroxyl radicals ($\cdot\text{OH}$) were the secondary radicals. (Mohammed et al. 2021).

200 mg/L of ternary composite α -SiW11Cr/ polyaniline /ZnO on 10 mg/L malachite green dye solution was used to check the pH effect on degradation rate. When the acidity of the solution was increased up to pH 1, the degradation rate was 90.8% due to the formation of cation

form of malachite green which was in favor of α -SiW11Cr/ polyaniline/ZnO negatively charged form. The degradation rate was found lowest at 5 pH, while the decolorization rate increased at pH > 7 because of the fusion of active hydroxide ion and malachite green cation in an aqueous solution. This combination resulted in a colorless alcohol base in basic condition (Zhang et al. 2020).

Some copolymers of conducting polymers were also hybridized with ZnO for degradation of dyes such as poly(aniline-co-o-aminophenol)/ZnO (Sivakumar et al. 2014), while poly(aniline-co-o-anthranilic acid)/ZnO was used for removal of Cr(VI) and Ni(II) and the pattern of reduction was well matched with a first-order kinetic model. The same nanocomposites also showed good results for the degradation of MB dye up to 82% in UV-light illumination (Haldorai et al. 2014). For the reduction of Cr (VI), some other researchers also used poly(aniline-co-o-toluidine) nanohybrids (Sivakumar et al. 2015). 100% degradation of Congo red dye was reported by Zor et al. (Sibel and Budak 2020) by polyaniline /ZnO nanohybrids prepared by chemical polymerization, and degradation studies were performed under ultraviolet–visible light irradiation.

Polyphenylenediamine/zinc oxide

Polyphenylenediamines are the derivatives of polyaniline and exist in 3 isomers; ortho, meta, and para (Riaz et al. 2017, 2018; Jadoun et al. 2021d). Polyphenylenediamines have two free amine groups for functionalization before and after polymerization to enhance the properties of the polymer such as electroactivity, conductivity, sensitivity, thermal stability for their application in metal ions adsorption, anti-corrosion coatings, sensors (Jadoun et al. 2021d), but the nanohybrids of polyphenylenediamines with ZnO are very rarely studied for photocatalysis (Jadoun et al. 2017a; Riaz et al. 2019; Sandoval et al. 2019). The bandgap of poly(o-phenylenediamine) (*ortho* isomer) is 2.2 eV which is quite low in comparison to ZnO (Olgun and Gülfen 2014). The photocatalytic activity of homopolymer was very poor under ultraviolet irradiation for the degradation of acid red 249 but the poly(m-phenylenediamine)/ZnO (1/80) (*meta* isomer) showed the highest degradation of 94.6% in 120 min. The other ratios and ZnO showed less activity than the previous one which was 88.9% for poly(m-phenylenediamine)/ZnO (1/60), 92.3% for poly(m-phenylenediamine)/ZnO (1/100), and 81.8% for pristine ZnO, as shown in Fig. 7a. Therefore, increasing the poly(m-phenylenediamine) content in nanohybrids increased the electron mobility due to conjugate structure and recommend the photogenerated electrons and holes recombination, but the intensity of ultraviolet light absorbed by ZnO particles was affected by more increment in poly(m-phenylenediamine) content.

Under visible light irradiation, both ZnO and poly(m-phenylenediamine) showed poor results with almost no degradation of acid red 249 dye. Although when PMPD/ZnO was irradiated with visible light, poly(m-phenylenediamine) absorbed photons to excite and electrons transferred to conduction band of ZnO, hence charge separation was improved along with photocatalytic activity too and the best results were shown by poly(m-phenylenediamine)/ZnO (1/80), Fig. 7b. The best nanohybrid was studied for photocatalytic stabilities after some cycles with the 50 mg of catalyst and 50 mg/L concentration of acid red 249. Photocatalyst was restored by centrifuge after each run and used for the degradation of acid red 249 under ultraviolet and visible light, Fig. 7c, d. After the 5th cycle, 79.4% acid red 249 was degraded by poly(m-phenylenediamine)/ZnO (1/80) which was 34.9% in the case of ZnO. This was due to inhibition of photo-corrosion in the presence of poly(m-phenylenediamine) (Peng et al. 2014). Poly (aniline-co-p-phenylenediamine)/ZnO nanohybrids were found more electrically conductive, thermally stable as compared to pristine copolymer, and a favored interaction between the ZnO nanoparticle and copolymer chains. These showed 80% degradation of methylene blue in 3 h under ultraviolet irradiation (Sivakumar et al. 2012).

Polypyrrole/zinc oxide

Polypyrrole is a widely explored conducting polymer having a bandgap of 2.2 eV (Jadoun et al. 2021a). The nanohybrids

Fig. 7 The degradation efficiency of acid red 249 versus irradiation time under **a** ultraviolet irradiation **b** visible light irradiation **c** using poly(m-phenylenediamine)/zinc oxide (1/80) composite as photocatalyst under ultraviolet irradiation at different recycling runs (the degradation efficiency of acid red 249 after 120 min irradiation in ultraviolet light at several recycling experiments is shown in inset) **d** using poly(m-phenylenediamine)/zinc oxide (1/80) composite as photocatalyst under visible light irradiation at several recycling runs (Reprinted from Peng et al. 2014 with permission from Wiley)

of polypyrrole/ZnO possessed 2 times higher rate constant than pristine ZnO for the degradation of diclofenac which is a non-steroidal anti-inflammatory drug extensively used as analgesics, resulting in 81% degradation in 60 min. ZnO alone was able to degrade 46% of diclofenac only. In 25:1 of polypyrrole: ZnO showed the best results while increasing the ZnO content (polypyrrole: ZnO/5:1) suppressed the surface of polypyrrole resulting in defects in which e^-/h^+ recombination occurred and revealed the photocatalytic activity to be decreased. The degradation of diclofenac can be seen in Fig. 8a, with increasing the time absorbance peak of diclofenac decreased suggested 81% degradation in 60 min. In the degradation of diclofenac, the main responsible species were trapped as h^+ in the scavenger test (Silvestri et al. 2019). Polypyrrole/ZnO prepared by ultrasonication technique was effective to reduce Cr^{6+} to Cr^{3+} under visible light irradiation. The electron moved in conduction band of ZnO participated in the reduction of Cr^{+6} to Cr^{+3} while the holes form hydroxide radical by absorbing water molecules on the surface but it could again oxidize Cr^{+3} to Cr^{+6} . Hence, the addition of citric acid as a radicle scavenging agent was done to enhance to photoreduction of Cr^{+6} and inhibit the oxidation process, Fig. 8b (Balakumar and Baishnisha 2021).

A flexible composite film of ZnO-Micro-rods/ polypyrrole with substantial durability, flexibility, and photocatalytic activity under visible light was developed in which ZnO microrods were coated with polypyrrole shell (400 nm thick) from the upper part and acted as a photosensitizer, while the lower part of ZnO was also implanted in polypyrrole layer which enabled the transfer of an electron from LUMO of polypyrrole to conduction band of ZnO, Fig. 9a. This

type of architecture enhanced the photocatalytic degradation of MB with a 0.22% rate per minute, Fig. 9b (Yan et al. 2017). Similarly, polypyrrole/ZnO nanohybrids were used to degrade the violet acid 7 dye for treatment of wastewater (González-Casamachin et al. 2019) and polypyrrole/1-D ZnO nanohybrids showed 97.13% degradation of crystal violet using 1 gL^{-1} of catalyst and 5 mgL^{-1} concentration of dye in 120 min (PATIL et al. 2016). Nanohybrids synthesized by polypyrrole, ZnO, and Ag were studied for the degradation of Rhodamine B resulted in 99% of dye degradation in 120 min under visible light irradiation with a rate constant of $k = 2.96 \times 10^{-2}\text{ min}^{-1}$ (Podasca et al. 2019).

The real untreated textile water containing azo dye direct black 22 was initially treated with the bacterial consortium and after 96 h polypyrrole/ZnO nanohybrids were employed for photocatalysis. The photocatalysis was carried out for 60 min and revealed 95.7% of decolorization efficiency and 99.8% of total organic carbon degradation. Hence, this can be an efficient alternative to put on before dumping textile wastes in water bodies (Ceretta et al. 2020).

Poly (ethylene dioxythiophene)/zinc oxide

Poly (3,4-ethylene dioxythiophene) is a conducting polymer and has been studied widely for its stability, high and tunable electrical conductivity. In its conducting state, this polymer remains optically transparent, with low redox potential and a moderate bandgap (Gueye et al. 2020). Ternary nanohybrids, poly (ethylene dioxythiophene)/ZnO/fly ash cenosphere (fly ash cenosphere) are very low-density materials which generally used to prepare very lightweight hybrids) was prepared by chemical oxidative polymerization method and utilized

Fig. 8 Nanohybrids of polypyrrole /zinc oxide **a** Synthesis of polypyrrole/zinc oxide nanocomposites for UV–visible photocatalytic degradation of diclofenac **b** Photocatalysis by polypyrrole /zinc oxide for reduction of toxic Cr^{6+} to benign Cr^{3+} (Reprinted from Silvestri

et al. 2019, (Balakumar and Baishnisha 2021) with permission from Elsevier). PPy: polypyrrole; ZnO: zinc oxide; HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital

Fig. 9 Photocatalytic activity and mechanism of carrier transport. **a** Degradation rates of methylene blue by photolysis, polypyrrole/polyethyleneglycol-borate film, zinc oxides microrod arrays, zinc oxide microrods/ polypyrrole (400) composite film, and zinc oxide-microrods/ polypyrrole (800) composite film under visible light. **b** A schematic illustration of carrier separation and transport mecha-

nism at the zinc oxide/ polypyrrole interface. (Reprinted from Yan et al. 2017 with permission from American Chemical Society). PPy: polypyrrole; PEG: polyethylene glycol; MB: methylene blue; ZnO: zinc oxide; HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital

for the photodegradation of methyl orange dye consisting of N=N azo group. The photocatalyst with maximum degradation efficiency was 2% poly (ethylene dioxythiophene)/ZnO/fly ash cenosphere composites which showed first-order kinetics and 0.0058 min^{-1} rate constant. These ternary nanocomposites were able to degrade 70% methyl orange dye in 120 min (Dagar and Narula 2016).

A simple solid-state heating method was adopted for the fabrication of poly (ethylene dioxythiophene)/ZnO nanohybrids with the variation of ZnO content from 10 to 20%. Its photocatalytic activity was measured against the methylene blue in wastewater under UV and solar irradiation. After 5 h of irradiation under ultraviolet light, the degradation efficiency was found 88.7% (poly (ethylene dioxythiophene)/10 wt% ZnO), 98.7% (poly (ethylene dioxythiophene)/15 wt% ZnO) and 98.2% (poly (ethylene dioxythiophene)/20 wt% ZnO), while in natural sunlight, 93.3% (poly (ethylene dioxythiophene)/10wt% ZnO), 96.6% (poly (ethylene dioxythiophene)/15 wt% ZnO) and 95.4% (poly (ethylene dioxythiophene)/20 wt% ZnO) were achieved which indicated that highest degradation was achieved in ultraviolet light for 15 wt % of ZnO in poly (ethylene dioxythiophene)/ZnO (Abdiryim et al. 2014).

For the treatment of reactive red 45 azo dye from wastewater, these nanohybrids were prepared by in situ methods and were used under ultraviolet-A and solar light irradiation, and surprisingly very low amount of photocatalyst was able to degrade the dye during wastewater treatment. Before starting the treatment, reactive red 45 dye was kept for maintaining equilibrium. In ultraviolet-A light the photocatalysis was done for 90 min with the initial concentration of catalysts at

1 g L^{-1} and 30 mg L^{-1} for the reactive red 45 dye. Poly (ethylene dioxythiophene)/ZnO (1–2) showed the best results as only 25% dye was left in 90 min while in the case of poly (ethylene dioxythiophene)/ZnO (1–3) and poly (ethylene dioxythiophene)/ZnO (1–5), 82% and 91% remained in the water, respectively. In the solar irradiation, the results were not satisfying that much as the highest degradation was achieved by poly (ethylene dioxythiophene)/ZnO (1–2) and 53% dye was remained in the water after 90 min (Katančič et al. 2017).

Other conducting polymers /zinc oxide nanohybrids

Polynaphthylamine is a derivative of polyaniline (Jadoun et al. 2017c) and much work has been reported previously on polynaphthylamine for photocatalytic activity (Riaz and Ashraf 2011, 2012). Its nanohybrids with ZnO were prepared by blending polynaphthylamine and ZnO via sonication for 2 h and then washed and dried to yield in powder form. These nanohybrids were used to degrade alizarin red dye by two distinct methods (1) photochemical reactor (2) microwave-assisted degradation. For degradation studies, alizarin red dye solution in a fixed concentration was taken for both microwave and ultraviolet irradiation. Firstly, the neat dye solution was exposed in both for 5, 10, 20, 30, and 40 min in the microwave while 30, 60, 90, 120 min for ultraviolet irradiation. The same process was repeated by adding 200 mg of ZnO, polynaphthylamine, and polynaphthylamine /ZnO nanohybrids. As well as the time increased, the absorption maxima of the peak of dye decreased revealed the degradation of dye, and the maximum decrease in the visible

Fig. 10 Degradation kinetic plot for alizarin red dye solution containing homopolymer and nanohybrid of polynaphthylamine/zinc oxide as catalyst exposed to **a** microwave irradiation **b** ultraviolet irradiation

c variation of fluorescence intensity of 2-hydroxy terephthalic acid upon microwave irradiation **d** ultraviolet irradiation (Reprinted from Riaz et al. 2016 with permission from Elsevier)

region was found in the case of microwave irradiation. The degradation kinetics showed first order in both cases, and the k values in ultraviolet exposure were found 0.005 for 300 nm peak while 0.004 for 500 nm peak, Fig. 10a, b. In the case of microwave irradiation, these were 0.009 and 0.007, respectively, for ultraviolet and visible region peak, and rate constants also followed the same pattern. In the degradation pathway, $\cdot\text{OH}$ was generated in both microwave and ultraviolet degradation. Terephthalic acid was used to trap $\cdot\text{OH}$ as it vastly reacts with the previous one to produce 2-hydroxyterephthalic acid which is highly fluorescent and gives emission on 415 nm with an excitation at 315 nm. The increment in peak intensity of 2-hydroxyterephthalic

acid with time under microwave and ultraviolet but surprisingly, the peak intensity was increased more than twice in case of the microwave which indicated the generation of $\cdot\text{OH}$ in microwave irradiation was high, Fig. 10c, d (Riaz et al. 2016).

The photocatalytic degradation of methylene blue under visible light was performed by polynaphthylamine/ZnO synthesized via in situ chemical oxidative polymerization. The surface properties were modified by adding ZnO to polynaphthylamine as well as the morphology and crystallinity were also found to enhance. The degradation rate was moderate and up to 22% dye was degraded under visible light irradiation by polynaphthylamine /0.39 wt % ZnO.

Polythiophene is an intrinsically conducting polymer having sulfur in its cycle and conjugated double bonds in its backbone. It attracted a lot of attention to researchers due to its good thermal stability, higher environmental stability, and narrow bandgap (2.5 eV) (Swager 2017). In nanohybrids of polythiophene /ZnO, the photons are easily absorbed by polythiophene upon irradiation with visible light, but still, it is very less studied with ZnO. Different weight ratios of polythiophene /ZnO were explored for the photocatalytic degradation of MB. Significant decrement in absorbance of methylene blue was attained after some time and almost diminished in 180 min. The charge carriers generated in conduction band and valence band moved toward the catalyst surface were responsible for redox reactions with other moieties. $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ reacted with methylene blue molecule to break the backbone of dye or pollutant, Fig. 11 (Faisal et al. 2020).

Shivakumar and coworkers fabricated Poly(aniline-co-o-toluidine)/ZnO nanohybrids for the reduction of Cr (VI) from wastewater and the patterns of reduction of Cr (VI) followed the first-order kinetics, as well as these nanohybrids, also showed outstanding degradation of MB. 65% reduction of Cr (VI) and 92% for MB dye were obtained in 3 h duration (Sivakumar et al. 2015). The poly(azomethyne)/ZnO (poly(azomethyne) is the Schiff's base or conjugated polymer achieved by condensation having conjugated nitrogen atom ($\text{CH}=\text{N}$) in a polymer backbone) was used for the decolorization and photocatalytic degradation of dyes containing wastewater in natural sunlight. The dose of the photocatalyst was taken 500 mg, while the dye was taken in 50 mg L^{-1} concentration. The degradation efficiency was found 97% for MB and 96%, 95% were found for malachite green and Bismarck brown dyes in 5 h and the rate constant of pseudo-first-order reaction kinetics was found 0.2803, 0.3232, and 0.3762 min^{-1} for methylene blue, malachite

green, and brilliant blue dyes, respectively (Pradeeba and Sampath 2019).

Various conducting polymers such as polyaniline, poly(o-phenylenediamine), polypyrrole, polythiophene, and polynaphthylamine possess a narrower bandgap of $\sim 2 - 2.5 \text{ eV}$, while ZnO possesses a wide bandgap of 3.37 eV, works as a synergistic relationship to each other and minimizes the recombination of charge by the synergistic charge transfer mechanism resulting in enhancement of redox reactions at the surface of catalyst for the removal of toxic pollutants and reduction of metals. Therefore, conducting polymers / ZnO nanohybrids are the best alternative to absorb the solar irradiation up to 53% due to its visible region lying bandgap.

Effectiveness of conducting polymers/ zinc oxide photocatalyst with other semiconductors

Conducting polymers possessed a narrow bandgap of $\sim 2 - 2.5 \text{ eV}$ (Guo and Facchetti 2020), revealing its potential for sensitization of ZnO having a wide bandgap of 3.2 eV (Khan et al. 2017). The excellent photocatalysis ability of conducting polymers /ZnO nanohybrids is attributed to the adequate charge separation capability and movement of electrons from HOMO to LUMO of conducting polymers followed by the transfer of electrons to conduction band of ZnO. The electrons from valence band of ZnO also transferred to conduction band of ZnO; hence, the holes created in valence band transferred to HOMO of conducting polymers. Consequently, on the surface of ZnO, hydroxides and superoxide radicals generate due to the excess of holes in valence band to enhance photocatalysis. These radicals are responsible for the redox reactions and degradation of organic contaminants from wastewater (Belabed et al. 2021; Khan et al. 2021). When compared to pristine poly (ethylene dioxythiophene) and ZnO with their nanohybrids for photocatalysis of methylene blue under ultraviolet light for 5 h, the efficiency of poly (ethylene dioxythiophene)/ZnO was 52%, while pristine poly (ethylene dioxythiophene) and ZnO revealed 14% and 31%, respectively, which were quite low (Ali et al. 2013).

For degradation of methylene blue and malachite green, polyaniline/ZnO nanohybrids showed an affective behavior under visible light illumination. The intermolecular interaction between polyaniline and ZnO resulted in $\pi - \pi^*$ transition of electrons from HOMO to LUMO of polyaniline which transferred in conduction band of ZnO resulting in hydroxide and superoxide anion radical's generation which were responsible for photocatalysis (Saravanan et al. 2016). The solar light on polyaniline /ZnO nanohybrids boosted the degradation of dyes up to 99% in 5 h (Eskizeybek et al. 2012). The nanohybrids of polyaniline / TiO_2 and polypyrrole / TiO_2

Fig. 11 Photocatalytic degradation of methylene blue dye or gemifloxacin antibiotic by polythiophene/zinc oxide nanohybrid photocatalyst, where [P] represents the pollutant molecule (Reprinted from Faisal et al. 2020 with permission from Elsevier). PTh: polythiophene; C.B.: conduction band; V.B.: valence band ZnO: zinc oxide; HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital

were employed for the degradation of methyl orange under solar light resulting in satisfactory results but less degradation efficiency when compared to polyaniline /ZnO and polypyrrole ZnO nanohybrids (Deng et al. 2012; Ovando-Medina et al. 2015; Kumar et al. 2018).

Conclusion

In the nutshell, nanohybrids of conducting polymers and zinc oxide seem to be the most promising materials for photocatalysis under, visible and solar irradiation. Numerous pieces of the literature suggested that minimizing the possibility of recombination of charge carriers is the easiest and effective way for enhancing photocatalytic activity. Therefore, conducting polymer-based zinc oxide nanohybrids is the best alternative in which the bandgap of nanohybrid lies in the visible region which increases the possibility to absorb solar irradiation up to 53%. This critical review demonstrated the use of conducting polymers and their paradigm shift to enhance the performance of zinc oxide-based nanohybrid photocatalyst for degradation of harmful chemicals, toxic pollutants, insecticides, etc. Along with zinc oxide, the combination of conducting polymers enhances the photogenerated charge carrier separation by extending the absorption of light from UV to the visible region, and hence, the visible-light-driven photocatalytic activity improved. A synergistic relation between conducting polymers and zinc oxide is also responsible for the enhanced efficiency of photocatalytic degradation. As the aggregation process is slowed down by using polymers due to its tendency, the use of conducting polymer during synthesis in high concentration is much helpful in the reduction of large aggregation in photocatalysis. Photoinduced holes can be easily trapped by π -conjugated chains of conducting polymers, supportive in inhibiting the self-oxidation process of photocatalysts hinders the photo-corrosion resulting in improving the photostability.

Though more than 90% of studies are related to the degradation of dyes, in reality, the removal of dye is a simpler process than some complex emerging organic contaminants such as personal care products, disinfection by-products, pesticides, drugs, and many other synthetic chemicals which should be more focused. Also, the photocatalysis on conducting polymers/ZnO nanohybrids and all other nanohybrids has been researched on a static system which is hard to apply on the water treatment in the real-world system due to the need for sustainability of catalyst in a flow-through system with the slight leakage of metals from the nanohybrids. Future soundings should be the study of the removal of major contaminants from real water systems by simulating the quality parameters from laboratory to field. The post-treatment retrieval of nanohybrids must be majorly focused

to scale it up. Some magnetic separation systems should be the key point for these types of post-treatment for recovery of nanohybrids so that by applying a magnetic field, these could be easily separated out.

In the field of solar energy harvesting and storage, photocatalysis can open new opportunities and there is wide space for development. Even, it can play a key role also in environmental diminutions by some routes to remove several types of organic and inorganic pollutants which are inorganic toxins such as arsenic, chromium, mercury and others in the freshwater system as well as for the reduction and harvesting of copper or noble metals. Some better new engineering concepts should be optimized for new materials for photocatalysis. To attain better solar radiation, there is a need to fabricate those materials which are shifting to the visible and near-infrared region as 43% of sunlight absorb in the visible region and 52% in the near-infrared region. In parallel with photocatalytic experiments, environmental toxicity valuation should also be carried out. All in all, conducting polymer/zinc oxide-based photocatalysis has shown a great potential to remove organic contaminants in laboratory-scale settings, however, its application in the real world would necessitate addressing various hurdles which should be focused on in the future.

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Declarations

Conflict of interest The author declares no conflict of interest.

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