Chapter 11

Nanomaterials as Photocatalyst

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Abstract

Clean and drinkable water is a big challenge in 21st century. A variety of organometallic compounds have been utilized by human being for rapid civilization and modernization. These hazardous waste discharges from the industries and directly mixed with environment especially in water reservoir and adulterate water, which is responsible for many contagious diseases. To vanquish this issue we needed an eco-friendly, safe, cost-effective nanomaterials for the degradation and removal of noxious waste. In this chapter emphasized on different nanomaterials as photocatalyst for photocatalytic performances, also critically discussed applicability of different nanomaterials for photocatalytic process comprising with types photocatalyst, light source, scavengers, trapping agents, photodegradation activity mechanism and its utility. Moreover, removal of toxic dyes, pharmaceutical drugs, agrochemical waste, heavy metal ions, and phenolic compounds have been discussed.

Keywords

Nanomaterials, Photocatalysts, Photodegradation, Pharmaceutical Drugs, Phenolic Compounds

Contents

Nanomaterials as Photocatalyst.................................................................................................304
1. Introduction.........................................................................................................................305
2. Historical background of photocatalyst ............................................................................307
3. Different Nanomaterials used as photocatalyst ..........................308
   3.1 Metal-based nanomaterials .........................................................308
   3.2 Metal oxide-based nanomaterials .................................................309
   3.3 Metal-polymer based nanomaterials .............................................310
4. Synthetic approaches towards photocatalysts ...............................310
   4.1 Sol-gel .....................................................................................310
   4.2 Hydrothermal ...........................................................................311
   4.3 Solvothermal ............................................................................312
   4.4 Chemical vapor deposition (CVD) ..............................................313
   4.5 Green Techniques .....................................................................313
5. Process of photocatalytic activity ....................................................315
   5.1 Types of photocatalyst used in photodegradation activity ..........315
   5.2 Source of light ..........................................................................315
   5.3 Mechanism of photocatalytic degradation ..................................315
     5.3.1 Photo excitation ....................................................................316
     5.3.2 Ionization of water ...............................................................316
     5.3.3 Oxygen ion sorption .............................................................316
     5.3.4 Protonation of superoxide .....................................................316
     5.3.5 Scavengers and trapping agent in photocatalysis ..................317
6. Photodegradation & photoreduction of toxic compounds .............317
   6.1 Photocatalysis ..........................................................................317
   6.2 Photocatalytic degradation of dyes .............................................319
   6.3 Degradation of antibiotics and pharmaceutical drugs ...............321
   6.4 Photocatalytic degradation of phenolic compound ....................321

Conclusion ..........................................................................................322

References ..........................................................................................322

1. Introduction

In recent advances, the scientific community has extremely focused on resolving environmental related issues, which are the major concerns of the 21st century. The biggest challenges are to get clean water owing to fast civilization and industrialization, which is the most vital resource for the existence of all beings’ water pollution has specified critical environmental concern, as the industrial gradual enlargements release of wastewater
streams without sufficient processing and their leaking into the natural water cycle [1].

Around the globe, an extensive use of carcinogenic organic dyes in the textiles industries increase gradually and the more amounts of polluted effluents were released into an aquatic ecosystem. It has become the chief carrier of all contaminants such as carcinogenic dye [2] effluent, heavy metals [3], and pharmaceutical waste [4] despite carrying vital natural minerals such as sodium, magnesium, calcium etc. It is mainly due to the release of unprocessed industrial wastage into the water bodies. It causes the depletion of dissolved oxygen content and results in adverse effects to aquatic creatures and mankind.

On the other hand, environmentalists are striving hard to combat the dye ill effects. The industrial discharges treatment has to be carried out to avoid the harmful effects of pollutants in water, eventually to save the planet, earth and to prevent diseases. Pesticides are one of the most essential groupings of organic pollutants present in waste water. There are numerous methodologies to treat industrial wastes such as precipitation ion-exchange, evaporation, reverse osmosis, ultrafiltration, microfiltration, solvent, extraction [5-6]. Photocatalytic degradation technique was employed for the treatment of water purification because other methods purely transfer the industrial waste from one phase to another phase i.e. detrimental sludge remains even after the treatment. Therefore, the photocatalytic technique is certainly more effective method to convert harmful organic impurities degradation into carbonaceous products [7]. Photocatalysis is an advanced oxidation process (AOP) that can be used for the destruction of pollutants in a simple and competent mode. It is one of the most economic and promising industrial effluent treatment processes. The p-type semiconductor nanomaterials which are being used as most effective photo-active catalysts for photocatalytic exclusion of various organic dyes, hazardous composites and venomous chemicals in water have been broadly studied. The phenolic compounds, color compounds are chemically stable so the technologies relating to UV radiation and hydrogen peroxide oxidation are not effectively deals with the degrade the colour dyes, at present photocatalytic method have paid the great attention due to its effective towards decolorization of the dyes by using semiconductor nanomaterials [8-10].

Recently, development and design of nanostructured semiconductor nanomaterials for potential applications such as environmental remediations, energy and water disinfection have been more attracting material for the degradation of various organic pollutant, pharmaceutical waste have shown effective results. Metal oxide NPs has been broadly used as an eco-friendly photocatalyst and attracted major attention because of their chemical stability, electron transfer capability, low cost, nontoxicity, and electro catalytic characteristics [11]. This p-type and n-type semiconductor metal oxide possesses a tunable band gap in the range 3.0-4.0eV, depending on the nature of the defects and density. Due to their wide band gap and high photosensitive nature, various semiconducting metal oxides such as ZnO, SnO₂, Co₃O₄, CeO₂, TiO₂, Bi₂O₃ and Fe₂O₃ are used in the photocatalytic degradation of organic pollutants [12-17].

In the photocatalytic reaction, the semiconducting photocatalyst absorbs light energy more than equal to band gap, which generate the hole, and the electrons, which further gives rise to efficient oxidizers of organic dyes. Due to the fast recombination of photo-induced CB
electrons and VB holes, it is challenging to obtain efficient degradation efficiency using semiconductor photocatalyst from the aqueous solution [27]. In the case of dye pollutants, the dye acts as a photosensitizer in visible light, and on the other hand, it injects an excited electron to an electron acceptor and converted to cationic dye radical (dye\(^{++}\)), followed by self-degradation or decomposition. Such a photocatalytic degradation process for dyes is different from that of the conventional semiconductor photocatalysis under UV irradiation, and has been demonstrated to be an efficient approach to remove textile dyestuff from aquatic environments [28-30].

2. Historical background of photocatalyst

Metal/metal oxides and graphene NCs have promising application as photocatalyst due to advanced arrangement of electronic structure, charge separation and transport and light absorption properties. A major breakthrough in photocatalysis research was occurred in 1972, when Fujishima and Honda discovers that TiO\(_2\) in connection with Pt electrode cause electrochemical photocatalysis of water under UV light radiations [104]. Verity of inorganic NPs (NPs) including TiO\(_2\), CuO, BiOCl, ZnO, CdO, CdS, ZnWO\(_4\), SnO\(_2\), NiFe\(_2\)O\(_4\), Bi\(_2\)O\(_3\)/BiOCl, MnFe\(_2\)O\(_4\) etc have been proposed to poses photocatalytic activity. In 1977, Nozik discovered that the combination of a noble metal in the electrochemical photolysis process, such as platinum, silver and gold, among others, could increase photoactivity, and that an external potential was not required [31-34]. Wagner and Somorjai (1980) and Sakata and Kawai (1981) delineated hydrogen production on the surface of strontium titanate (SrTiO\(_3\)) via photogeneration, and the generation of hydrogen and methane from the illumination of TiO\(_2\) and PtO\(_2\) in ethanol, respectively.

The photocatalysis were originally used by fujishima and Honda in 1972, the history of photocatalysis can be divided by different ways as an illustration, the relatively effective division proposed by Serpone and Emeline [36], as a function of the type of accoutrements used to carry out the photocatalytic processes is frequently cited. In particular, three different generations of photocatalysts have been proposed. The first is composed by pristine inorganic semiconductors (in the morning substantially ZnO, WO\(_3\) and TiO\(_2\) and also substantially TiO\(_2\) only), of which the photocatalytic parcels have been delved in depth, frequently with introducing experimental approaches, with the main end to give perceptivity into the medium of product and transfer of the charge carriers generated inside the material and into the nature of the reactive species operative in the delved photocatalyzed processes. The alternate generation of photocatalysts is substantially composed by doped semiconductors synthesized to push the onset of immersion toward longer wavelengths introducing intra-band gap countries, the nature and energetic positioning of which have been deeply delved , indeed though the first report of their discovery remained unnoticed for a long time,[36] while a consecutive report entered more recognition( and 16 times further citations!), being the most cited photocatalysis paper of its decade(videinfra) [37]. The doping strategies proposed were grounded on the preface of non-metal or essence centers inside the crystallographic structure of the pristine material with the end to induce color centers (localized countries located between the valence and
conduction bands [38-40] and/or oxygen vacancies with the conformation of centers where the essence cations have different oxidation countries, e.g., Ti$^{3+}$ centres in a TiO$_2$ structure [42]. The third and last generation proposed is grounded on the product of mongrel heterostructures formed by two or further inorganic semiconductors [43-45]. In this case, the dynamics of the charge carriers came extremely complex, especially if the number of the accoutrements composing the mongrels is advanced than two. In some cases, these photocatalysts have shown both high effectiveness and a better capability to gather solar irradiation with respect to the pristine and doped semiconductors.

3. Different Nanomaterials used as photocatalyst

3.1 Metal-based nanomaterials

The different nanomaterials used as photocatalyst has been shown in Fig. 1. Many works are published on metal NPs as photocatalysts. For instances, Mongal et al., [46] investigate the photocatalytical behaviour of silver doped TiO$_2$ NPs via convenient single step sol gel method. Doping concentration of silver significantly change the photocatalytical properties of TiO$_2$. In terms of efficient photocatalyst for organic compounds under UV rays and air conditions, 0.75 wt% silver doped TiO$_2$ shows the best performance. Further study reveals that studied doping of gold can exhibit much higher photocatalytical activity as compared to silver. Kowalska et al., [47] reported photodeposition of 2 wt% doping gold on the surface of TiO$_2$ with controlled temperature conditions. In comparison to silver monometallic and Au/Ag bimetallic photocatalysts, gold monometallic photocatalysts
demonstrated significantly higher activity during alcohol dehydrogenation under UV irradiation. Montoya and Gillan [48] studied the surface modification of doping of 1 or 2 wt% cobalt, nickel and copper enhances the photocatalytical hydrogen evaluation. The photoinduced TiO₂ conduction band electrons in solution are likely to be transferred to protons in solution that are reduced to H₂ through the photodeposited 3d metal species on the TiO₂ surface. Dholam et al., [49] investigated the photocatalytical activity of chromium and iron doped TiO₂ nanocomposites (NCs) synthesized by physical and chemical method. Radio frequency magnetron sputtering and a sol gel method were used to synthesized nanocomposite and study the effect of different percentage of metal dopant (up to 5 wt %) for hydrogen generation under visible light irradiation. Salas et al., [50] reported a synthesis of platinum doped TiO₂ photocatalyst by using incipient wetness impregnation method. 1 wt % doping of platinum in TiO₂ decreases the band gap from 3.20 to 2.73 eV and shows favourable photocatalytical properties for water splitting.

3.2 Metal oxide-based nanomaterials

Manivel et al., [51] reported the synthesis of CuO-TiO₂ nano-catalyst, with high photocatalytical properties via easy impregnation method. Compared with bare TiO₂, CuO-TiO₂ nano-catalyst is much more effective in photocatalytic degradation of Acid Red 88. This nano-catalyst provides more surface-active sites for photocatalytical activity. Liu et al., [52] demonstrated the synthesis of ZnO/TiO₂ NPs via two different methods viz., sol-gel and solid phase reaction method. Using a sol-gel method, the photocatalytic activity of ZnO/TiO₂ particles was nearly the same as that of pure TiO₂, whereas, the photocatalytic activity of ZnO/TiO₂ particles prepared by solid phase reaction was significantly higher. Doping of 0.5% of ZnO in mole with 500 °C calcinations shows excellent photodegradation of Rhodamine B. Using CeO₂ doped anatase TiO₂ with exposed (001) high energy facets, Wang et al., [53] reported selective reduction of NO by NH₃ with its catalytic properties. Initially TiO₂ was prepared hydrothermally by using its precursors and then it is exposed with (001) high energy facet. Photocatalytic activity was monitored with doping of different molar ratio of cerium into the titania (Ce/Ti molar ratio) surface. It was found that at unit molar ratio, catalyst show excellent selective catalytic reaction NO with NH₃ at high temperature. Using an easy aqueous sol-gel synthesis at ambient temperature, Mahy et al., [54] synthesized TiO₂ materials doped with different mol % of zirconia precursors. As a result of better charge separation between TiO₂ and ZrO₂ oxides under UV/visible light, zirconia improved the p-nitrophenol degradation in water efficiency. In addition, photocatalytic activity was evaluated on the degradation of methylene blue dye under UV-A light, the most doped sample demonstrating 4 times greater degradation compared to the pure TiO₂ sample. Gnanasekaran et al., [55] synthesized the TiO₂@Fe₃O₄ NCs by mixing the precipitation and sol gel method with higher surface area value 115.7 m².g⁻¹. The TiO₂ and Fe₃O₄ was prepared separately via sol gel and precipitation method respectively and then it mixed with isopropanol with the ratio 1:0.2:5 with constant stirring. This reaction mixture then converted to sol gel by drop wise addition of citrate solution. The TiO₂@Fe₃O₄ NCs were studied with a UV-abs spectrometer, revealing 2.70 eV as the band gap for the material.
3.3 Metal-polymer based nanomaterials

Using TiO$_2$ NPs as initiators to photopolymerize 2-(tert-butylamino)ethyl methacrylate and ethylene glycol dimethacrylate, novel TiO$_2$/biocidal polymer core/shell NPs were synthesized by Kong and his co-worker [56]. In the preparation, the monomers were adsorbed onto TiO$_2$ surfaces through interactions between ester groups and metal oxide surface sites. During UV light irradiation, the excited TiO$_2$ NPs produced electron-hole pairs, which simultaneously initiated the surface polymerization of the monomers on the surface. Tekin et al., [57] prepared the PVA/TiO$_2$ and PEG/iO$_2$ nanocomposites via sol gel method and studied their thermal, antibacterial and photocatalytic properties in detailed manner. The study compared the antibacterial and photocatalytical activity of PVA/TiO$_2$ is much better than bare TiO$_2$ and PEG/TiO$_2$ for *E. coli* and Acid Black I dye respectively.

Using ammonium persulfate as an oxidant in the presence of ultrafine grade powder of *anatase* TiO$_2$ cooled in an ice bath, Zhang et al., [58] synthesised polyaniline-*anatase* TiO$_2$ NCs in a series of different ratios of polyaniline:TiO$_2$ by 'in-situ' deposition oxidative polymerization of aniline hydrochloride and *anatase* TiO$_2$. The study reveals that photocatalytic degradation of polyaniline solid-phase products could be achieved as well as polyaniline-TiO$_2$ NCs having potential to be used as photodegradable products. Also, the photodegradation rate is increases as the ratio of polyaniline:TiO$_2$ is decreases. Saravanan et al., [59] reported a synthesis of TiO$_2$/Chitosan NCss with different weight ratio of TiO$_2$ and chitosan by two step method. In first step, TiO$_2$ NPs prepared via sol gel method using 1:2 ratio of acetic acid and isopropanol. In next step, different weights of TiO$_2$ and chitosan were weighed and dissolve in acetic acid. The pH of solution was increased by addition on NaOH to precipitate out the TiO$_2$/Chitosan NCs. As mass of chitosan increases, the crystallinity of NCss was decreased. Fischer et al., [60] demonstrated the easy scale-up methods with highly efficient crystalline TiO$_2$ NPs on polyethersulfone microfiltration membrane to remove pollutants in a continuous way. A mixture of titanium (IV) isopropoxide and hydrochloric acid was used for the purpose. After heating and cooling to 210 °C, the membrane became thoroughly dipped into the dispersion of TiO$_2$. Photocatalytic activity of ultrasound-treated NPs was highest in degrading carbamazepine, and degradation did not decrease after nine repetitions.

4. Synthetic approaches towards photocatalysts

4.1 Sol-gel

Among the most commonly used methods for synthesizing photocatalysts is the sol-gel method. Since it is possible to regulate many parameters, it is an effective way to tailor metal oxides to specific applications. These parameters include, for example, precursor composition, pH, temperature and reaction time, concentration of reagents, nature and concentration of catalysts, aging time and temperature, addition of organic additives, and water amount. Sol-gels are primarily used because they produce polycrystalline particles with special properties due to their homogeneous mixing of metal ions at the molecular level. Additionally, the sol-gel method has the advantage of incorporating different types
of dopants during some stages. During the gelation stage, active dopants are introduced into the sol, allowing direct interaction between them and the support, enhancing the photocatalytic properties of the material [61]. As defined by the sol-gel method, it involves the inorganic polymerization reaction induced by water to convert a precursor solution into an inorganic solid; an aqueous or alcoholic mixture of metal-organic salts (alkoxides) or inorganic salts (chloride, nitrate, sulfate, acetate, etc.) is used as a precursor. After preparing a homogeneous solution, the next steps in the sol-gel process are: (a) converting the homogeneous solution into a sol by using a suitable reagent (generally water with or without acid/base), (b) aging, (c) shaping, and (d) thermal treatment/sintering [62]. As a result of hydrolysis and condensation, M-O-M bonds are formed inorganic polymers, which are further condensed to form gels. Aerogels can be synthesized by drying the gels under extremely harsh circumstances. A xerogel is fabricated when the gel is dried at room temperature. The desired material is then produced by thermally treating the gel, and it can then be formed into a variety of shapes such as monoliths, films, fibres, and monosized powders. Using titanium (IV) n-butoxide as a precursor, Candrappa K. G. et al., and Chen Y. C. et al., synthesised TiO₂ using the sol-gel method [63, 64]. Depending on the synthesis conditions and calcination temperature, anatase or rutile phase can be produced. TiO₂ was synthesised by the sol-gel method from two different alkoxide precursors, titanium (IV) n-butoxide and titanium (IV) isopropoxide, and Chen Z et al., investigated the impact of the nature of the oxide precursors throughout this process [65]. Also, the sol-gel approach was used by Clayton Farrugian et al., to fabricate W, Ag, and W/Ag co-doped TiO₂ nanopowders. [66]. Choi J et al., used the sol-gel method to blend gold particles into Ti₁ₓZnₓO₂ films [67].

4.2 Hydrothermal

Any heterogeneous reaction occurring under high pressure and temperature circumstances with aqueous solvents or mineralizers is typically referred to as hydrothermal. With the reaction taking place in aqueous solutions, this synthetic process is often carried out in steel pressure containers called autoclaves with or without Teflon liners under regulated temperature and/or pressure. It is possible to raise the temperature beyond the point at which water starts to boil and achieve vapour saturation. The internal pressure generated by the autoclave is mostly determined by its temperature and the volume of solution supplied [68]. The experimental temperature and pressure settings and the corrosion resistance in that pressure-temperature range in a certain solvent or hydrothermal fluid are the most crucial factors for choosing an appropriate autoclave. The corrosion resistance is a key consideration in the selection of the autoclave material if the reaction is occurring directly in the vessel. High-strength alloys, such as stainless steel, iron, nickel, cobalt-based superalloys, titanium and its alloys, are the most effective materials for resisting corrosion [69]. By hydrothermally treating peptized precipitates of a titanium precursor with water, Han C. et al., synthesized TiO₂ NPs [70]. Through hydrothermal processing, Horikoshi S. et al., synthesised phosphorus-doped TiO₂ (P-TiO₂) having a mesoporous structure [71]. Well-crystallized mesoporous P-doped titania NPs were developed by Hu L. et al., using both hydrothermal and sol-gel techniques [72]. Alternately, using a combination of the sol-
and hydrothermal techniques, ternary Bi$_2$WO$_6$ photocatalyst has been formed as microspheres. In contrast, Bi$_2$WO$_6$ was also produced directly by a hydrothermal reaction without using the \textit{sol-gel} method. Sol-gel-hydrothermal (SH) Bi$_2$WO$_6$ was composed of hollow monodispersed hierarchical microspheres, whereas hydrothermal (H) Bi$_2$WO$_6$ has an uneven platelike structure. The results of the degradation of methylene blue (MB) in the presence of the various Bi$_2$WO$_6$ catalysts revealed that SH-Bi$_2$WO$_6$ demonstrates higher photocatalytic activity over H-Bi$_2$WO$_6$. It was determined that SH-improved Bi$_2$WO$_6$'s photocatalytic activity was due to the unique hierarchical structure that was developed by the fusion of \textit{sol-gel} and hydrothermal processes [73].

4.3 Solvothermal

The hydrothermal method is a derivative of the solvothermal method, which uses a nonaqueous solvent. Due to the wide range of organic solvents with high boiling points that can be chosen, the reaction temperature can be increased to much greater levels than in the hydrothermal approach. In general, the solvothermal technique is superior to the hydrothermal method for controlling the photocatalyst particle size, shape, distribution, and crystallinity [74]. With or without the use of surfactants, the solvothermal approach has been used to create TiO$_2$ NPs and nanorods. It has been proven to be a practical method for the synthesis of a range of NPs with narrow size distribution and dispersity. Otherwise, the solvent has a significant impact on the crystal shape. The solubility, reactivity, and diffusion behaviour of the reactants can be affected by solvents with various physical and chemical properties; in particular, the solvent's polarity and coordinating ability can affect the morphology and crystallisation behaviour of the end products. A high concentration of ethanol not only has the ability to modify the solvent's polarity but also has a significant impact on the reactant particles' potential values and raises the viscosity of the solution. For instance, instead of nanowires, short and wide flakelike structures of TiO$_2$ were produced in the absence of ethanol. TiO$_2$ nanorods were synthesized by Kappe using chloroform [75]. It is typically easier to regulate the size, crystallinity, and agglomeration behaviour of the NPs using nonaqueous solvothermal methods. Since there are more active sites accessible for photocatalytic processes, mesoporous TiO$_2$ microspheres with rough surfaces often exhibit high specific surface area, which is a crucial characteristic for the photocatalytic activity. Solvothermal techniques were used to create a number of distinct types of mesoporous TiO$_2$ samples in various sizes [76, 77, 78]. Using tetrabutyl titanate as a precursor in a polyethyleneimine solution diluted with 100% ethanol, hierarchical mesoporous TiO$_2$ microspheres with high crystallinity and high BET specific surface area were synthesized in this context. Methyl orange (MO) and phenol aqueous solutions were degraded using the produced TiO$_2$ microspheres, and the activity of this process was assessed. The solvent's physicochemical behaviour qualities are altered in solvothermal circumstances, which involve high pressure. A nanocatalyst made of bismuth oxyiodide (BiOI) by Li X et al., has high photocatalytic activity when exposed to visible light [79]. According to a report by Mera et al., they developed BiOI microspheres using a solvothermal process (2014) [80].
4.4 Chemical vapor deposition (CVD)

Chemical vapor deposition (CVD) is another method that has been exploited for the fabrication of supported titanium dioxide materials. In CVD, thin films prepared on glass, metallic substrates, or semiconductive substrates, composites fabricated from activated carbon/titanium dioxide, amine polymers synthesized from titanium dioxide, and titanium dioxide nanorods fabricated from titanium precursor using CVD method. A chemical vapor deposition technique combines physical and chemical methods of producing materials. Due to their simplicity of control over synthesis, narrow particle size distribution, and low cost, chemical methods are the most popular method of synthesis of photocatalysts. While physical methods have been less explored, they are particularly relevant to large scale production of materials because highly specialized equipment and operators are required. High purity materials can be produced by CVD; besides, it does not require post-heat treatment to improve crystallinity. A few of these techniques include atmospheric pressure chemical vapor deposition (APCVD), plasma-enhanced chemical vapor deposition (PECVD), metal-organic chemical vapor deposition (MOCVD), which uses metal-organic precursors, and hybrid physical chemical vapor deposition (HPCVD). In cases requiring conformal deposition of the material, CVD is considered one of the most precise techniques. Molecular precursors are needed for CVD film growth. In order to transport precursor molecules, a chain of inert or reactive gas used. Chemical reactions in the gas phase near the surface convert them into a thin solid film of the desired material. The deposition reaction in CVD technologies is driven by hot carrier gases. TiO$_2$ thin films were synthesized by Sarantopoulos et al., utilising borosilicate glass and silicon wafers as substrates and titanium (IV) isopropoxide as the molecular precursor in an isothermal, isobaric, horizontal low-pressure CVD reactor. Visible light assisted photocatalytic activity of various dyes using Boron-doped TiO$_2$ nanotubes reported by Q. Zhang et al. The synthesis of TiO$_2$ nanotubes was achieved by using electrochemical anodization technique [82]. Zhu Y. et al., synthesized B-doped samples displayed stronger absorption in both UV and visible ranges. Additionally, the CVD techniques may quickly and at low deposition temperatures create coating materials that are single-layer, multilayer, composite, nanostructured, and functionally graded with precise dimension control [83]. Foster et al., (2010) provided information on the atmospheric pressure thermal CVD development of TiO$_2$/Ag and TiO$_2$/CuO thin films. Even against MRSA (methicillin-resistant staphylococcus aureus) and a few other infections, the movies had good microbicidal action [84]. The degradation of methylene blue was tested using a modified CVD technique to create V$_2$O$_5$/TiO$_2$ NCs particles and films, according to Lianjie Zhou et al., [85,86]. By using CVD, ZnO and other chalcogenide films have been created.

4.5 Green Techniques

Green synthesis technique is an eco-friendly approach for the synthesis of photocatalyst or NMs. This exploited natural or biological resources for the synthesis of NMs (Fig. 2) This technique has nontoxic, efficient and environmentally benign. In a recent time, scientific community have been described to accomplish the success of synthesis of NMs from plant
extracts like leaves, roots, stem, fruits, peels, and seeds [87-89]. The notable success in this field has opened new route to advance “greener” approaches for the manufacturing of NMs with impeccable structural properties using milder and cheaper initial constituents [90].

Indeed, the biogenic or green technique is commendable approach in the area of nanoscience and nanotechnology due to the concern of cost-effectiveness, fast, use of non-hazardous biochemicals, and their implausible properties. However, the conventional methods are being widely used for fabrication of nanomaterials like metal, metal oxide, metal oxides-polymer NCs, quantum dots, and carbon-based NMs [91-93], although, these methods encompasses with several pitfalls like expensive reagents, harmful chemicals, ominous effects on the medical equipment, and environment hazardousness. Considering the precedent apprehensions, exploration interest is being paid to develop a green, sustainable, non-toxic, inexpensive, and biocompatible technique. One of the best green synthesis techniques of nanomaterials; is a biogenic synthesis, it is a substitute technique to traditional or orthodox methods [94-97]. The biogenic synthesis of NMs involves bacteria, algae, fungi, enzymes, animal mass cultures, yeasts, and plant extracts. Among
These, plant/microbial-assisted synthesis is convenient, rapid, cheaper, green, easy to handle, and non-hazardous approach. The biochemicals present in extract of plants can play disparate roles during fabrication NMs like reducing, surfactant, capping, and stabilizing agents [98-99].

5. Process of photocatalytic activity

5.1 Types of photocatalyst used in photodegradation activity

The photocatalytic responses can be distributed into two types on the base of appearance of the physical state of reactants. Homogeneous photocatalysis, when both the semiconductor and reactant are in the same phase, i.e. gas, solid, or liquid, similar photocatalytic responses are nominated as homogeneous photocatalysis [100]. Different photocatalysts likewise ZnO, ZnS, CdS, SrO$_2$, WO$_3$ and Fe- TiO$_2$ have been used for treatment of air adulterants. The most popular among them is TiO$_2$ due to its low cost, high stability, environmental benevolence. It's a semiconductor which is used for print-convinced redox responses for declination of VOCs [101].

5.2 Source of light

Ultraviolet LED (UVLEDs) are mainly employed for the photocatalytic degradation of organic pollutants present in air and water. Recent findings have shown that visible LEDs, like blue, red, green, and white, can also be used for photocatalytic applications [102]. Photodegradation is degradation of a photodegradable molecule caused by the absorption of photons, particularly those wavelengths found in sunlight, such as infrared radiation, visible light, and ultraviolet light. However, other forms of electromagnetic radiation can cause photodegradation [103]. Methylene blue is brought into contact with the photocatalytic active surface of a test sample that is irradiated through the supernatant solution (320 nm $<< 400$ nm). The solution is decolourated in the process. Throughout the measurement, the colour concentration of the solution is measured by UV-vis spectroscopy [104]. Photocatalytic semiconductors can be prepared in the form of powders, fibers, and films by different synthetic methods including sol-gel process, hydrothermal and solvothermal techniques, direct oxidation reactions, sonochemical method, microwave method, chemical vapor deposition method, and electrodeposition method [105].

5.3 Mechanism of photocatalytic degradation

The dye degradation by GMO photocatalyst as depicted in exemplifies oxidation process, adopted by the reactive oxygen species, for example hydroxyl radicals, superoxide, anions, and singlet oxygen species that formed in the reactor. Photocatalytic oxidation mechanism using semiconducting material can by summarized as:
5.3.1 Photo excitation

In photocatalytic reaction, electron promoted from the filled valance band (VB) of photocatalyst to the conduction band (CB) because of light irradiation. The absorbed photon has energy ($h\nu$) are either greater than the band gap of the semiconductor photocatalyst. The excitation process leaves behind a hole in the $h^+(VB)$ thus electron and hole pair ($e^-/h^+$) is generated as shown below in equation.

\[
M/MO^+ + h\nu (UV) \rightarrow M/MO (e^- (CB) + h^+ (VB))
\] ………… (1)

5.3.2 Ionization of water

The photo-generated holes at the valance band then react with water to produce OH$^-$ radical.

\[
H_2O (ads) + h^+ (VB) \rightarrow M/MO + OH^- (ads) + H^+ 
\] ………… (2)

The produced hydroxyl/superoxide are radical anion further react with remaining water molecules to produce the active hydroxyl ion exclusively which has been acted as a strong oxidized agent. Owing to their strong oxidation property, the toxic dye molecules have been break down and resulted corresponding CO$_2$ and H$_2$O.

5.3.3 Oxygen ion sorption

The photogenerated hole ($h_{VB}^+$) reacts with surface bound water or OH- to produce the hydroxyl radical, electron in the conduction ($e_{CB}^-$) is taken up by the oxygen in order to generate anionic superoxide radical ($O_2^-$). This superoxide ion may not only take part in the further oxidation process but also prevent the electron hole recombination, thus, sustaining electron neutrality within the graphene based NCs.

\[
O_2 (ads) + M/MO (e^- (CB)) \rightarrow M/MO + O_2^-(ads)
\] ………… (3)

5.3.4 Protonation of superoxide

The superoxide ($O_2^-$) produced gets protonated forming hydroxyl radical ($HO_2^-$) and then subsequently H$_2$O$_2$ further dissociates into highly reactive hydroxyl ions (OH$^-$).

\[
O_2^- (ads) + H^+ \rightarrow HOO^- (ads)
\] ………… (4)

\[
2HOO^- (ads) \rightarrow H_2O_2 (ads) + O_2
\] ………… (5)

\[
H_2O_2 (ads) \rightarrow 2OH^- (ads)
\] ………… (6)

\[
\text{Dye} + OH^- \rightarrow CO_2 + H_2O (\text{Dye intermediate})
\] ………… (7)
Dye + h\(^+\) (VB) \rightarrow Oxidation product…………………….. (8)

Dye + e\(^-\) (CB) \rightarrow Reduction product…………………….. (9)

Both oxidation and reduction process take place on the photo excited semiconductor photocatalyst.

5.3.5 Scavengers and trapping agent in photocatalysis

The part of hole scavengers in photocatalysis is frequently regarded to be removing the holes in photocatalysts by giving electrons to them. Mureithi et al., show that the effect of hole scavengers goes beyond junking of holes to affecting the response time, pathways, and products in photocatalytic responses. Utmost photocatalytic nanosystems reported so far employ a hole scavenger a sacrificial chemical which is oxidized in the photocatalytic process and therefore removes the hole from the nanostructure [106]. Fastening on the influence of different species, similar as scavengers (t- butanol, formic acid, methanol, p-benzoquinone, oxalate, superoxide dismutase, and azide), snooping species (sulfite, dichromate, bromate, carbonate, chloride, and iodide) and inorganic ions (nitrate, sulfate, and phosphate), this work delved the product of hydroxyl revolutionaries and singlet oxygen during TiO\(_2\)/UVA responses. Electron paramagnetic resonance spectroscopy (EPR) was applied to probe revolutionaries formed in the presence of each snooping/scavenger species. Some scavengers and snooping species were studied during phenol declination, chosen as a model substrate. All species, except bromate, hindered the declination. Para-benzoquinone showed an increased hydroxyl radical product, attributed to the print- reduction of quinones. revolutionaries other than hydroxyl revolutionaries, similar as carbon dioxide, hydroxymethyl, azide, and semiquinone, were linked in the presence of oxalate, methanol, azide, andpara-benzoquinone, independently. Some of these revolutionaries can conceivably interact with organic substrates due to their reduction eventuality; as a result, a critical interpretation must be done when these species are added to a miscellaneous photocatalysis process.

6. Photodegradation & photoreduction of toxic compounds

6.1 Photocatalysis

In recent years, a great deal of effort has been dedicated to solve the widespread pollution caused by effluents from urban and agricultural industries, which includes bio recalcitrant and organic pollutants [107]. Development in industrialization and continuous progression of newer technologies coupled with poor environmental policies have led to the generation of toxic effluents in huge amount which are discarded into natural water bodies. The main component of this chemical discharge from textile, chemical, petroleum and many other industries are azo dyes. These toxic dyes not only disturb the aquatic ecosystem but also has a devastating effect on human life and terrestrial biota. These dyes are mutagenic, carcinogenic, and highly toxic to CNS and can cause respiratory diseases, cancer, genetic
disorders, chromosomal abnormalities and many acute disorders. Moreover, these dyes remain in environment for longer periods of time without degrading [108]. In view of this situation, it has become imperative to reduce and remove these chemical pollutants (synthetic dyes) from environment. In this regard, semiconductor assisted photocatalysis has received global attention, since these dyes are resistant to biological and physical treatment methods [109].

Heterogeneous semiconductor photocatalysts can absorb solar radiation to generate electron-hole pairs which can accelerate the remediation of these dyes. A simple mechanism of heterogeneous photocatalysis includes absorption of light by semiconductor, leading to the excitation of electrons from valence band to conduction band leaving behind holes in VB. Figs. 3 & 4 depicts the process of dye degradation on a semiconductor photocatalyst involving direct and indirect pathways. In the indirect pathway, dye is degraded by reactive oxygen species formed on the catalyst surface. Photogenerated holes react with adsorbed water or hydroxyl ion to generate hydroxyl radicals whereas electrons in CB reacts with oxygen to form superoxide radicals. These reactive oxygen species quickly, and non-selectively reduces the pollutants, including dyes, antibiotics, drugs, and phenolic compounds. In the direct pathway under light irradiation, shaded organic dyes such as RhB, EBT, IC, TB, MO, CR and MB can also be excited in the process called photosensitization, where dye is excited from the ground state to the excited state. Charge transfer occurs from the highest occupied molecular orbital (HOMO) of excited state dye to the conduction band of the photocatalyst providing more electrons to generate superoxide radicals, as a consequence enhancing the photocatalytic degradation activity [110]. Still, the quick recombination rate of photogenerated electron – hole dyads within photocatalytic accoutrements results in its low proficiency, therefore limiting its practical operations. Thus, repression of recombination of charge carriers is crucial for the improvement of photocatalytic exertion of semiconductor PCs. Besides the conventional doping and adding co-sorbents, carbon – semiconductor mongrel accoutrements have come a new class of photocatalysts, which lately has attracted a lot of attention [111]. Among carbonaceous materials, graphene has received attention due to its unique properties, such as high charge-carrier mobility, high thermal and electronic conductivity, and high specific surface area. These unique properties of graphene make it an ideal support material for semiconductor photocatalysis. Furthermore, interaction of graphene with semiconductor materials give rise to unique properties such as an extended light absorption and decreased charge carrier recombination rates along with high stability [106]. Therefore graphene-semiconductor hybrid materials have been widely used for the degradation of organic pollutants, antibiotics, organic compound, photocatalytic hydrogen generation and photocatalytic disinfection. In this segment the main applications of graphene-based semiconductor photocatalysts like PANI, NiO, TiO₂, Fe₃O₄, and ZnO etc., are briefly summarized.
6.2 Photocatalytic degradation of dyes

Nowadays, we are facing huge inadequacy of pure and potable water and its accessibility is becoming more and more luxurious day by day. This is due to the disposal of several toxic wastes from many industries, pharmaceutical laboratories and agricultural field. Among these effluents the inorganic and organic dyes are issue of major concerned. Scientists are focusing on biodegraded dyes and dye derived components. Biopolymers are the most preferable choice for the degradation of dyes as their enhanced catalytic activities are reported by so many researchers so far. Millions of people in the developing countries decease due to unavailability of clean and pure drinking water and safe hygienic environment. We need an eco-friendly, cheap and easy process to biodegrade these toxic dyes for purification of water as day by day the sources for portable water is vanishing and turning into the ponds of eutrophicated, toxic, dirty and polluted water bodies. The pollutants which are majorly found in water bodies consist of pesticides, herbicides, dyes, surfactants etc., [112]. To overcome these problem, recent past year’s graphene-based photocatalyst have gained significant importance for the photocatalytic application. Due to their high photosensitivity, high surface area and excellent optical, mechanical and electrical properties and stability, eco-friendly tactic, nontoxic, low cost and enhanced catalytic properties, they are being widely used in water cleansing, photodegradation of toxic dyes and chemical effluents (Figs. 3&4) [113]. Chaudhary et al., synthesized ZnO-rGO NCs for photodegradation of methylene dye using visible irradiation, study revels methylene blue dye was degraded about 85% in 70 min by using ZnO-rGO NCs [114]. Sonkusare et al., microwave-mediated synthesis, photocatalytic degradation activity of α-Bi2O3 microflowers/novel γ-Bi2O3 microspindles, theα-Bi2O3 MFs show enhanced photocatalytic activity than γ-Bi2O3 MSs under UV light irradiations [115]. Rahimi et al., projected rGO/NiO nanowires for photocatalytic disintegration of methyl orange (MO). For Photocatalytic decomposition of MO requires both hydroxide and superoxide radicals [116]. Mitra et al., have synthesized a new PCs based on Polyaniline/reduced graphene oxide (PANI/rGO) composites by oxidative polymerization. They have reported that 5 wt % rGO(PG2) can be engaged with outstanding photocatalytic efficiency percentage 99.68, 99.35, and 98.73 for MG, RhB, and CR within 15, 30, and 40 min, respectively. The experimental results showed that rGO can reduce accretion of PANI and increased surface area which enriches the photocatalytic activity [117].

In another study, Elshypani et al., [118] described solid state mediated magnetite zinc oxide (MZ) (Fe3O4/ZnO) with different ratios of reduced graphene oxide (rGO). Results revealed that the photodegradation activity of Magnetite Zing Graphene MZG was more than 98.5% against Methylene Blue. This was due to synergic effect of magnetite and zinc oxide in attendance of rGO.

Hamed et al., [119] have reported Gr/Pd/TiO2-NPs and Gr/Pd/TiO2-NWs were prepared via combination of hydrothermal & photodeposition method. They have compared degradation capacity of TiO2-NWs, Gr/Pd/TiO2-NPs and Gr/Pd/TiO2-NWs towards Rhodamine B dye in UV light irradiation. Results showed that Gr/Pd/TiO2-NWs have high excellent photocatalytic activity due to high surface area. Zhang et al., [120] have studies
the photodegradation of MB in water by CuO.ZnO.Fe$_2$O$_3$/rGO and CuO.ZnO.Fe$_2$O$_3$/CNT. The degradation efficacy of composite with CNT is better than rGO.

Chandra et al., demonstrated that the photodegradation profile of eosin, methylene blue, and Rhodamine B is almost 80% in the presence of graphene-Mn$_2$O$_3$ NCs [121]. Fu and co-workers have been prepared magnetically separable ZnFe$_2$O$_4$/graphene PCs by a facile hydrothermal method. The PCs displayed 88% of MB degradation by adding H$_2$O$_2$ as a scavenging agent in 5 min and reached up to 99% at 90 min in irradiation of visible light. It assists a dual function as photoelectron-chemical degrader and generator of hydroxyl radicals via photo electrochemical decomposition of H$_2$O$_2$ [122].

Fig. 3. Indirect dye degradation

Fig. 4. Direct dye degradation
6.3 Degradation of antibiotics and pharmaceutical drugs

Besides adsorption, antibiotics can be efficiently decayed or perished into non-toxic small molecular species under the sun, visible light and ultraviolet (UV) light, due to the presence of active groups (e.g. superoxide ions ($O_2^-$) and hydroxyl revolutionaries (.OH) produced by photocatalysts. So photocatalytic declination is one of the most operative, green, and generally used ways for antibiotics pollutants junking in the terrain. Graphene, as a promising PCs, has been extensively explored for photo catalytic declination of antibiotic poisons in water, due to their large specific face area for invariant distribution, narrow band- gap powers and exceptional electrical conductivity in storehouse and fast transport of electrons, and low manufacturing cost for large scale products. Therefore, graphene is frequently combined with other photocatalysts to form new photocatalysts in order to overcome these downsides and ameliorate the catalytic performance of antibiotics. In recent times, colourful attempts have been devoted to designing and fabricating graphene-grounded semiconductor photocatalyst in order to increases the declination capacity of antibiotic adulterants. In this regard, Song et al., set MnO$_2$/ grapheme NCs by an In-situ hydrothermal system, and it successfully removed up to 99.4 of the tetracycline residues in pharmaceutical wastewater [123]. In another study, Shanavas et al., examined the declination capacity of ibuprofen and tetracycline motes efficiently under visible light irradiation within 90 min using ternary Cu/ Bi$_2$Ti$_2$O$_7$/ rGO NCs. The attained results suggested that the Cu NPs and the rGO wastes play a major part in the photocatalytic capability of Cu/ Bi$_2$Ti$_2$O$_7$/ rGO PCs by acting as charge carrier fowlers and the repression of $e^- - h^+$ recombination [124].

6.4 Photocatalytic degradation of phenolic compound

Principally organic colourings have been substantially named as a model emulsion to estimate the photocatalytic exertion of graphene-grounded NCs [125]. Among the dangerous organic pollutants set up in artificial backwaters, phenol and phenolic composites are veritably important [126]. The discharge quantum of phenol in water must be maintained at 0.1 –1 mg/ L(ppm) grounded on the environmental protection rules of the Pollution Control Board (1992) thus, semiconductor PCs displayed bettered photocatalytic declination of phenol under dissembled solar/ UV/ Visible irradiation after objectification of graphene. Graphene-grounded TiO$_2$/ ZnO NCs were prepared via hydrothermal system by Malekshoar et al., [127] the photocatalytic profile of the coupled NCs with an optimized rate of the mechanisms was explored. The results reveal that the coupled mixes (Graphene-ZnO/TiO$_2$) with 0.95 to 0.05 rate) outpaced, when compared to a single compound by a factor of 2. Also, the parametric study was carried out to optimize the response conditions. Experimental results showed that 1 h of 100 mW/ cm$^2$ solar irradiation was needed to degrade 40 ppm phenol at neutral pH, when1.25 g/ L of coupled ZnO-G/ TiO$_2$-G mixes Li. Fen Chiang et al., synthesized Cu–TiO$_2$ nanorods for bisphenol degradation under UV-visible light irradiation [128].
Conclusion

In a conclusion, the nanomaterials are the alternative for degradations of various organic pollutants from the contaminated waters. There are several types of nanomaterials can be used as active photocatalysts. The better catalytic activity of the nanomaterials is depends on its optical properties. Every nanophotocatalyst must have ideal bandgap. A simple mechanism of heterogeneous photocatalysis includes absorption of light by photocatalyst, leading to the excitation of electrons from valence band to conduction band leaving behind holes in valence band. A heterogeneous photocatalysts can absorb light radiation to generate electron-hole pairs which can accelerate the remediation of these dyes or macromolecules. The photocatalytic degradation of toxic compounds can be processed under different light irradiations, for instance antibiotics dyes, drugs, and phenolic compounds can be efficiently decayed or perished into non-toxic small molecular species under the sun, visible light and ultraviolet.

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