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PHOTOCATALYTIC ACTIVITY OF TiO_2 NANOMATERIAL

ABHILASHA JAIN[1)] AND DIPTI VAYA[2)]

[1)]Department of Chemistry, St. Xavier's College, Mumbai-400001 India
[2)]Department of Applied Science, THE NORTHCAP UNIVERSITY, Gurugram-122017 India*

ABSTRACT

Nanomaterials synthesize by different techniques exhibit excellent photocatalytic activity. These catalysts could be employed for environmental remediation, renewable energy sources, photocatalysis and many other applications in various fields. Nanophotocatalyst has been used for the treatment of hazardous materials such as industrial effluents containing complex organic compounds, dyes and metal ions successfully. The multidimensional study of composition, shape, size, surface area and nanostructure and different operating parameters like pH, concentration, temperature etc, of these photocatalyst help in current and further development of photocatalysts for different applications . The photocatalytic activity of nanoparticles has made a great contribution in providing definitive mechanistic information about the photocatalytic processes.

The main aim of this review paper is to give an overview of the enhanced photocatalytic activities of titanium dioxide (TiO_2) nanoparticles. This review includes the basic properties of photocatalyst and mechanim of photocatalysis process followed by unique photocatalytic properties and research of TiO_2 nanoparticles as photocatalysts. An effort has also been made to give an overview of expedient photocatalytic activity of these doped nanoparticles. Many investigators have reported the enhanced photocatalytic activity by the degradation of dyes as a model compound.

Key Words: photocatalysts, TiO_2, nanoparticles, AOPs.

1. INTRODUCTION

Today, the industrial revolution is putting its negative impacts on the entire globe. Over the year's complexities, varieties and the amount of hazardous compounds are increasing in wastewater discharged by various printing, dyeing, textile and other chemical industries into the ecosystem. These compounds are highly carcinogenic and mutagenic. Apart from aesthetic pollution, they are causing eutrophication, high Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD). In addition to that, these compounds absorb sunlight strongly which affects the photosynthetic activity of aquatic plants and seriously threatening the whole ecosystem [1, 2]. Now days the perilous effects of organic dyes to the environment is a particular concern. To resolve this problem, the photocatalytic decomposition processes are being employed by many researchers to degrade the organic pollutants of industrial wastewater before discharge into receiving media [3]. Although various chemical and physical process are available for the degradation of textile effluents but they generate non-biodegradable contaminations and further require treatment involving expensive procedure. Conventional techniques such as coagulation/ flocculation, membrane separation, absorption methods as well as biological methods are also inefficient for removal of complex organic compounds [4-11]. To resolve such types of problems Advanced Oxidation Processes (AOPs) are proven to be most promising technique which is based on the generation of highly reactive hydroxyl radicals ($^{\cdot}OH$) [12-19]. This is the most cost effective chemical method which is extensively used for treatment of textile effluents and variety of organic pollutants [14, 20-25]. Faster degradation of dye is achieved due to the high oxidative power of ($^{\cdot}OH$) radicals (2.83 V) and it can be further improved by using UV-visible radiations that generate additional hydroxyl radicals. The major advantages of the photocatalytic process is that there is no further requirement of secondary disposal methods and also not require expensive oxidizing chemicals. In addition to that, these photocatalysts are self-regenerated and can be recycled. To improve the quality of drinking water this photocatalytic process can be used to remove nuisance odors, taste and naturally existing organic matter, which contain the precursors to trihalomethanes formed during the chlorine disinfection step [26].

2. General Mechanism of Photocatalysis and Photocatalytic Activity of TiO_2

Various semiconductors have been used as a photocatalyst i.e. TiO_2, ZnO etc. The electronic structure of a semiconductor plays a key role in photocatalysis. A semiconductor consists of Valance Band (VB) and Conduction band (CB) and the energy difference between these two levels is called the band gap having energy less than 3.5 V. Both the electrons and holes are in valence band without excitation. When semiconductor surface is exposed to light, then by absorbing particular wavelength electrons are transferred from the VB to the CB, leaving behind a holes (h^+) in the valence band and thus form electron–hole pairs. Electrons and holes migrate to the surface of the semiconductor and can reduce and oxidize the reactants which are adsorbed by the semiconductor, respectively. The reduction and oxidation potential of these photo-induced electrons and holes is much higher than that of hydrogen and ozone, respectively. Therefore, these electron–hole pairs act as a strong redox system. The photo-produced holes generate hydroxyl radicals by the oxidation of OH^- and H_2O molecules which are absorbed on TiO_2 surfaces. Simultaneously, the electrons in the conduction band could facilitate reduction of O_2 molecules which exist in absorbed air on TiO_2 surfaces and finally form peroxyl radicals. These photo-produced hydroxyl and peroxyl radicals in turn oxidize and degrade organic/inorganic materials. The reduction and oxidation reactions are the fundamental mechanisms of photocatalytic hydrogen production and photocatalytic water/air purification, respectively. The schematic representation is shown in **Fig. 1**[27]. These photo-generated electrons and holes can rejoin in bulk or on surface of the semiconductor within a very short time, releasing energy in the form of heat or photons.

Investigations reveal that among various photocatalysts, TiO_2 is the most efficient photocatalyst. Titanium dioxide ($TiO_{2)}$ was discovered in 1791 from ilmenite. In 1929, the photoactivity of TiO_2 was first noticed when it was used as white pigments in buildings [28]. Many polymorphs of TiO_2 exist. The well-known phases of titanium dioxide are anatase, rutile and brookite which was discovered in 1801, 1803 and 1825 respectively. The metastable anatase and brookite forms can irreversibly convert to stable rutile which is the naturally occurring phase of TiO_2 by heating [29].

TiO_2 exhibit low cost, stable and safe to humans and environment. There are enormous fields where the photocatalytic activity of TiO_2 nanoparticles have been explored e.g. in photocatalytic water splitting [30, 31], photocatalytic self-cleaning [32], purification of wastewater [32-37], photo-induced super hydrophilicity [33, 36, 38], photovoltaics [37, 39-42], Gap before photosynthesis [36] and antibacterial / antimicrobial activity [32, 37, 38, 42, 43]. The most promising area of TiO_2 photocatalysis is the photodegradation of a large variety of environmental contaminations such as complex organic compounds and inorganic material turn into CO_2 and harmless inorganic anions respectively [32, 2-27]. TiO_2 as a photocatalyst has shown a great potential for detoxification or remediation of wastewater. TiO_2 nanoparticles can be freely suspended in wastewater or deposited on substrates during the decontaminations process [35, 44, 45].

3. Properties of TiO_2 Nanomaterial as a Photocatalyst

Nanosized material size range between 1 and 100 nm. They exhibit properties which lie into the region of transition between the molecular and the bulk phases [46]. In the bulk material, the electron excited by light absorption could possess with different kinetic energies in conduction band [47]. As the particle size of nanoparticles is same or smaller than the size of the first excited state then, the electron and hole generated upon irradiations cannot fit into such a particle until or unless they assume a state of higher kinetic energy. Hence,

e-mail : diptivaya08@gmail.com

as the size of the semiconductor particle is reduced below a critical diameter, the spatial confinement of the charge carriers within a potential well [48], like a ‘particle in a box’ [49], causes them to behave quantum mechanically [50]. According to solid state terminology it means that the bands split into discrete electronic states (quantized levels) in the VB and CB [51] and the nanoparticle behaves more and more like a giant atom [47]. Nanosized semiconductor particles which exhibit size-dependent optical and electronic properties are known as quantized particles (Q-particles) or quantum dots [52]. Such type of researches explains their quantum-mechanical aspect to understand the activity of nanoparticles.

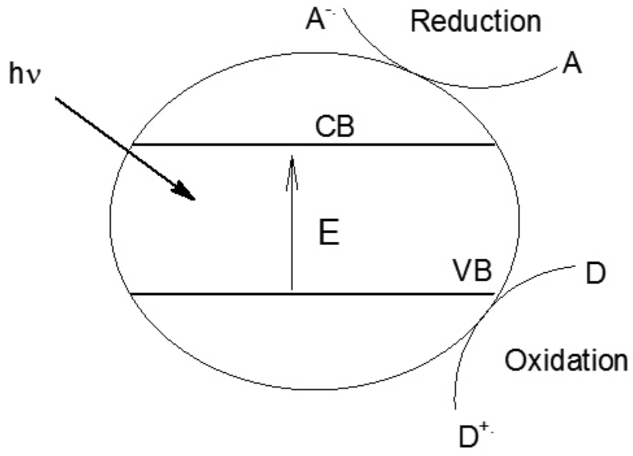

Fig. 1: Mechanism of Photocatalytic Activity.

Various investigations have shown that various properties of nanocrystalline semiconductor particles are different from those of bulk materials. Both surface adsorption as well as photocatalytic reactions can be increased by nanosized semiconductors because of having more available reactive surface area.

In recent scenario nanoscience has more advantages than ongoing technologies because nanomaterials completely mineralize most of organic compounds [53] and completely removed from polluted water [54]. Nanophotocatalyst are non-toxic, chemically and thermally stable [55]. In addition, these photocatalyst are easily available, inexpensive and resist for corrosion in the presence of water and other chemicals [56].

Nano-TiO_2 have been synthesized in various sizes and shapes such as nanoparticles [57-58], nanotubes [59- 60], nanowires [60], inverse opals [61], nano ribbons [62] and nanosheet arrays [63]. Some of them are shown in Fig.2**.** [64]. There are different methods such as hydrothermal, sol-gel, precipitation etc are available to synthesize different shape of *NPs*. Generally, nano-TiO_2 is synthesized by using various titania precursors such as titanium tetra-iso-propoxide (TTIP) [65], tetrabutyl titanate (TBOT) [66] and titanium tetrachloride ($TiCl_4$) [67].

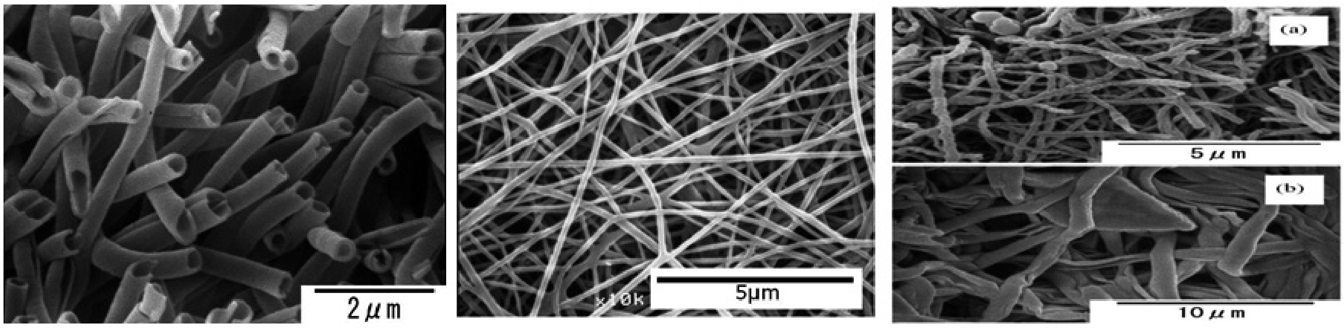

Fig. 2: (i) SEM image of TiO_2 nanotubes formed by calcination of PVA-TTIP hybrid nanofibers.
(ii) SEM image of TiO_2 nanofibers obtained by calcination at 400°C for 5 hours in air.
(iii) SEM images of (a) non-hollow TiO_2 nanofibers and (b) wall-broken TiO_2 nanotubes.[64].

TiO_2 nanostructures due to high surface-volume ratio offer increase light absorption rate, increasing surface photo-induced carrier density which lead to higher surface photoactivity and enhanced photocatalytic activity of TiO_2 nanocatalysts. Some researches reported that smaller crystallite size of nano doped TiO_2 induced a larger band gap due to the increased redox ability [68]. Moreover, the quantum size effect of nano-doped-TiO_2 increases its photocatalytic activity [69].

The anatase and rutile forms are the common crystallographic phases found in the formation of nano-TiO_2, where anatase phase is favored for its high photocatalytic activity [70] and exceptional thermodynamic stability in nanoscale dimensions [71]. The crystalline structure of nano-TiO_2 is shown as a octahedral TiO_6. In order to achieve high photocatalytic degradation efficiency, nano-TiO_2 should be mesoporous and should exhibit high crystallinity and specific area [72]. Nano- TiO_2 having large specific surface area, high percentage of anatase phase and small crystallite size although give favorable contribution towards high photocatalytic activity.

Photocatalytic properties of nano-TiO_2 can be effectively utilized in the removal of the environmental pollutants under UV-visible irradiation. Catalytic TiO_2 nanoparticles could also oxidize hydrocarbons, alcohols, carbon monoxide [73-74], ammonia [73], SO_2 [75] and bacteria [76] in air under UV irradiations/solar light. TiO_2 nanoparticles can destroy various organic species directly under light irradiation and have been employed in photocatalytic cancer therapy [77].

The most significant reason for the low conversion efficiency of TiO_2 under visible light is due to the width of the band gap, which is 3.2 and 3.0 eV for the anatase and rutile phase, respectively [78]. The rutile form of TiO_2 absorbs till 405 nm, while the anatase form absorbs till 385 nm [79] (Fig. 3). Thus, the further need to modify TiO_2 to adsorb visible light region.The following conditions requires are:

(i) The band gap to less than 3.0 eV

(ii) Suitable potentials of the conduction & valence band edges

(iii) Higher mobility of the charge carriers within in the valence and the conduction bands.[80]

In various investigations TiO_2 *NMs* showed their enhanced photocatalytic activity and in few researcher reported doping and modification require to achieve high rate of photocatalytic process. Some of them are highlighted in the following sections.

4. Photocatalytic activity of TiO_2 Nanomaterial

The synthesis of TiO_2 nanoparticles by a combined sol–gel ball milling method has been done by Farbod and Khademalrasool [81]. It was found that that the ball milling has an important role in preparation of nanosized TiO_2 powder. The photocatalytic activity of TiO_2 NMs with different sizes was studied by photocatalytic degradation of Congo red dye. The maximum photocatalytic activity was shown by those nanopowders which were synthesized at 550 °C with average particle size of 55 nm. The efficient photocatalytic degradation of methylene blue (MB) by TiO_2 NMs in aqueous suspension was studied. The maximum degradation of MB was observed when the concentration of TiO_2 in the aqueous suspension was 0.5 g L^{-1}.

A comparative study has been done by Fathinia and Khataee for removal of phenazopyridine (PhP). It was reported that photocatalytic ozonation showed the highest efficiency (85% at 35 min) in PhP removal than photocatalysis and ozonation process. In this technique TiO_2 nanoparticles were immobilized on ceramic plates and irradiated by UV-A light in the proximity of oxygen /ozone. By study of the chronic phytotoxicity of PhP and its intermediate compounds formed in ozonation and photocatalytic ozonation it was also concluded that photocatalytic ozonation efficiently reduce the phytotoxicity of the PhP from aqueous solutions.[82] Photocatalytic activity of novel TiO_2 nanoparticle-coated titanate nanorods has been reported by Yu *et al*., [83]. Here, Anatase TiO_2 nanoparticles were uniformly coated on the surface of the titanate nanorods using TiF_4 and H_3BO_3 as the precursors via a simple solution route. Investigations were carried out the study of effects of the precursor concentration, deposition time and deposition temperature on the morphology and phase structure of this material. It was found that rutile TiO_2 nanoparticle modified anatase TiO_2 nanorods shows an expedient photocatalytic reduction of CO_2. Bimodal structured TiO_2 microsphere has been used for the degradation of phenol rate. The increase in rate of degradation was due to the nano-sized anatase crystallite which has been incorporated into the TiO_2 microsphere [84].

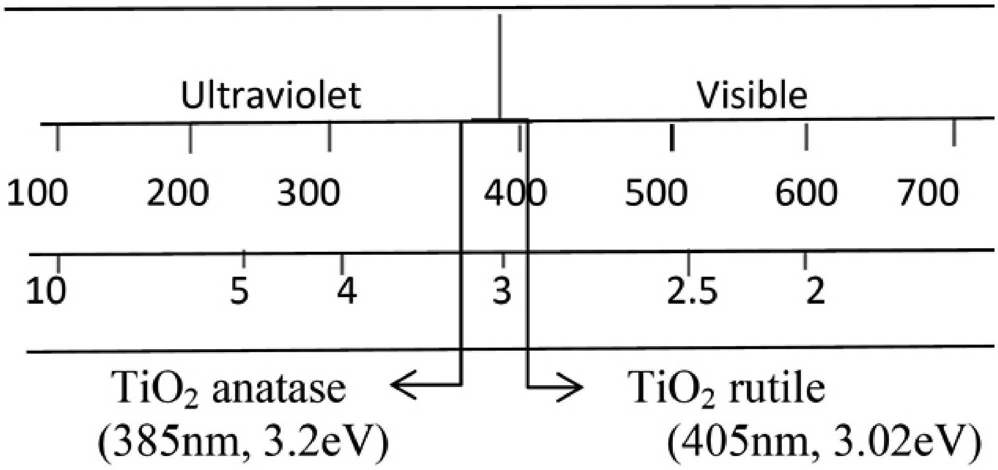

Fig. 3: UV region for photoactivity of TiO_2.

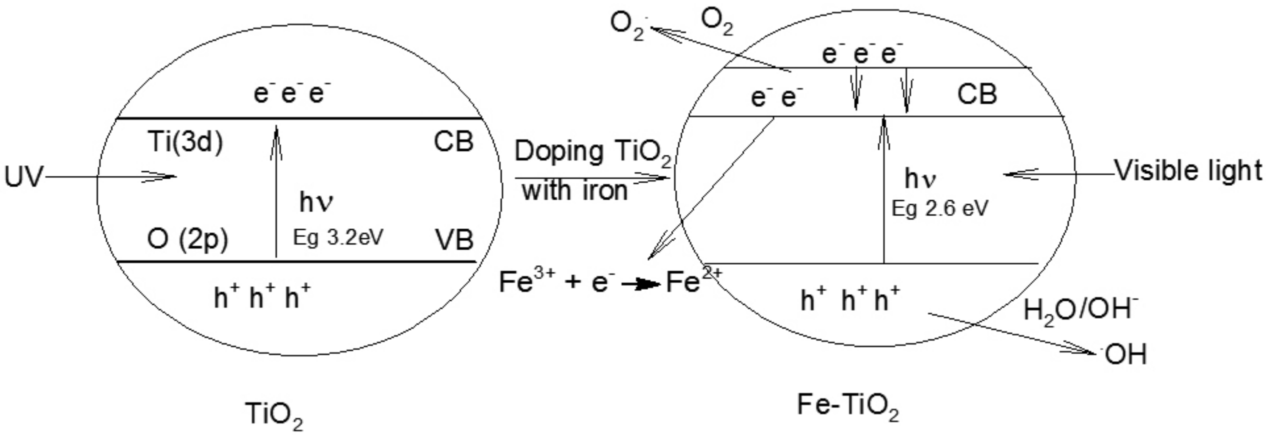

Fig. 4: Energy Level of iron doping with TiO_2.

Photocatalytic activity of TiO_2 nanoparticles for the decomposition of methyl orange (MO) in fixed film batch reactors was studied. These nanoparticles showed a red shift in UV–vis light reflectance spectra, which would be beneficial for photocatalytic reactions. Experimental results indicate that TiO_2 nanoparticles with different shapes and sizes showed different photocatalytic activities. Cubic nanoparticles show higher photocatalytic activity than other TiO_2 nanoparticles, which were prepared with the use of sodium dodecyl sulfate [85]. The photocatalytic efficiency of nanocrystals can be significantly improved by tailoring the shape and the surface structure of nanocrystals. The nanobelts exhibit a lower electron−hole recombination rate than the nanospheres [86]. A shell of anatase nanocrystals on the fibril core of a single TiO_2 crystal was obtained by Yang *et al.,*[87] via two consecutive partial phase transition processes. It is a noval efficient photocatalyst where nanofibril morphology has an additional advantage that they can be separated readily after reaction & reuse by sedimentation. For TiO_2 nanoparticle fabrication, low-pressure control methods such as combined arc submerged nanoparticle synthesis system (ASNSS) was developed by Chang *et al.,*[88]. It was observed that the TiO_2 nanoparticle fluid exibit excellent photocatalytic activity in photodegradation of MB. By using immobilised nanoparticle TiO_2 films photocatalytic inactivation of E. coli in surface water was achieved by Alrousan, *et al.,*[89].

5. Photocatalytic activity of doped - TiO_2

The performance of photocatalyst can be improved by depositing or incorporating metal ion or non-metal dopants into the TiO_2 [90, 91]. Doping techniques have been applied in photocatalysis to overcome limitations of nano TiO_2 such as wideband gap, ineffectiveness of photocatalysis under the sunlight and thermal instability [92, 93]. Most of the dopants have the potential to increase the photocatalytic efficiency of nano-doped- TiO_2. To broaden the effective range of light sensitivity of photocatalyst from the ultra-violet (UV) region to the visible light region, dopants can modify the electronic structure of nano- TiO_2 [94]. Dopants having their worth for their ability to confer excellent physicochemical properties such as high crystallinity (high percentage of anatase phase), high specific surface area and small crystallite size [95- 97]. Dopants could create a charge space carrier region on the surface of TiO_2 and prohibits the recombination of the photogenerated electron-hole pairs, which in turn accelerate the formation of hydroxyl radical and thus enhance the rate of photocatalytic process**.** In addition to this, dopants can act as active site for the adsorption of pollutants and increase the rate of photodegradation [98].

Different parameters of doping require to achieve high photoactivity of *NPs* :

- Calcination temperature
- Initial reactant concentration
- Dosage of doped TiO_2
- Doping concentration

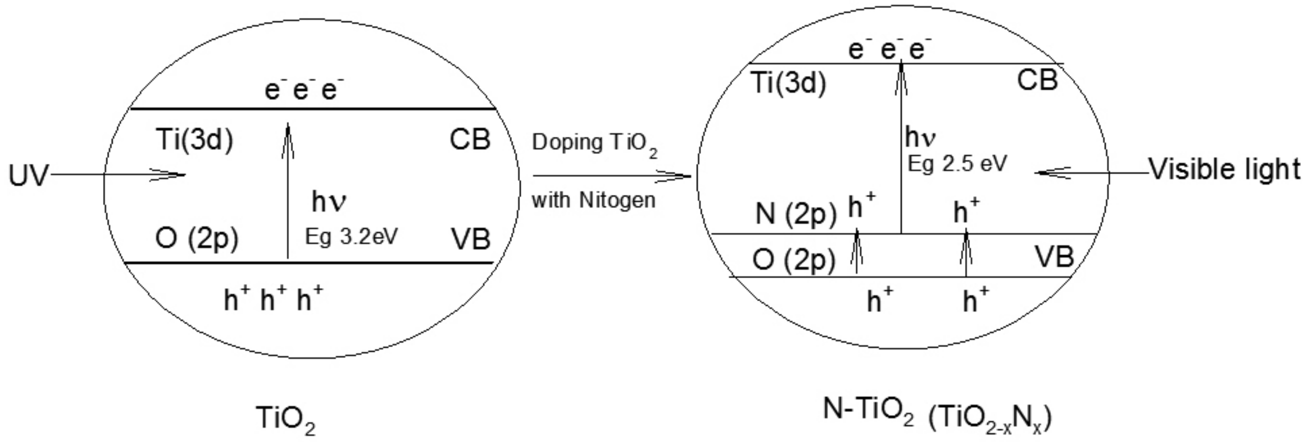

Fig. 5: Energy Level of Nitrogen doping with TiO_2.

Various metals and non-metals have been used for doping to get excellent photocatalytic activity of TiO_2 *NMs* as shown in Table-1. Some of these investigations have been discussed in following section.

5.1 Photocatalytic activity of metal doped TiO_2 NMs

Metal doped TiO_2 is promising photocatalyst especially metals having variable valency .i.e. Iron acts as a trap for the electron−hole pairs and consequently inhibits their recombination (Fig. 4)[103]. On the other hand, the radius of Fe^{3+} (0.79 Å) is similar to that of Ti^{4+} (0.75 Å). This trait increases the easy incorporation of Fe^{3+} ions into the crystal lattice of TiO_2 [104,105]. It was found that[106] Fe^{3+} doped TiO_2 prevents the agglomeration of the particles, forming well nanocrystalline particles with high surface area and thus ensuring high photocatalytic efficiency with band gap of 2.6 eV.

The effects of the co-addition of Zn^{2+} and Sodium dodecyl benzene sulphonate on the photocatalysis performance and wetting properties of the resulting TiO_2 nanoparticle films were investigated [110]. It was reported that both the photocatalytic activity and the hydrophilicity was improved with the addition of Zn^{2+}, which can be attributed to surface oxygen vacancies.

Kerkez and Boz[112] synthesized the Cu^{2+}-modified TiO_2 nanorod array thin films by a hydrothermal method and then modified with an ultrasonic-assisted sequential cation adsorption method. It was reported that the efficiency of degradation of MB under visible light was increased 40% with respect to the efficiency of the pure sample.

Amphiphilic TiO_2 nanotube arrays (TiO_2 NTs) were fabricated through electrochemical oxidation of Ti in solution containing H_3PO_4 and NaF. It was found that the TiO_2 NTs have the capability of self-cleaning due to amphiphilic and the photocatalytic activity[113].

It was reported that for methyl orange (MO) degradation the sulfated Mo-doped TiO_2@fumed SiO_2 composite shows good photocatalytic activity under UV and visible light irradiation. The high surface area and high active sites on the composite surface are considered as the key factors [114]. Umadevi and Christy [115] reported that the photocatalytic activity of TiO_2 nanoparticles can be enhanced by Silver nanoparticles. Heterostructures based on Ag_3PO_4 nanoparticles and TiO_2 nanobelts was prepared by a co-precipitation method [116]. Electron microscopic studies showed that the Ag_3PO_4 nanoparticles and TiO_2 nanobelts was in intimate contact which might be facilitated charge transfer between the two semiconductor materials. The heterostructures showed markedly enhanced photocatalytic activity for the photodegradation of MO under UV irradiation as compared with unmodified TiO_2 nanobelts or commercial TiO_2 colloids. However, the heterostructures exhibited significantly better stability and reusability in repeated tests than the Ag_3PO_4 nanoparticles.

Smith *et al*., [120] investigated the effect of Ag nanoparticle loading on the photocatalytic activity of TiO_2 nanorod arrays. It was observed that Ag loading of 0.25 wt.% shows maximum photodecay. Excellent photocatalytic performance was found for the Ag–TiO_2 nanocomposites for the degradation of MO under UV-light irradiation. It can be explained by promoted separation of photogenerated electron-hole pairs and higher reductive power due to the formed heterostructure between TiO_2 and Ag as well as the advanced absorption of light due to surface plasmon effect of Ag nanoparticles

An enhanced degradation of MO was achieved by Sb_2O_3/TiO_2 nanoparticles. Due to the Sb_2O_3 coupling the separation of photoinduced electron–hole pairs on the Sb_2O_3/TiO_2 photocatalyst surface occur which leads to high rate of degradation [121].

Photocatalytic activity of nanoglued Sn-doped TiO_2 was studied by Li et al., [122]. The nanoglued photocatalyst showed high photocatalytic activity during the degradation of penicillin under UV light. The effect of different Sn content on the amount of hydroxyl radical was also observed and it was found that an appropriate amount of Sn dopant can greatly increase the amount of hydroxyl radicals which responsible for the increase of photocatalytic activity.

Photocatalytic activities of Ce or Co doped nanocrystalline TiO_2–SiO_2 composite films has been investigated by Yao *et al*.,[123]. As compared to Co doped TiO_2–SiO_2 film Ce doped TiO_2–SiO_2 film exhibited excellent photocatalytic activity for the degradation of an organic dye in solution. Photocatalytic activity of laponite pillared by CeO_2 modified TiO_2 has been investigated by Yingguang Lin *et al.,*[124]. It was reported that the addition of Ce as a dopant can slowed the crystallization and thus prevent the growth of crystal of TiO_2. It also promotes the stability of active phase as well as formation of mesoporous materials. Ce doping can also inhibit the thermal loss and phase transformation of anatase to rutile phase. All these characteristics are accountable for enhancement in photodegradation processes through rhodamine B [125].

The solar photocatalytic activity of WO_3/TiO_2 photocatalysts was used for the degradation of an organophosphorus pesticide by using malathion as a model compound. With WO_3 doping the enhanced photocatalytic activity and long-term stability of TiO_2 nanoparticles was observed [126]. La-doped nanorods and nanotubes calcined at 973 K have been used for photocatalytic degradation of formic acid. It was observed that the presence of La inhibits TiO_2 crystallite growth and increases the lifetime of photo-generated electron–hole pairs [127].

Table -1 Different Transition metal dopant over TiO_2 NMs.

	Transition metal& Anionic Dopant	Organic pollutant	Ref. No.
1.	Ag	Methyl orange (MO), Methylene blue (MB), Dye acid 7	99,115,116.117,118,119,120
2.	Au	MB, Dye Acid-7	117,118
3.	Fe	Reactive orange 6, Acetone, Active yellow XRG, Oxalic Acid (OA)	101, 102, 107,131
4.	Cu	OA, MO, MB	107, 111, 112
5.	Pd	Organic Waste,	99
6.	Sn	Pencillin, MB	124,128
7.	Sb	MO	121
8.	Mn_2O_3	MB	130, 132
9.	Co	MB	130
9.	WO_3	Organophosphorous pesticides	126
10.	La	Formic acid	131
11.	Cd	MO	100
12.	Zn	MO, OA, Rhodamine B (RhB)	100, 107, 108, 110
13.	V	RhB, 3,4-chloroaniline	108, 109
14.	Ce	3,4-chloroaniline,	109
15.	Nitrogen	MB, MO	133,136,137,138
16.	Sulphure	MO, MB	138,139
17.	Floride	Phenol, Chlorophenol	140,141
18.	Carbon	Basic Red 18,Basic Red 46, Acid Orange7	142,143

Sm^{3+}-doped TiO_2 nanocrystalline has been employed for the degradation of MB [128].The significantly enhanced in the photocatalytic activity can be attributed to the larger specific surface area and the greater the formation rate of OH radical which were simultaneously obtained for Sm^{3+}-doped TiO_2 nanocrystalline. Cao *et al*.,[129] studied the photocatalytic degradation of 4-chlorophenol. It was found that TiO_2-N–x%Ni photocatalyst shows a higher activity than both pure TiO_2 and nitrogen doped TiO_2 (TiO_2-N) under visible-light irradiation. The unique chemical species, such as N–O_x and O–Ni–Cl, existed on the surface of TiO_2-N–x%Ni. The energy levels of N–O_x and O–Ni–Cl surface states locate above the valence band and below the conduction band of TiO_2, respectively. This could lead to strong visible-light absorption and enhanced charge carrier separation.

5.2 Photocatalytic activity of non metal doped TiO_2 NMs

The photocatalytic activity of nitrogen-doped TiO_2 nanomaterials was investigated by degradation of MB aqueous solution under visible light irradiation [133]. It was observed that the wavelength range of nitrogen-doped TiO_2 was shifted to visible light.

It is difficult to make the substitution of O by N because the ionic radius of N (1.71 Å) is so much greater compared to O (1.4 Å) [134]. Thus, to maintain the electroneutrality and to form an oxygen vacancy, three oxygen atoms should be replaced by two nitrogen atoms. In the presence of nitrogen in titania, the energy of oxygen vacancies is reduced from 4.2 to 0.6 eV, showed that nitrogen favors the formation of oxygen vacancies.[135] As shown in Fig. 5, these oxygen vacancies promote the absorption in the visible region (from 400 to 600 nm) and ensure the activation of N-doped TiO_2.

By two-step process of hydrothermal and post-impregnation method Cr and N-codoped TiO_2 nanotubes were prepared. The enhanced photocatalytic activity for the degradation of methyl orange up to 97.16%, has been reported. [137].

The photocatalytic activity of nanocrystalline S, N-codoped TiO_2 thin films and powders under visible and sun light irradiation was evaluated by the degradation of MO. It was found that MO solution was discolored completely under sun light in 75 min in the presence of the modified TiO_2 powder [138]. It was reported that sulphur doping can generate the small particle size with great surface area which accelerate the photodegradation process. The methylene blue dye degradation ability of sulfur doped hollow TiO_2 nanocatalyst is shown to be 98.6% compared to that of standard Degussa P25 (30%). This catalyst is able to degrade 71% methylene blue dye during fifth times recycling without any further treatment [139].

Photocatalytic activity of a noval immobilized composite photocatalyst, titania (TiO_2) nanoparticle/activated carbon on the degradation of Basic Red 18 (BR18) and Basic Red 46 (BR46) was reported by Mahmoodi *et al.,*[142]. Results showed that for the degradation of textile dyes, the immobilized composite photocatalyst with 2 wt.% of activated carbon was the most effective for degradation of toluene in air. The Pt/C-doped $TiO_2/PtCl_4$ three-component nanojunction system has been developed by Dong *et al.,*. This system system exhibited six times higher visible light activity than that of the pristine C-doped TiO_2 , due to the increased utilization of visible light, the enhanced charge carrier separation and transfer process[143]. In some research it was reported that after combined with graphene oxide (GO), the GO–TiO_2 showed much higher photocatalytic activities for the degradation of Acid Orange 7 under UV irradiation[144].

6. Photocatalytic activity of Coupled TiO_2

6.1 Photocatalytic activity of TiO_2 with organic compounds

Photodegradable polyvinyl chloride (PVC)–vitamin C(VC)–TiO_2 nanocomposite film show high photocatalytic activity which can be explained on the basis of the formation of a Ti^{IV}–VC charge-transfer complex with fivemember chelate ring structure and followed by rapid photogenerated charge separation [145]. Enhanced photocatalytic activity of the novel 1,3-bis(*N*-3*H*-3,3-dimethyl-2-methylene indolenine) squaraine dye (ISQ) sensitized TiO_2 nanocomposites was reported by Li *et al.,*[146] for the degradation of MB under the visible-light irradiation. These particles showed superior photocatalytic stability after 5 successive cycles under visible-light.

Efficient decolorization of an ordinary dye Reactive Brilliant Red X-3B in aqueous solution under visible light irradiation has been achieved by TiO_2 nanoparticles modified by pre-oxidized polyacrylonitrile. UV–Vis DRS shows that pre-oxidized polyacrylonitrile can absorb more visible light to enhance visible light photocatalytic activity of TiO_2 nanocomposites [147]. Liu *et al.,*[148] observed that the TiO_2 nanoparticle modified with phthalic acid resulted in enhanced photocatalytic reduction activity for Cr(VI).

6.2Photocatalytic activity of TiO_2 Nanocomposites

Different nanocomposite utilize to remove organic pollutant from waste water as given in table 2.

Table 2 Different Nanocomposite use to remove Organic Pollutants.

	Nanocomposite	Organic Pollutant	Ref.no.
1	Cu–Zn–S/TiO_2 NTAs	2,4-dichlorophenoxyacetic acid, anthracene-9-carboxylic acid	149
2	γ-Fe_2O_3@SiO_2@TiO_2–Ag	MO	150
3	Ag/TiO_2–Cu	4-nitrophenol	153
4	Cellulose fiber TiO_2 nanobelt –Ag NPs	MB	154
5	Ag-TiO_2	MB, Toluene, Rhodamine -B	154,157,155,156
6	SnO_2/TiO_2	Rhodamine B	158
7	CdS/TiO2	MO	159, 160
8	TiO_2–$LaFeO_3$	MB	161
9	CeO_2/TiO_2,ZrO_2/TiO_2, $H_3PW_{12}O_{40}$-CeO_2/TiO_2, $H_3PW_{12}O_{40}$-ZrO_2/TiO_2	Methanol	162

It was reported that the γ-Fe_2O_3@SiO_2@TiO_2–Ag nanocomposites showed stronger photocatalytic activity than pure TiO_2 for the degradation of MO solution under UV irradiation [149]. It was reported that Fe doping can prohibits the crystal growth and also slow down the phase transformation of anatase to rutile form [150]. Moreover, ferric ions act as shallow charge traps and enhance the lifetime of photoinduced electron – hole pair [151].

It was observed that at 400 °C, the SnO_2/TiO_2 composite films showed the highest photocatalytic activity due to synergetic effects of low sodium content, good crystallization, appropriate phase composition and slower recombination rate of photogenerated charge carriers [151]. It was reported CdS/TiO_2 nanocomposites showed seven times increase rate of photochemical degradation when sample prepared by the CV method [153]. It was reported that the laponite pillared by the CeO_2 modified TiO_2 (Ce-Ti-lap) showed the best photocatalytic activity in the degradation of MO as compared with the pure TiO_2, the laponite only pillared by TiO_2 (Ti-lap) and the laponite only pillared by CeO_2 (Ce-lap). Photocatalytic performance of TiO_2 catalysts modified by $H_3PW_{12}O_{40}$, ZrO_2 and CeO_2 has been reported by Tiejun *et al.,*[155].

7. CONCLUSION

In recent decades, serious concern has been given to water pollution. Different methods and techniques have been employed for the wastewater treatment out of which AOPs have been proven as the most effective and promising method. It has many advantages over the other techniques. In this series, photocatalytic activity of nanomaterial comes under the light. These nanoparticles can serve as a excellent photocatalyst for the degradation of variety of organic pollutants which are giving grave threat to the environment due to the having more available reactive surface area, inexpensive and stable to corrosion in the presence of water and other chemicals. Their photocatalytic activity can be further improved by using some metal and non-metal ions as a dopant. These dopants can modify the morphology and electronic structure of TiO_2 nanoparticle to achieve high rate of photocatalytic processes. In the same sequence, some modification has also been done by using inorganic-organic compounds but the interlinkage between the various parameter which accelerate the rate of photodegradation process are yet to be investigated. More researches should be done to harness/harvest the full potential of TiO_2 nanoparticles as a photocatalyst and to understand the mechanism of photocatalysis.

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