# A Comprehensive Review: Recent Updates on Photocatalytic Degradation of Pollutants Using TiO$_2$ Photocatalyst

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## Abstract

Environmental sustainability is a challenging task for worldwide researchers. The photocatalyst is a promising technique, which can accomplish this task and resolve the problem in an ecofriendly way. Volatile organic compounds (VOCs) and some inorganic gases are the most hazardous compounds in the environment, which can be abated through photocatalysis. Metal oxide photocatalysts are extensively used for the photocatalytic degradation of VOCs and inorganic gases. Among the metal oxide photocatalysts, Titanium oxide (TiO$_2$) is the most commonly used semiconductor photocatalyst due to its structure, unique properties under ultra-visible light, nontoxicity, and high acid-base properties, good chemical and thermal stabilities, easy availability, and high metal-support interaction. This review elucidates the morphology, reactive facets, reaction mechanism, structural modifications, surface properties, and key issues related to understanding the importance of TiO$_2$ as a photocatalyst for the degradation of VOCs and inorganic gaseous pollutants.

**Keywords**: Titanium oxide; Photocatalysis; Photodegradation; Volatile organic compounds; Catalyst design; Pollution

## 1. Introduction

Nowadays, the increasing concentration of gaseous organic pollutants is a raising challenge for developing countries and their developing economies and it is the field of interest for many researchers to address the challenges regarding air pollution, toxicity and corresponding mitigation [1, 2]. The degradation of air and water pollution by the solar photocatalytic oxidation approach in the field of interest because it destroys the pollutants completely, while other processes can only separate them. Mostly, volatile organic compounds (VOCs), $CO_x$, $NO_x$ and $SO_x$ are considered to be responsible for the greenhouse effect; especially, researchers interest increased when they learned to know that acetaldehyde is the major cause of indoor pollution [3-6].

Photocatalysis is the process in which the reaction occurs through the solar & UV energy without using the toxic chemicals and any extra energy. Volatile organic compounds such as acetaldehyde, formaldehyde, and toluene are some important typical organic compounds that are the root of indoor air pollution and are needed to be photo catalytically cleaned to purify the air [2, 7]. These VOCs are emitted from the consumer's goods and construction materials, which not only deteriorate the air quality by forming photochemical smog and atmospheric $PM_{2.5}$ but they are also carcinogenic and, hence, they cause serious effects to the cardiovascular system [8, 9]. It is reported that the VOCs contents in indoor air is 5-10 times higher than that of outdoor air as estimated by the United States Environmental Protection Agency (U.S.EPA), and currently, it is recommended that about 50% of precedent controlled pollutants are VOCs [10, 11].

Various techniques were applied and studied for the removal of VOCs including biological treatment, physically adsorption, chemically absorption, non-thermal plasma and catalytic combustion [12, 13]. The aforementioned methods have certain limitations, such as high cost and energy consumption, the formation of secondary pollution and the inherent difficulty to deal with low VOC concentration, i.e., to have sufficient conversion [8]. Another

abatement technique is heterogeneous photocatalysis, where Nano semiconductors are used for VOC degradation, using air as oxidant. This process happens under mild conditions at ambient temperature and atmospheric pressure [1, 14].

Transition metal oxides have shown promising properties in catalytic oxidation reactions for the degradation of VOCs [15-17]. Titanium oxide ($TiO_2$) is one of the most important and active semiconductor photocatalysts having low cost, high chemical stability, nontoxicity, easy availability, high ultraviolet absorptivity, excellent photocatalytic activity, unique physical and electronic properties with larger band gap of 3.2eV [18-21]. $TiO_2$ under irradiation of UV and near UV light can oxidize VOCs and varied organics into the non-toxic $CO_2$, $H_2O$ and mineral acids at ambient temperature and atmospheric pressure [22, 23].

It is widely known that $TiO_2$ can degrade the pollutants of air and water and that it does not only absorb UV light, but it can also absorb in the visible wavelength area and effectively absorb natural sunlight [24, 25]. As $TiO_2$ is abundantly used as suspended particles in solution, an effective immobilization of $TiO_2$ on an adsorbent can largely increase its efficiency to remove pollutants. Since photocatalysis is an emerging technology using $TiO_2$ as a photocatalyst to oxidize VOCs into $CO_2$ and $H_2O$ under irradiation of UV light for the purification of indoor air at room temperature and pressure. Currently, the focus of scientists is to enhance the efficiency and selectivity of photocatalysts [26]. The focus of this review is to provide a comprehensive overview of current advances in photocatalytic treatment of gaseous pollutants using $TiO_2$ as a photocatalyst. After a brief introduction to photocatalysis fundamentals, the $TiO_2$ photocatalyst, modification, and kinetic analysis are explored mechanistically in terms of organic and inorganic gas phase applications. This review is intended to facilitate as both a solid introduction for newbies to the area and a summary update for professional scholars.

## 2. Methods for the degradation of gaseous pollutants

Some of the most major anthropogenic pollutants produced in urban and industrial regions are volatile organic compounds (VOCs) [27]. Because they are widespread compounds used as industrial cleaning and degreasing solvents, these VOCs are widely used (and produced by) both industrial and home activities [28]. Cooking and cigarette smoke, building materials, furnishings, dry cleaning agents, paints, glues, cosmetics, fabrics, plastics, polishes, disinfectants, household insecticides, and combustion sources are all sources of VOCs [28, 29]. According to the definition of U.S. EPA, VOCs are volatile nature hydrocarbons at normal indoor conditions of temperature and pressure. According to European Union (EU) VOCs are the volatile compounds having boiling point less than or equal to 250°C at 101.3 kPa vapor pressure. VOCs are naturally produced due to wetlands, oceans, forests, and volcanoes. While some major toxic VOCs are formed due to human activities such as emissions through vehicles, manufacturing industries and petrochemical industries [U.S.EPA, 2012] (Table 1). Usually, when VOC is exposed to $NO_x$, ozone and other chemicals are formed [30]. The formation of carcinogenic smog on the ground by ozone is a major concern.

$NO_x$ + VOC + sunlight $\rightarrow$ $O_3$ + NO + other products                     (1)

Common VOC degradation methods, used in the commercial and industrial sector, are membrane separation, adsorption, liquid absorption, thermal oxidation, bio-filtration and catalytic combustion [31, 32]. New technologies use air or controlled environment chambers for the removal of VOCs. Satisfactory results were not achieved by single based removal system due to the variations and complexity of VOCs characteristics. Therefore, an affective, cost-effective method and environmentally friendly method must be required for the degradation of VOCs. Table 2 provides brief information related to the methods used for the degradation of VOCs [10].

The most traditional technique for the degradation of VOCs is adsorption method. Adsorption techniques required porous materials such as silica gel, activated carbon, and

molecular sieve as a medium for the chemical and physical adsorption. Inorganic salts (e.g., ammonium and sulfurous) along with amine groups such as urea and its derivatives, amino-containing polymers and hydrazine are the commonly used adsorbents [33].

**Table 1:** Annual concentration limits of air pollutants excluding heavy metals [34].

| Pollutants | WHO (mg.m$^{-3}$) | US EPA (mg.m$^{-3}$) | China MEP (residential area) (mg.m$^{-3}$) |
|---|---|---|---|
| $PM_{10}$ | 0.02 | N/A | 0.04 |
| $PM_{2.5}$ | 0.01 | 0.012 | 0.04 |
| $NO_2$ | 0.04 | 0.053 | 0.04 (24h) |
| $SO_2$ | 0.02 (24h) | 0.5 (3h) | 0.02 |
| CO | N/A | N/A | 4 (24h) |
| VOCs | N/A | N/A | Benzopyrene 0.000001 |

The catalytic oxidation method and thermal process are the most effective techniques for the degradation of VOCs. Reacting formaldehyde with oxygen in the existence of noble metal results in the formation of $CO_2$ and water [35]. Such reactions occur at high temperatures, so energy consumption is the major issue in such reactions. Particles, atoms, molecules, and free radicals require high chemical activation energy thus it is difficult to control under normal conditions due to the slow reaction rate [10]. Microbial degradation is also a feasible technique used in industries and laboratories for formaldehyde removal from exhaust gas and wastewater. Acidity is the most significant factor in the selection of biological enzymes for degradation. According to experimental data, the removal rate for the enzymes for the degradation of formaldehyde was 80% in 8h. However, these techniques are not applicable to the cleaning of indoor air [36, 37].

**Table 2:** Summary on current control methods for volatile organic compound degradation [10].

| Techniques | By Products | Advantages |
| --- | --- | --- |
| Catalytic Combustion | $CO_2$, $H_2O$ | Wide range of applications, high efficiency, no secondary pollution. |
| Activated carbon-based adsorption | Carbon and collected organics | Recovery of compounds, which may offset annual operating costs. |
| Absorption | Water waste | Product recovery can offset annual operating costs. |
| Botanical purification | Organics, $CO_2$ and amino acids | Economical, no pollution, improving the indoor environment. |
| Bio filtration | Biomass | Little or no energy needs to be added in the form of heat or radiation to support this process. |
| Zeolite based adsorption | Zeolite and collected organics | Effective in more than 90% RH as the adsorbent might be too specific. |
| Membrane separation | Exhausted membrane | The stability of the membrane was poor. |

Photocatalytic oxidation (PCO) being a cost-effective, environmentally friendly has received the attention of scientists these days due to its exceptional properties. Removing indoor air VOCs, PCO technology is considered as the most promising technique during recent years. PCO oxidize even low concentrations of VOCs, inorganic, organic nature of gases and convert harmful gases into harmless $CO_2$ and water [2].

### 3. General characteristics of Titanium Oxide

Photocatalysts are materials used for degradation of harmful air pollutants into less harmful or harmless form in the presence of UV irradiations [38, 39]. Many scientists have synthesized different photocatalysts for the degradation of VOCs. Various mono component semiconductor photocatalysts e.g., $TiO_2$ [40-42], $ZnO_2$ [43, 44], $WO_3$[45, 46] and $SnO_2$ [47, 48] have shown the efficiency for the degradation of VOCs. Photocatalytic oxidation of gas phase VOCs can widely be studied by using $TiO_2$ as photocatalyst [49, 50]. $TiO_2$ is a well-known for its easy synthesis, it is well researched, it has photo corrosion resistive, photocatalytic and strong

oxidizing material, and it is mainly used for environmental remediation due to its chemical structure, properties and biocompatibility [51, 52].

## 3.1 Morphology

The proper applications of $TiO_2$ depend mainly on the morphology, crystalline polymorphs, and dimensions. In various studies, $TiO_2$ is prepared to have different forms, shapes, sizes and dimensions like cubes, spheres, tubes, rods, wires, sheets, needles, flakes, flowers, chestnuts, belts, and urchins [19, 53-55]. $TiO_2$ can exist in three mineral forms i.e., anatase, brookite and rutile (Figure 1)[56-58]. Anatase is the tetragonal crystalline form of $TiO_2$ and is used as a photocatalyst under UV illumination. Anatase $TiO_2$ is inexpensive, non-toxic, high surface area, photochemically stable and has a high tendency to generate photoelectrons and have a negative conduction band potential. Anatase can disinfect, purify, and remedy the toxic pollutants in water and air because of its highly photo-induced redox power. Rutile has also a tetragonal crystalline structure and is used in paints with white pigment, whereas brookite has a crystalline orthorhombic form of $TiO_2$[56, 59, 60].

In catalytic applications, anatase $TiO_2$ showed the highest photoreactive activity[61], whereas rutile $TiO_2$ showed a lesser surface affinity for organic compounds and have high electron-hole recombination rate (Table 3) [62]. It has been investigated that $TiO_2$ photocatalytic activity is because of its crystalline nature but several authors also reported a controversial result in the literature. Some researchers have reported that the anatase form performs better than the rutile form [63], while others reported the opposite [64]. Some other researchers have noticed and reported that the anatase-rutile hybrid form has best photocatalytic activity [65], but it was recently reported that when the activity of both crystalline forms was compared, the photocatalytic activity depends upon the oxidant composition, e.g., anatase form of $TiO_2$ showed better photocatalytic activity in the presence of $O_2$, while the rutile form of $TiO_2$ shows highest photocatalytic activity with $H_2O_2$ [66]. It was

reported that the high photoactivity of anatase was due to the position of the Fermi level, which is higher for anatase than rutile [67].
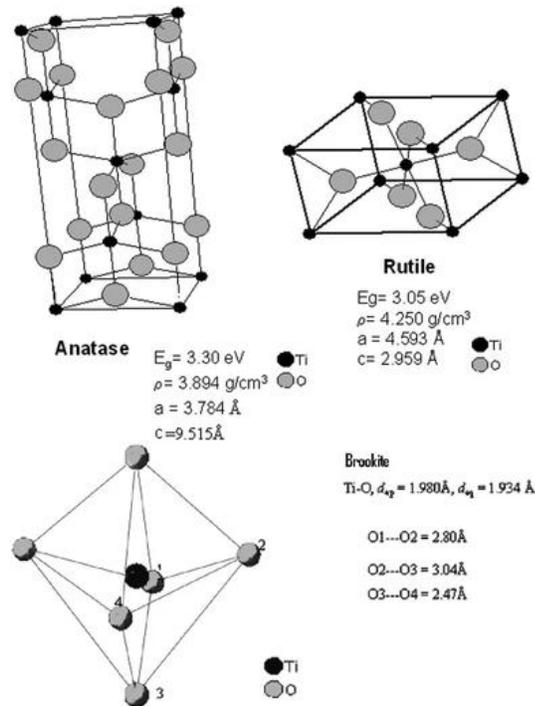


**Figure. 1** Different forms of TiO$_2$. [58] Copyright 2018 Elsevier.

**Table 3.** Physical Properties of anatase and rutile forms of TiO$_2$ [66].

| Properties | Anatase TiO$_2$ | Rutile TiO$_2$ |
|---|---|---|
| Molecular weight (g/mol) | 79.88 | 79.88 |
| Crystal structure | Tetragonal | Tetragonal |
| Melting point (°C) | 1825 | 1825 |
| Boiling point (°C) | 2500–3000 | 2500–3000 |
| Light absorption (nm) | <390 | <415 |
| Refractive index | 2.55 | 2.75 |
| Ti-O bond length (Å) | 1.95 (4) | 1.95 (4) |

| | | |
|---|---|---|
| | 1.98 (2) | 1.98 (2) |
| Lattice constant (Å) | a = 4.59 | c = 2.96 |
| | a = 4.*59* | c = 2.96 |

The physicochemical properties of a catalyst depend upon the preparation method and the used precursors. Degussa P25 $TiO_2$ is a non-porous 70% anatase –30% rutile compound and it is proven to have higher reactivity than pure anatase and was set as a standard material in the environmental applications of photoreactivity [68]. Hence, the anatase-rutile hybrid form has higher photocatalytic activity, the electrons jump from the conduction band of anatase to the less positive rutile thus recombination rate of electron and hole reduces in the anatase part. The morphology design of the TiO2-based materials has been synthesized by sol-gel, solvothermal hydrothermal, direct oxidation, micelle and inverse micelle usage, electrodeposition, emulsion or hydrolytic precipitation, chemical/physical vapor deposition, microwave, and ultrasonic techniques [19].

Monodispersed nanoparticles of $TiO_2$ are the most frequently used morphology due to their small crystalline size and large surface area. The recombination of electrons and holes in bulk is strongly reduced, so that detrimental effects such as surface recombination and low crystallinity due to small size can be avoided [69]. The most preferable titania was synthesized by electrochemical anodization on titanium metal foils using self-assembled nanotubular films where one dimensional (1D) $TiO_2$nanotubes, nanowires nanorods, nanoneedles, nanobelts were also synthesized by hydrothermal method. Vectorial charge transfer, controlled porosity [70, 71] and lower recombination rate, enhanced their advantages in photo-induced especially in photocatalysis applications due to their morphology [70-72]. The SEM, TEM, and XRD characterization methods are used for the study of surface morphology and physical properties such as crystalline forms, crystal sizes, facets, and surface area of prepared $TiO_2$. Nguyen-Phan and Eun Woo Shin [73] reported that by hydrothermal process pure anatase $TiO_2$ was formed by using a low volume of HCl (DTC-2.15) having quantity >100µm while pure rutile $TiO_2$ was

prepared by using a high volume of HCl (DTC-15) with spherical morphology (6-8 μm). Changing the volume of HCl from 5-9ml (DTC-5.0, DTC-6.0 and DTC-9.0), the morphology of $TiO_2$ nanoparticles was changed from a flower-like shape to a cauliflower-like shape where the crystal size became enlarged.

The visible light-responsive $TiO_2$ can be formed by adding a small quantity of cations and metal oxide by doping and physical ion implantation methods. Visible light-responsive thin film $TiO_2$ photocatalyst can convert $H_2O$ into pure $H_2$ and $O_2$ using sunlight radiations where single site $TiO_2$ zeolite framework can reduce carbon dioxide and hydrogen into oxygen and hydrocarbons. $TiO_2$ is among those few materials with photo-induced super hydrophilicity, where photo-functionalized titanium can be used in bone-implant fixation to allow quick bone-titanium integration [26]. Super hydrophilicity and photo-induced redox potential are the two main properties which is the basis of photocatalyst environmental application [19, 25].

## 3.2 Reactive facets

Spherically shaped $TiO_2$ has high photocatalytic properties due to its large surface-to-volume ratio and larger number of active sites [74].The small size of the nanocrystals favors the recombination of electrons and holes having low quantum efficiency and wider band gap, which can deactivate $TiO_2$ under UVA light [75]. Such complications limit the commercial use of $TiO_2$and, hence, modifications to enable UV light absorption will improve electron-hole separation which enhances the corresponding photocatalytic performance. The modification methods like transition metals doping [76, 77], non-metals deposition [78], incorporation of noble metals [79], semiconductor heterojunctions [80], co-catalyst loading and changes of crystal structures were applied to improve the photocatalytic activity of pure $TiO_2$ (Table 4) [81].(001), (010) and (101) are the low index fundamental facets of $TiO_2$. Morphologically controlled crystal facet structure of anatase $TiO_2$ and fabrication at the atomic level, i.e., micro and nanoscale level is the topic of scientific research interest these days. According to Wulff

construction [82, 83] anatase $TiO_2$ is naturally the most dominant with lesser reactivity and thermodynamically stable surface (101), which consist of more than 94% of the surface exposed area. The most commonly and naturally existing shape of $TiO_2$ is octahedral bipyramid having eight (101) side facets and two top and bottom (001) facets [84]. Meanwhile, the crystal growth during equilibrium the high energy (001) facet disappear and transferred into the specific low surface free energy minimizer shape with bare facets [85-87].

The aspect ratio of the crystal is well-defined as the ratio between the truncation facet sides ((b) and the bipyramidal sides ((a) in Figure 2. The degree of truncation (B/A) ranges from 0.3 to 0.4 with wide range of conditions having less than 10% bare facets (001) [88]. Thus, theoretical and experimental investigation showed that anatase $TiO_2$ with facets (001) results in a higher catalytic activity, compared to the thermodynamically stable facets (101) due to lower atomic coordination numbers of the bare atoms, active high density unsaturated coordination Ti atoms and surface-active oxygen atoms with broad bond angles of Ti–O–Ti in the facets (001) [89-91]. The modification, applications, and properties of highly energetic (001) facet depends upon the shape of the facets. The reported average surface energy order of the anatase $TiO_2$ is 0.90 J $m^{-2}$ for (001), >0.53 J $m^{-2}$ for (100), and >0.44 J $m^{-2}$ for (101) [92, 93]. The low defect $TiO_2$ nanosheet can decrease the recombination rate of photo generated electrons and holes at the grain boundaries and attain the high energy conversion efficiency. By doping anatase $TiO_2$ nanosheets with bare energetic facets (001) with metals and non-metals, the absorption of UV light enhanced. Carbon [94], nitrogen, sulfur [92, 95] nickel [96], molybdenum [97], platinum [98] and aurum [99] are the metals used to dope the faceted $TiO_2$. Many novel forms of the anatase $TiO_2$ (001) facet received much attention of the researchers from the past few years and published different reviews on the pure anatase $TiO_2$ facet (001) [100, 101].

**Table 4.** Photocatalytic oxidations of volatile organic compounds on $TiO_2$-based photocatalyst [34].

| Photocatalyst | Pollutants | Performance | Reference |
|---|---|---|---|
| Silica glass fibers doped P25 Degussa $TiO_2$ | Acetylene | 85% acetylene was degraded with the formation of formaldehyde, formic acid and glyoxal as intermediates | [102] |
| A monolithic catalytic bed coated with P25 and PC500 | n-decane and perchloroethylene (PCE) | n-decane decomposition rate was 100% where PCE was degraded by 69% | [103] |
| Graphene oxide on $TiO_2$ nanocrystals | Benzene and ethanol | 95% conversion | [104] |
| PVC sheet coated by $TiO_2$ | Toluene and benzene | Rate constant of $7.65 \times 10^{-5}$ and $1.07 \times 10^{-4} min^{-1}/cm^2$ | [105] |
| Optical fiber coated by $TiO_2$ | Isopropanol | 22% conversion | [106] |
| $TiO_2$ film on window glass | Benzene and acetone | 100% Benzene and acetone was degraded in 25 min and 110 min | [107] |
| $TiO_2$ film mechanically robust | Acetaldehyde and ethanol | Under UV 100% conversion in 70 min for ethanol and 125 min for acetaldehyde | [108] |
| Nano and micro- sized $TiO_2$ | Acetaldehyde, toluene and Acetone | PC105 (Cristal) > P25 (Evonik) > 1077 (Kronos) > AT-1 (Cristal) | [109] |
| $TiO_2$ microfiber | Heptane, toluene and acetone | Quantum efficiencies on $TiO_2$ fiberfor acetone 0.0106, heptane 0.0027 and toluene 0.0024 | [110] |
| Mesoporous $TiO_2$ | Benzene | 80% conversion on TS-400 | [111] |
| F-doped anatase $TiO_2$ nanosheets | Acetone, benzene and toluene | Highly efficient under both UV and visible light | [112] |
| Nanocomposites of $TiO_2/SiO_2$ | Benzene | 92.3% conversionforTi/Si = 30: 1 in 2 h, conversion rate is 6.8 times higher than P25 | [113] |
| $TiO_2$ doped with $Fe_2O_3$ | Trichloroethylene (TCE) | 95% degradation of TCE | [114] |
| $TiO_2$ doped with transition | Benzene | 58% conversion by $Mn/TiO_2$ | [115] |

metal

| | | | |
|---|---|---|---|
| $TiO_2$ doped by Cu | TCE | Both TCE and water mobility was favored by 0.2 wt% Cu content where 0.5 wt% Cu blocked the active sites strongly | [116] |
| V-doped $TiO_2$/porous polyurethane | Toluene | 80% degradation | [8] |
| $Sn^{2+}$-doped $TiO_2$ | Benzene | 27% conversion by TS-40 (Ti/Sn = 40: 1) | [117] |
| $TiO_2$ doped with Pt | Cyclohexane N-doped | 100% decomposition and platinum endorsed the $CO_2$ selectivity | [118] |
| N-doped and O-deficient $TiO_2$ | Benzene | 72% benzene converted and yields $CO_2$ of 190ppmv for 5 h reaction | [119] |
| Spray-coated polyester fiber supported non- metal doped $TiO_2$ | Formaldehyde | 38% conversion at C-$TiO_2$ | [120] |
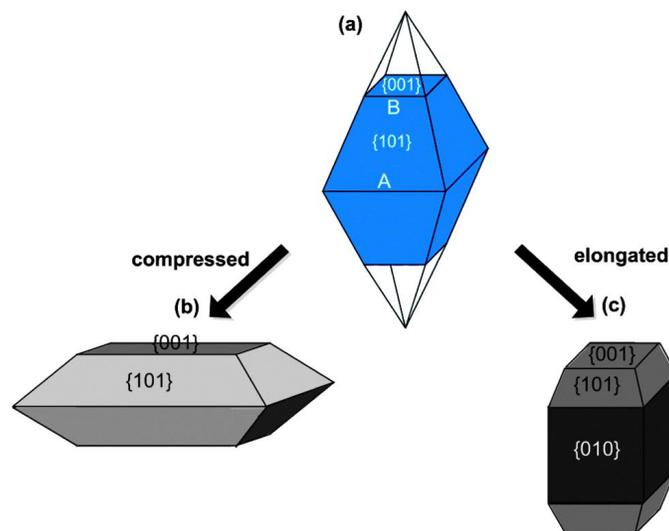


**Figure 2:** Evolution of an anatase $TiO_2$ crystal nucleus nucleated as a truncated octahedral bipyramid seed: (a) under equilibrium conditions, the high energy (001) facets diminish rapidly, and the crystal evolves into thermodynamically stable (101) facets. (b and c). Under non-equilibrium conditions, the high energy (001) and (010) facets are stabilized by selective adhesion of capping agents. The side lengths labelled as (A) and (B) are used to estimate the

degree of truncation (B/A) and calculate the percentage of exposed (001) facets [121]. Copyright 2014 Royal Society of Chemistry.

## 3.3 Engineering of oxygen vacancies

Oxygen vacancies in photocatalytic reactions play an important role and get the attention of scientists to engineers. $TiO_2$ is the most used semiconductor oxide for the degradation of environmental pollution and the generation of hydrogen gas photo-catalytically. Reduction of electron-hole recombination and the introduction of oxygen defects are the most promising ways to enhance photocatalytic activity [122, 123]. Surface oxygen vacancies can trap the photoinduced charge and subsequently provide sites for the adsorbed compounds by transferring the charge which inhibits the recombination of the charges, leading to an increase in photocatalytic activity. Oxygen vacancies in the bulk play an important role as charge trappers and decrease the photocatalytic performance due to the recombination of photo-generated electrons and holes [124-126]. However, it is important to control the surface oxygen vacancies to increase the performance of the photocatalyst. The disordered layer was formed by Mao et al. in $TiO_2$ by hydrogenation method which improved the photocatalytic performance of $TiO_2$ [127]. Surface oxygen vacancies of $TiO_2$ get more attention than bulk oxygen vacancies. Two different types of intrinsic defects (surface oxygen vacancy $V_O^{\bullet\bullet}$ and $TiO^{3+}$) are formed on the surface of $TiO_2$ simultaneously when reacting with hydrogen or any other reducing agent at high temperature [128]. The simplest and widely studied method for the generation of surface vacancy is to treat the nanocrystals of $TiO_2$ by hydrogen thermal method [127, 129, 130]. Surface vacancy/reduced $TiO_2$ nanomaterials with different shapes, sizes and morphology are also formed by chemical reduction or oxidation and electrochemical reduction method with $V_O^{\bullet\bullet}$ [129, 131-133].

A literature study showed that both surface and bulk oxygen vacancy increases light absorption, but they have different effects on photocatalytic activity. The oxygen vacancy

defects in $TiO_2$ were theoretically studied by first-principles calculations [134, 135], electron paramagnetic resonance spectroscopy (EPR), scanning tunnelling microscopy (STM) [136-140]and time-resolved photoluminescence spectroscopy (PL) [125, 127] are the experimental techniques used for the study of oxygen vacancy defect in $TiO_2$. These defects may also affect the electronic properties[141], reactivity, adsorption and desorption of anatase and rutile with $O_2$ [135-139], $H_2O$ and $CO_2$ has been reported. Li et al. [142]investigated that the oxygen vacancy defect level is situated below the conduction band in $TiO_2$. Studies have been reported that the free electrons on oxygen vacancy are localized to form $Ti^{3+}$center [143]. The $TiO_{2-x}$ contained oxygen vacancy under visible light showed enhanced photocatalytic activity [127, 144]. Due to the defects caused by oxygen vacancy, visible light absorption increased in $TiO_2$, where the catalytic activity was improved due to the absorption of solar light. Fukushi et al. [145] reported the results contrary to the above with the reduction of photocatalytic activity under fluorescence lamp for the degradation of organic materials in gas phase. This result was due to the different illuminating material used. For defect less $TiO_2$ UV light can be used, whereas for defected $TiO_2$ visible light is effective. Due to the presence of oxygen vacancies, free electrons can move between the surface and the bulk and, hence, more electrons were absorbed by the holes after light incidence [146-148]. The above literature studies reveal that the holes, affecting the degradation of organic materials, decreased and, as consequence, this corresponded to an enhanced photocatalytic activity.

Li et al. [149] explored the three different kinds of $TiO_2$ nanocrystals for the photocatalytic reduction of $CO_2$ by two different vacancy defects: the surface oxygen vacancy (SO) and bulk single-electron-trapped oxygen vacancy (SETOV). The former was prepared by the reduction of anatase $TiO_2$ (SO-$TiO_2$) using $NaBH_4$. Nanotubes titanic acid were dehydrated to form bulk-SETOV (SETOV-BO) at 400°C whereby reducing pristine$TiO_2$ the surface and bulk oxygen vacancy (SBO) were produced at high temperatures. After investigation the high photocatalytic reduction was shown by the photocatalyst with both surface and bulk defects and the increase of the surface defects over the bulk enhanced the photoreduction of $CO_2$as

shown in Figure 3. Huang et al. [150] reported that a $CuO_2$ ultrathin layer on $TiO_2$ nanorods surface was formed by the redox reaction between $Ti^{3+}$ induced by oxygen vacancy and $Cu^{2+}$. The oxygen vacancy modulation defect could obviously increase the efficiency of anatase/brookite heterophase junction 12 times higher than pristine $TiO_2$ [151].
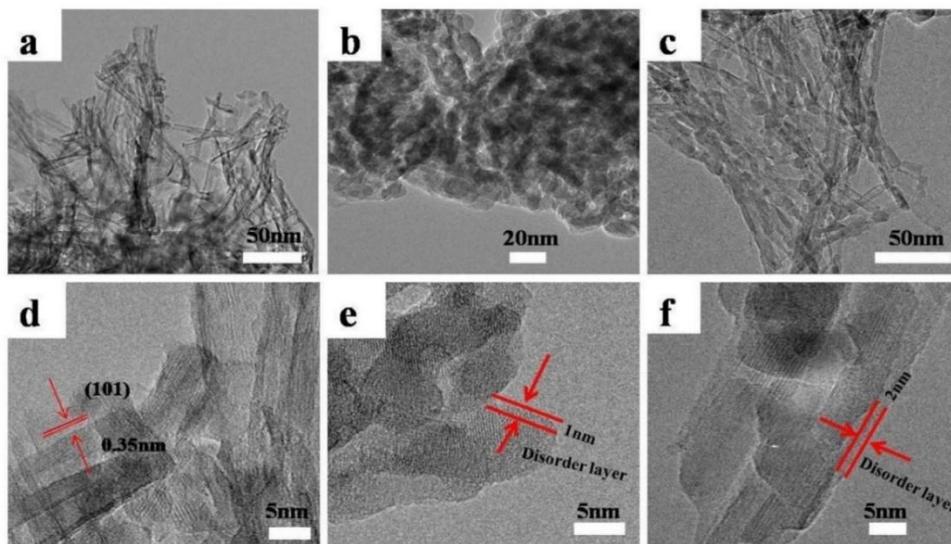


**Figure 3:** TEM and HRTEM images of $TiO_2$-BO (a, d), $TiO_2$-SO (b, e), and $TiO_2$-SBO (c, f) [149]. Copyright 2017 Elsevier.

## 4. Reaction mechanism of $TiO_2$ photocatalyst

Mechanism of photocatalytic oxidation reactions (PCO) have key importance in the real applications. During the PCO, the formation of electron and hole between the valance (VB) and conduction band (CB), is the significant step and needs energy to overcome the band gap energy $(E_g)$[56]. The oxidation and reduction process can occur at the same time in PCO reactions. The free photoelectron in the CB and a photohole in the VB are created in the semiconductor by the absorption of photon of energy equal or greater than the energy

difference between the VB and CB. The photo-redox reaction occurs between the air, pollutant and oxygen simultaneously. The hydroxide (HO⁻) or hydroxyl radical(HO•) formed during the PCO reaction is very reactive while the superoxide ($O_2^-$) formed by reducing oxygen ($O_2$)as a result of the electron reducing ability [66]. The organic or inorganic pollutants and microorganismscan be destroyed by the highly reactive HO• and $O_2^-$ species (Figure4) [152-154]. $TiO_2$has the ability for the complete degradation of organic pollutants, and the activation can be expressed by Equation(2) [66]:

$$TiO_2 + hv \longrightarrow h^+ + e^- + TiO_2 \qquad (2)$$
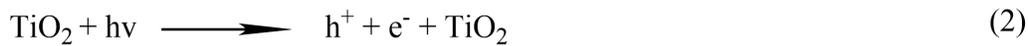
The photonic excitation in the above reaction is the initiating step for the catalytic reaction, where $h^+$ and $e^-$ are the strong oxidizing and reducing agents correspondingly:

$$HO^- + h^+ \longrightarrow OH \qquad (3)$$

The reduction reaction:

$$Ti^{4+} + e^- \longrightarrow Ti^{3+} \qquad (4)$$

$$Ti^{3+} + O_2 \longrightarrow Ti^{4+} + O_2^- \qquad (5)$$

$$OH^+ \text{ Pollutants} \longrightarrow \text{Oxidize Pollutants } (CO_2, H_2O, \text{etc}) \qquad (6)$$
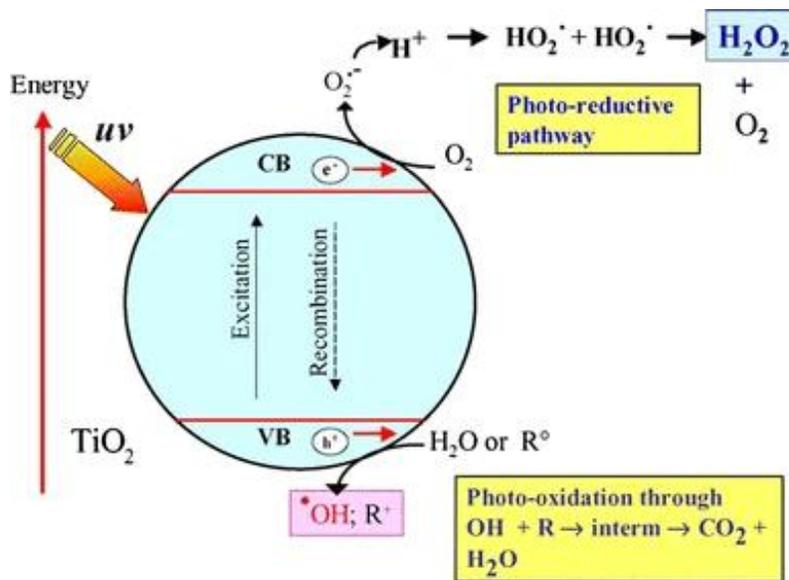
**Figure 4:** Classical scheme for the production of highly oxidative species by $TiO_2$ under light irradiation with wavelengths <400 nm. [56] Copyright 2011 Springer.

## 5. Photocatalytic degradation of organic gaseous pollutants

In the early 1970's gas-phase heterogeneous catalysis was examined by Teichner et al. [155] for the incomplete oxidation of paraffins and photocatalytic oxidation of isopropanol and photo-adsorption of oxygen and the formation of reactive species after the adsorption of water on the surface of $TiO_2$ were studied by Stone et al. on rutile surface [156, 157]. Firstly, surface $OH_s^-$ and bulk $OH_L^-$ were reported to be formed on the surface of $Ti^{4+}O^{2-}$. On the reactive surface of $TiO_2$, the positive hole was trapped by $OH^-$ to form $^\bullet OH$ while $O_{2, ads}$ after getting electron produced $O_{2, ads}^-$. The reactive radicals, present in the photodegradation process, are produced during water and oxygen adsorption at the surface and are capable of the degradation of VOCs in the air by PCO reaction [157]. Further studies of chemisorption and photochemistry of $CO_2$, $O_2$, and $H_2O$ can provide concepts about the degradation of VOCs in the air purified by PCO (Figure 5). The World's attention is attracted by indoor air pollution for the PCO of VOCs due to

its health effect [34].Indoor and outdoor air pollutants mainly consist of VOCs i.e., aldehydes, aromatics, and halocarbons. Benzene, toluene, formaldehyde and tetrachloroethene are the frequently used VOCs in PCO studies used for the better understanding of the photocatalysts and reactors.
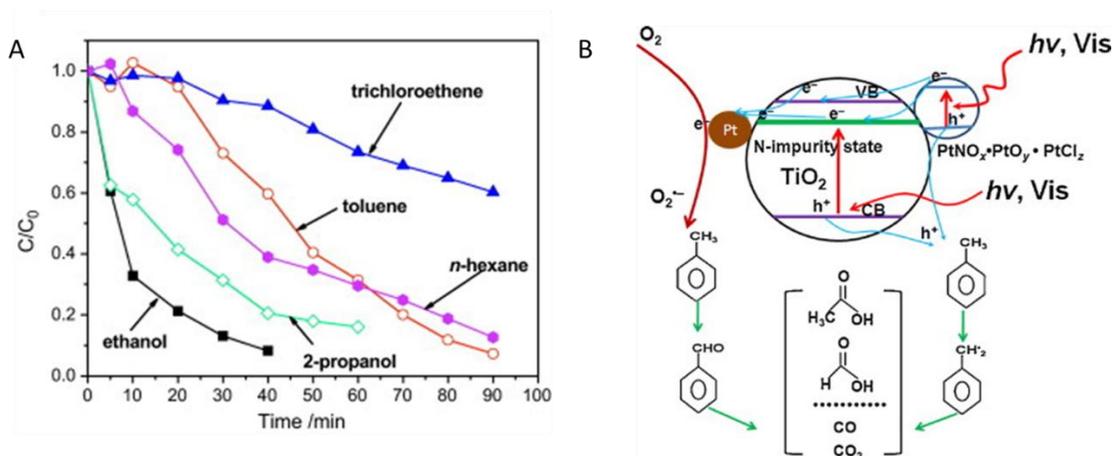


**Figure 5:** (A) Degradation of various chemicals using Pt/N-TiO$_2$ photocatalyst. (B) Mechanism of photodegradation of gaseous toluene over Pt/N-TiO$_2$ under visible light irradiations. [158] Copyright 2011 Elsevier.

### 5.1 Photocatalytic Degradation of Aldehydes

Environmental pollution due to aldehydes is the main concern of scientists these days. Formaldehyde is the most important air pollutant among carbonyl compounds that causes serious sickness and cancer [159].The World Health Organization (WHO) limit for formaldehyde in air is 80ppb or 0.1mgm$^{-3}$ [66]. Peral and Ollis [160] were the first to study the heterogeneous photocatalytic oxidation of various pollutant gases e.g., formaldehyde and butyraldehyde as well as m-xylene, acetone and 1-butanol. Gas phase photocatalytic degradation of these compounds was studied by the Langmuir-Hinshelwood rate forms by using anatase TiO$_2$ powder under UV radiation [161].

Yuanwei Luet al. [22] investigated the adsorption of formaldehyde on the $TiO_2$ film coated on activated carbon filters and $TiO_2$ film coated on glass under UV irradiation. $TiO_2$ coated with activated carbon filters can work efficiently as compared to $TiO_2$ film coated on glass. Activated carbon-coated coated $TiO_2$ significantly increased the degradation of formaldehyde, due to the absence of adsorption saturation over the activated carbon. Elfallah et al.[162] reported the TiO2-impregnated polyester (PES) and glass fibre (GFT)-$TiO_2$ for the photocatalytic degradation of butyraldehyde and isovaleraldehyde. GFT-$TiO_2$ has enhanced the performance as compared to PES-$TiO_2$. The by-products formed during the reaction were analyzed by gas chromatography-mass spectrometry (GC-MS). Shi and coworkers [163] studied the photocatalytic oxidative conversion of aldehydes into carboxylates using $TiO_2$ as a catalyst by the oxygen isotope labelling method. The dehydrogenation of aldehydes takes place first, followed by the oxidation of aldehydes by a two-electron transfer process. The photocatalytic oxidation is initiated by $^{\bullet}OH$ and $SO^{\bullet-}$ single electron radicals. DFT studies defined a new way for the oxidation of aldehydes using $TiO_2$ as a catalyst. The aromatic aldehydes (benzaldehyde and p-methoxybenzaldehyde) showed much lower photodegradation performance and yield as compared to aliphatic aldehydes (acetaldehyde and propionaldehyde) as shown in Figure 6. The first order rate constant for p-methoxybenzaldehyde was $2.34 \times 10^{-4}$ $min^{-1}$, $3.09 \times 10^{-4}$ $min^{-1}$ for benzaldehyde, $27.1 \times 10^{-4}$ $min^{-1}$ for propionaldehyde and $30.4 \times 10^{-4}$ $min^{-1}$ for acetaldehyde, respectively.
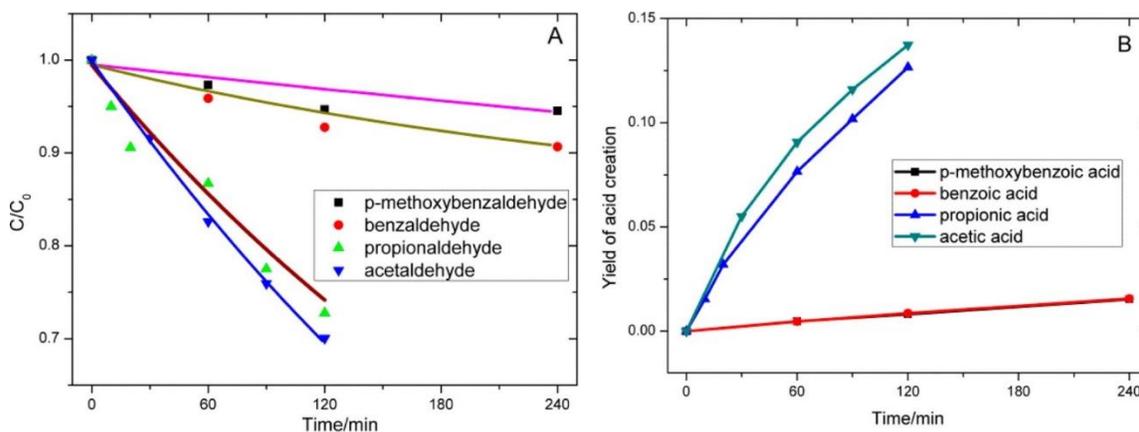
**Figure 6.** (A) Degradation kinetics of p-methoxybenzaldehyde, propionaldehyde, benzaldehyde, and acetaldehyde and (B) yield of corresponding acids: concentration ratio of the formed acids to theinitial aldehydes [163].Copyright 2015American Chemical Society.

The proposed mechanism for the photodegradation of formaldehydeis given by Equation (7-11) [34, 164]:

$$HCHO + \cdot OH \longrightarrow \cdot CHO + H_2O \qquad\qquad (7)$$
$$\cdot CHO + \cdot OH \longrightarrow COOH \qquad\qquad (8)$$

$$\cdot CHO + \cdot O^-_{2ads} \longrightarrow HCO_3^- (+ H^+) \longrightarrow HCOOOH (+HCHO) \longrightarrow HCOOH \qquad (9)$$

$$HCOOH(-H^+) \longrightarrow HCOO- (\cdot OH) \longrightarrow H_2O + \cdot CO_2^- \quad or \qquad (10)$$
$$HCOO^- + (+ h^+) \longrightarrow H^+ + \cdot CO_2^-$$

$$\cdot CO_2 + [O] + \cdot OH + h^+ \longrightarrow CO_2 \qquad\qquad (11)$$
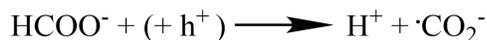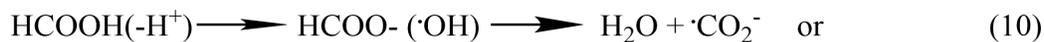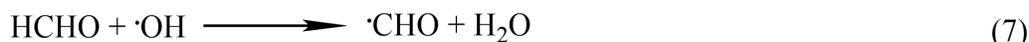
## 5.2 Photocatalytic degradation of toluene

Toluene is a pollutant, occurring in both indoor and outdoor environments, and it is the most well-known and recommended pollutant by the French normalization group in the standard AFNOR, XP-B44-013 for the study of PCO was prepared the surfaces of $TiO_2$ nanoparticles by loading $TiO_2$quantum dots (QDs) with a two-step method [163, 165]

Quici et al.[166] reported the effect of low concentration of toluene under UV light of 254 nm and 185 nm for indoor air purification using two different forms of $TiO_2$, one coated with P25 aqueous suspension and the other with thin films organic/inorganic sol gel mesoporous anatase. The efficiency for the removal of toluene was enhanced by increasing the thickness (i.e., mass) of the $TiO_2$ till 500 nm, while further increase in thickness could not enhanced the removal efficiency. Zhong et al [167] studied removal of toluene using co-alloyed

TiNbON under visible light with radiance 42-95W/m$^2$ at room temperature with a relative humidity of 25-65% and flow rate of 0.78cm/s to 7.84cm/s. Visible light can degrade the 58% of toluene. Seunghyun et al. investigated the degradation of toluene using Pt/TiO$_2$ and F-TiO$_2$ as a photocatalysts. The Pt/TiO$_2$ exhibits a greater photodegradation activity as compared to pristine TiO$_2$, but it rapidly deactivates when repeatedly used. On the other hand, F-TiO$_2$ initially showed less photodegradation activity, but only a slight deactivation was observed after several runs. The Pt/TiO$_2$ catalyst showed higher photodegradation activity for toluene (Figure 7).
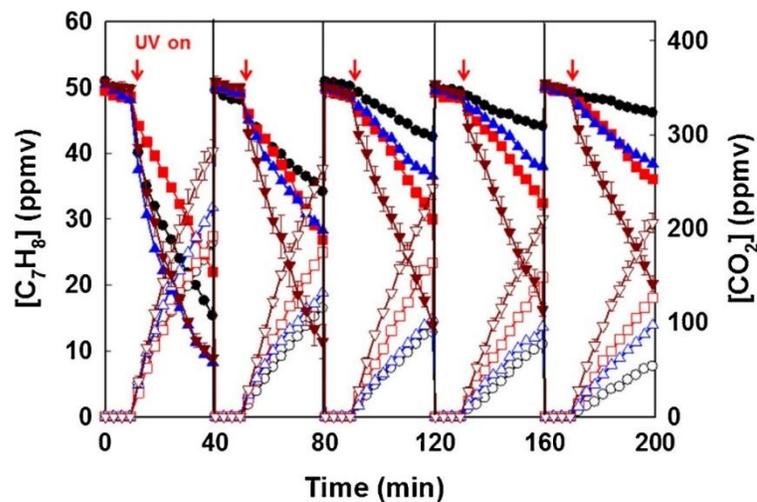


**Figure 7.** Repeated photocatalytic degradation cycles of gaseous toluene on F-TiO$_2$/Pt (▼), Pt/TiO$_2$ (▲), F-TiO$_2$ (■), and bare TiO$_2$ (●)[168]. Copyright 2018 Elsevier.

The mechanism for the PCO of toluene gasses provided in (Eq.12-23) [34],

$$2H_2O\cdot \longrightarrow O_2 + H_2O_2 \qquad (12)$$

$$H_2O_{2,ads} + O^-_{2,ads} \longrightarrow OH^- + \cdot OH + O_2 \qquad (13)$$

$$OH\cdot_{,ads} + C_6H_5CH_{3,ads} \longrightarrow H_2O + C_6H_5CH_2\cdot \qquad (14)$$

$$C_6H_5CH^-_2 + O_{2,ads} \longrightarrow C_6H_5CH_2OO\cdot \qquad (15)$$

$$C_6H_5CH_2OO^{\cdot} + e^- \longrightarrow C_6H_5CH_2OH + OH^- \tag{16}$$

$$C_6H_5CH_2OO^{\cdot}_{ads} + {\cdot}OH \longrightarrow C_6H_5CO^{\cdot} + H_2O \tag{17}$$

$$C_6H_5\overset{\cdot}{C}O + O_{2,ads} \longrightarrow C_6H_5COOHO^{\cdot} \tag{18}$$

$$C_6H_5CO\overset{\cdot}{O}O + C_6H_5CHO_{ads} \longrightarrow C_6H_5\overset{\cdot}{C}O + C_6H_5COOOH_{ads} \tag{19}$$

$$C_6H_5\overset{\cdot}{C}O + O_{2,ads} \longrightarrow C_6H_5COO\overset{\cdot}{O} \tag{20}$$

$$C_6H_5COO\overset{\cdot}{O} + C_6H_5CHO_{ads} \longrightarrow C_6H_5\overset{\cdot}{C}O + C_6H_5COOOH_{ads} \tag{21}$$

$$C_6H_5COOOH_{ads} + C_6H_5CHO_{ads} \longrightarrow 2C_6H_5COOH_{ads} \tag{22}$$

$$C_6H_5COOH_{ads} \longrightarrow C_6H_6 + CO_2 \tag{23}$$

According to the proposed mechanism, benzoic acid and small amount of benzyl alcohol, phenol and benzaldehyde will be produced as intermediates, due to partial oxidation during the degradation of toluene.

## 5.3 Photocatalytic degradation of Benzene

Chemical factories produce fuel gas, gasoline vapours, automobiles, cigarette smoke, plastics, rubber, and paints are the sources of benzene production, as well as benzene derivatives, such as toluene, benzoic acid, chlorobenzene, phenols and chlorophenols. Health problems like leukaemia due to even a small amount of benzene are reported [169].

To perform PCO of gaseous benzene, Wang and Ku [168] used a batch-type photoreactor with a bundle of TiO₂-coated quartz fibre. The principal intermediate was suggested to be phenol; however, the final products were CO₂, CO, and H₂O. The degradation routes were seen using gas chromatography-mass spectrometry (GC–MS) and Flourier transform infrared spectroscopy, as shown in Scheme 1. Jian et al. [12] prepared mesoporous TiO₂ photocatalyst by changing the calcination temperature for the removal of benzene (Figure 8). Mesoporous TiO₂ shows more catalytic activity and stability as compared to commercial TiO₂ for the degradation of benzene. Yanhui et al. [20] reported that the graphene-TiO₂ has higher

stability and photocatalytic activity towards gaseous benzene, the higher the content of graphene. $TiO_2$ lower its photocatalytic activity.
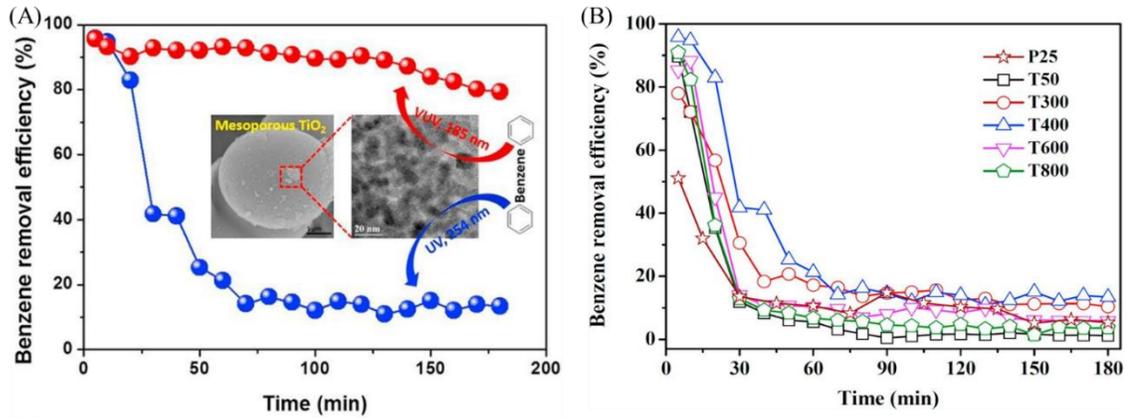


**Figure 8:** (A) Photodegradation of benzene using mesoporous $TiO_2$ under UV and VUV irradiation. (B) Benzene removal efficiency over $TiO_2$ calcined at different temperatures under UV-PCO system [12]. Copyright 2017 Elsevier.

**Identified by GC-MS**



**Scheme 1:** Gas-phase PCO of benzene by UV/TiO$_2$ processes [170].

## 5.4 Photocatalytic degradation of Trichloroethene

The organochloride compound trichloroethene (TCE) is used as a solvent, cleaning and degreasing agent. TCE is the typical chlorinated VOC emitted from industrial wastes, indoor air and hazardous waste sites [171]. Tomoaki et al [172] investigated the porous Pt ion doped $TiO_2$ under visible light for the photocatalytic degradation of TCE, which was 100% degraded under visible light (Figure 9).

Being a chlorinated compound, TCE was studied as an air pollutant in PCO. It was observed that the most hazardous and toxic chlorinated VOCs intermediates are formed i.e., carbon monoxide (CO), chloroform ($CHCl_3$), carbon tetrachloride ($CCl_4$), dichloroacetyl chloride (DCAC), tri-chloroacetyle chloride (TCAC) and phosgene ($COCl_2$) during PCO degradation reaction of TCE. The proposed TCE mechanism is given in the scheme given below. It was observed that the toxic effect of intermediates is reduced due to oxygen and relative [90-92].The effects of oxygen and relative humidity (RH) on the formation of DCAC and phosgene were examined by Ou and Lo [171]. As shown in Scheme 2 [171], a TCE degradation process has been proposed. The number of hazardous intermediates can be reduced by optimizing oxygen and relative humidity.
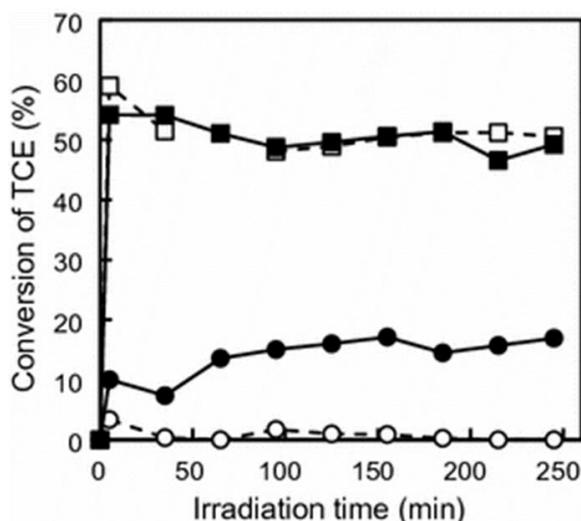
**Figure 9:** Time course of TCE conversion on Pt-TiO$_2$(filled circle) and TiO$_2$(open circle) under VL irradiation and Pt-TiO$_2$(filled square) and TiO$_2$ (open square) under UV irradiation [172]. Copyright 2017 Springer.

$$TiO_2 \xrightarrow{h\nu} h^+ + e^-$$

Trichloro ethylene, TCE

$$Cl^- + h^+ \longrightarrow \dot{C}l$$

$$O_2 + e^- \longrightarrow O_2^- + Cl$$

Russel mechanism

Cl elimination

C—C bond rupture

C—C bond rupture

(DCAC)

(Phosgene)

$$\dot{C}l + O_2$$

$$CH_2\dot{C}l + \boxed{Cl_2 + CO_2} \quad \text{(Final Products)}$$

$$+$$

$$H_2O \longrightarrow CH_2\text{---}CH_2 + \boxed{HCl}$$

(Final Product)
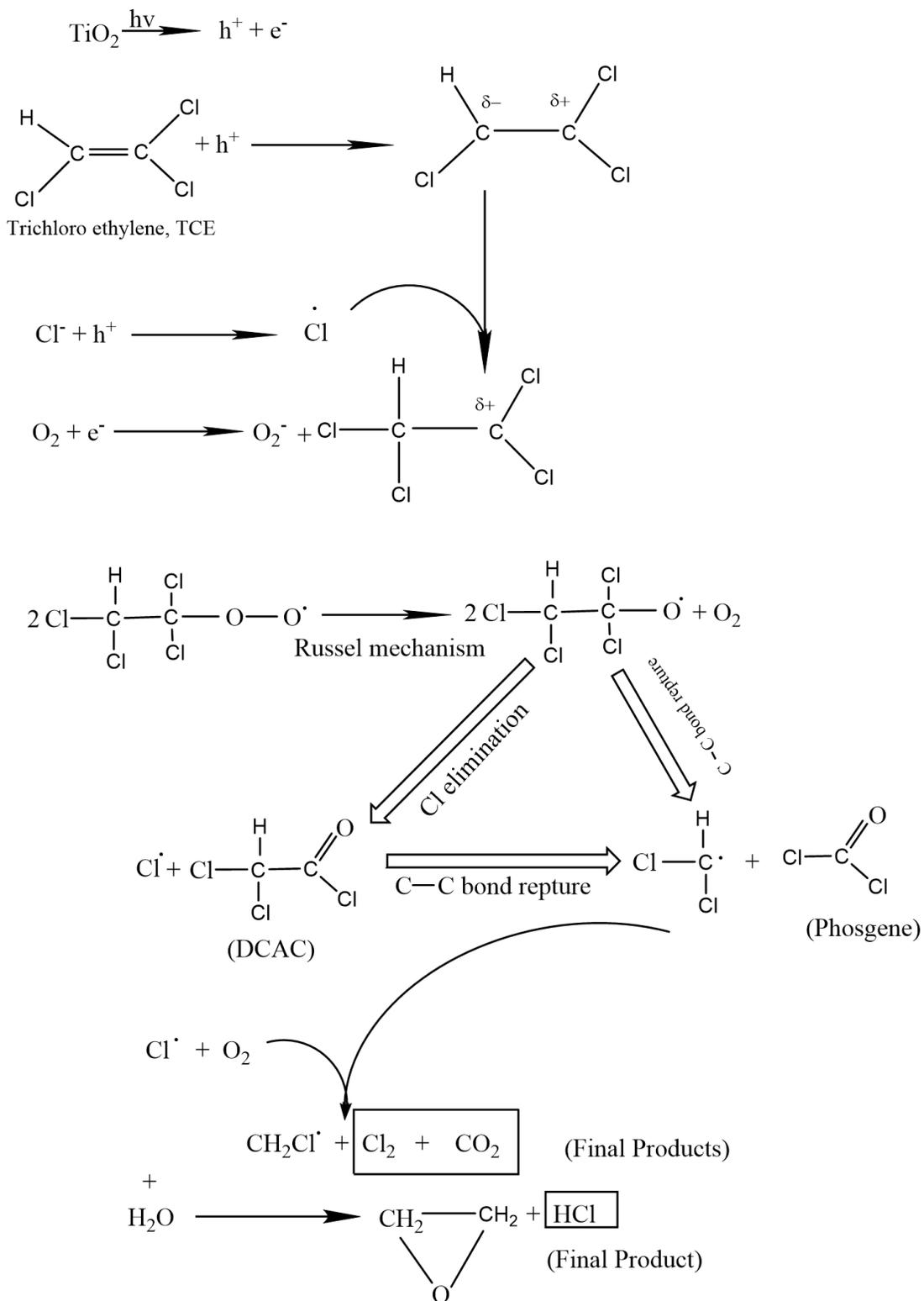
**Scheme 2:** Proposed mechanism of TCE photodegradation [173].

## 6. Photocatalytic degradation of inorganic gaseous pollutants

The massive intrusion of harmful contaminants into environmental matrices is a global threat that is becoming increasingly alarming due to the increase in industrialization. Besides organic pollutants, every year a considerable number of different types of harmful inorganic pollutants, such as $NO_x$, $SO_x$, CO, and others, are released. TiO2-based photocatalysts are widely used for the photodegradation of these inorganic pollutants (Table 5).

**Table 5.** Photocatalytic oxidations of inorganic gas pollutants on $TiO_2$-based photocatalysts [34].

| Photocatalyst | Pollutants | Performance | Reference |
|---|---|---|---|
| Polymeric nanofibers supported anatase $TiO_2$ | $NO_x$ | 16% of NO decomposed | [174] |
| Oxygen-deficient $TiO_2$ | NO | 75% of NO degraded | [175] |
| Fe/$TiO_2$ | $NO_x$ | 38% of NO decomposed | [176] |
| Molybdenum-doped $TiO_2$ nanotubes | $NO_2$ | 77% decomposition of $NO_x$ | [177] |
| Pt-doped $TiO_2$ | $NO_x$ | Pt-$TiO_2$0.4% decomposed about 30% NO while P25 5% under the irradiations of visible light | [178] |

| Material | Gas | Result | Reference |
|---|---|---|---|
| Au/CeO$_2$-TiO$_2$ | NO | 83% of NO decomposition where 48% over | [179] |
| Cobalt imidazole complex functionalized GO supported TiO$_2$ film | NO$_x$ and CO | pure TiO$_2$ 51% of NO$_x$ decomposition and 46% of CO greater | [180] |
| WO$_3$/TiO$_2$ | H$_2$S | than pure TiO$_2$ film 70% decomposition of H$_2$S and 60% sulfur was removed | [181] |
| RuO$_2$/TiO$_2$/Pt | CO SO$_2$ and | by 5%WO$_3$/TiO$_2$ 100% degradation of CO in 60 min | [182] |
| Multi-walled carbon nanotubes supported Cu/TiO$_2$ | NO | | [183] |
| | NO | 62% SO$_2$ and 43% NO was removed | [184] |
| Dye-modified TiO$_2$ | | 99% of NO decomposed with 99% N$_2$ selectivity | |

## 6.1 Photocatalytic degradation of NO$_x$

The nitric oxides (NO$_x$) mainly include NO and NO$_2$ [185]. Emission of NO$_2$ may occur due to the activities of both human beings and natural sources, e.g., volcanic emissions, and NO$_x$ and can be emitted by the decomposition of organic compounds by the microorganisms by solar energy and the ecosystem. Human activities and automobiles can emit NO$_x$. Emission of NO$_x$ can cause human health problems like immune and respiratory problems and environmental issues e.g., global warming, formation of tropospheric ozone and acid rain [186]. The removal of NO$_x$ can be done by controlling NO$_x$ emission by reducing NO$_x$ into N$_2$ or

oxidizing it into $HNO_3$ [185, 187]. $NO_x$ can be reduced by heterogeneous photocatalytic oxidation (PCO), HCs-SCR, $NH_3$-SCR, photoselective catalytic reduction (photo-SCR) and photodecomposition [5, 111, 188].

Luevano-Hipolito et al. [189, 190] studied the photocatalytic degradation of NO and their $Bi_2Mo_3O_{12}$ catalyst was reported to remove 88.9% NO and is considered to be an excellent photocatalyst under UVA PCO. The $TiO_2/WO_3$ was studied for nitrogen oxide ($NO_x$) removal under UV and visible light. Mendoza et al. [191] examined surface-modified $WO_3/TiO_2$ for $NO_x$ removal under visible light. Host $TiO_2$ was modified by using NaOH as a modifying agent. The performance of NaOH-modified $WO_3/TiO_2$ was increased by increasing the concentration of NaOH which can remove more than 90% of $NO_x$ while non-modified $WO_3/TiO_2$ can remove ~ 72% of $NO_x$. The greater proficiency for the removal of $NO_x$ was due to the oxygen vacancies on the surface of $TiO_2$ which facilitates $WO_3$ particles to bind efficiently. Ma et al. [192] prepared oxygen-deficient $TiO_2$ ($TiO_2$-200) at low temperatures for the degradation of NO at the level of 400 ppbv under visible light irradiations (420 nm < λ < 700 nm). Visible light irradiations can be absorbed efficiently due to oxygen vacancies on $TiO_2$ surface which facilitates the separation of photoelectrons and holes. Larger the surface area larger are the active sites for reaction. The enhanced photocatalytic oxidation ability of $TiO_2$-200 is due to oxidation of NO to $NO^{-3}$ as shown in Figure 10. Marco et. al. discusses the production and characterization of sodium titanates (ST) as well as their application in the photocatalytic reduction of NO. The photocatalytic studies revealed that virgin ST (tri and hexa-titanate) was the photocatalyst with the best performance in terms of NO reduction when compared to the impregnated samples (STAg, ST-Zn). When 1 g of photocatalyst was used with a flow of 280 ml/min and a light of 253 nm, maximum degradation efficiencies of 80 percent were achieved [193].

**Figure 10.** (A) Photocatalytic removal of $NO_x$ over visible light responsive oxygen deficient $TiO_2$. (B) NO conversion, $NO_x$ conversion, and $NO_2$ selectivity at 0.5h for various catalysts [192]. Copyright 2014 American Chemical Society.

The photocatalytic conversion of $NO_x$ into $HN_3$ by photooxidation via the following steps and mechanism (Eq.24 -37)[34, 186].

$$NO \longrightarrow HNO_2 \longrightarrow NO_2 \longrightarrow HNO_3 \tag{24}$$

$$NO + \overset{\cdot}{O}H \longrightarrow HNO_2 \tag{25}$$

$$HNO_2 + \overset{\cdot}{O}H_{ads} \longrightarrow NO_2 + H_2O \tag{26}$$

$$NO_2 + \overset{\cdot}{O}H_{ads} \longrightarrow HNO_3 \tag{27}$$

$$NO + O^-_{2,ads} \longrightarrow NO_3^- \tag{28}$$

$$2NO + \overset{\cdot}{O}^-_{2,ads} + 3e^- \longrightarrow 2NO_2 \tag{29}$$

$$3NO_2 + 2OH^- \longrightarrow 2NO^{-3} + NO + H_2O \tag{30}$$

Other mechanisms that are used in photocatalysis for the photoreduction of $NO_x$ into $N_2$ is,

$$NO_{ads} + e^- \longrightarrow N_{ads} + O_{ads} \qquad (31)$$

$$NO_{ads} + N_{ads} \longrightarrow N_2O_{ads} \qquad (32)$$

$$NO_{ads} + O_{ads} \longrightarrow NO_{2,ads} \qquad (33)$$

$$2O_{ads} \longrightarrow O_{2,ads} \qquad (34)$$

$$2NO_{ads} \longrightarrow NO_{2,\ ads} \qquad (35)$$

$$2NO_{ads} \longrightarrow O_{2,ads} + N_{2,ads} \qquad (36)$$

$$2NO_{2,ads} \longrightarrow O_{2,ads} + 2N_{2,ads} \qquad (37)$$

## 6.2 Photocatalytic degradation of $SO_x$

The US EPA declared gaseous $SO_x$ as a hazardous pollutant because it can cause damage to the vegetation, acid rain and corrosion to the buildings. Exposure to $SO_x$ can cause respiratory problems like asthma and bronchi tightening. $SO_x$ can also form airborne particles which create problems in visibility and change the climate.

Wang et al. [194] studied photochemical removal of $SO_2$ over $TiO_2$-based nanofibers with a dry photocatalytic oxidation process. Results revealed that the degradation of $SO_2$ under UV light was mainly influenced by the oxidation of NO to $NO_2$. The researchers found that adding $TiO_2$ to mortars increased their physical, mechanical, and photocatalytic capabilities, as well as allowing them to be decontaminated by the $SO_2$pollutant [195].Cerium-based $TiO_2$ nanofibers showed 100% efficiency for the removal of $SO_2$ and are resistive to humidity while using copper-based $TiO_2$ nanofibers the photocatalytic activity decreased when humidity is less than 4% where $SO_2$ dissolution occurs under 8% humidity (Figure 11).

Topalian et al.[196] investigate the photo fixation of $SO_x$ on the surface of anatase $TiO_2$. Studies have shown active oxygen can facilitate the sulfides and sulfates formed by the photooxidation of $SO_2$.

$$SO_{2,ads} + {}^{\cdot}O^{2-}_{2,ads} \longrightarrow SO^{2-}_{4,ads} \qquad (38)$$

$$SO_{2,ads} + OH^-_{ads} \longrightarrow HSO^-_{3,ads} \qquad (39)$$
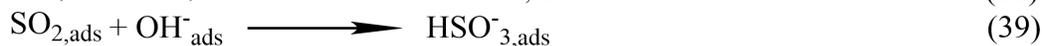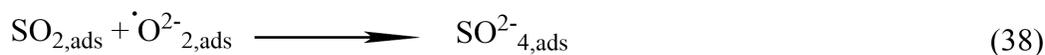
Xia et al. [197] described their investigations on the photocatalytic evacuation of vaporous NO and $SO_2$ utilizing $BiOI/Al_2O_3$ as a photocatalyst under visible irradiations. The proposed mechanism and the conversion of $SO_2$ is given below (Equations 40-42),

$$SO_2 + h^+ + 2H_2O \longrightarrow H_2SO_4 + 2H^+ \tag{40}$$

$$SO_2 + \overset{\cdot}{O}H_{ads} \longrightarrow HSO_3 \tag{41}$$

$$SO_2 + \overset{\cdot}{O}^-_{2,ads} \longrightarrow SO^{2-}_4 \tag{42}$$
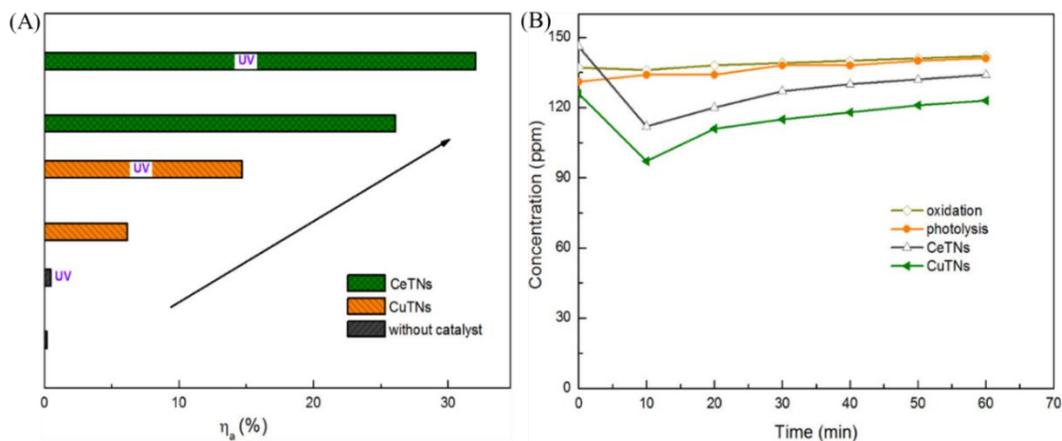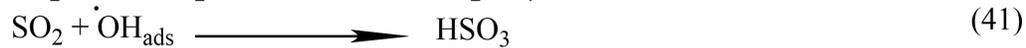


**Figure 11:** (A) Characteristics of $SO_2$ photocatalytic removal process. (B) Photocatalytic removal of $SO_2$ under basic fuel gas (BFG) atmospheres [194]. Copyright 2017 American Chemical Society.

## 6.3 Photocatalytic Degradation of CO and Ozone

The carbon monoxide is a major air pollutant in the environment and fatal for living beings because it can accumulate oxygen in the blood. CO is emitted by the partial combustion/oxidation of volatile organic compounds, i.e., hydrocarbons. Hassan et al. [198] reported a Ti-MCM-41 mesoporous framework which hindered the crystal growth of $TiO_2$. This

property can make Ti-MCM-41 more favorable for the photocatalytic degradation of methylene blue and carbon monoxide (Figure 12).

Ozone is a pungent smell blue colour gas located in the atmosphere above 30,000-150,000 feet and is responsible for the absorption of UV rays and protecting the earth from the harmful effects of UV rays. Ozone is a hazardous pollutant and varies with region, temperature and weather. Ozone concertation higher than $0.214g/m^{-3}$ is poisonous and can cause headaches, eye, nose and throat irritation and chest pain [199]. Ozone has a strong oxidizing property and oxidizes VOCs in the atmosphere. Simultaneous degradation of pollutants is a topic of interest in this field.
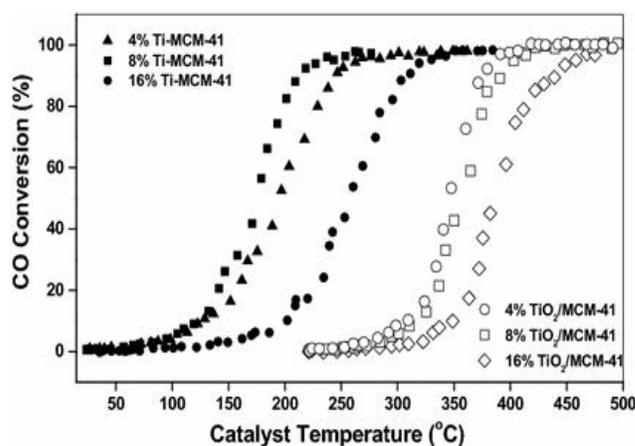


**Figure 12:** CO conversion % in relation to the reaction temperature over $TiO_2$/MCM-41 prepared by post impregnation and Ti-MCM-41 prepared by one pot method containing different $TiO_2$ content (4,8 and 16 wt%) using gas mixture CO and $O_2$ with amount (4:20 wt% respectively) at a rate of 100 mL $min^{-1}$ [198].Copyright 2017 Springer.

Carbon monoxide under UV irradiations converts to $CO_2$ which is the last step in the photooxidation/ photodegradation of CO (Equations 43-46) [200]:

$$CO + h^+ \longrightarrow CO^{\cdot} \qquad (43)$$
$$^{\cdot}O^-_2 + h^+ \longrightarrow 2O \qquad (44)$$
$$O + e^- \longrightarrow O^- \qquad (45)$$
$$O^- + CO \longrightarrow CO_2 \qquad (46)$$

Ozone can be photo-catalytically degraded due to the formation of reactive radical. Following is the pathway used for the photodegradation of ozone (Equations 43-49),

$$CO + h^+ \longrightarrow CO^{\cdot} \qquad (43)$$
$$^{\cdot}O^-_2 + h^+ \longrightarrow 2O \qquad (44)$$
$$O + e^- \longrightarrow O^- \qquad (45)$$
$$O^- + CO \longrightarrow CO_2 \qquad (46)$$
$$O_3 + e^- \longrightarrow {}^{\cdot}O^-_3 \qquad (47)$$
$$OH + O_3 \longrightarrow O_4 + H^+ \qquad (48)$$
$$^{\cdot}O^-_3 + O_3 \longrightarrow {}^{\cdot}O^-_4 + O_2 \qquad (49)$$

Other reported pathway for the photodegradation ozone are as follow(Equations 50,51) [199],

$$^{\cdot}O^-_4 + O_3 \longrightarrow {}^{\cdot}O^-_3 + 2O_2 \qquad (50)$$
$$^{\cdot}H^+ + O^-_3 + O^-_4 \longrightarrow 3O_2 + OH^- \qquad (51)$$

## 6.4 Photocatalytic degradation of H$_2$S

H$_2$S is a highly poisonous, odorous, and corrosive gas and is responsible for odour pollution which can affect human health and the environment. H$_2$S in the range of 0.0004 ppm can cause H$_2$S corrosion, acid rain and global warming.

Gaoyuan et al [201] described the degradation of H$_2$S over transition metals (Mn, Cu, Ni and Co) modified TiO$_2$ prepared by sol gelatin method under VUV-PCO and UV-PCO. Among all the Mn-TiO$_2$ showed the highest activity for the degradation of H$_2$S under VUV-PCO. Haiboet al. [202] investigated the hollow double organic metal framework [MIL-101(Cr)] of TiO$_2$

nanoparticles [TiO$_2$@MIL-101(Cr)] having high adsorption capability for H$_2$S under UV irradiations (Figure 13). Naeem et al. [203] reported the comparative studies of photocatalytic degradation of H$_2$S on the pure and 2% S-doped TiO$_2$ nanoparticles and nanofibers. The S-doped nanoparticles and nanofibers showed higher H$_2$S degradation activity as compared to pure nanoparticles and nanofibers where results showed that nanofibers have 10% higher efficiency than nanoparticles.
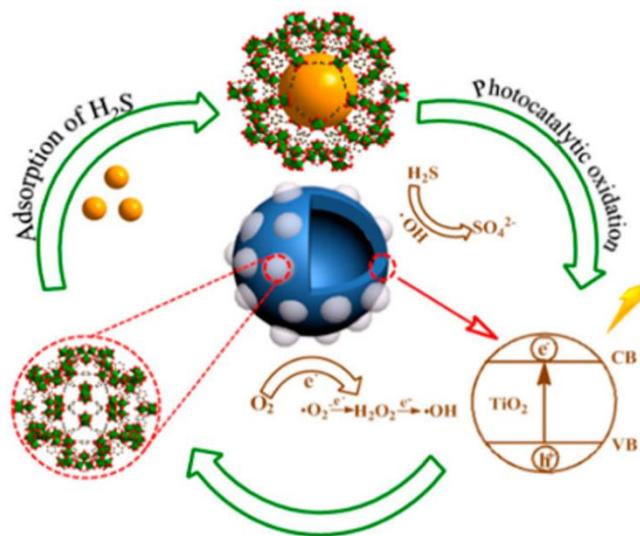


**Figure 13.** Schematic of the Reaction Mechanism for the removal of H$_2$S [202].Copyright 2017American Chemical Society.

Photocatalytic decomposition of hydrogen sulfide with the evolution of hydrogen gas was discussed by Bhirud et al.[204] as follow (Equations 52-58):

$$H_2S + OH^-_{ads} \longrightarrow HS^-_{ads} + H_2O \qquad (52)$$

$$2HS^-_{ads} + 2h^+ \longrightarrow 2S + 2H^+ \qquad (53)$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad (54)$$
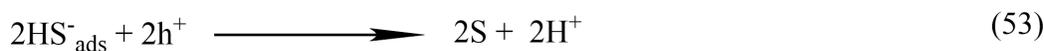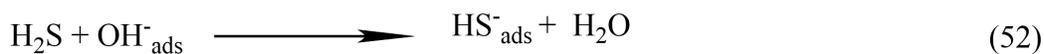
The process of photocatalytic oxidation is more favourable for energy revolution because it does not form the explosive hydrogen gas,

$$H_2S_{ads} + h^+ \longrightarrow H_2S^+ \longrightarrow H\dot{S}_{ads} + H^+ \qquad (55)$$

$$\dot{O}H_{ads} + H_2S^+{}_{ads} \longrightarrow H_2S_{ads} + H_2O_{ads} \qquad (56)$$
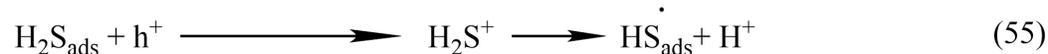
The resultant PCO product of $H_2S$ is sulfate, which leads to $SO_x$ conversion.

$$H\dot{S}_{ads} + O_{2,ads} \longrightarrow HS\dot{O}O_{ads} \qquad (57)$$

$$HS\dot{O}O_{ads} + O_{2,ads} \longrightarrow SO_{2,ads} \qquad (58)$$

## 7. Modification techniques

Ultraviolet light only consists of 4-5% of solar spectra whereas visible region accounts for about 40% of the solar photons. For the preparation and development, visible light reactive photosensitizing dyes are adsorbed on the $TiO_2$ surface where the photosensitizing dye in this system is photochemically and thermally unstable [26, 205]. In the early 90's, Grätzel used a dye photosensitize $TiO_2$electrode for the preparation of solar cell [206].Since then, various studies have been conducted such as the reports of Borgarelloet al [207], Hoffman and Bahnemann [208], who synthesized visible light-responsive photocatalysts by using different cations and metal oxides in a small quantity, but some limitations were also reported.

In advanced research, metal-ion implantation methods have been applied by using high-energy metal ions to change the electronic properties for the synthesis of doped-$TiO_2$. Apno et al. [209] studied implantation of $TiO_2$ by using numerous transition metal ions such as Fe, V, Cr, Co, and Ni at high voltage of 50-200 keV, which shifts the absorption band in the visible spectrum for these photocatalysts. In recent studies, the chemical doping method was used to improve the electronic properties of $TiO_2$ for the synthesis of visible light reactive $TiO_2$ by using metals, metal ions, non-metals and metal oxides [182].

**7.1 Metals Doping**

**7.1.1 Transition and Noble Metals Doping**

The $TiO_2$ doped by transition metals like V, Co, Cr, Fe and Ni, shifts the spectrum of $TiO_2$ to the visible band region and enhances the photocatalytic behavior of $TiO_2$ [210]. Transition metals can decrease quantum efficiency by providing the sites for charge recombination for photoinduced charge carriers. Transition metals doped anatase $TiO_2$ show thermal stability [211]. The doping of transition metals on $TiO_2$ can form a new level between the valence band and conduction band, which shifts the spectrum towards the visible region.

Photocatalytic behavior depends upon the nature and quantity of the doping agent. Kang [212] reported that metal doping not only decreases the band length and increases the photocatalytic activity of $TiO_2$, but it also cannot destroy the framework of $TiO_2$ the only drawback is that the metal remaining on the surface of $TiO_2$ can hinder the reaction sites. Morikawa et al.[213] studied the doping of Cr on $TiO_2$ for the degradation of NO. The result showed that the Cr doping could decrease the photocatalytic performance on the other hand doping of Cr with V on $TiO_2$ can improve the photocatalytic activity of the $TiO_2$ catalyst.

Doping of $TiO_2$ with transition metal ions can increase the photocatalytic response under visible light. Earlier, Choi et al. [214] investigate the 21 transition metal ions doped on $TiO_2$ to study the photocatalytic oxidation of chloroform and photocatalytic reduction of tetrachloride. It was reported that $Fe^{3+}$, $Mo^{5+}$, $Ru^{3+}$, $Os^{3+}$, $Re^{5+}$, $V^{4+}$, and $Rn^{3+}$ ions increased the photocatalytic degradation of $CHCl_3$. Yan et al. [215] doped cerium metal ion on $TiO_2$ by sol-gel method. It was investigated that Ce doping forms an energy band between valence and conduction bands. This avoids the recombination of electron-hole pairs by capturing the photo-generated holes, while the electrons in this energy band can easily jump to the conduction band of $TiO_2$. As shown in Figure 14, Ce doping increases the photocatalytic activity of $TiO_2$.

Iron in a trivalent state was doped on $TiO_2$ by sol-gel hydrothermal method, the titanium metal ($Ti^{4+}$) in $TiO_2$ is substituted by $Fe^{+3}$ thus the concentration of $Fe^{+3}$ decreases from the surface and shifts towards the $TiO_2$ deep bulk. It was also studied that doping concentrations and structures have significant influences on the doping of Fe on $TiO_2$. Cr and V also show good performance as a metal for $TiO_2$. The 3d electrons of $Cr^{3+}$ jump to the conduction band of $TiO_2$, thus increasing the visible light absorption ability of Cr-$TiO_2$ for the photodegradation of active yellow XRG dye [216].The $V^{4+}$ can be doped on $TiO_2$ by different methods such as the sol-gel, flame spray pyrolysis (FSP) [217] and by other chemical methods [218]. $TiO_2$ doped with $V^{4+}$ shift the conduction band of $TiO_2$ towards the visible light spectrum, thus $V^{4+}$ ion increases the visible light-induced photocatalytic activity of $TiO_2$ [219].
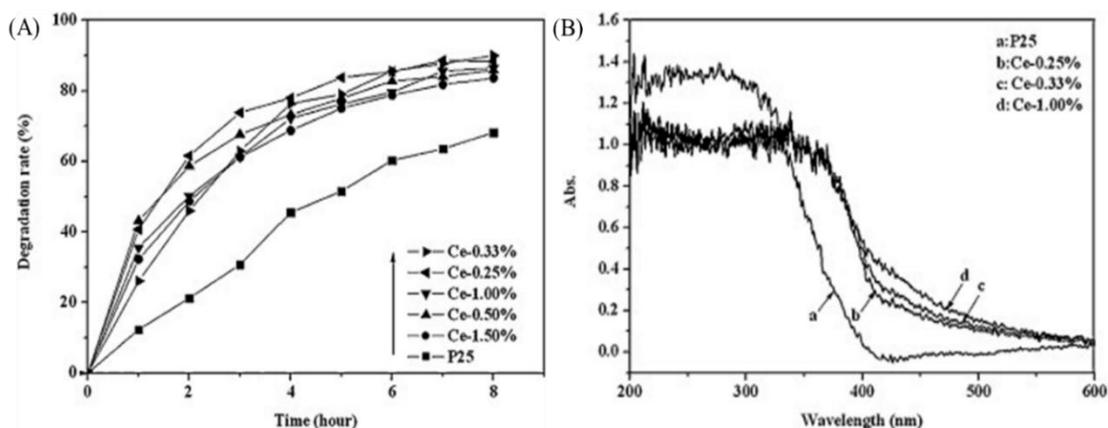


**Figure 14:** (A) UV-VIS spectra of Ce-$TiO_2$ samples with different Ce ion doping concentrations.(B) Curves showing the methylene blue degradation by Ce-$TiO_2$ catalyst with different Ce ion doping concentrations [215].Copyright 2012 Elsevier.

$Sn^{4+}$ doped $TiO_2$ replaces the $Ti^{4+}$ ion in the $TiO_2$ lattice, causing the expansion of the lattice in $a$ and $c$ directions and changing the binding energy [220]. Zhuang et al. [117] investigated the $Sn^{2+}$ doped anatase $TiO_2$ nanoparticles by using the sol-gel approach for the photodegradation of benzene under UV irradiations. The $Sn^{2+}$ doped anatase $TiO_2$ nanoparticles

showed good photostability when examined for six days in a constant cyclic run. $TiO_2$ doped with $Sn^{4+}$ enhances the hydroxyl group on the surface and the oxygen vacancies absorb in the UV light spectrum region. The results showed that the $Sn^{4+}$ doping enhances the visible light absorption on $TiO_2$ [221]. The $Ti^{3+}$ doped $TiO_2$ has also been studied and published.

Noble metals like Pd, Ag, Pt and Au can behave as electron trappers and increase the photocatalytic activity by transferring the charge and inhibiting the recombination of electron-hole pairs [213]. Hwang et al. [222] described that the Pt doped on the $TiO_2$ can enhance the transfer of the photo-generated electrons. Au-Pt alloy doped on the $TiO_2$ nanocomposite was studied by Fenglong Wang and coworkers [223] and its photocatalytic performance was compared with undoped $TiO_2$. Results showed a tenfold increase in the photocatalytic activity of Au-Pt alloy doped $TiO_2$. Choi et al. [224] studied the photocatalysis and dark reaction for the decomposition of organic pollutants such as 4-chlorophenol (4-CP) under UV irradiations using Ag/$TiO_2$ and reduced hexavalent chromium (Cr (VI)) in the dark. The intermediates were formed by the photocatalytic oxidation of 4-CP where electrons stored in Ag/$TiO_2$ were used for the reduction of Cr (VI). Karmaoui et al. [225] investigate the noble metals Ag, Pt and Au for the photocatalytic and plasmonic gas sensing to degrade $NO_x$. The Au-doped anatase-$TiO_2$ showed high photocatalytic activity for the degradation of $NO_x$ as compared to other noble metals doped $TiO_2$ (Figure 15).
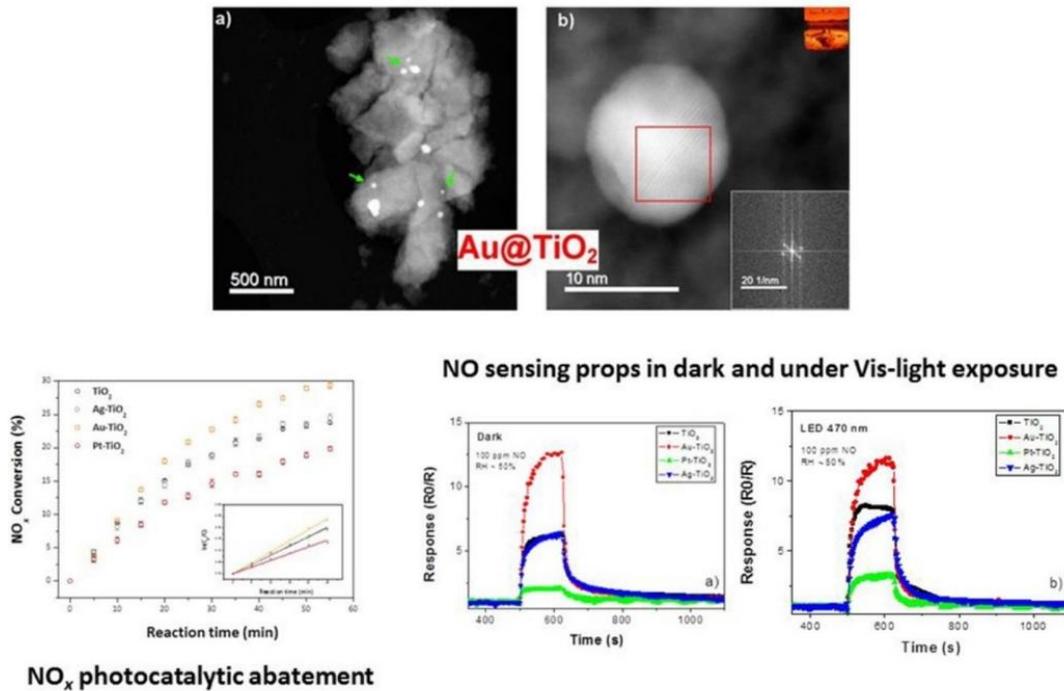
**Figure 15:** Noble metals modified $TiO_2$ NPs [225]. Copyright 2017 Elsevier.

### 7.1.2 Rare-Earth Metals Ions Doping

So far, there has been a lot of work reported on rare-earth metals like lanthanide doped on $TiO_2$ [226]. Sun et al. [227] studied La doping on $TiO_2$ and its substitutional effect on the electronic state of $TiO_2$ and its photocatalytic activity by using the density function theory (DFT) method. It was observed that the increase in visible light absorption and photocatalytic activity is attributed to the adsorption of La doping rather than replacing La doping. Zhang et al.[228, 229]studied the photocatalytic activity of Sm, Eu and Yb dopants on $TiO_2$. Sm-doped $TiO_2$ was synthesized by the chemical co-precipitation method. It was observed that the electrons from $Ti^{4+}$ jump into the electronic structure of $Sm^{3+}$, increasing the binding energy of $Sm^{3+}$. The Yb-doped $TiO_2$ was prepared by the use of evaporation induced self-assembly process, and the

results showed that (1) Yb decreased the recombination of photoelectrons and holes, increasing the photocatalytic activity, and (2) the Yb dopant also stabilized the mesoporous structures.

Anandan et al. [230] reported the La-doped $TiO_2$which under visible light irradiations reduces the recombination of electrons and holes and thus can photodegrade the salicylic acid. Parida and Sahu [231] doped $La^{3+}$, $Pr^{3+}$ and $Nd^{3+}$ on $TiO_2$ and studied their photocatalytic activity towards Cr (VI) and methylene blue. $La^{3+}$ doping on the mesoporous surface of $TiO_2$ enhanced the surface area, reduced the crystalline size and inhibited the $TiO_2$ phase transformation. Results showed that the photocatalytic degradation of Cr (VI) and methylene blue was increased by doping rare earth metals ions ($La^{3+}$, $Pr^{3+}$ and $Nd^{3+}$) on $TiO_2$, while the highest photocatalytic activity was shown by $La^{3+}$.

El-Bahy et al. [232] synthesized rare earth metal ions ($La^{3+}$, $Nd^{3+}$, $Sm^{3+}$, $Eu^{3+}$, $Gd^{3+}$and $Yb^{+3}$) doped $TiO_2$by sol gel technique. Lanthanide ions doped $TiO_2$ showed the highest photocatalytic activity for the photodegradation of organic dye as compared to pure $TiO_2$, where $Gd^{3+}$ doped $TiO_2$ showed the promising photocatalytic activity among other lanthanide ions doped $TiO_2$ (Figure 16). Baiju et al. [233] reported the $Gd^{3+}$ doped $TiO_2$ photocatalyst prepared by the sol-gel method showed higher photocatalytic activity than undoped $TiO_2$.
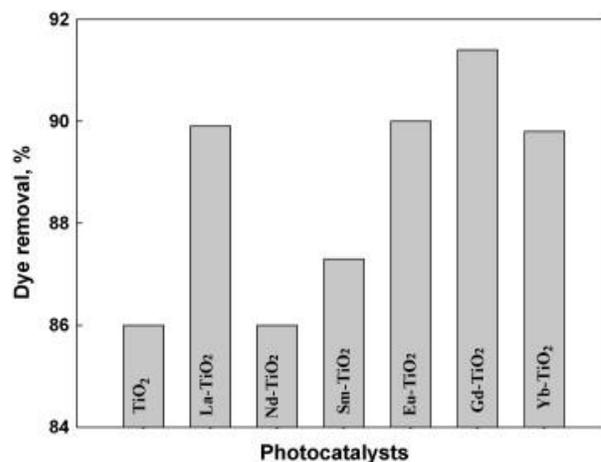
**Figure 16:** Effect of lanthanide ion-doped $TiO_2$ on the photodegradation of DB53[232]. Copyright 2009 Elsevier.

## 7.2 Non-Metals doping

Non-metals ions doping on $TiO_2$ is a hot topic for researchers nowadays. Due to the high cost and poor thermal stability of metal ions dopants, the use of non-metals has recently attracted wide attention from scientists to the band gap modification of $TiO_2$. Boron(B), carbon(C), nitrogen(N), sulfur(S), fluorine(F) and other non-metals having atomic radius equal to an oxygen atom [78]. Among all the non-metals N has attracted the interest of researchers and it has widely been studied due to stability and low ionization energy.

### 7.2.1 Nitrogen doping

Earlier N-doped compounds were prepared and studied under visible light to check the photocatalytic activity to their parent species [234, 235]. Later, Sato discovered the visible light-responsive material through the calcination of $NH_4OH$ and $TiO_2$ solution [236]. Asahi et al. [78] reported that N doping $TiO_2$ increased the photocatalytic activity of $TiO_2$ by increasing the visible light absorption. After further investigations, it was studied that N-doped $TiO_2$ within the bulk enhanced the photocatalytic degradation of 2,4-dichlorophenol under visible light, while chemically absorbed N is harmful to the photocatalysts (Figure 17A) [237]. It was also reported that the source of N has beneficial effects on the doping of N. Urea, triethylamine, thiourea, and hydrazine hydrate are the sources used for N doping on $TiO_2$ by using the microemulsion-hydrothermal method [238]. Among these triethylamines are the most favorable source for N doping on $TiO_2$ showing the highest peak for photo-induced degradation of Rhodamine B under visible light as shown in (Figure 17B). N-$TiO_2$ can be prepared in two simple steps: firstly, to

synthesize $TiO_2$ and then doping with N by using an N-containing source at a high temperature [239] or using a nitrogen precursor inductivity-coupled plasma [240].
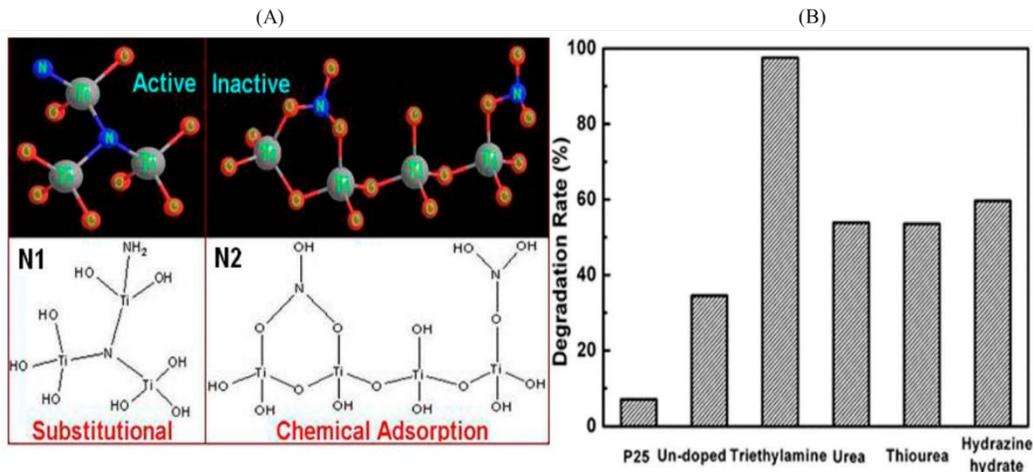


**Figure 17:** (A) Left part of the figure shows how nitrogen may be present in N-doped $TiO_2$ [190]. Copyright 2009 Elsevier. (B) The right part of the figure shows the photocatalytic activities of N-doped $TiO_2$ prepared from different nitrogen sources at the respective optimal doping values[238]. Copyright 2007 American Chemical Society.

For significant N doping on $TiO_2$ on the surface or bulk, both dry and wet methods have been used. Nitrogen ions can directly react with $TiO_2$ using physical techniques such as ion implantation [241, 242] and sputtering [243, 244], other techniques like atomic layer deposition [245], gas phase reactions [246, 247] and pulse-layered deposition [248] have also been used for the synthesis of N-doped $TiO_2$. The most promising method for the preparation of N-doped $TiO_2$ nanoparticles is the sol-gel technique which requires an easily operating machine which controls the porosity and morphology of the nanoparticles. Titanium salts ($TiCl_4$) and alkoxide precursors (titanium tetra isopropoxide $Ti[OCH(CH_3)_2]_4$, tetrabutylorthotitanate$C_{16}H_{36}O_4Ti$) are used for the growth of N doping. In addition to the aforementioned titanium alkoxide is also

hydrolyzed for N doping with the source of nitrogen, e.g., aliphatic amines, ammonia, ammonium salts, nitrates and urea [249, 250].

To enhance the nitrogen quantity in the lattice of $TiO_2$, $Ti^{4+}$ is treated with ligands having N like $Ti^{4+}$-amine complexes or $Ti^{4+}$-bipyridine [251]. Another way for N doping is to react with urea, and the N is doped during the condensation process of the alkoxide precursor, shifting the spectrum towards the visible region (3.2 to 2.3 eV). Sol-gel technique is used to synthesize the visible light active $TiO_2$ nanostructure doped with N surfactant. Simply, visible light active N-$TiO_2$ is formed by using dodecylammonium chloride (DDAC) (Figure 18) [252]. The pore-templating material DDC simultaneously changes the structural properties. Hence the N-doping activates the $TiO_2$ for visible light absorption and increases its photocatalytic activity, reactivity and functionality for various environmental applications [253, 254]. The most reported and published research on N-doped $TiO_2$ may occur on the polymeric anatase form of N-doped $TiO_2$. The anatase-rutile mixed form was also synthesized and was made visible light active by changing the parameters of the sol-gel method [237]. Such a combination of anatase-rutile photocatalysts transfers the electrons from anatase to rutile by photoexcitation, decreasing the recombination of electrons and holes and increasing the photocatalytic activity under visible light irradiations. synthesized N doped.
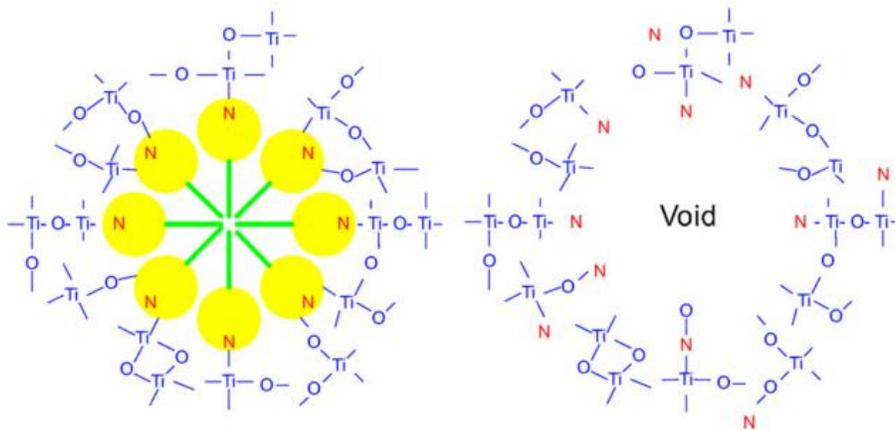
**Figure 18.** Templating sol-gel method utilizing nitrogen-containing surfactants as both nitrogen source and pore template material [252]. Copyright 2007 American Chemical Society.

Anatase/rutile $TiO_2$ photocatalyst which showed nine times greater photocatalytic activity with a high range of λ greater than 430nm as compared to Evonik P25. Plasmonic $Au/TiO_2$ was synthesized for the photodegradation of formaldehyde by single pass continuous flow reactor under visible light. The highest activity of 83.3% formaldehyde conversion was noted when the air was wet and the rate of humidity (RH) was equal to 44%, while in dry air, $Au/TiO_2$ became inactive even under the visible light irradiations (Figure 19) [256]. The situ DRIFT studies revealed that the formaldehyde oxidization terminated at Dioxymethy l (DOM) production in a dry environment and the presence of $TiO_2$. For $Au/TiO_2$, formaldehyde oxidation stops at format and carbonate without the formation of $CO_2$ in the dark, while in the wet air, the continuous formation of $CO_2$ was noted. Linsebigler et al. [221] studied that treating $TiO_2$ with $NH_3$ for N doping under visible irradiations by calcination method increased the photocatalytic activity while doping $TiO_2$ with $N_2$ reduced the photocatalytic activity due to the widening of the bandgap. Hirai et al. [257] synthesized mesoporous N doped $TiO_2$ by calcination method which showed better performance due to large surface area than doped $TiO_2$ prepared by sol-gel technique under visible irradiations.
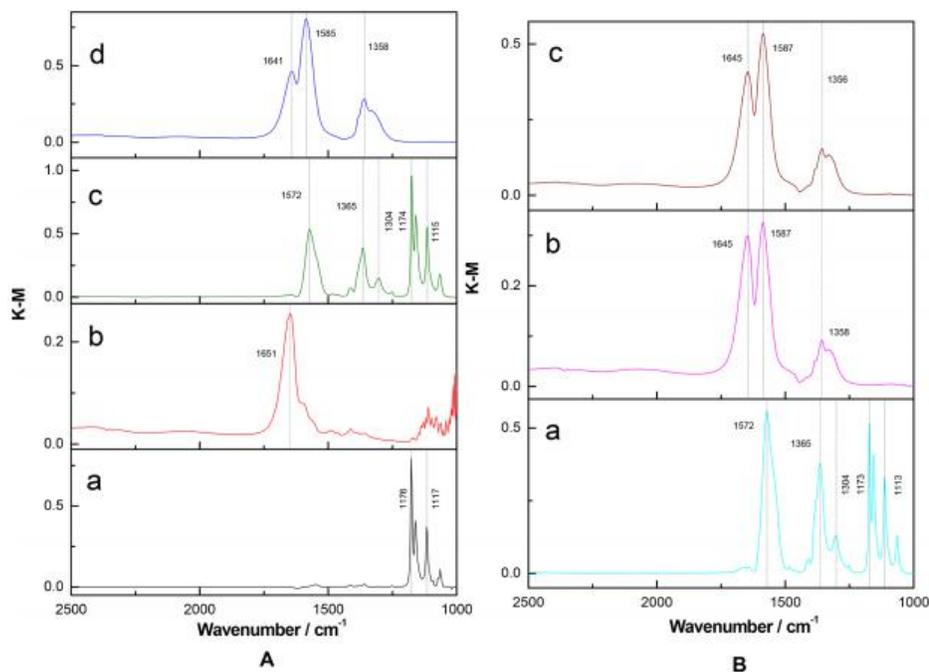
**Figure 19.** In situ DRIFT spectra at wavenumbers between 2500 and 1000 cm$^{-1}$ of formaldehyde oxidation (A) at 120 min of TOS under dark at (a) dry, (b) wet over TiO$_2$, and (c) dry, (d) wet over Au/TiO$_2$; (B) at 90, 180, and 210 min of TOS under subsequent conditions of (a) light and dry, (b) light and wet, and (c) dark and wet over Au/TiO$_2$, respectively [256].Copyright 2017American Chemical Society.

### 7.2.2 Carbon Doping

Carbon has also been reported as an active dopant for visible light utilization and photocatalytic performance of TiO$_2$. Nagaveni et al.[258] prepared C-doped TiO$_2$ using sol-gel techniques for the photocatalytic degradation of methylene blue under UV-Vis irradiation. Kamisaka et al. [259] studied the structural and optical properties using the DFT technique. The DFT results showed that by C doping four structures were assumed to be obtained. Among them, Ti and O, the substitutes of C doping, have not found any clues for visible light utilization due to titanate anions formation. On the other hand, C doping substitutes O and does not cause

any change in the structure, which is beneficial for $TiO_2$ to absorb visible light. Xia et al [260] synthesized a monodispersed C doped rutile $TiO_2$hierarchical structure uncovered facet (110) for the evolution of $H_2$ photo catalytically from water. About 450 mL of $H_2$ was released in 196 min. Yu et al [94] prepared a novel type of C-doped $TiO_2$ with uncovered facet (001) sheets by a hydrothermal method having enhanced efficiency for the absorption of the entire visible range along with redshift edge. Lin et al [261] prepared novel visible light-responsive C-doped mesoporous $TiO_2$ by using sol-gel and hydrothermal methods for the photodegradation of the dye-reactive bright Red X-3B.

### 7.2.3 Fluorine Doping

Doping of F on $TiO_2$ is the most interesting topic which has recently attracted the attention of researchers, where the direct doping of F on $TiO_2$ for photocatalytic degradation activity using a UV-VIS source is rather controversial [262, 263]. In the solvothermal process, fluoride ions are doped on the $TiO_2$ photocatalyst surface, rather than in the lattice. A single-step solvothermal method was adopted using a hydrophobic $NH_4F$ modifier and an isopropanol solvent to form super hydrophobic mesoporous MCF doped with fluorinated $TiO_2$ nanoparticles [264]. The synthesized photocatalyst exhibits an enhanced photocatalytic activity, high adsorption, and super hydrophobic properties for the degradation of Rhodamine B degradations as shown in Figure 20. It was reported that the substitution of F in the $TiO_2$ lattice neither introduces impurity nor shifts the band gap [265]. However, when studying $SnO_2$ and $ZnO_2$, it turns out that the replacement of oxygen vacancies by F would introduce impurities in the band gap [266]. It was summarized that F was substituted in the O vacancies which remove the recombination sites to induce vacancies and impurities in the $TiO_2$ lattice [267].
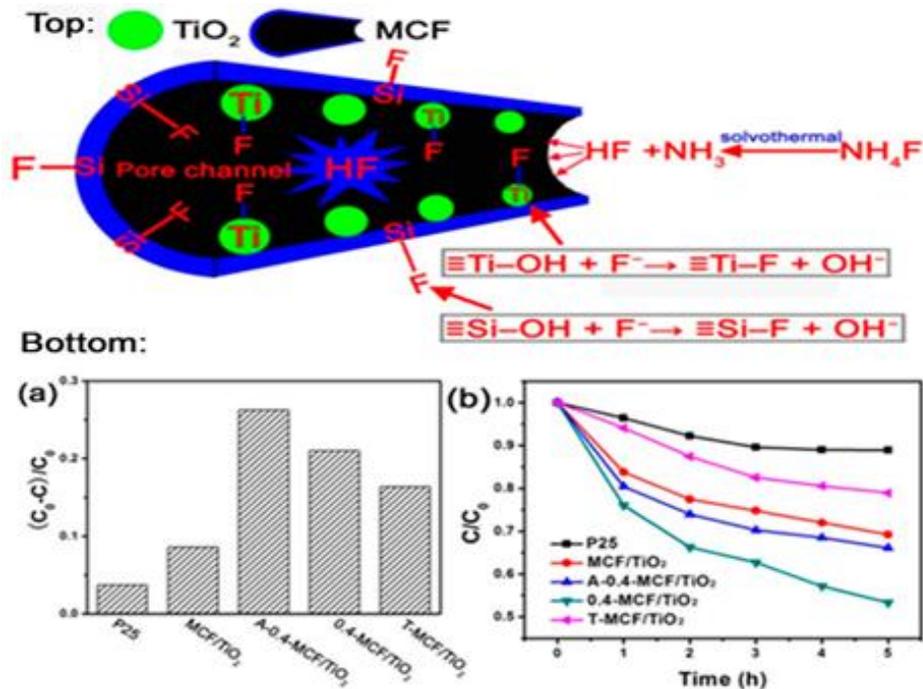
**Figure 20.** The top figure shows a schematic diagram of the fluorination reaction occurring in the pore channels of MCF; the bottom figure shows the adsorption capacities of RhB (20 mg/L, catalyst concentration: 0.25 g/L) on different samples (a); visible light photocatalytic activities of different samples (b) [264].Copyright 2012 Elsevier.

**7.2.4 Sulphur Doping**

Due to the larger ionic radii sulfur addition in the $TiO_2$ lattice, is difficult as compared to N. Cationic sulfur ($S^{6+}$) may be chemically easily inserted than anionic sulfur ($S^{2-}$). Periyat et al.[268]synthesized cationic-anionic doped $TiO_2$ using ammonium sulfate by sol-gel method. In other work of the same group [269], it was also reported S doped $TiO_2$ by modifying titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$) using $H_2SO_4$. It was concluded that the anatase was maintained at a high temperature (≥800∘C) through the formation of titanyl oxysulfate($TiOSO_4$). Thus, the presence of sulfur increases the photocatalytic activity of the synthesized materials under visible light irradiations. Han et al.[270] prepared the visible light active S-doped $TiO_2$ film from

non-ionic surfactant and $H_2SO_4$ as an inorganic source of sulfur using a novel sol-gel technique based on a self-assembled method. Both anionic $S^{2-}$ and cationic species$S^{6+}/S^{4+}$ were doped uniformly on the surface of the S-doped $TiO_2$ film. Due to the doping of anions or oxygen vacancies, strong EPR significantly limits the energy band in $TiO_2$. For the photocatalytic degradation of microcystin-LR (MC-LR), the most reliable photocatalyst is mesoporous S-doped $TiO_2$ under visible light irradiations (Figure 21).
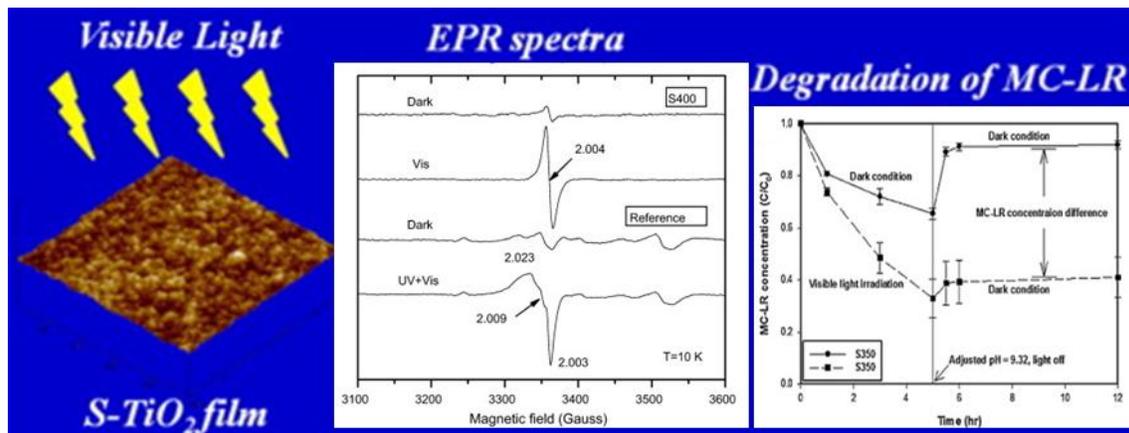


**Figure 21:** Visible light-activated sulfur-doped $TiO_2$ films for water treatment[270]. Copyright 2011 Elsevier.

### 7.2.5 Boron Doping

Compared with other non-metals, $TiO_2$ is rarely doped with boron. While investigating B-doped $TiO_2$, it was observed that the absorption of visible light leads to redshift, which causes the overlapping of 2p electrons of O with the impurities of B. Besides this, it was also studied that the B-doped $TiO_2$ showed a spectrum in the blue shift instead of the red shift that reduced the size of the crystal (Quantum size effect) due to the presence of B [271, 272]. Miguel et al.[273] prepared an interstitial boron-doped $TiO_2$thin films and found an improvement in the

photocatalytic activity of TiO₂. The promising effect of coating B on TiO₂ increases the atmospheric chemical vapor pressure deposition which thus enhances the photocatalytic activity of $B_{int}$-TiO₂. Stengl et al. [274] synthesized B-doped nanosized TiO₂ by the reaction of TiOSO₄ with urea and amorphous boron by the process of homogenous hydrolysis followed by annealing at 700 °C. Results showed that B-doped TiO₂ owing to the better utilization of visible light have good photocatalytic activity as compared to reference TiO₂. Recently, researchers have been interested in studying the modification of TiO₂ by boron and other co-dopants and non-metallic ions [275, 276]. Nasr et al. [277] synthesized highly active BN/TiO₂ nanofibers for the degradation of methyl orange by the electron spinning method. The results indicated that the BN coating on TiO₂ nanofibers increased the band gap between electrons and holes as compared to pure TiO₂ nanofibers. Compared with TiO-P25 and TiO₂ nanofibers, the photodegradation of methyl orange under UV irradiation of BN/TiO₂ is increased by 5 times and 3.8 times, respectively (Figure 22).
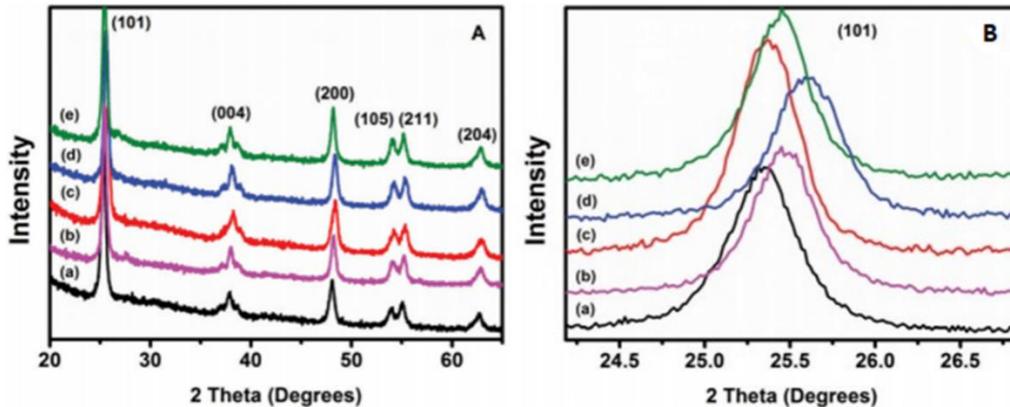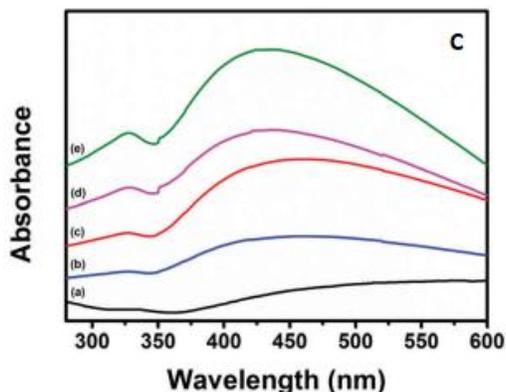
**Figure 22:** (A,B) XRD pattern (C) UV-VIS absorption spectra of (a) $TiO_2$, (b) BN (3 wt%)/$TiO_2$, (c) BN (5 wt%)/ $TiO_2$, (d) BN (7 wt%)/$TiO_2$ and (e) BN (10 wt%)/$TiO_2$ annealed nanofibers in air for 4 h at 500°C [277]. Copyright 2018 Royal Society of Chemistry.

**7.3 Co-doping**

To improve the photocatalytic performance of $TiO_2$, multiple components were used, i.e., co-doped to modify$TiO_2$ to utilize the visible spectrum region of sunlight. Co-doping of $TiO_2$is the recent interest of researchers in the field of photocatalysis. It was reported that the co-doped $TiO_2$ has a higher photocatalytic activity as compared to singly doped $TiO_2$ due to the synergistic effect and electron/hole separation [227, 229, 278-280]. According to the band theory for semiconductors, it was explained that the Ti contributes its 3d energy orbital while the oxygen shares its 2p orbital to form a valance band of $TiO_2$ while the other doping non-metals impurities like N, C, S, P and F also contributes there 2p orbitals having much higher negative energy substitute in the lattice of oxygen along with other non-metal dopants. Thus, new energy bands are formed above the $TiO_2$ valance band which facilitates the utilization of visible light and increases the photocatalytic activity of $TiO_2$ [26]. Cong et al. [281] suggested the energy levels of 1s energy orbital of C doping and 1s energy orbital of N doping in the valance band for co-doping of $TiO_2$. The band gap of $TiO_2$ became smaller while the visible light photocatalytic activity enhanced. Liu et al. [282]and In et al. [283]investigated the B and N co-

doped $TiO_2$ (Ti-B-N) on the surface have higher photocatalytic activity and showed higher absorption of UV-Vis light. Bikramjeet Singh and coworkers [284]studied BN-doped $TiO_2$ for the photodegradation of methylene blue. The large surface pores favor the catalytic oxidation reactions. Decrease of the band size, higher photocatalytic activity, pore structure optimization and reusability were due to B-O-Ti-O. Results showed that BN-$TiO_2$ photodegrade the 79% methylene blue in 200 min, while pure $TiO_2$ degrades 32% under visible light (Figure 23).
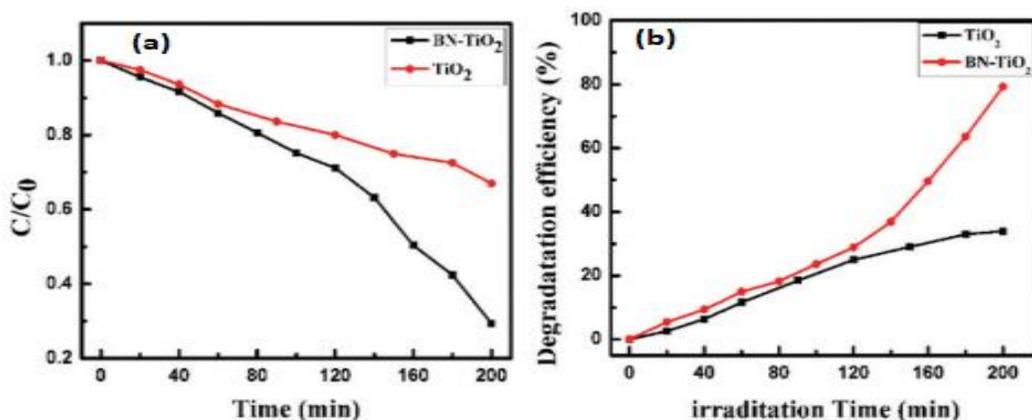


**Figure 23:** (A) Concentration vs. irradiation time and (B) degradation efficiency vs. irradiation [284]. Copyright 2017 Royal Society of Chemistry.

Komai et al. [285] reported the N and S co-doped $TiO_2$ having improved photocatalytic activity for the degradation of methylene blue under visible irradiations. It was proposed that the N and S could form an anodic co-doping thereby narrowing the band gap of $TiO_2$ and thus enhancing its photocatalytic activity by increasing the visible light absorption. Yang et al. [286] proposed the S and F co-doped mesoporous $TiO_2$. By maintaining and controlling the structure and morphology, the ability of mesoporous $TiO_2$ to absorb visible light is enhanced with the decrease of electron-hole recombination. S and F co-doping absorbed visible light with the redshift and shows the ability the degrade many organic pollutants and dyes. N and F co-doped

TiO$_2$ microspheres have a synergetic effect on TiO$_2$ and were prepared by solvothermal technique [287]. It was proposed that co-doping of N and F on TiO$_2$ increased the photocatalytic activity and visible light-induced photodegradation of AO7. C and B co-doped TiO$_2$ prepared by gel hydrothermal method have also high photocatalytic activity due to the narrowing of the band gap because of B doping [288]. Vanadium, V and N co-doped TiO$_2$ showed higher photocatalytic activity under visible irradiations than singly doped TiO$_2$ and were synthesized by sol-gel technique. The increase in photocatalytic behavior is due to the shortening of the band gap by inducing V and B in the TiO$_2$ lattice [220]. Lanthanum, L and N co-doped TiO$_2$ not only have a higher photocatalytic activity under visible light but also reduce the recombination of electrons/holes and increase the surface area for better absorption of visible light irradiation, thereby improving its photocatalytic ability [289]. Biswas and co-workers [290] investigated the N and F co-doped TiO$_2$ nanoparticles and adjusted the ammonium fluoride-urea concentration and the reaction time at 300 °C between 1-7%. The results showed that N/F doped TiO$_2$ nanoparticles exhibited a higher redshift band spectrum of >600nm, where their colloidal dispersion was absorbed in UV to near IR irradiations. Reactive oxygen was produced in the presence of UV irradiation which was used for the photodegradation of toxic chemicals, pathogens, and cells (Figure 24).
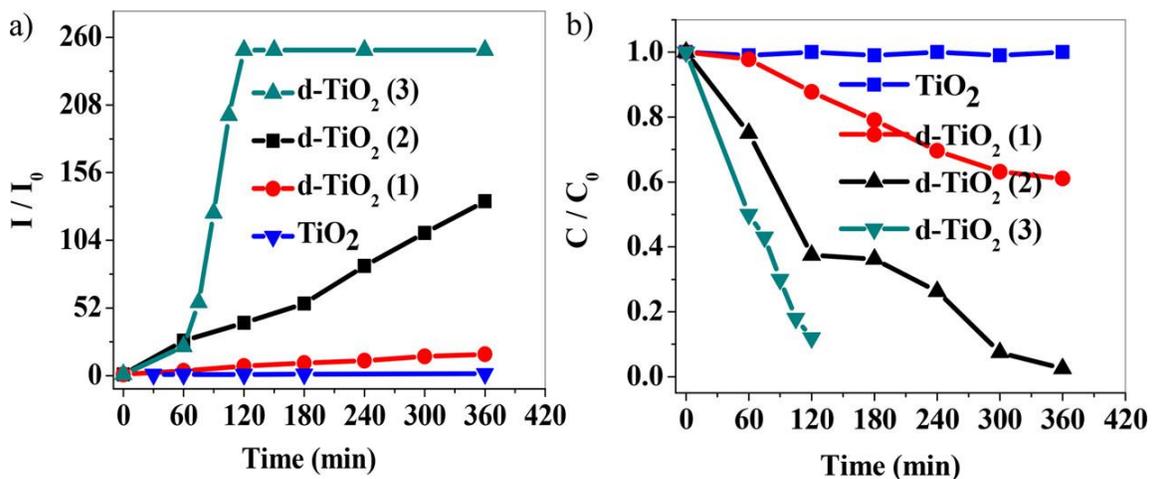
**Figure 24:** (A)Visible light-induced reactive oxygen species generation by N, F co-doped $TiO_2$nanoparticle.(B) Visible light photodegradation of bisphenol A using N, F co-doped $TiO_2$nanoparticle as photocatalyst showing that bisphenol A degradation kinetics by nanoparticles is in the order of d-$TiO_2$(3) > d-$TiO_2$(2) > d-$TiO_2$(1) > undoped $TiO_2$ [290]. Copyright 2017 American Chemical Society.

Cong et al. [291]synthesized N and 0.5% $Fe^{3+}$ co-doped $TiO_2$ for the first time using homogeneous precipitation hydrothermal technique, thereby lowering the band gap of $TiO_2$ and increasing the separation between electrons and holes. Such N and $Fe^{3+}$ co-doped $TiO_2$ showed better photocatalytic activity as compared to pure $TiO_2$ with an increase of 5% under UV light and 75% under visible light irradiations. Wong et al. [292] reported that doping of Ag on the surface of N-doped $TiO_2$ improved the visible light absorption ability. Wang and coworkers reduced the limitations by sandwiching Ag between [$TiO_2$(N)] like $TiO_2$ (N)/Ag/$TiO_2$(N). Hoang et al. [293]reported the higher photocatalytic activity of co-doped $Ti^{3+}$ and N on $TiO_2$ nanowires. The oxidation state of N is lower but occupies a higher energy level due to the Coulombic force. Thus, electrons of singly N-doped $TiO_2$ can be excited with high energy longer wavelength photons. Dhandole et al. [294] studied the Rh and Sb co-doped visible light active nanorods of rutile (Rh–Sb: $TiO_2$ NR) for the photocatalytic degradation of organic pollutants and microbial pathogens. To improve and increase the photocatalytic activity of Rh–Sb:$TiO_2$ NR was treated with acid and $Cu_xO$ ($Cu_xO$/A–Rh-Sb:$TiO_2$ NR). The results showed that the $Cu_xO$/A–Rh-Sb:$TiO_2$ NR photocatalyst was eco-friendly and had a high capability for the removal of environmental organic pollutants and microbial pathogens inactivation (Figure 25).
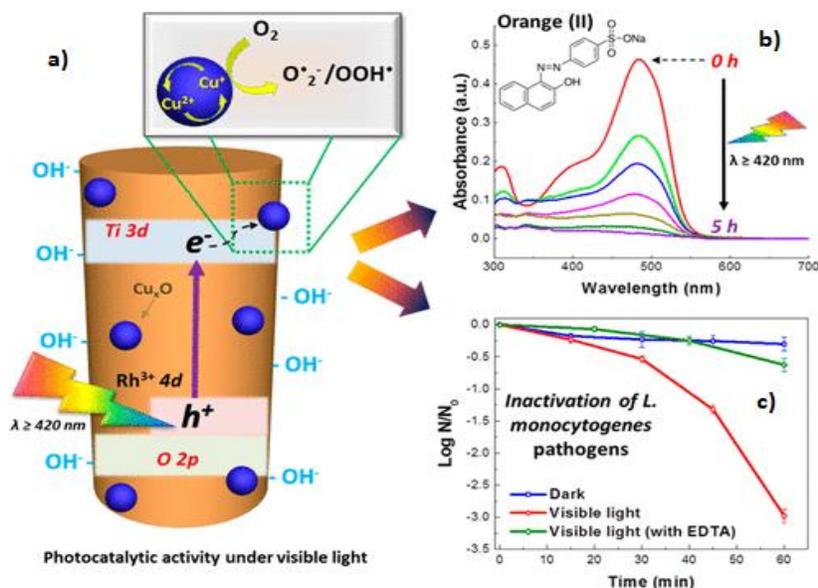
**Figure 25:** (A) Schematic diagram of photocatalytic degradation of Orange (II) dye by copper oxide loaded A-Rh-SbTiO$_2$ NRs under visible light irradiation, (B) Orange (II) dye degradation under visible light absorbance spectrum of 2 wt % of Cu$_x$O/A–Rh-Sb:TiO$_2$ NR, (C) Inactivation of L. monocytogenes using Cu$_x$O/A–RhSb:TiO$_2$ NRs in dark condition, visible light condition and visible light with EDTA [294]. Copyright 2018 American Chemical Society.

## 7.4 Modification of Oxygen-Rich TiO$_2$

Recently, oxygen has been generated by per oxo titania complex using situ thermal decomposition [295]. This process enhanced the strength of the Ti-O-Ti bond, thereby mounting the valance band (VB) shifts and thus increasing the visible light absorption ability. The upward shift of VB due to oxygen-enriched TiO$_2$ is the main factor for the increased visible light absorption capability which in turn increases the photocatalytic activity. Oxygen-rich TiO$_2$ and controlled TiO$_2$ were synthesized as shown in Figure 26.
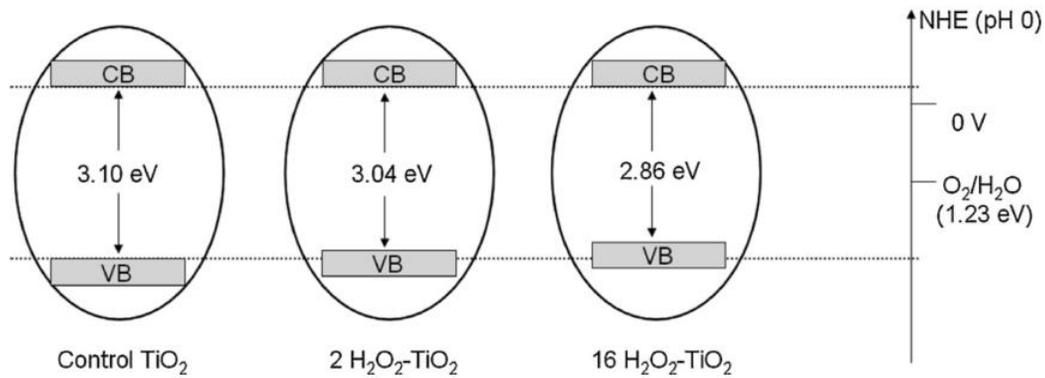
**Figure 26:** Mechanism of band gap narrowing by oxygen excess [295]. Copyright 2011 Wiley.

## 8. Kinetic studies on the photodegradation of gaseous pollutants

The rate of the photocatalytic reaction depends on the pollutant molecules covering the surface of the catalyst particles at a steady state. That's why, the adsorption modelling and the kinetic modelling look nearby similar, thus literature studies showed the wide applications of the Langmuir-Hinshelwood (LH) relationship for this purpose. LH is used in the photocatalytic reactors for the local light effect,

$$- r_p = [I(x,y,z)]^n \frac{kKC_{p,s}}{1 + KC_{p,s}} \tag{52}$$

Where the apparent rate constant is denoted by k, Langmuir adsorption equilibrium constant by K, the impurities concentration at the catalyst surface is denoted by $C_{p,s}$. The concentration of pollutants in the bulk fluid is equal to the concentration of the pollutants adsorbed on the surface in the absence of mass transfer limitation. Researchers explored that no mass would transfer unless the rate of the reaction is independent of the air volume flow rate in the reactor. Nevertheless, the simple model to transfer the mass and rate of photocatalytic reaction and has a constant area of cross-section [296]. The n in the equation above is the intensity of the

incident light. The higher the incident light, the greater the recombination of electrons and holes (n < 1), whereas the lower the intensity of light, the stronger the degradation of pollutants (n=1). When the concentration of the pollutants is small the above equation (52) becomes [297],

$$- rp = [I(x,y,z)]n\ k'\ C_{p,s} \tag{53}$$

Three different types of equations i.e., namely the two types of sites where the LH bimolecular competes and the two types of sites where the LH bimolecular does not compete and were obtained by the expansion of LH model due to the water vapor adsorption competition (Equations 54-56)[296, 298-300].

$$- rp = [I(x,y,z)]^n\ k \left( \frac{K_p K_w C_p C_w}{(1+ K_p K_w C_p C_w)^2} \right) \tag{54}$$

$$- rp = [I(x,y,z)]^n\ k \left( \frac{K_p C_p}{(1+ K_p C_p)} \right) \left( \frac{K_w C_w}{(1 + K_w C_w)} \right) \tag{55}$$

$$- rp = [I(x,y,z)]^n\ k \left( \frac{K_p C_p}{1+ K_p C_p + K_w C_w} \right) \left( \frac{K'_w C_w}{(1 + K'_p C_p + K'_w C_w)} \right) \tag{56}$$

Where p in the subscript represents the water and pollutant. Thus, the above equations for certain rectors fit satisfactorily in the experiments but were not suitable for the reactions occurring on the surface of the catalyst. That's why if some authors used different rectors and operating systems, they can't compare their experimental data with the LH model. However, limitations were found when formaldehyde degradation was done on a monolith-type reactor [301, 302], used on glass plate reactor [303]. The Intrinsic parameters contained in the reaction

kinetic equations are independent of fluid dynamics, radiation field and reactor geometry. The reaction kinetic scheme was simplified by the addition of different species in a reaction.

Passalia et al. [304] studied formaldehyde degradation by using a single-pass plate photocatalytic reactor. The intrinsic kinetic model plausible reaction approach was applied to kinetic steady pathways that utilize the kinetic steady state approximation for the next generation of electrons and holes. The reaction rate model is used to replicate the experimental results obtained by the corrugated plate photocatalytic reactor [305-307]. Imoberdorf et al. [308, 309] investigated the degradation of perchloroethylene (PCE) by attacking the chlorine radical using the laboratory flat-scale plate for the derivation of intrinsic kinetic expression. Studying the TCE of the LH models in the literature showed effects on photocatalytic rate due to the concentration of water vapors and another equation for the degradation of TCE by the reaction of electrons and hole pairs in the absence of water vapors, exhibited the first-order reaction kinetics, linear TCE adsorption/desorption equilibrium, and steady-state concentrations of holes and adsorbed intermediates [310]. Proposed intrinsic reaction expression schemes for the degradation of toluene [311] and cyclohexane [312] have also been used. Hence, in the future, it is very important to use the intrinsic kinetic expression for the reaction mechanisms of scientific and engineering research.

## 9. Techniques for Immobilization of $TiO_2$

Immobilization of $TiO_2$ is a technique used to fabricate the reactors for air purification. Doping $TiO_2$ with supportive materials or $TiO_2$ fabrication into thin film. $TiO_2$ fabrication itself is an excellent technique for the immobilization of photocatalysts for air purification. Thevenet et al. [102] studied the PCO reaction for the elimination of acetylene by loading P25 $TiO_2$ on glass fibers. A 50% dry mixture of both P25 $TiO_2$ and colloidal silica was used for the synthesis and was loaded on silica glass fibers. Other supporting materials that can be used for immobilization of photocatalyst powders include graphene oxide [104], optical fibers [19], PVC sheets [105] or

monolith [103]. Antonello and coworkers [108] proposed gas phase PCO of VOCs by using the novel method for electrochemical fabrication of transparent and mechanically robust $TiO_2$ film. $TiO_2$ film showed self-cleaning and promising properties for the degradation of VOCs. Xie et al. [107] investigated the window glass PVP(polyvinylpyrrolidone) modified thin film $TiO_2$ by sol-gel method for the degradation of benzene and acetone. It was observed that the rate of decomposition increased due to enhanced crystallinity as compared to those reactions where PVP was not added.

The most important methods for immobilization of catalysts are chemical vapor deposition (CVD), sol-gel, thermal, layer-by-layer (LBL) and electrophoretic deposition methods (EPD). Support was introduced into the gaseous catalytic atmosphere by the chemical vapor deposition method at a high temperature which decomposed on the surface of support [313]. The N-doped $TiO_2$ was prepared by CVD method by using different precursors [247]. It has also been used to control the thickness of $TiO_2$ film [314] and $TiO_2$situ crystallization [315, 316]. Glass plates and glass rings are used as catalyst support materials which fabricate with $TiO_2$ precursor and high calcination temperature (>450$^{O}$C) in the sol-gel method. Sol-gel technique is cost-effective, flexible and available in a variety of shapes [313, 317, 318]. Recently, a hybrid sol-gel suspension method at low temperature (<150 $^{O}$C) was introduced and applied on different substrates such as glass fibers, aluminium, $Al_2O_3$ monoliths, stainless steel, etc. to synthesize thick, highly photo-catalytically active and stable layers from various commercial $TiO_2$ nanoparticles [319].

In the thermal synthesis method, the catalyst is directly scattered onto the support and thermally treated [313, 320]. Catalyst performance depends upon the temperature of calcination which affects the physical properties of $TiO_2$ such as structure, crystal phase, oxygen adsorption capacity and BET surface area [321].The support material is dipped or sprayed several times in the colloidal solution of the catalyst till the desired layer is achieved. Catalyst and support are bound together electrostatically. The Nanoparticle's dispersion in the porous

matrix and thickness of the catalyst are controlled in the LBL method easily, thus, providing a high surface area without the need for high calcination temperature [322-325]. In the electrophoretic deposition (EPD) technique, charged particles move when an electric field is applied through stable suspension. In the EPD method, the thickness of the film is controlled, and it can also be used on complex shapes and is environmentally friendly. EPD can be used inside the array of $TiO_2$ nanotubes [326], for the deposition of chitosan/h-BN/ $TiO_2$ composite on metals [327], on a plastic substrate [328] and can also be used to coat the biological molecules in future [329].

## 10. Concluding Remarks and Perspectives

Pure $TiO_2$ can only be activated by using high-energy photons in the UV region having $\lambda \leq$ 387 nm for anatase. This is due to the large band gap of pure $TiO_2$ although its practical use and applications are minimized [330, 331]. Different strategies were adopted to improve the photocatalytic performance of $TiO_2$. They include the modification in the morphology of $TiO_2$ such as enhancing the surface area and porosity, or chemical modifying the structure of $TiO_2$ by adding the components additionally. However, the performance of visible light active (VLA) $TiO_2$ can be improved by controlling the morphology of the semiconductor through the chemical modification method. The one-dimensional $TiO_2$ morphology is preferred due to its high surface area and reduction in the recombination process. Despite the progress and great interest of the scientists in the field of photocatalysis, still it cannot be commercialized due to some complications such as visible light absorption ability, low quantum efficiency, selectivity towards $CO_2$ and $H_2O$ formation and stability. Combine work is needed in photocatalysis from different fields of specialization such as chemists, material scientists, chemical engineers and bandgap engineers [34].

Environmental pollution, especially VOCs and indoor air quality is a hot topic of attention for the scientist these days. The best way for the degradation of VOCs and refining

the quality of indoor air is PCO. Extensive research has been done to understand the charge separation and mechanism for the photodegradation of VOCs and other pollutants. $TiO_2$ is the most promising photocatalyst under UV irradiation. There is a great demand to develop a photoactive $TiO_2$ with doping or other methods to prepare the novel $TiO_2$ that can enhance its efficiency for the degradation of VOCs under visible light. Nano-scaled $TiO_2$ exhibited higher photocatalytic performance in PCO reactions and further efforts are required to modify them either by fabricating and analyzing them under different reaction conditions to achieve better performance and commercialization. Discovering different ways of doping and fabrication to modify nano-scaled $TiO_2$ is the current and future interest in research and further applications.

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