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Recent Progress in Semiconductor Photocatalysis for Organic Fine Chemical Synthesis

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Abstract

Photocatalytic process is a well-known reaction in photosynthesis by plants and algae. Artificial photosynthesis is a chemical process that mimics the natural plant photosynthesis to make important chemicals by using man-made materials. One of the most promising methods of artificial photosynthesis is synthesis of organic chemicals, including biodegradable plastics, pharmaceutical drugs, liquid fuels and intermediates for valuable chemicals, etc. In 1972, Fujishima and Honda discovered photocatalytic process using TiO_2 semiconductor oxide electrodes to generate hydrogen from water. Researchers have achieved a single-step system that uses semiconductor particles for organic fine chemical synthesis under UV or visible radiation. This chapter summarizes the recent research trends on artificial photosynthesis by photocatalytic process for organic fine chemical synthesis on selected photocatalytic organic transformations, especially photocatalytic transformations by oxidation, carbon-carbon and carbon-heteroatom coupling, cyclization, etc.

Keywords: artificial photosynthesis, photocatalysis, organic synthesis, oxidation, cyclization, UV light, visible light, C-C bond formation

1. Introduction

The Earth receives energy of about 3×10^{24} joules in a year from sun, which is higher than the global energy consumption. Plants utilize the solar energy to fix atmospheric carbon dioxide and produce carbohydrates and oxygen by photosynthesis. Warburg and Negelein disclosed the photosynthesis, in which reaction occurs between CO_2 and H_2O in the presence of chlorophyll and form O_2 and carbohydrates [1]. It is worth to utilize the solar energy for various energy-consuming processes, since it is clean, sustainable and abundant resource. Artificial

photosynthesis is a process in which fundamental scientific principles of natural photosynthesis are applied to design a solar energy conversion to make important chemicals by using man-made materials. Many approaches are reported. One of the successful reports provides an outline for solar energy storage in fuels [2]. Another important approach is finding a new route for the chemical production and synthesis by utilizing solar energy, which is an energy-decisive industrial process. The method to synthesize organic chemical by photochemical process was first reported by Giacomo Ciamician in 1912 [3]. Presently, photochemistry is a well-developed field of chemistry and the majority of the experiments use direct excitation of molecules by UV light [4]. To activate the photoreaction under visible light, sensitizers are applied, which transfer energy or an electron from the excited state to the molecule to be converted. Various homogeneous sensitizers are successfully used for various organic transformations [5]. The homogeneous sensitizers are substituted by heterogeneous photosensitizers using photocatalytic process and which are easily separable and therefore recycled. In 1972, Fujishima and Honda reported a photocatalytic process using TiO$_2$ semiconductor oxide electrodes to generate hydrogen from water [6]. Semiconductors can act as photocatalysts for light-induced chemical transformations because of their unique electronic structure, which is characterized by a filled valence band and an empty conduction band. When a photon with an energy of hv matches or exceeds the band gap energy (Eg) of the semiconductor (SC), an electron in the valence band (VB) is promoted to the conduction band (CB), leaving a positive hole (h$^+$) in VB. The photo-excitation can be written as [7]:

$$SC + hv \rightarrow SC\left(h^+\right)_{(vb)} + SC(e^-)_{(cb)} \tag{1}$$
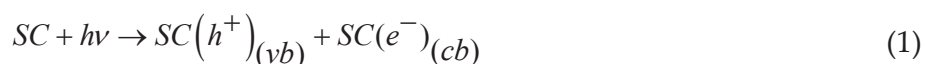
Where SC is semiconductor, vb and cb represent the valance band and the conduction band, respectively. The reactive species, h$^+$ and e$^-$ are powerful oxidizing and reducing agents, respectively. Subsequently, various oxidizing species such as $^\bullet OH$, $O_2^{\bullet-}$, various forms of active oxygen species, such as HO$_2$, H$_2$O$_2$ and O, are produced [8,9].

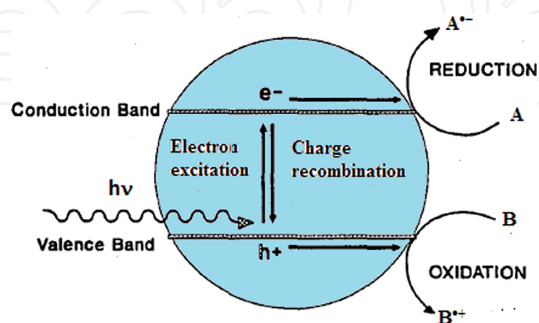The photo-excitation process over semiconductor photocatalyst is presented in **Figure 1**.

Figure 1 Semiconductor photocatalysed reaction.

Different semiconductors (e.g., TiO$_2$, ZnO, α-Fe$_2$O$_3$ and WO$_3$) are considered for their potential use as photocatalysts. In early 1980s, great effort was placed on organic synthesis by semicon-

ductor photocatalysis [10]. Photocatalysis in synthetic route has attracted many researchers, because this method presents a greener approach to organic synthesis [11,12]. Recent studies have revealed that highly selective redox reactions could be achieved by visible light irradiation. The studies employed in photocatalytic organic transformation includes, oxidation, reduction, carbon-carbon and carbon-hetero atom coupling, cyclization, isomerization, etc. This chapter deals with various studies performed in oxidation, carbon-carbon and carbon-heteroatom coupling, cyclization by UV and visible light-induced photocatalysis.

In photocatalytic process, photo-oxidation is the most studied because the VB edge in most of the semiconductor catalysts have more positive than the oxidation potential of the functional group in the organic compounds. The oxidation reactions are mainly focused on the oxidation of alcohols, amines, cyclohexane and aromatic alkanes. The conversion and product selectivity could be controlled by tuning the reaction conditions, such as nature of solvent, excitation wavelength of the light, interface engineering such as surface modification to change the adsorption mode or electron transfer pathway.

2. Oxidation of hydrocarbon

Selective partial oxidation of hydrocarbon into its oxidation products, such as aldehyde, ketone, and carboxylic acid, by photocatalytic process is of great importance for chemical industries. Selective oxidation of methane into its useful oxygenates such as methanol and formaldehyde by photocatalytic method is of great challenge. Gondala et al. [13], for the first time, reported the photocatalytic transformation of methane into methanol over WO_3, TiO_2 (rutile) and NiO semiconductor photocatalysts, at room temperature, under the irradiation of a strong UV laser beam at 355 nm. The methanol yield in all three catalysts observed was low due to the degradation of methanol immediately after its formation in the aqueous suspension. Methane activation at low temperature and at atmospheric pressure using supported molybdena TiO_2 catalyst [14] excited by band gap illumination motivated the researchers to test this reaction with various catalysts [15,16]. However, the conversion of methane was low and an advancement in the source of methane such as methane hydrates was used. Methane hydrates available in the ocean at depths between ~280 and 4000 m have higher concentration of methane in water, which is higher than that of water–methane pressurized systems. Comparison of photocatalytic conversion of methane dissolved in water and methane hydrate showed that the conversion of methane dissolved in water was observed at temperatures below 70°C. On the other hand, the photocatalytic conversions of the methane hydrate occurred at temperatures below −5°C [17]. The comparison of the photocatalytic reaction under visible and the full spectrum of UV-visible showed that the production of methanol was 50% greater in visible compared to that with the full spectrum lamp of UV-visible. Complete oxidation of methane could be avoided by changing the atmospheric condition. V-MCM-41 (acid) catalyst prepared under acidic conditions resulted in the selective formation of methanol with NO oxidant compared to O_2 as oxidant under UV radiation accompanied by the formation of trace amounts of CO_2 and acetaldehyde. Metal doping is used to improve the photocatalytic activity by avoiding charge recombination and to achieve visible-driven photocatalysis. Silver-

impregnated WO_3 was studied for the conversion of methane to methanol under laser illumination (100 mJ) in the aqueous medium [18]. The overall photonic efficiency of photo-catalytic conversion process based on hydroxyl radicals is ~8%. The remaining portion of photogenerated hydroxyl radicals is consumed in oxygen formation, interaction with metha-nol, interaction with methanol by-products such as formaldehyde and recombination.

Photocatalytic oxidation of cyclohexane to cyclohexanol and cyclohexanone is an important commercial reaction, used as precursors in the synthesis of adipic acid and caprolactam, in turn used in the manufacture of nylon 66 and nylon 6, respectively. The selective oxidation of cyclohexane to cyclohexanol and cyclohexanone both under liquid and gaseous phase at room temperature and pressure by photocatalytic process was studied [10,19–21]. The product selectivity depends on the nature of the catalyst, irradiation wavelength and presence of solvent and O_2, etc. The comparison of oxidation of cyclohexane with and without TiO_2 photocatalyst showed that under photolytic oxidation at $\lambda < 275$ nm (i.e., in the absence of catalyst) yielded a high selectivity to cyclohexanol (>85%). However, under photocatalytic condition with TiO_2 catalyst at $\lambda < 275$ nm, the selectivity shifted to the ketone (>95%) [21]. In cyclohexane oxidation, nature and composition of the solvent plays an important role in the distribution of products and by-products [20]. The composition of the mixed solvent has a strong influence on the selectivity of the process: an increase in the content of dichloromethane up to 50% brings an enhancement in the rate of formation of mono-oxygenated products. At the same time, the alcohol to ketone ratio increases in the mixed solvent. Studies performed with various polar and nonpolar solvents showed that in nonpolar solvents, cyclohexanol preferentially adsorbed onto the titanium dioxide particles and underwent deep oxidation, ultimately to carbon dioxide and water. Therefore, in nonpolar solvents, the selectivity of the reaction to cyclohexanol was very low. However, in polar solvents, cyclohexanol adsorbed to the titanium dioxide particles to a lesser extent due to the competition for adsorption sites with the solvent, and the selectivity of the reaction to cyclohexanol significantly increased. Of the various solvents studied such as acetone, isopropanol, dichloromethane, chloroform, carbon tetrachloride, benzene and n-hexane, dichloromethane was the best solvent with regard to the formation rate of cyclohexanol and cyclohexanone. The most unfavorable solvents were isopropanol, chloroform and benzene [21]. Studies under different O_2 partial pressures showed that the process is unaffected for O_2 partial pressures >200 Torr. For lower values, the formation of dicyclohexyl becomes significant and reaches a maximum at a pO_2 of 60 Torr. In O_2-free media containing $C(NO_2)_4$ as the electron scavenger, the formation of cyclohexanone decreases markedly while that of cyclohexanol is essentially the same as that in oxygenated media. Studies on cyclohexane photocatalytic oxidation with $^{18}O_2$ over anatase TiO_2 was analyzed by in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy suggests that oxygen incorporated in cyclohexanone, as well as in deactivating carbonates and carboxylates, originates from the catalyst surface, rather than from dissolved O_2. The proposed Mars-van Krevelen cycle is completed by regeneration of surface sites by reaction with $^{18}O_2$ [22]. In studies conducted at dry nitrogen containing 10–20% of oxygen, cyclohexanone is produced with high selectivity (>90%). In humidified nitrogen/oxygen gas, the cyclohexanol selectivity was increased [23]. This suggests the participation of surface hydroxyl group in the reaction mechanism. A recent study by She et al. [24] showed that the Cl$^\bullet$ radicals enhance the

oxygenation of cyclohexane by N_2O to cyclohexanone. Metal doping influences the catalytic activity and selectivity in the photocatalytic oxidation of cyclohexane. Silica-entrapped Cr catalyst for cyclohexane in acetonitrile prevents the decomposition of cyclohexane, there by increased selectivity was observed. The highest turnover number of 2.5 with cyclohexanone selectivity of 68% was observed. Increasing the Cr content resulted in red shift absorption between 500 and 800 nm, which is due to the d-d transition of octahedral Cr^{3+} in Cr_2O_3. Comparison of V-doped hollow TS-1, sulfated hollow TS-1 and sulfated V-doped hollow TS-1 demonstrated that sulfated V-doped TS-1 catalysts are more efficient for selective formation of valuable products (alcohols and ketones) [25].

3. Oxidation of alcohol

Selective oxidation of various primary and secondary alcohols in a gas-phase photochemical reactor using immobilized TiO_2 catalyst at 463 K showed that in the absence of UV light radiation 8% conversion was obtained [26]. Irradiation of the catalyst with the UV light increased the conversion dramatically to 48%. In the presence of UV light, benzaldehyde was formed in preference to phenyl acetaldehyde, in addition to small amounts of other secondary and tertiary reaction products. Benzylic alcohols gave higher conversions, however, with more secondary reaction products. The presence of oxygen was found to be critical for photo-oxidation. The conversion increased from 13 to 20% when a very small quantity of oxygen (O_2/alcohol = 1) was added to the nitrogen carrier gas. There was significant improvement in the conversion, from 13 to 36%, when nitrogen was replaced by air as the carrier gas. Aldehyde is formed only in the presence of O_2. Mohamed et al. [27] studied the photocatalytic oxidation of selected aryl alcohols, such as benzyl alcohol, 1-phenylethanol, benzhydrol, 4-chlorobenz-hydrol, hydrobenzoin, 4,4'-dichlorohydrobenzoi and 4,4'-dimethoxyhydrobenzoin, in a polar, nonhydroxylic solvent (CH_3CN). The main products formed are aldehydes or ketones; the carboxylic acids are formed in small amount. The selective oxidation of alcohol to aldehyde by photocatalytic process was demonstrated for the conversion of 4-methoxybenzyl alcohol (MBA) into 4-methoxybenzaldehyde (p-anisaldehyde, PAA) in organic-free water containing aqueous suspensions of commercial and home-prepared TiO_2 [28]. The home-prepared catalysts, obtained under mild conditions, showed to be much more selective than TiO_2 Merck and TiO_2 Degussa P25 with highest selectivity to PAA. The nanostructured anatase TiO_2 samples synthesized by simply boiling the aqueous solutions of titanium tetrachloride ($TiCl_4$) showed a yield much higher (42% mol for conversions of ca. 65%) than the commercial TiO_2 samples. The least crystalline sample showed higher quantum efficiency (0.116%) [29]. Wang et al. [30] showed that the photocatalytic oxidation of alcohol with O_2 is accelerated by Brønsted acids adsorbed onto TiO_2 or TiO_2/SiO_2 photocatalysts.

The photocatalytic oxidation of benzyl alcohol and its derivatives, such as 4-methoxybenzyl alcohol, 4-chlorobenzyl alcohol, 4-nitrobenzyl alcohol, 4-methylbenzyl alcohol, 4-(trifluoro-methyl)benzyl alcohol and 4-tertiary-butylbenzyl alcohol, into corresponding aldehydes was achieved at stoichiometric conversion and selectivity (>99%) on a TiO_2 photocatalyst under irradiation of light from a blue LED (λmax = 460 nm) in O_2 atmosphere [31]. A red shift of the wavelength of light could be achieved by Au/CeO_2, which exhibited stronger photo-absorption

due to SPR than Au/TiO$_2$ [32]. Aromatic alcohols (benzyl alcohol and substituted benzyl alcohol such as o-CH$_3$, m-CH$_3$ and p-CH$_3$, m-Cl and p-Cl substituted benzyl alcohol) oxidized to corresponding aldehydes almost quantitatively (>99% conversion, >99% selectivity and >99% carbon balance), in an aqueous suspension of Au/CeO$_2$ under irradiation of green light [33]. The electronic properties of the substituent groups play a very significant role on the reaction rate, which is enhanced by electron donating substituents and retarded by electron-withdrawing substituents [34].

4. Hydroxylation of aromatics

Conversion of benzene to phenol is an industrially important reaction. With TiO$_2$ based photocatalysis, the yield and selectivity of phenol production from benzene were about ca. 0.5 and 80%, respectively [35], which are lower than the conventional Fenton process (5% and 80–90%) [36]. The by-product formed in the photocatalytic oxidation of benzene is biphenol. The efficiency of the photocatalytic phenol synthesis can be enhanced by structural modification of the catalyst, and by using additives. Noble metal deposits on TiO$_2$ surface often enhance the photocatalytic reactivity because they trap CB electrons with reducing charge pair recombination and promoting interfacial electron transfer. Pt/TiO$_2$ exhibited an enhanced yield (1.7 times, i.e., 4.4%) and selectivity (96%). The addition of various electron acceptors such as O$_2$, Fe^{3+}, H$_2$O$_2$, Ag$^+$ and N$_2$O further enhanced the yield and selectivity. TiO$_2$ along with polyoxometalate PW$_{12}$O$_{40}^{3-}$ increased the phenol production yield (i.e., 11 and 70% selectivity) [37]. Here, polyoxometalate performs dual roles of both as a photocatalyst and as an electron shuttle. 2 atom % vanadium incorporated into the lattice of disordered mesoporous titania, 1 wt% Au incorporated into Ti$_{0.98}$V$_{0.02}$O$_2$ (TV2), showed two times higher activity than bare TV2 [38]. Zheng et al. [39] compared three photocatalysts M@TiO$_2$ (M = Au, Pt, Ag) for the oxidation of benzene to phenol in aqueous phenol under visible light ($\lambda \geq 400$ nm). Au@TiO$_2$ exhibited a high yield (63%) and selectivity (91%) compared to Pt@TiO$_2$-(yield = 34% and selectivity = 53%). Ag@TiO$_2$-microspheres resulted in negligible activity. The optimum Au loading for higher yield and selectivity was 2 wt% in Au@TiO$_2$ loading and this catalyst exhibited enhanced visible-light absorption as well as the strongest SPR effect. Comparison of the photocatalytic activity of Au@TiO$_2$-nanosheets and Au@TiO$_2$-microspheres showed that Au@TiO$_2$-nanosheets resulted in lower activity compared with that of Au@TiO$_2$-microspheres. The Au@TiO$_2$-microspheres produced a strong interaction between Au and TiO$_2$. Comparison of the synthesis of Au@TiO$_2$ by two different methods such as Ti^{3+} ion-assisted method and direct photodeposition route showed that the catalyst prepared by direct photodeposition route produced only traces of phenol. The direct photodeposition route leads to an inhomogeneous loading of noble metal on TiO$_2$, and the Au NPs exhibit a wide size distribution in the range of 20–80 nm. By changing the hydrophobicity of the catalyst, the adsorption of reactants (benzene, hydrophobic) and the desorption of the desired products (phenol, hydrophilic) could be improved [40]. With this idea, titania is incorporated in hydrophobically modified mesocellular siliceous foam (MCF) and is used for the photocatalytic hydroxylation of benzene to phenol in aqueous solutions. The inner environment of the MCF cage was turned hydro-

phobic by surface organo-grafting with silylation agent (TiO_2-MCF/CH_3). The hydrophobically modified TiO_2@MCF/CH_3/UV sample showed the highest phenol selectivity (70%) and phenol yield (12.5%) after 2 hours of irradiation. $FeCl_3$ and mesoporous carbon nitride ($FeCl_3$/mpg-C_3N_4) hybrids exhibited 38% benzene conversion with 97% selectivity for phenol under visible light [41], which is due to faster reduction of Fe^{3+} to Fe^{2+} by light-irradiated electrons from mpg-C_3N_4. Metal-exchanged BEA zeolites dispersed in benzene-acetonitrile-water mixtures at room temperature with O_2 as oxidant showed that Pd^{2+}-, Fe^{3+}- and Cu^{2+}-exchanged BEA were shown to be effective for the formation of phenols (hydroquinone, resorcinol, catechol and phenol) [42].

5. Epoxidation of alkenes

Epoxidation of alkenes to epoxide is a very useful transformation in organic synthesis. A series of highly dispersed transition metals such as Ti^{4+}, Cr^{6+}, Mg^{2+} and Zn^{2+}, in SiO_2 matrix, exhibited photocatalytic activity for propene oxide formation [43]. Various studies reported on silica supported that metal oxide catalysts are effective photocatalysts for propylene epoxidation in a closed reactor system. Studies on silica supported on V, Ti and Cr showed that the conversion rate of propylene and the formation rate of propylene oxide were increased in the order Cr < Ti < V oxides on silica [44]. Gradual deactivation was observed for CrO_3/SiO_2 with the course of the photoreaction, although the initial activity was almost same as that of TiO_2/SiO_2. Shiraishi et al. [45] prepared Cr-SiO_2 catalyst containing highly dispersed chromate species by a sol-gel method and when subjected to photocatalytic oxidation reaction under visible light irradiation ($\lambda > 400$ nm) showed very high selectivity (>90%), which is higher than Cr/SiO_2 catalysts prepared by an impregnation method or Cr/MCM-41 prepared by a templating method. The yield and selectivity to propylene oxide were improved significantly by modification of silica with 1 wt% magnesium oxide loading [46]. Photo-oxidation of propene over V_2O_5/SiO_2 with O_2 under UV irradiation in a closed circulation reactor produced ethanal (acetaldehyde, AA), acrylaldehyde (AL) and propanal (propionaldehyde, PA). However, propene oxide was not detected as a product [47]. On the other hand, the same catalyst system with flow reactor system, which provide short contact time between the substrates and the catalysts produced acetaldehyde and propene oxide as main products; the selectivities were 43 and 30%, respectively [48]. The non-loaded amorphous SiO_2 did not show any photocatalytic activity. It is clear that the surface vanadium oxide species are the photocatalytic active sites. Comparison of commercial and home-prepared TiO_2 catalysts for partial photo-oxidation of cyclopentene oxidation produced cyclopent-2-en-1-one, cyclopent-2-en-1-ol, 6-oxabicyclo[3.1.0]hexane, penta-1,5-dial (glutaraldehyde) [49]. The commercial catalysts showed lower photo-activity in terms of cyclopentene conversion (51–57%) compared to the home-prepared ones (53–69%). The commercial photocatalyst produced ketone as the major fraction in the range of 35–49% and epoxide fraction in the range of 12–17%, while the home-prepared catalysts gave mainly the epoxide fraction in the range of 26–49% and ketone fraction in the range 9–16%. The difference in catalytic behavior of TiO_2 commercial and TiO_2 homemade is due to the difference in structural properties, which resulted in different reaction mechanisms. Selective epoxidation was achieved by Shiraishi et al. [50] in Ti-containing MCM-41 mesoporous silica (T-S) with

isolated and tetrahedrally coordinated Ti-oxide species (Ti-O4), when photo-activated in acetonitrile (MeCN) with molecular oxygen. The high epoxide selectivity (>98%) of the T-S system is due to a "shield effect" driven by MeCN. TiO_2 photocatalyst incorporated in highly hydrophobic Y zeolite under UV-light irradiation using molecular oxygen as an oxygen source exhibited a markedly enhanced photocatalytic activity compared with bare TiO_2 [51].

6. Oxidation of amines to imines

In organic synthesis, selective oxidation of amines to imines are considered as important reactions, because imines and their derivatives have immense applications in the synthesis of nitrogen heterocycles, especially alkaloid synthesis, which are biologically important compounds. Lang et al. [52] have studied extensively and achieved highly selective photocatalytic conversion of various amines into its corresponding imines on TiO_2 using 1 atm of air as the oxidant in acetonitrile under UV irradiation. It is documented that it is a challenging task to achieve high selectivity in water medium as complete degradation is potential to occur by over oxidation. The reaction rate in terms of conversion of amine is much higher in water medium than in CH_3CN with high selectivity of imine formation [53]. However, the selectivity decreased to some extent because of free radical intermediates, which are comparable to photocatalytic oxidation of amine in CH_3CN. Studies on substituents' effect on the catalytic activity of amine to imine showed that substituents on the benzylic amines did not affect the selectivity significantly both in CH_3CN and in water medium [59]. The presence of electron-donating substituents (CH_3– and CH_3O–) and electron withdrawing substituents (F– and Cl–) on the phenyl ring had little effect on the reaction rate and product selectivity of the oxidation reaction. The halo-substituted benzylamines provided good selectivity, as the halo-substituted positions along with the imine functionality are useful for further transformations. Comparison of benzylic and nonbenzylic amines showed that no imines formation occurred in nonbenzylic amines such as cyclohexylamine and n-hexylamine and only fragmentation products were detected by unselective auto-oxidation at multiple reactive sites. Utilization of visible/solar energy is the prime concept to make the synthesis a economically and environmentally viable process. Nb_2O_5 converts amine to imine with high selectivity under visible light >390 nm to about 460 nm in benzene [54]. Studies on the photocatalytic activity and selectivity in the aerobic oxidation of benzylamine over various metal oxides illustrate that TiO_2 exhibited higher yield than Nb_2O_5 and ZnO. However, the selectivity to N-benzylidene benzylamine was comparatively low because benzaldehyde was formed as a by-product. In V_2O_5, benzylamine-N-carbaldehyde was formed as a main by-product. Hiroaki Tada and his research group have used the "plasmon photocatalysts", in which noble metal nanoparticles are dispersed into semiconductor photocatalysts, which possesses two prominent features: a Schottky junction and localized surface plasmonic resonance (LSPR) [55]. Au NPs supported on various metal oxides (anatase and rutile TiO_2, $SrTiO_3$, ZnO, WO_3, In_2O_3, Nb_2O_5) under visible-light irradiation (λ > 430 nm) showed that Au supported on rutile TiO_2 exhibited high level of visible-light activity for aerobic oxidation of amines to yield the corresponding imines with high selectivity (>99%) compared to other supports. The high activity of Au NP on rutile

TiO_2 is due to multiple factors such as significant red shift of the LSPR peak of Au/ rutile TiO_2 due to its very large permittivity ($\varepsilon = 114$) as compared with that of anatase TiO_2 ($\varepsilon = 48$), smaller Au particle size, good adsorptivity of rutile TiO_2 for amine owing to the presence of acid sites on the surface.

7. Oxidation of polycyclic aromatic hydrocarbons

Polycyclic aromatic compounds (PHA) are compounds containing multiple aromatic rings which are fused together. The highly efficient photocatalytic method was adopted to various PAHs and it was found that it can be degraded under UV or visible light irradiation [56]. The reaction mechanism illustrated that the toxic PAHs degraded through various useful intermediates. The selectivity of the product depends on the type of catalysts used. Other factors which influence the catalytic activity are solvent medium, atmospheric condition and wave length of light radiation, etc. Photocatalytic oxidation of naphthalene in water medium with Degussa P25 under UV radiation (345 nm, 500 Watt) produced 2-formyl-3-hydroxycinnamaldehyde and 5,8-dihydroxy-2,4-naphthaquinone as stable intermediates [57]. Bahnemann and coworkers found 15 different intermediates when naphthalene is in water medium with Degussa P25 under UV radiation (366 nm, 50 Watt) [56]. The main intermediates observed are coumarin, 1,4-naphthalenedione, 2,3-dihydro-2,3-epoxy-1,4-naphthalenedione, 2-formyl-Z-cinnamaldehyde, 1,2-benzenedicarboxaldehyde and phthalic acid. Karam et al. synthesized 1,4-naphthaquinone in a closed system reactor under UV radiation [58]. Solvent plays an important role in the photocatalytic degradation of naphthalene. In water containing 1% MeCN produced significant amounts of three intermediates: isomeric 2-formylcinnamaldehydes and 1,4-naphthoquinone. In organic solvent, the oxidation rate was almost an order of magnitude slower than in water and produced significant amount of naphthoquinone and phthalic anhydride [59]. In acetonitrile and water mixture, with UV light ($\lambda < 340$ nm) produced 2-formylcinnamaldehyde (85%), Z isomer is the original product that is spontaneously transformed into the thermodynamically more stable E isomer. Addition of acetone can cause an accumulation of intermediates. For example, higher concentrations and more types of intermediates were found in degradation of naphthalene with the high acetone level [60]. In mixed solvents such as acetonitrile and water bubbled with molecular oxygen, naphthalene is efficiently oxidized to 2-formylcinnamaldehyde when irradiated with 500 W super-high-pressure mercury lamp ($\lambda < 340$ nm) light [61]. Under the same condition, phenanthrene was converted into a coumarin compound with 45% yield [62]. Photocatalytic activity of different kinds of TiO_2 powders for naphthalene oxidation showed that Degussa P25 TiO_2 powders, which contain mixture of anatase and rutile, showed the highest photocatalytic activity for the production of 2-formylcinnamaldehyde from naphthalene. Similarly, powders containing both rutile and anatase phases showed high activity, even if the component of the anatase phase is a few percent. Pure anatase particles and pure rutile particles exhibited lower activity for the photocatalytic oxidation of naphthalene into 2-formylcinnamaldehyde [63]. Visible active photocatalysts are developed to convert the PAHs to useful compounds. Kohtani and coworkers showed that $BiVO_4$ (band gap 2.4 eV) [64] and Ag-loaded $BiVO_4$ photocatalysts are

visible light-driven for photo-oxidation of various PAHs in acetonitrile in O_2 atmosphere. Compared to pure $BiVO_4$, Ag-loaded $BiVO_4$ photocatalyst remarkably improves adsorptive and photo-oxidative performance on the degradation. Anthraquinone is obtained in both pure and Ag-loaded $BiVO_4$ solutions, while the amount of formation using Ag-$BiVO_4$ is much larger than that using pure $BiVO_4$. Anthrone is obtained only from the irradiated Ag-$BiVO_4$ solution but not from the pure $BiVO_4$ one. The amount of anthraquinone formation is largest in O_2-saturated solution compared to that in N_2 atmosphere. Bz[a]A was degraded by Ag-$BiVO_4$ and converted into a considerable amount of 7,12-dione. Substituent effects on the photocatalytic oxidation of naphthalene demonstrate that in dinitronaphthalene isomers, namely 1,3-dinitronaphthalene (1,3-diNN), 1,5-dinitronaphthalene (1,5-diNN) and 1,8-dinitronaphthalene (1,8-diNN), the photocatalytic oxidation rates followed in the order 1,3-diNN > 1,8-diNN > 1,5-diNN [65].

8. C-C bond formation

The C-C bond formation between an electrophilic alkene and adamantane was achieved by the irradiation of TiO_2 suspensions in the presence of isopropylydenmalonitrile (IPMN, 0.02 M, with adamantane likewise 0.02 M) and under nitrogen forms a new product as an adduct, 2-[1-(1-adamantyl)-1-methyl)]ethylpropanedicarbonitrile (35% yield), together with traces of oxygenated products, such as 1-adamantanol, 2-adamantanol and 2-adamantanone [66]. By adding silver sulfate as a sacrificial electron acceptor, the yield increased to 75%. The single-electron transfer oxidation of adamantane is followed by deprotonation leading to the 1-adamantyl radical that couples with isopropylydenmalonitrile.

9. Cyclization reaction

Intramolecular cyclization of N-(β-hydroxypropyl)-ethylenediamine in the presence of a semiconductor (TiO_2 or CdS or ZnO)-zeolite composite catalysts in O_2 atmosphere produces 2-methylpiperazine and piperazine [67]. The yield of 2-methylpiperazine and piperazine depends on the type of semiconductor and zeolite. Zeolites modified with TiO_2 (5 wt% TiO_2–Hβ) composite considerably facilitated the intramolecular cyclization with a yield of 31.9%. Zeolites modified with semiconductors ZnO and CdS showed lower activity. This is due to moderate hydrophobicity and acid site strength offered by TiO_2-zeolite composite for the cyclization reaction. Selvam and Swaminathan have shown one-pot synthesis of quinaldines from nitroarenes by combined redox-cyclization reaction assisted by photocatalytic method using pure TiO_2 and Au-loaded TiO_2 catalyst in absolute ethanolic solution under UV radiation (λ = 365 nm) [68]. The Au-loaded TiO_2 catalyst exhibited higher efficiency and selectivity for the formation of quinaldine and substituted quinaldine from nitrobenzene and substituted nitrobenzene. For instance, TiO_2 produced 60% yield and Au/TiO_2 produced 75% yield. The reaction involves two steps: in the first step nitro group is reduced to amine, which is followed by condensation with aldehyde and cyclization occurs. The substituted nitrobenzene influen-

ces the activity and selectivity. The authors suggested that the electron-releasing group at para-position inhibits the condensation of amino group with aldehyde. 4-Methoxynitrobenzene has a strong electron-releasing group at para-position and showed lower quinaldine yield (60%). Steric effect also plays an important role in product formation. In 3,5-dimethylnitrobenzene and 3-nitrotolune, the cyclization reaction is hindered due to steric effect in 3,5-dimethylni-trobenzene and decreased the product yield (70%) when compared to 3-nitrotolune (80%).

10. Conclusions

There is an extensive research and dramatic growth going on in the field of heterogeneous photocatalysis. This method has been commercialized in various aspects of environmental detoxification. Photocatalysis method can be successfully applied for fine organic chemical synthesis. The advantages of photocatalysis method in organic synthesis include the possibility of utilizing clean and abundant renewable energy source, harmless chemicals used as catalysts, reaction can be carried out at room temperature, product type and its selectivity can be tuned by varying the nature of solvent, atmospheric condition, and wavelength of light source used, catalyst reusability, etc. Various challenging aspects have to be considered before implementing in industrial scale. Most commonly, simulated sunlight or UV sources are used in the laboratory. Experiments need to be devised to monitor the performance of the catalyst in sunlight. In future, more catalysts need to be devised that can trap the visible radiations as well. Since organic solvents are utilized in organic transformations, the band gap of the metal oxide photocatalysts in organic medium has to be explored. Systematic study has to be conducted to optimize the reaction parameters and understand the reaction mechanism, thereby the product yield could be improved.

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