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Prospective of titania based photocatalyst for environmental reduction reactions

TRILOCHAN MISHRA*
Functional Material Group, AMP Division, CSIR-National Metallurgical Laboratory, Jamshedpur-831007, India

Abstract : In the last two decade photocatalysis is widely studied so as to evolve a green chemical rout to deal with the environmental and energy problem faced by the mankind. Among all the studied photocatalysts anatase TiO_2 is most attractive even today though limited to UV light absorption in pure form. However, easy availability, high aqueous stability and nontoxic nature attracted the researchers to go for different possible modifications. Effort has been made by number of researcher to modify titania through metal, nonmetal doping and mixing with other oxides and sulphides to engineer the band gap, band potential and delay the charge separation through Z-scheme and hetero-junction formation so as to achieve the goal of producing stable and highly active photocatalyst for energy and environmental application. In recent past, various strategies have been tried to extend the solar light absorption from visible to NIR range by using appropriate material so as to ultimately promote the solar photocatalytic performance of TiO_2 based composites. Keeping these in view, present review will discuss the past and present development in the area of material modification to deal with band gap engineering, heterojunction formation, required porosity, powder catalyst separation and better charge separation with special objective of improved environmental reduction reactions. In addition future prospect of these materials has been discussed in details for new generation researchers. In particular material based on MOFs, two dimensional materials and metal halide *perovskites* based titania composites are emphasized for future evaluation to address both air and water pollution.

Key wards: *Titania, doped oxide, heterojunction, band potential, Z-scheme, photocatalyst, environmental, reduction reaction.*

INTRODUCTION

Report on photo-induced water splitting by Fujishima and Honda on titania in presence of UV light [1] opened the area of photocatalysis for future environmental and energy application. Till date though a lots of semiconductrs are available but TiO_2 is considered as the most promising photocatalyst for large scale application due to its appropriate electronic band potential, better chemical inertness, high photo-stability and easy market availability [2]. In general TiO_2 acts as an n-type semiconductor because of the presence of oxygen vacancies. For the photocatalytic reaction semiconductor is required with proper band gap and band potential for appropriate light absorption. In TiO_2 valency band and conduction band are constituted by the overlapping of the O 2p and Ti 3d orbitals, respectively. In general titania found in the form of anatase, brookite and rutile[3-4] having distorted octahedral structure (TiO_6) with different symmetries [5]. The band gap of pure rutile, anatase and brookite are 3.0, 3.2 and 3.3 eV, respectively. Though brookite is reported to be a better photocatalyst than anatase but the stability is questionable [6]. However anatase form is well studied as photocatalyst because of easy of synthesis, better thermal stability at least up to 500°C and photocatalytically active than other polymorphs [7]. Due to the revival of more interest on the TiO_2 photocatalyst Fujishima again reviewed [8] the subject in 2012 with new prospective for future application highlighting the importance of different forms including 0D, 1D and 2D titania.

To make TiO_2 photocatalyst more attractive for larger application number of researchers extensively investigated surface characteristics by various techniques in the last few years so as to provide important insights to the TiO_2 photocatalyst in molecular level [9]. All these discussion in recent years revives the importance of the traditional material. As per the basic principle a semiconductor produces electron and hole in presence of light which can facilitates both oxidation and reduction reaction to address both air and water pollution as schematically presented in Fig-1.

* Corresponding Author Email :tmishra@nmlindia.org

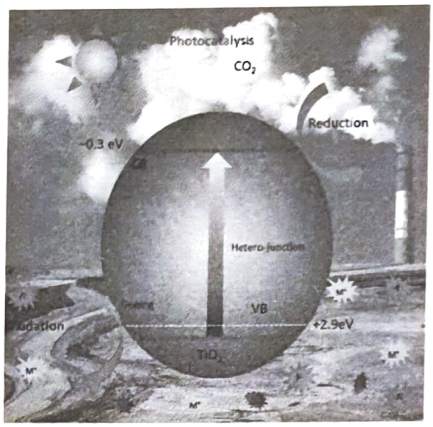

Fig-1: Schematic presentation of TiO_2 based photocatalyst for environmental remediation.

TiO_2 with conduction band (CB) potential level of -0.3 eV is more negative and hence suitable for the redox reaction $H+ /H_2$ (0 eV). On the other hand valency band (VB) potential of +2.9eV which is more positive with respect to O_2/H_2O (1.23 eV) standard redox potential, makes it suitable for oxidation reactions. Due to its favourable CB and VB potential level TiO_2 is capable of splitting water, oxidation of organics and converting CO_2 to fuel[10]. However it suffers with the main disadvantage of absorbing in UV light region thus making it inactive for much desired solar photocatalysis. Moreover, TiO_2 suffers with the large band gap (3.2 eV) with limited utilization of solar light (2%) and fast recombination of photoinduced charges which significantly limits the practical applications. In addition, phase change of anatase to rutile at moderate temperature (500–600°C) resulting in the drastic decrease in photocatalytic activities limits the large scale application of pure anatase as photocatalyst [11]. Therefore anatase based mixed oxides and hetero-junctions were explored by number of researchers to extend the thermal stability and visible light absorption[12]. In this context size and shape of the nanoparticles also plays an important role in modifying the electronic properties of different semiconductor oxides [13]. This recent review highlights the importance of pure oxide semiconductors, solid solution, heterostructures including Z-scheme catalyst fabrication for prospective photocatalytic applications. However, if one will look at the solar light, it is clear that around 46% is contributed by NIR region and hence for proper utilization of solar radiation we requires materials to absorb in the broad spectrum of visible to NIR so as to improve the efficiency. In this regard important strategies (Fig 2) include metal/ nonmetal doping, noble metal deposition, structural modification, heterostructure/ heterojunction formation with other semiconductor oxides and sulphides and dye sensitization with a primary objective of increasing the practical efficiency under solar light through better light absorption and charge separation. Here we will concentrate on the applicability of different modified catalysts for environmental reduction reactions so as to deal with the different waste water containing toxic metal ions and other anions.

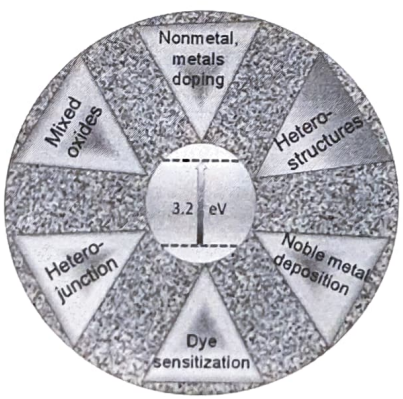

Fig 2: Important strategies to improve photocatalytic activity of titania based photocatalyst.

MODIFICATION OF TIO_2

TiO_2 based mixed oxides

Initially titania based mixed oxides are well studied with a objective of anatase phase stabilization and visible light absorption so as to project titania as a potential solar photocatalysts. Recently a number of critical reviews are published [11, 12] with different objectives and applications. Subsequently new innovative approaches are explored to improve the solar light absorption, charge separation and photo-stability of several composites, core shell structures involving Z-scheme and heterojunctions. In our lab we have demonstrated different titania based mixed oxides with attractive shape and surface morphology (Fig 3) for enhanced photo-induced catalytic activity under visible light. Shape and surface morphology control the much required porosity as demonstrated in spherical to nodular shaped materials. Titania and silica mixed oxide has attracted the researchers due to the extensive application as both catalyst support and active catalyst [14-15]. Due to the similar oxidation state (+4) of both Ti and Si with similar oxidation state are compactable to each other in the lattice and can easily interlink through oxygen bridge [16]. Silica lattice at the interface confined the TiO_2 species in nanoscale preventing from further growth. In addition, Si^{4+} with smaller ionic radius (0.042 nm) can easily enter into the lattice of TiO_2 and substitute the Ti^{4+}. Possibly this is one of the cause of high thermal stability of anatase phase in SiO_2 mixed titania[17]. Moreover, formation of Ti–O–Si hetero bridges gives rise to the Brønsted acidity as silica tetrahedra is chemically coordinated with the titania octahedral. Ultimately, this also contributes towards enhanced photocatalytic activity of silica-titania mixed oxides.

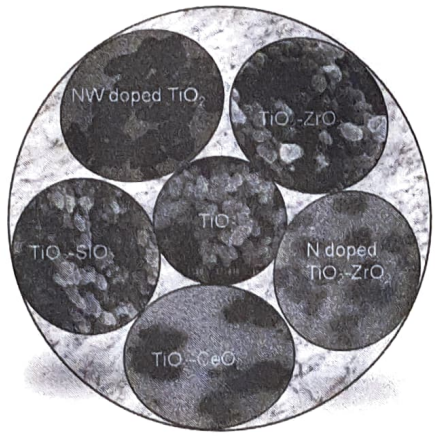

Fig-3: Different mixed oxides of titania as photocatalysts. Some of the figures are reproduced from ref (18, 47 & 53) with copyright permission.

For photocatalytic activity crystallinity of particular titania phase is a critical factor. In general addition of silica to titania enhances anatase phase stability at higher temperature by suppressing phase transformation to rutile and thereby maintains the high surface area and surface acidity. Addition of 10-20 wt% silica resulted in the stabilization of anatase phase [18] up to 900°C with high surface area. Interestingly the spherical shape of the titania and the mixed oxides are retained in a controlled sol-gel synthesis. Surprisingly presence of silica mostly facilitates the formation of Ti-O-Si bonds thus stabilizing the anatase phase and porous structures [19] even at high temperature. On the other hand pure titania easily transforms to nonporous rutile phase even at 600°C calcination thereby decreasing the photocatalytic activity. Similarly, in the periodic table zirconium and titanium belong to the IVB group of elements. Moreover, both TiO_2 and ZrO_2 come under n-type semiconductors having band gap of 3.2eV and 5.0eV respectively and exhibit close physicochemical properties. Wide band gap ZrO_2 with sufficient conduction band and valence band potential of -1.0 V and 4.0 V vs NHE, respectively emerges as a promising photocatalyst particularly for the pollutants degradation. Therefore ZrO_2 works better in a composite system where photoinduced electron can transfer from other semiconductor to facilitates the required reactions. Due to

this importance TiO_2-ZrO_2 materials are synthesized by several methods which include sol-gel [18, 20-21] and co-precipitation [22-23]. In sol-gel processes, typical problem arises due to the different hydrolysis and condensation rates of Zr and Ti alkoxides which gives rise to separate domain formation. In co-precipitation technique homogeneous colloids are formed where zirconia is mostly segregated within the titania matrix. On the other hand, ZrO_2 is distributed on the titania surface in case of heterogeneous colloids formation [24, 25]. Recently effect of other semiconductors oxides with TiO_2 for solar photocatalysis has been reviewed in details [19]. Mostly interfaces of other oxides like WO_3, Cu_2O, CeO_2 or Fe_2O_3 with anatase controls the electronic properties and hence influence the photocatalytic properties. Therefore it is essential to understand the change in electronic properties of a mixed oxides system.

Among all the mixed oxides TiO_2-WO_3 [26] and TiO_2-CeO_2 [27] system is well studied due to some inherent interesting properties of WO_3 and CeO_2. In particular these oxides when combined with titania exhibit improved photocatalytic properties under solar light. It is observed that nanosized WO_3 crystallizes in the form of orthorhombic or monoclinic phases with TiO_2. Presence of different oxidation states, oxygen vacancies and different surface phases on TiO_2 creates the variable surface properties [26]. Moreover monoclinic phase of WO_3 exhibits band gap of 2.7-2.8eV which is ideal for solar light absorption and hence can be used as solar photocatalyst [28]. In addition defect chemistry of WO_3 and CeO_2 [11] make these materials more interesting. Mixed oxides systems are explored with a objective of better photocatalytic activity because of fast charge recombination on pure WO_3 and CeO_2. Recently WO_3 based photocatalysts are reviewed [29] particularly in relation to doping and composites formation for various solar photocatalytic application. In case of TiO_2-WO_3 system surface acidity and size in nanoscale plays a decisive role for enhanced sunlight absorption and photocatalytic activity. In addition, Schumuki group reported on unidirectional Ti-W oxide nanotubes grown on TiW alloy through controlled anodization process[30]. Ti-W mixed oxide nanotubes with as low as 0.2wt% WO_3 showed improved ion insertion and photocatalytic activity in comparison to the pure TiO_2 nanotubes. Similarly doping of lanthanides can significantly enhance the photocatalytic activity of TiO_2 [31-32]. In a reported result high photocatalytic activity is noticed for 5wt% cerium oxide mixed titania material calcined at 600°C towards selenium reduction. Photocatalytic activity is found to be mainly dependant on the variable oxidation states like Ce^{4+}/ Ce^{3+} rather than only visible light absorption. Moreover, an important role is also played by oxygen vacancy created by the presence of mixed oxidation states [27]. Among the lanthanides ceria and lanthanum oxide mixed titania is well studied due to some interesting properties like variable oxidation states and easy formation of labile oxygen vacancy. Interestingly, pure ceria nanomaterial also acts as good photocatalyst [33]. In addition $SrTiO_3$ with band gap of 3.4 eV is also studied as photocatalyst in combination with TiO_2 [34–35] having improved photocatalytic activity due to better charge separation in $SrTiO_3$-TiO_2 heterojunction. Similarly, photocatalytic activities of TiO_2 [36–37] can be substantially improved due to the coupling of SnO_2 through better charge separation. On the other hand hematite having narrow band gap (~2.1 eV) has attracted the attention of researchers due to its advantages of natural abundance, low-cost, high stability towards visible light active photocatalytic and photo-electrochemical (PEC) [38, 39] applications. Coupling of Fe_2O_3 to TiO_2 has been studied by number of researchers for different applications. Branch shaped Fe_2O_3-TiO_2 nanocomposites synthesized by a combination of electrospinning and hydrothermal techniques were reported recently [40]. Even Bi_2O_3 with titania [41] can improve the photocatalytic activity under visible light with improved H_2 evolution efficiency. Therefore scope of designing an inovative mixed oxides with controlled heterostructure and porosity is enormous at present in exploration of new photocatalyst.

Doping with metals and nonmetals

Since the report of Ashi et al [42] several researcher investigated the doping of nonmetals like S, C, N and B so as to extend the light absorption by titania to visible region. Due to close atomic diameter these elements can easily substitute the O atoms of titania lattice. Typically, these types of doping results in decreased band gap and

changed electronic properties due to the contribution of p-orbitals [43-44]. In some cases surface doping takes place resulting in the surface functionalisation thereby altering the photocatalytic properties. Sometimes it is difficult to distinguish the surface and lattice doping of the materials. XPS is the most important tool used to identify the types of nonmetal doping in oxide semiconductors. Typically C1s, N1s spectra [45-46] is used to see the type of doping. Recently O1s spectra also showed the indication of doping and oxygen vacancy resulted from doping and partial Ti^{4+} reduction [47].

In this effort new strategies like plasmonic metals (Au, Ag etc) deposition on TiO_2 [48, 49], dye sensitisation and combination of low band gap semiconductor with TiO_2 making a heterojunction are extensively tried in last few years [50]. Recently graphitic carbon doping of semiconductor oxides are reported with tuneable band gape using coordination polymers. Amount of graphitic carbon in the interface of the oxide controls the band gap [51]. Titania based nanotubes synthesized by anodisation process is an interesting 1D material as presented in Fig 4. Obtained tubes are uniform in size and the length can be controlled with anodisation time and choice of electrolyte. Transition metal doped TiO_2 nanotubes also attracted the attention of researchers with increased photo-current and photocatalytic activity [52]. In situ chromium doping through anodisation of Ti-Cr alloy increases the crystalinity and electronic conductivity of the oxide tubes. Non-metal (N) doping on TiO_2-ZrO_2 mixed oxide improved the photocatalytic activity due to the creation of oxygen vacancy [47]. Formation of Ti^{3+} and oxygen vacancy with increased porosity is possible when reducing agents like hydrazine is used as nitrogen source. Similarly N and W doped titania is reported to be highly active for photocatalytic nitrate reduction reaction under visible light [53]. This indicates the beneficial effect of simultaneous doping of metal and nonmetal for different applications.

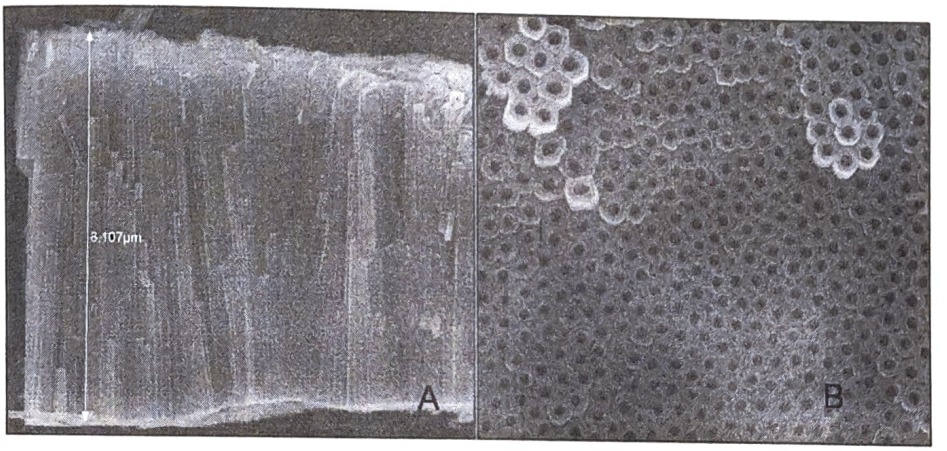

Fig 4: Anodized titania nanotubes (A) side view and (B) top view

Different hetero-junctions

In the recent years a lot of hetrojunction based photocatalysts are studied based on Z-scheme [54] and P-N junctions so as to improve the solar photocatalytic activity. Titania based heterojunction with more positive valence band and conduction band potential than TiO_2 exhibit better charge separation and photocatalytic activity [55]. Typically low band gap semiconductors like Fe_2O_3, WO_3, Ag_3PO_4, $BiVO_4$ and Bi_2WO_6, have been used by number of researchers to create a better heterojunction system for different photocatalytic applications [55-57]. However, most of these efforts are targeted for increased visible light absorption only. On the other hand copper hydroxy phosphate $Cu_2(OH)PO_4$ with libethenite structure is reported to extend the solar light absorption up to NIR range [58] thus increasing the photocatalytic activity. $Cu_2(OH)PO_4$ acts as an n-type semiconductor as reported from photo-eletrochemical study with optical band gap in the range of 3.4 to 1.52 eV [59]. Heterojunction based on TiO_2-$Cu_2(OH)PO_4$ reports the efficient photoreduction of Cr(VI) under solar light through better charge separation [60]. CdS with narrow band gap (2.4 eV) and sufficient negative conduction band potential become a well studied

solar photocatalyst for practical applications in the field of water splitting and CO_2 reduction. However, the poor aqueous stability and high charge recombination rates are the main bottle neck for photocatalytic solar water splitting application [61]. In a recent report [62] one dimensional CdS-TiO_2 having core shell structure synthesized via solvo-thermal method showed improved chromium (VI) reduction under visible light. Therefore, hetreojunction formation with other stable semiconductors is well studied with increased stability [63-65]. In particular heterojunction with metal chalcogenides and 2D C_3N_4 [64] are well reported in recent times due to their improved performance under solar light for variety of phtocatalytic reactions. Efficiency of a catalyst also depends on the shape and size of the material and the type of heterojunction formation which is well controlled by different synthetic techniques.

Environmental reduction reactions

Initially the photocatalysis process is mostly investigated for organic dye decomposition resulting in colour removal, purification and decontamination of indoor air, decontamination of soil and destruction of other hazardous organics such as through oxidation process. In this context photodecomposition of chlorinated organic like chlorophenol, tricloroethylene in contaminated water has been investigated at different pH by several researchers using titania based materials like TiO_2 [66], SiO_2-TiO_2 [67], ZrO_2-TiO_2 [68] and CdS-TiO_2 [69] with increased efficiency. Subsequently researchers extended the applications to environmental reduction reaction.

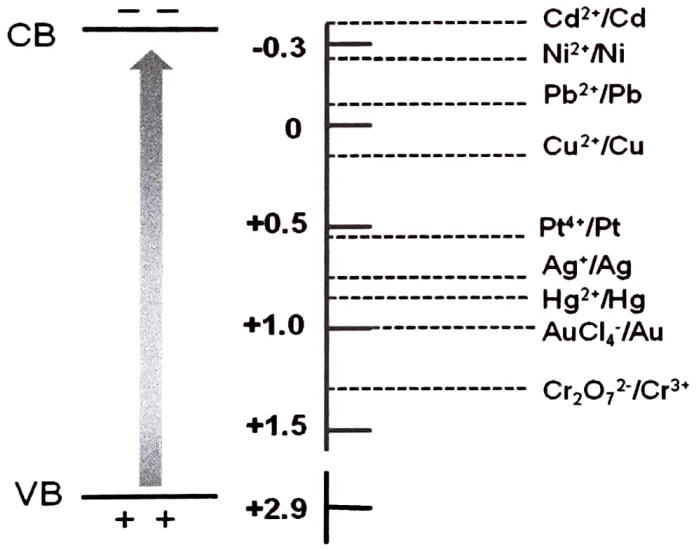

Fig 5: Positions of the redox potentials of metallic couples with respect to TiO_2 at pH = 0.

For efficient photoreduction of any metal ion to metallic form, the energy of the CB electron should be more negative than the E0 (Mn+/M couple). It is well known that these metallic couples are controlled by the pH of the solution. Thus pH is important for better reduction reaction efficiency. Reduction possibility of different cations is presented with respect to CB and VB of TiO_2 in Fig-5. It is understood that [70] metal ions having redox potential more than 0.4 V can possibly be reduced on anatase titania. Accordingly, the photo-induced reduction of dofferent inorganic cations and anions are investigated with a objective of recovery or removal application has been discussed. Even dye sensitized TiO_2 is also used for chromium ion reduction [71] under visible light. Fabrication of triphenylamine [72] and tetramethylpiperidin [73] based organic dyes with TiO_2 composites improves the photocatalytic efficiency to many fold under visible light.

Lead and cadmium are most commonly used toxic metal ions usually found in the waste and drinking water. Therefore, removal of these ions is important and mostly adsorption process is used for the same. However based on their reduction potentials (Pb: 0.126 V, Cd: -0.403 V) it is very difficult to reduce these applying

titania based photocatalyst. Efficient photoreduction of Pb(II) using Pt–TiO_2 suspensions [74] was reported. Mostly reduction process is enhanced in presence of a hole scavenger like organic molecules. Simultaneous oxidation of nitrobenzene and reduction of Pb^{2+} at pH-6 was demonstrated with the deposition of PbO_2 [75]. Whereas, cadmium reduction is only possible in presence of selective organics as hole scavengers. Importance of the hole scavenger is well noticed as presence of methanol is not capable of reducing Cd to metallic form whereas formate can do the same [76]. In one of our work importance of mixed oxides for lead and cadmium ions reduction were demonstrated using SiO_2-TiO_2 and ZrO_2-TiO_2 materials. In particular mixing of 10wt% silica and zironia with TiO_2 increases the surface area of the material which ultimately helps in increasing photoreduction activity in presence of formate under UV light [15, 18]. Similarly mercury is considered as a serious pollutant (0.005 mg/l) due to its biological or chemical non-degradability. Presence of other metal ions such as Cr(VI) [77], Fe(III) [78] etc. inhibits the photocatalytic reduction of Hg(II). In addition presence of hole scavengers increases the Hg(II) photoreduction activity. Among the hole scavengers presence of EDTA [78] enhances the photoreduction of mercury in comparison to the methanol, 4-nitrophenol, and salicylic acid.

In wastewater most common selenium species are selenate, selenite and their protonated forms. The toxicity of Se species is related to their mobile nature and oxidation states. So among the selenate and selinite Se(VI) is more stable towards reduction and more toxic than Se(IV). Efficient selenium reduction to red Se(0) on N doped TiO_2-ZrO_2 was reported under visible light [47]. Improved efficiency was credited to the synergistic effect of partial Ti^{3+} formation, oxygen vacancy and high surface area. Amal et al also reported the comparative study on the role of hole scavengers towards photo-reduction of Se ions [79]. However presence of hole scavenger is essential. Photo-reductions of different aqueous oxyanions which includes nitrate, chromate, nitrite, bromate, selenate and perchlorate in waste water is reported on TiO_2 based photocatalyst [80]. At the same time photocatalytic reduction of copper ion is only possible in presence of hole scavenger like EDTA, sodium formate, sodium oxalate or alcohols [81] and organic dyes [82]. Complete reduction of nitrate to nitrogen gas with 94.6% selectivity was reported with Wand N co-doped TiO_2 material under visible light [53]. Improved nitrate reduction with formic acid as hole scavenger is credited to the $CO_2^{\bullet-}$ free radical formation with high reduction potential. Simultaneous photocatalytic reduction of Cu(II) and Se(IV) using spherical binary oxide materials was first time reported by Aman et al [83]. Only formic acid and EDTA are found to be better hole scavengers for the reduction process among other organics. A comparative study is reported using both the hole scavengers varying reaction time, concentration, pH etc. In independent reaction formic acid is found to better hole scavenger for Se(IV) reduction while EDTA is the best for Cu(II) reduction. However, in a mixture solution both EDTA and formate performs equally in presence of visible light.

Similarly chromium (VI) is carcinogenic and a lot of catalysts are tried with improved photoreduction in UV [66, 70] as well as visible light [60, 62, 69]. In presence of hole scavenger Cr(VI) is reduced to less toxic Cr(III) which is easily removed through precipitation or adsorption. TiO_2-$Cu_2(OH)PO_4$ based hetero-junction[60] improves the photo reduction of Cr(VI) under solar light as $Cu_2(OH)PO_4$ extend the light absorption from visible to NIR range. In addition various new types of catalysts like MOFs [84] and halide pervoskite [85] based titania composites are tried for the photocatalytic reduction reactions. Possibly these materials will emerge as prospective catalyst in the future if the aqueous stability and other problems will be solved through modifications. These new catalysts are good for the CO_2 reduction reaction which is the one of the most critical environmental problem. CO_2 reduction to fuel has been well studied in recent time with a objective of improved efficiency to deal with the practical problem [69]. Among the oxyanions arsenate and arsenites are important due to their high toxicity and availability in the drinking water of eastern India. Recently total arsenic removal of 3 ppm using an innovative $BiVO_4/TiO_2$ system under LED light irradiation from aqueous solution was reported [86]. In this context titania based photocatalysis as an effective and green method is reviewed by Litter highlighting the mechanism and practical applicability [87].

Efficient arsenic reduction within two hours of reaction offers the possibility of practical application. Moreover, titania composites with two dimensional materials like metal chalcogenides [88] are important and need proper evaluation for various photocatalytic applications. In addition to catalysts materials development reactor designing is also important for practical application. Recent progress on continuous flow based slurry reactors attracted a lot of researchers towards flow reactor designing [89]. In this regard a plug flow reactor was designed where hematite nanomaterials as photocatalysts were used in the suspension [90].

FUTURE PROSPECTS

Presently, designing of modified titania based photocatalyst is mainly concentrated on doping, mixed oxides and hetero-structure formation with one dimensional, two dimensional semiconductors. Possible approaches to enhance solar photocatalytic activity and separation of photocatalysts from reaction mixture are discussed to provide a future direction in highly efficient photocatalyst design. The TiO_2 based heterostructure materials is an important and attractive subject for future development in the area of photocatalysis and photo-electrocatalysis. However, a breakthrough research is essential for material designing based on z-scheme and heterojunctions maintaining the required band potential to solve the renewable energy based environmental problems at the earliest. One need to emphasize on the stability of materials, porosity, sufficient solar light absorption and better charge separation in heterostructure designing based on binary and tertiary system. This review focused on the future scope of development and use of low-cost TiO_2 based material for different reduction reaction in particular. Photocatalytic removal of different toxic oxyanions needs more investigation with respect to efficiency and catalytic material deigning. In addition designing of continuous flow reactor is emphasized for practical application with increased photon and mass transfer. Flow type photoreactors reduces the safety hazards and simplify the process in large scale in comparison to batch reactors. As far as material is concerned MOFs and metal halides pervoskite titania composites are emerging photocatalyst which need in depth study with respect to aqueous stability and appropriate application. In addition titania and two dimensional material composites are versatile photocatalyst and need extensive research in fine tuning the heterojunction formation for improved solar photocatalysis towards toxic metal ions, oxyanions and CO_2 reduction to address both air and water pollution.

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