

Strategies developed on the modification of titania for visible light response with enhanced interfacial charge transfer process: an overview

Review Article

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Received 11 March 2011; Accepted 7 June 2011

Abstract: The modification of titania by metal / non metal ion doping, coupling with narrow band gap sensitizer, surface fluorination, metal deposition, and together with recent ventures on application of {001} facets of anatase titania for visible light response with enhanced charge carrier separation are briefly overviewed.

Keywords: Titania • Doping with metal / non metal ion • Surface fluorination • Metallization • {001} anatase facet

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1. Introduction

Since the photoelectrochemical splitting of water using TiO_2 was first reported by Fujishima and Honda in 1972 [1], the application of TiO_2 in several fields has drawn significant interest by several research groups. However, the high density of charge carrier recombination and also the large band gap of TiO_2 impair its commercial applications. Recently intense research has been devoted to modification of the titania band gap as well as to utilization of the large fraction of solar light with high quantum efficiency for commercial applications. In this regard, main landmark achievements are represented in Scheme 1.

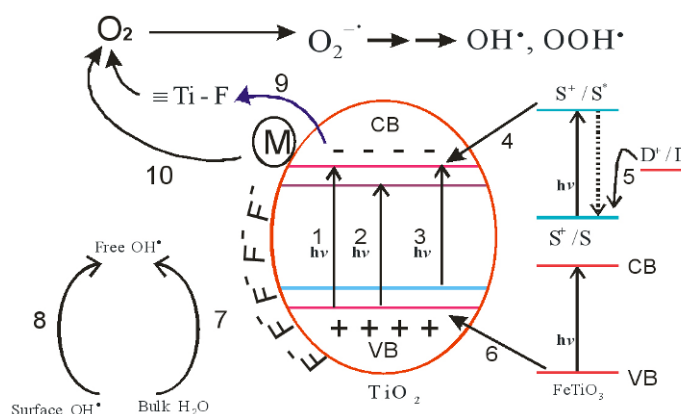
2. Strategies developed to harvest solar light with enhanced separation of charge carriers in titania

The band gap excitation of TiO_2 by UV light generates charge carrier pairs with robust redox properties. Those pairs may recombine, become trapped in the metastable surface state or react with electron acceptors / donors adsorbed on the surface of the photocatalyst (Path 1). Doping of metal ions within certain limits prolongs

the charge carrier life time and also extends the band gap absorption to the visible region either through d-d transition or interband transition from dopant level to band gap states of TiO_2 (Path 2) [2a]. Metal ion doped titania prepared by applying ion-engineering techniques such as ion-implantation and an Radio Frequency magnetron sputtering deposition method showed high efficiency for water splitting under visible light [2b]. Although, reports on enhanced activity of metal ion doped TiO_2 compared to the benchmark photocatalyst Degussa P25 is widely reported [2c], the thermal instability as well as increased recombination due to metal ion inclusions limits its scope [2d].

Asahi *et al.* reported the $\text{TiO}_{2-x}\text{N}_x$ films prepared by sputtering the TiO_2 target in a N_2 (40%) / Ar gas mixture for the degradation of methylene blue and gaseous acetaldehyde under UV / Visible light [3a], while Khan *et al.* reported the water splitting using rutile TiO_2 doped with carbon as substitutional impurity [3b]. In contrast to the metal ion doped TiO_2 , wherein metal ion forms a localized electronic level, the p orbital of substituted non metal atom hybridize with O 2p orbital resulting in visible light response. Although it is recently argued that in the case of doped titania visible light response mainly originates from color centers [3c]. Non metal ion doping into anatase titania lowers the oxidation power of holes

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Scheme 1. Charge transfer process in modified TiO_2 . (Recombination processes are not shown for clarity). Path 1, 2 and 3 corresponds to band gap excitation of titania, metal ion doped titania and non metal doped titania respectively; Path 4- Electron transfer from excited state of sensitizer to CB of titania; Path 5- Regeneration of sensitizer in the presence of sacrificial electron donors; Path 6- Hole transfer from sensitizer to VB of titania; Path 7- Oxidation of solvent water molecules by hole to generate free hydroxyl radicals; Path 8- Desorption of surface adsorbed hydroxyl radicals in the Helmholtz layer by surface fluorination to generate free hydroxyl radicals; Path 9- Surface $\equiv\text{Ti-F}$ as reactive electron trapping site; Path 10- Metal deposits on the titania surface serving as passive electron sink.

as the dopant electronic level lies just above the valence band edge (Path 3). However, nitrogen doped rutile TiO_2 seems to increase the oxidation power of holes due to the downward shift of valence band maximum. This indicates the phase structure dependence of titania in tuning the redox properties of the charge carriers [3d]. Choi *et al.* for the first time reported *in situ* doping of carbon into TiO_2 lattice *via* sol-gel hydrolysis of titanium tetrabutoxide without using external carbon precursor which showed visible light photocatalytic activity for the degradation of 4-chlorophenol [3e]. Liu and co-workers suggested that dense localized surface states with favorable surface structure in the non metal ion doped titania promote the separation of photoexcited charge carriers thereby enhancing the photocatalytic activity [3f].

Surface sensitization of titania by narrow band gap semiconductor [4a], organic dyes [4b], inorganic metal complexes [4c] or conjugated polymers [4d] enables utilization of the large fraction of solar spectrum. The metal chloride complexes adsorbed on titania surface serve as visible light absorbing sensitizers and titania matrix functions as a charge trap resulting in better photocatalytic activity [5]. The coupling of TiO_2 with quantized WS_2 or MoS_2 showed superior activity for the degradation of organic compounds under visible light [6]. Although the bulk WS_2 has conduction band edge lower than that of TiO_2 , the size quantization of WS_2 results in the shift of its CB edge to a higher value compared to that of TiO_2 facilitating interparticle electron transfer, which is otherwise not possible in bulk WS_2 . For this kind of coupled semiconductors with quantized structure the use of highly toxic CdS in photocatalysis could be avoided. In the above cases [4-6], interfacial

electron transfer takes place from the excited state of the sensitizer to conduction band of titania with charge separation followed by dioxygen reduction (Path 4). The self degradation and lower adsorption of the sensitizers on titania surface and their relative physical / chemical instability hinders its practical application. In most of the cases, sacrificial electron donor should be continuously added to regenerate the sensitizers (Path 5), although in few cases, water [4c] or organic pollutant [5] itself could act as electron donors. Another novel version of coupled semiconductor is $\text{FeTiO}_3 / \text{TiO}_2$ [7], wherein transfer of holes from sensitizer to titania takes place (Path 6). This kind of coupled semiconductor can have practical significance compared to the previous composite systems [4-6].

Chelating compounds like H_2O_2 [8a] or chlorophenol [8b] with surface Ti-OH groups can result in visible light response for titania *via* ligand to metal charge transfer transition which is critically dependent on the nature of the groups anchored on the titania surface and their electron density. However, achieving complete mineralization of the targeted compounds is rather difficult [8c].

Surface fluorination of TiO_2 has drawn significant attention in recent years since it facilitates the generation of free hydroxyl radicals which are highly oxidative as compared to the surface bound hydroxyl radicals [9a]. The replacement of isovalent hydroxyl groups by fluoride ions forces the holes to oxidize solvent water molecules (Path 7) and adsorbed fluoride ions desorb the surface bound hydroxyl radicals in the Helmholtz layers generating free hydroxyl radicals (Path 8) [9b]. In addition, surface $\equiv\text{Ti-F}$ serves as reactive electron trapping site (Path 9) and also suppresses the formation of deep traps [9c]. Surface fluorinated TiO_2 is also known

to enhance the formation of singlet oxygen and lead to the degradation of cyanuric acid under UV irradiation [9d], which is otherwise inert for photocatalytic degradation in TiO₂ suspension [9e].

Noble metal deposition on titania serves as passive sink for electrons *via* Schottky barrier (Path 10) and also shifts the band gap absorption to visible region due to the surface plasmon resonance effect. The photocatalytic activity critically depends on the work function of the deposited metal and on the ratio of M / Mⁿ⁺ distributed on the semiconductor surface [10]. Synthesis of titania by co-doping with two or more foreign ions has drawn significant attention for its multifunctional electronic properties and favorable surface structure. This type of doped titania can be actually beneficial in terms of stability, reusability and for enhanced efficiency [11]. Furthermore, it is suggested that the defects and imperfections within the lattice caused by co-doping have little adverse effects on the activity of titania [11d].

Towards the end of this century, exploring the photocatalytic application of anatase {001} facet was another recent venture in TiO₂ photocatalysis. The {001} facet have higher surface energy compared to widely reported {101} facet and, hence, {001} nano sheets with a low density of defects can reduce the recombination of photogenerated electron-hole pairs

on grain boundaries thus improving the photocatalytic efficiency [12]. The traditional method of using highly corrosive HF as capping agent to synthesize {001} facet by most of the research groups [12b] was overcome by the use of tetrafluoroborate-based ionic liquid by Yu and co-workers [12c]. The visible light active {001} TiO₂ facet doped either with N [12d] or Mo [12e], or C [12f], or N / S as codoped [12g] nanomaterials exhibited superior activity for pollutant degradation, while Pt deposited {001}TiO₂ facet was found to be efficient in water splitting [12h]. Recent work by Yu and co-workers, showed that fabricated dye sensitized solar cells based on {001} titania nanosheets exhibited higher photoelectric conversion compared to titania nanoparticles and Degussa P25 [12i].

3. Conclusions

In conclusion, researchers are optimistic that wide variety of known strategies of TiO₂ modification by tailoring, tuning and structuring it is possible to alter the electronic, chemical, bulk and surface structure for effective utilization of solar light with hindered charge carrier recombination.

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