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Photocatalysis of TiO_2Nanoparticles

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ABSTRACT

Titanium dioxide is a wideband gap semiconductor that can be excited to produce electron– hole pairs when irradiated with light.Such photoinduced electron–hole pairs have been utilized to generate electricity in solarapplicationss, to split water into hydrogen and oxygen, to oxidize and degrade inorganic /organic/biologicalcompounds in environments aswell as to create superhydrophilicity. This review would assist the readers to obtain an overview of this exciting and promising field.

Keywords- *Superhyrdophilic, Titanium dioxide, Photoactivity, Photocatalyst.*

I.INTRODUCTION

Titanium, the world's fourth most abundant metal (exceeded only by aluminium, iron, and magnesium) and the ninth most abundant element (constituting about 0.63% of the Earth's crust), was discovered in 1791 in England by Reverend William Gregor, who recognized the presence of a new element in ilmenite[1].Titanium dioxide is the oxide of titanium with a chemical formula of TiO_2. It is also known as titanium (IV) oxide, titania. Photoactivity ofTiO_2 was first noticed in 1929[2]when it was used as white pigments in buildings. Compared with the bulk TiO_2 materials, theTiO_2nano-materials have attracted moreattentions. Because of high surface-volume ratio,TiO_2 nanostructures provide increased surface area at which photo-induced reactions may occur, enhancing light absorption rate increasing surface photo-induced carrier density,enhancing thephoto-reduction rate, and resulting in higher surface photoactivity.At the same time,the high surface-volume ratio of the nanoparticles enhance the surface absorption of OH^- and H_2O, increasing the photocatalytic reaction rate.Upto nowTiO_2 nanoparticles have been applied in photocatalytic water-splitting [3], purification of pollutants[4], photocatalytic self-cleaning[5], photocatalytic antibacteria[6], photo-inducedsuperhydrophilicity[7] as well asin photovoltaics[8] and photosynthesis[1].

II.PROPERTIES OF TITANIA

1. Physical Properties of TiO_2.

The polymorphs of $TiO_2$are,

- Anatase (tetragonal),
- Rutile (tetragonal),
- Brookite (orthorhombic).

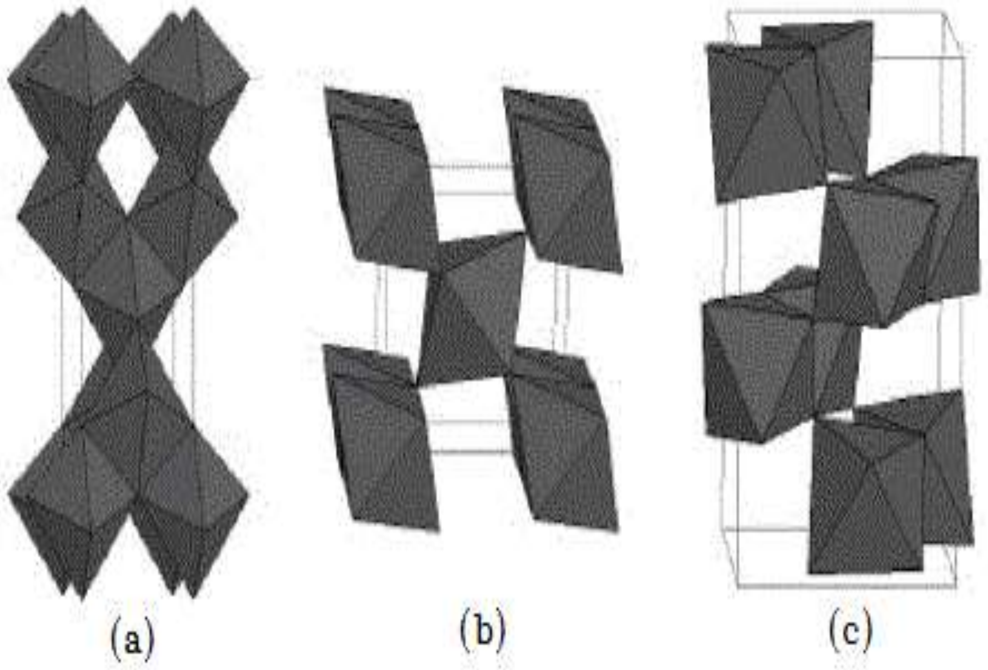

Figure 1: (a) Anatase, (b) Rutile, (c) Brookite.

The metastable anatase and brookite phases can irreversibly convert to stable rutile upon heating[9]. Among these polymorphs, only rutile and anatase showphotocatalytic effects. Both of them are inexpensive, chemically stable, harmless and photocatalytic. The crystallographic structure of rutile consists of cornershared TiO_6octahedra in a tetragonal cell[10]. The structure of anatase consists of edge-shared TiO_6octahedrainatetragonalcell[11]. Rutile and anatase show very similar physical properties while slight differences exist. The physical property causes rutileTiO_2 nanoparticles absorb violet visible light while anatase absorb UV to show photo-induced catalytic effects[12].

2. Photoactivity of TiO_2 Nanoparticles.

Anatase possesses an energy band gap of 3.2eV with an absorption edge at 386 nm which lies in the near UV range. Rutile has a narrower energy band gap of 3.02eV with an absorption edge in the visible range at 416 nm[13]. Both forms are photocatalytic. When TiO_2 is exposed to an UV light with a wavelengthof 280–400 nm (3.10–4.43eV), the UV light will be absorbed by TiO_2 and an electron is elevated from the valence band to the conduction band of TiO_2, leaving behind a hole in the valence band, as shown in Fig. 2, to form electron–hole pairs.

$$TiO_2 + h\upsilon \rightarrow e + h^+ \quad (1)$$

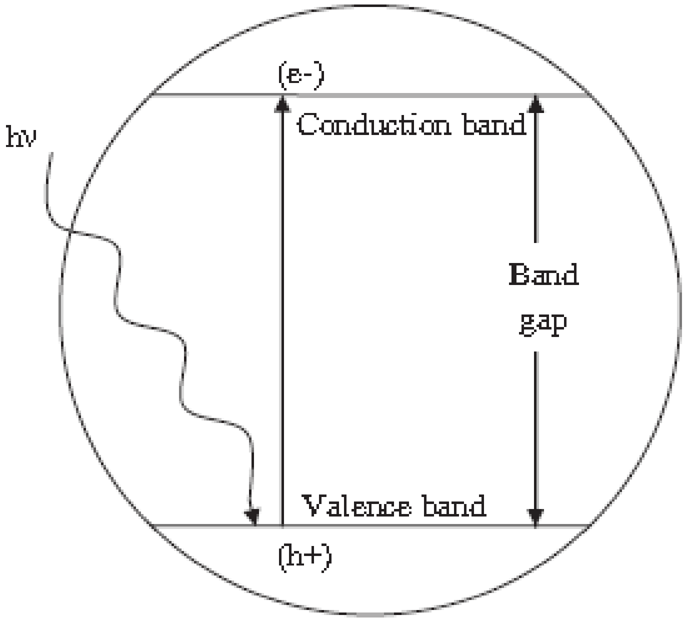

Figure 2: Illustration of photo-generation of charge carriers in a Photocatalytic TiO_2 nanoparticle.

This excited electrons and holes can either be used directly to create electricity in photovoltaic solar cells or drive a chemical reaction, which is called photocatalysis. In the photo-activated applications, reactive species are usually adsorbed on TiO_2 surfaces to enhance photo-induced performances[14].

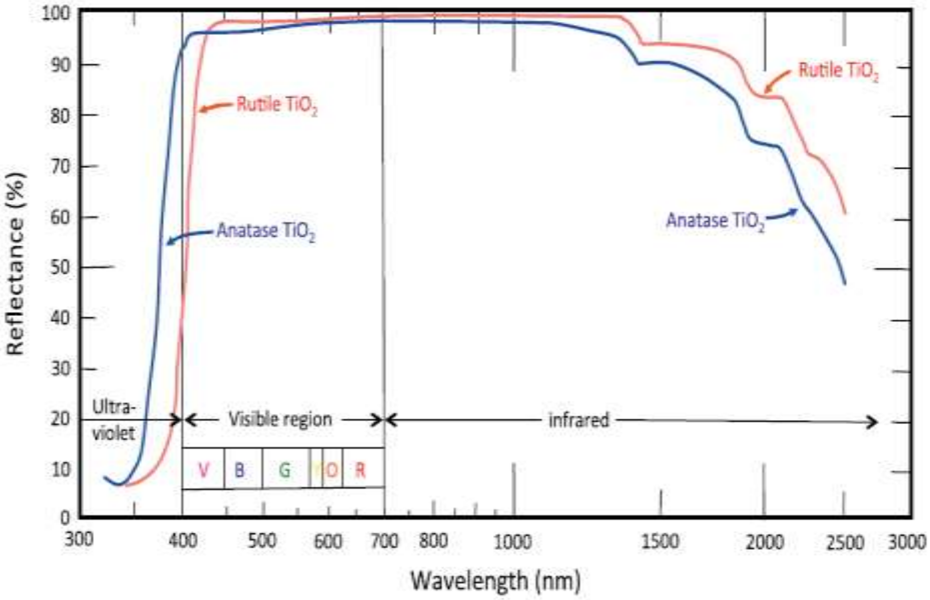

Figure 3: Reflectance of TiO_2[15].

3. Applications on Photocatalysts.

Among various photocatalysts,TiO_2 has the most efficient photo-activity, the high estability,guaranteed safety to humans and environment,and the lowest cost.Therefore TiO_2 photocatalysts are almost the only photocatalyst suitable for industrial applications at present and also probably in the future [16].

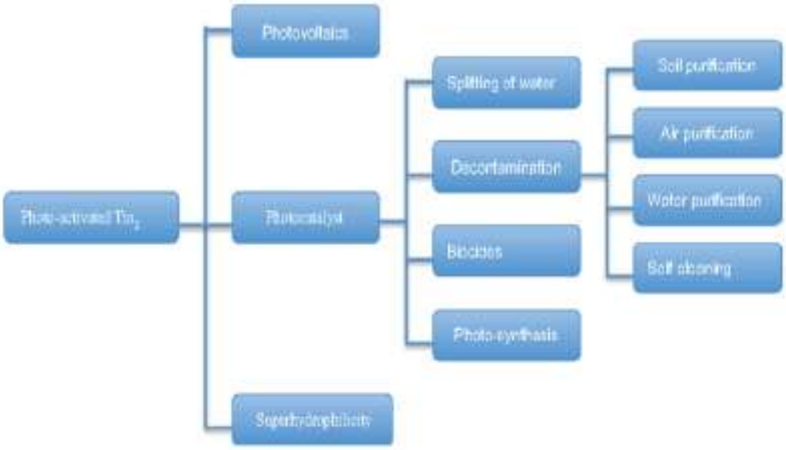

Figure 4: Applications ofTiO_2 photocatalyst.

As showninEq. (1), under an UV irradiation, electrons in the valence band of TiO_2 will be activated to the conduction band, forming electrons(e−) with high activity. At the same time, holes(h+) will be created in the valence band. Therefore the formed electron–hole pairs are strong redox systems. The photo-produced holes h+ on TiO_2 nanoparticle surfaces can oxidizeOH^- and H_2O molecules absorbed onTiO_2 surfaces into hydroxyl radicals $^{\cdot}OH$.

$H^+ + OH \rightarrow {}^{\cdot}OH$ (2)

The holes can also facilitate oxidation through the presence of absorbed water onTiO_2 surfaces

$H^+ + H_2O \rightarrow {}^{\cdot}OH + H^+$ (3)

At the same time, the electrons in the conduction band can facilitate reduction of electron acceptors through the presence of absorbed air onTiO_2 surfaces to form adsorbed radicals

$e + O_2 \rightarrow {}^{\cdot}O_2$ (4)

These formed hydroxy and peroxy radicals are atomic species with a free unpaired electron, possessing strong ability to degrade organic pollutants and to split water. These photo-activities occur on Ti atom surfaces. In order to emphasize the location of the photo-activities, the chemical formation of the high-active radicals at Ti surfaces are also expressed as

$Ti4+ \ldots OH + h\upsilon \rightarrow Ti3+ + {}^{\cdot}OH$ (5)

$Ti3+ + O2 \rightarrow Ti4+ + {}^{\cdot}O2$ (6)

$Ti4+ \ldots O2 + H2O \rightarrow Ti4+ + {}^{\cdot}OH$ (7)

On combining these equations,

$H_2O + O_2 + h\upsilon \rightarrow {}^{\cdot}OH + {}^{\cdot}O_2$ (8)

These photo produced hydroxyl and peroxyl radicals, expressed in Eqs. (2-8), in turn oxidize and degrade organic/ inorganic materials.

4. Self cleaning of Organic compounds.

The initial process of self-cleaning of organic compounds is the generation of electron–hole (e−/h+) pairs on theTiO_2 nanoparticle surfaces expressed inEq. (1). The produced holes react with absorbed water to produce hydroxyl radicals $^{\cdot}OH$. The produced hydroxyl radicals have enough oxidizing power to convert any organic compounds toCO_2 and water

[17].

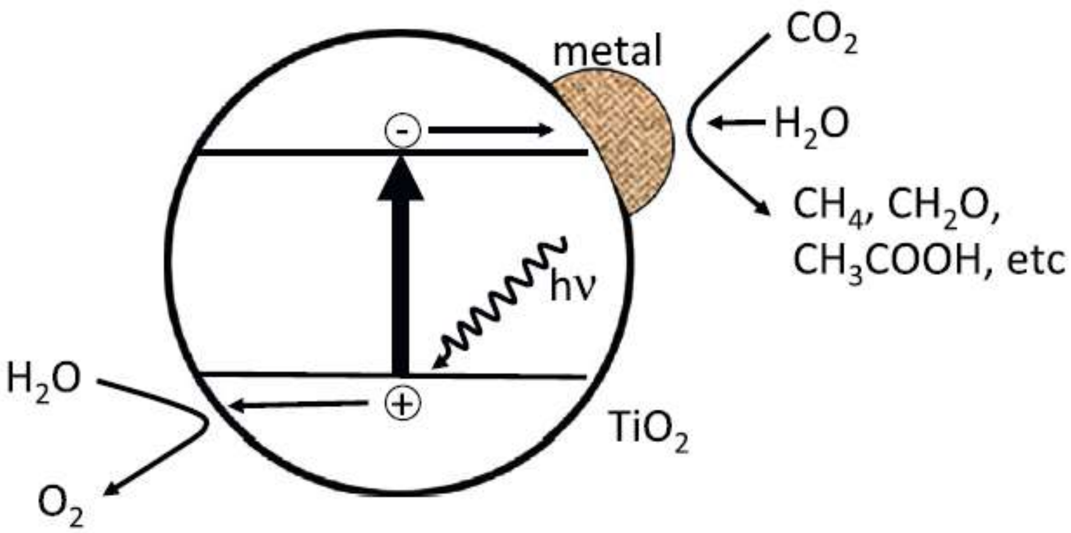

Figure 5: CO_2 photo-reduction on aTiO_2nanocatalyst[13].

The photo-inducedradicals($^{\cdot}OH$ and $^{\cdot}O_2$) expressed in Eq. (8) oxidize the organic compoundsinto CO_2 and H_2O. Thus it is practical, through TiO_2 coating, to maintain clean windows and windshields, remove finger marks off walls, reduce colony density ofmicro-organisms on hospital walls, oxidise oil films of water. The self-cleaning application and photocatalytic mechanism of TiO_2 self-cleaning have been reviewed[18].

5. Superhyrdophilicity

UV illumination of TiO_2 may induce a patchwork of superhydrophilicity (i.e.,photoinducedsuperhydrophilicity or PSH) across the surface that allows both water and oil to spread [18]. This PSH is accompanied by photocatalyticactivity, as both phenomena have a common ground; so the surface contaminants will be either photomineralized or washed away by water. A possible application is self-cleaning windows[19].

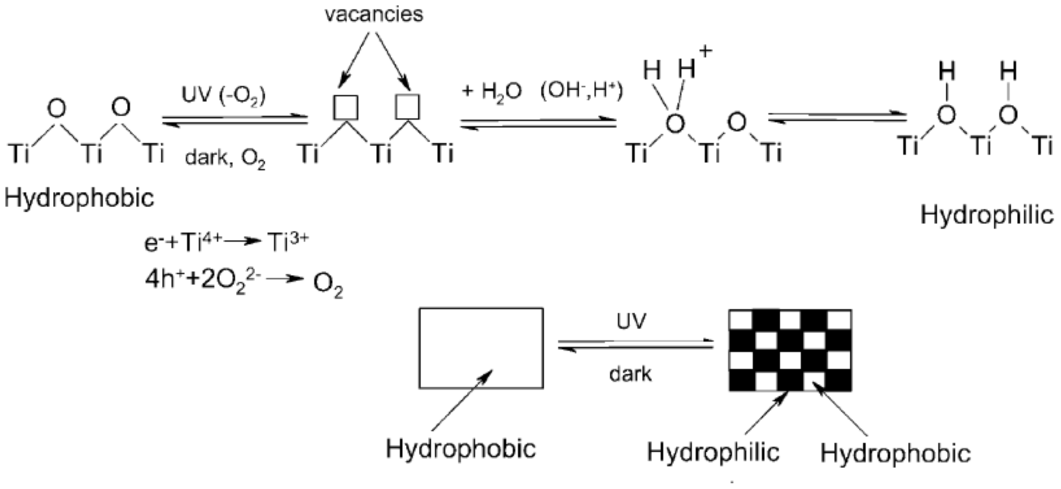

Figure 6: Mechanism of photoinducedsuperhydrophilicity of TiO_2[20].

PSH involves reduction of Ti(IV) cations to Ti(III) by electrons and simultaneoustrapping of holes at lattice sites (usually bridging oxygen) or close to thesurface of the semiconductor[21]. Such trapped holes weaken the bond between theassociated titanium and lattice oxygen, allowing oxygen atoms to be liberated, thus creating oxygen vacancies[22]. The subsequent dissociative adsorption of water at the site renders it more hydroxylated. An increased amount of chemisorbed OH^- leads to an increase of van der Waals forces and hydrogen bonding interactions between H_2O and OH^-. Water can easily spread across the surface and hydrophilic properties will be enhanced[23].PSH was found to be of primary commercial importance due to the anti-foggingand self-cleaning properties of the deposits. The technology is now being increasingly used in commercial applications, particularly in Japan[24].

6. Future aspects of TiO_2 Photocatalysts

TiO_2photocatalysts are stable and highly efficient. However TiO_2 catalysts can only be excited by UV light, which only occupies as small part of thesolar spectrum. In order to improve the utilization of solar energy, TiO_2 catalysts should work under visible light in the future. Morphology of TiO_2 nanocrystals affects the photocatalytic activities of TiO_2 catalysts. It is reported that the crystallographic facets affect photocatalytic activities of TiO_2[25]. The electron and hole relaxation rate strongly depend on size of TiO_2 nanocrystals too[26], affecting the efficiency of TiO_2nanocatalysts. TiO_2 nanocrystals with controlled morphology and controlled size are expected in the coming decades to increase the photocatalytic activities of TiO_2[27]. With the rapid developments of nano-engineering and nanotechniques, highly sufficient TiO_2 catalysts are expected towork undervisiblelight in the21stcentury.

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