

## Brief Review on Some Major Factors Affecting Visible Light Activity of Titania Photocatalyst

Review Article

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## Abstract

As sunlight is an excellent source of clean energy, research for harnessing the energy via an efficient photocatalyst that is active under visible light is actively underway. Titania is well accepted as a photoconductor and photocatalyst under ultraviolet light. Effort to make it visible light active has been growing. This review article presents some factors involving the photocatalytic activity of titania which is active under visible light in terms of crystallography. Based on recent progress, several suggestions are made for a better visible light active titania.

**Keywords:** Titania; Photocatalyst; Visible Light; Crystal Lattice; Hetero Junction; Excitons; Charge Separation.

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## Introduction

Titania is well known for its usefulness as a photocatalyst under ultraviolet light (UV). For more practical and broader applications, the photocatalytic activity (PCA) under visible light (VL) has been actively pursued over a decade. Interest in VL active photocatalysis has been motivated in part by the realization that sunlight is effectively an inexhaustible energy source. Most frequent effort to boost visible light photocatalytic activity (VLA) included doping the titania crystal lattice. More successes have been shown by anions and nitrogen in particular [1-3]. Hydrogenated titania surface and increased the solar absorption. Dye-sensitization technique [4-6] is well utilized. Surface incorporation of high electrical conductivity metal nanoparticles is well known for its surface plasmonics [7-10].

For high PCA, one of the requirements for a catalyst is high specific area (SSA). In the synthesis of high SSA nanoparticles, one chooses to use a low temperature method such as solution or sol-

gel process. A dilemma encountered in this is that the particles produced at a low temperature contain much residual impurities such as water ( $H^+$ ,  $H_2O$ ,  $OH^-$ ,  $H_3O^+$ ), solvent, and any additives that had to be present to optimize the process [11,12]. Conventionally these are removed by the subsequent calcinations steps which are also used to promote crystallinity. These steps involving elevated temperatures will cause the surface area reduction as well as any unwanted phase transformation. This may be overcome by nonaqueous solution process followed by low temperature drying or dehydration processes [12-19].

Another major factor known to affect the PCA is efficient separation of the photogenerated charges, i.e., excitons of  $e^-$ s and  $h^+$ s. Heterojunctions are shown to be effective site in reducing the recombination rates of the photogenerated  $e^-$ s and  $h^+$ s [13,20-32]. Heterointerfaces between crystallographic phases are critical to many photocatalyses including solar energy conversion. Understanding structure/composition at the metal/metal oxide or metal oxide/metal oxide interfaces, the ability to tailor and tune those interfaces are then essential elements in developing more efficient photocatalysts [28-32]. In this review article, the major factors contributing to the VLA are mentioned and crystallographic features directly related to VLA are discussed.

Titania is known to have three polymorphs: Anatase (An), rutile (Ru), and brookite (Br) [33,34]. These three  $TiO_2$  crystallographic phases have similar chemical properties, but have different crystalline structures. An and Ru are tetragonal, whereas Br is orthorhombic [33]. An phase  $TiO_2$  is photocatalytically the most active under UV [29,33-37]. At an ambient condition, Ru  $TiO_2$  is thermodynamically the most stable phase [33-35]. An is most widely utilized as photocatalyst under UV because it exhibits the highest SSA with an ease of production [33-35]. As one calcines An, it begins to transform to Ru at a temperature near 400°C depending on the SSA and/or the crystallite size [33]. Br phase is metastable, least well known, and is the most difficult to synthesize [33-35]. There are conflicting reports on the photo-

catalytic properties of Br phase of titania [33-40]. Some claim Br is the most photocatalytically active [34,38-40] and some report An is [28]. However, An exhibits the largest band gap energy and hence the least active under VL. A low temperature solution process often yields mixed phase of titania with different proportions depending on the experimental variables [11,33,38,39]. By varying the synthesis conditions, e.g., time, temperature, and pH, the polymorphic phases in titania can be controlled [11,33,38,39].

Along the line can a mixed phase titania be more photocatalytically active than a single or pure phase An? Based on heterojunctions promoting the charge transport in the excitons across the phase boundary, a mixed phase structure could be more photocatalytically active [35]. One well known example of this is Degussa Aeroxide TiO<sub>2</sub>, also known as P25, which consists of 79% An and 21% Ru [41].

## Results and Discussion

A low temperature synthesis method, called the “water based ambient condition sol” (WACS) process, yielded well crystallized high surface area polymorphic nanoparticle titania with Br as the predominant phase [11,33,38,39]. However, this water based low temperature synthesis method incorporates water or protons from the solvent water into the lattice [11,33,38,39] as shown in Figure 1. The extraneous protons will create cation vacancies, e.g., 4 H<sup>+</sup> ions creating 1 Ti<sup>4+</sup> ion vacancy by the charge neutrality principle. Upon calcination the protons bonded to oxygen anions can be removed as water by the reaction 2OH → H<sub>2</sub>O + O<sup>2-</sup>. Removing the lattice protons and/or synthesis in a lesser water environment has enhanced optical [42], dielectric [43-47], and/or catalytic properties in other metal oxides [17,47,48].

A polymorphic titania with Br as the major phase, i.e., polymorphic brookite Titania (PBT) - produced by WACS process [11-14] followed by a post-treatment in hot N-methylpyrrolidone (NMP) solvent, labeled as SACS200 - is shown to much enhance VLA [12-14]. Table 1 lists the titania samples discussed in this review with the corresponding phase compositions, crystallite sizes, and SSAs of PBT as compared with other reference titanias. Figure 2 shows UV-Vis spectra of these titania [38]. PBT200 which is titania with 53% Br and 45% An before the proton extraction shows some VL absorption while NMP treated PBT, i.e., SACS200 showed much increased VL absorption. Postech TiO<sub>2</sub> that is N-doped An titania showed some VL absorption while P25 showed no VL absorption. Nanoparticle titania with crystallite size <10 nm of Br as the predominant phase exhibits a moderate VL absorption. A polar anhydrous solvent NMP treatment of PBT enhanced VLA significantly. These titanias tested for photocatalytic degradation of methyl orange (MO) under VL irradiation with a 14 W fluorescent lamp are shown in Figure 3 [12]. SACS200 which is An/Br mixed phase shows superior VLA to NMP treated TiO<sub>2</sub> (TiO<sub>2</sub>SACS200) despite its higher SSA. The difference between the two titanias is that SACS200 is An/Br mixture and TiO<sub>2</sub>SACS200 is single phase An. P25 treated with NMP (not shown here) hardly showed any enhanced VLA [12-14]. This means that the superior VL PCA of SACS200 must be attributable to the mixed phase of Br and An.

The superior VL photocatalytic activity was explained as the effective charge separation by the intercrystalline electron transport from Br to An grains complemented by the strong VL absorption with the nitrogen species incorporated from NMP. The NMP here had a dual role of removing the entrapped protons from the crystal lattice of titania and introducing VL absorbing nitrogen

Figure 1. Protonated Titania crystal lattice from WACS process

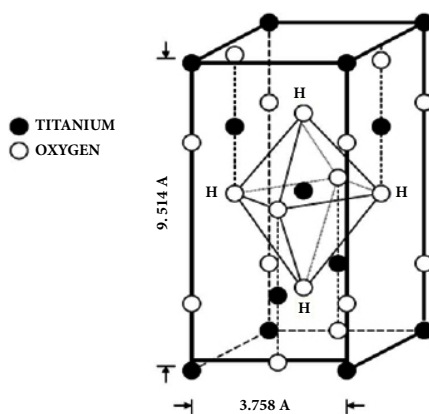


Table 1. Titania samples with phase compositions, the corresponding crystallite sizes, and specific surface areas

| Sample ID                | Phase content in wt%, |       |        | Crystallite size in nm | BET surface area<br>m <sup>2</sup> /g |
|--------------------------|-----------------------|-------|--------|------------------------|---------------------------------------|
|                          | An                    | Br    | Ru     |                        |                                       |
| PBT200                   | 45, 6                 | 53, 7 | 2, 18  | 157                    |                                       |
| SACS200                  | 44, 6                 | 53, 8 | 3, 11  | 138                    |                                       |
| P25                      | 79, 21                | -     | 21, 40 | 56                     |                                       |
| Postech, N-doped         | 100, 22               | -     | -      | 93                     |                                       |
| TiO <sub>2</sub> SACS200 | 100, 7                | -     | -      | 173                    |                                       |
| HBK                      | 100, 9                | -     | -      | 200                    |                                       |

Figure 2. UV-Visible spectra of various titanias

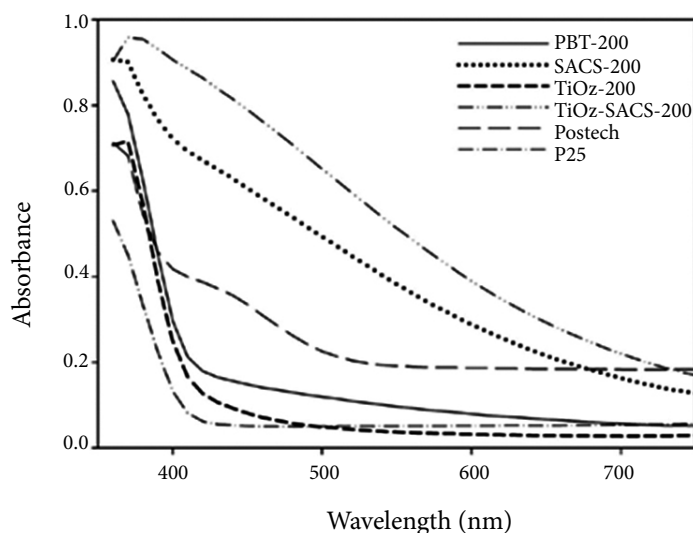
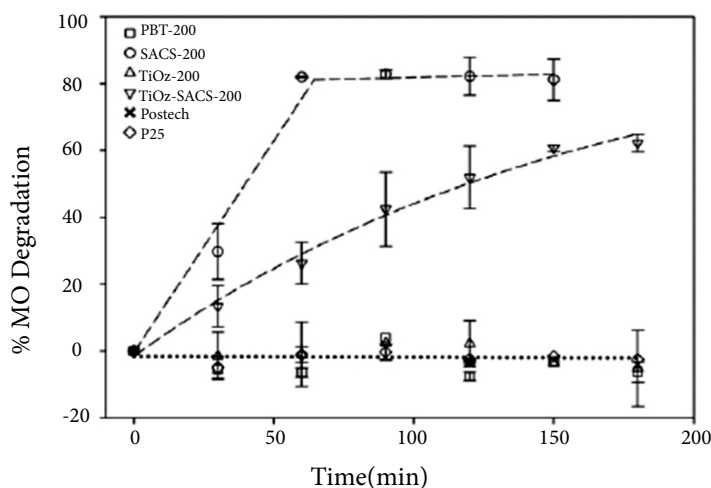
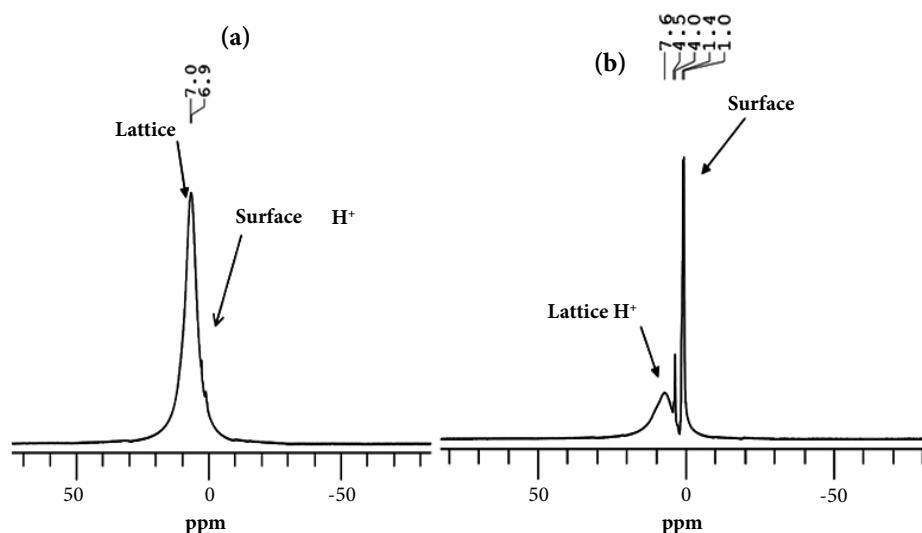


Figure 3. Degradation rate of methyl orange dye by VL photocatalytic action of various titanias.

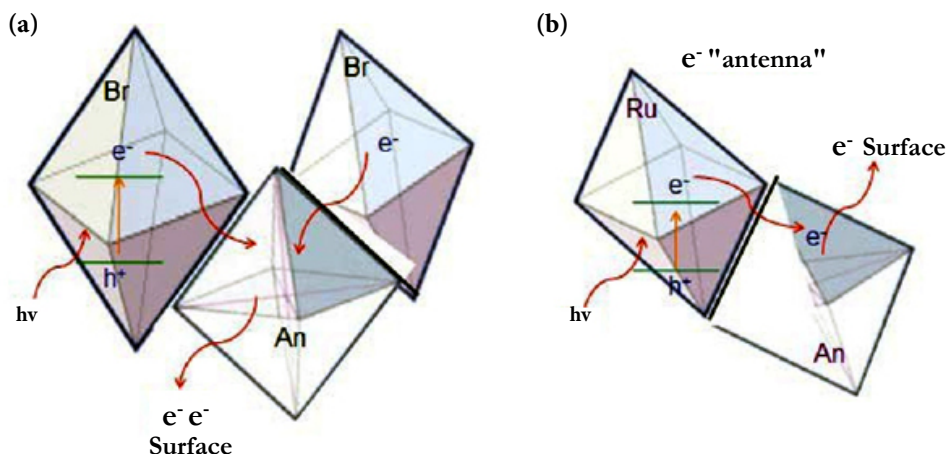
Figure 4. Solid state  $^1\text{H}$  MAS NMR spectra of (a) before NMP treatment and (b) after NMP treatment of PBT.

doping effect. These lattice protons extracted by NMP at a low temperature was confirmed by TGA, FTIR and solid state proton MAS-NMR spectroscopy as shown in Figure 4 [14].

The significance of this technique is tailoring the defect chemistry without sacrificing the surface area and the optimum polymorphic composition. This crystallographic composition has also shown

superior antimicrobial activity to single phase reference titanias [49]. The Br/An mixed phase titania is analogous to the An and Ru mixed phase in P25 as shown in Figure 5. The superior UV photocatalytic activity of P25 has been delineated by the efficient intercrystalline electron transport and charge separation by the minor rutile phase acting as the electron "antenna" [50]. Ozawa et al. [51] proposed strong coupling between An and Ru in their

Figure 5. Illustration of charge separation mechanism for the enhanced VLA in (a) SACS200 analogous to (b) P25 under UV [13].



mixed phase titania. Xia *et al.* [52] supported the efficient charge separation in P-25 titania via molecular dynamic simulation and density functional theory along with Raman spectroscopy. Gai *et al.* [36] also showed superior PCA for an N-doped An/Br polymorph by efficient electron transport of the excited  $e^-$ s from Br to An. The probable mechanism, analogous to the commercial reference titania P25, suggests an effective intergrain electron transfer and charge separation. This, in turn, reduced the electron-hole recombination rate [12,13,35,36,39].

The importance of charge separation via heterojunction in photoconductors for a more efficient PCA has been emphasized by many researchers [20-29,50-52]. Xia *et al.* [52] showed by density of states computed by DFT that the band gap in a mixed phase titania decreased from 3.2 eV of An to 2.0 eV as the proportion of rutile phase increased up to about 50%. Li *et al.* [40] presented Br having indirect band gap energy of 2.85 eV. These suggest the band gap of Br/An polymorph is significantly below that of An (3.2 eV) to absorb VL.

As the calcination temperatures of PBT increased, Br and An in PBT transformed to Ru [11]. Also as Ru phase increased and Br phase decreased in the polymorph, the VLA decreased [33]. Postech sample, which is a hydrothermal nitrogen doped single phase An, absorbed some VL as shown in Figure 2 of UV/Vis spectra. However, it was VL inactive under the 14 W VL source for MO degradation (Figure 3). SACS200 titania has shown to be superior to all other reference titanias in generating hydrogen from aqueous EDTA solution under VL [13]. Hydrogen generation rate from water was shown to follow the same trend as shown for MO photocatalytic decomposition in Figure 3. HBK titania is a commercial anatase titania with the name Hombikat having SSA > 200 m<sup>2</sup>/g. Despite the high surface area of HBK, the hydrogen generation under VL was only that of untreated PBT, which has SSA of ~160 m<sup>2</sup>/g. The crystallographic difference between HBK and PBT is the phase composition. HBK is fully An but PBT is An with more than 50% brookite.

Therefore, the major contributing factors for the observed superior VL-PCA from the An/Br polymorphic SACS200 are listed as: (1) the lower lattice hydroxyl content [11-13], (2) nitrogen doping [12] from NMP for enhanced VL absorption, and (3) the effective charge separation and intergrain transfer of VL excited electrons from one phase to the other [11-13,36]. So several opportuni-

ties to further enhance VL-PCA and photochemical reactions in titania are:

- Tailoring the crystallography of polymorphic titania with respect to crystallographic phase composition during the synthesis, though the optimum phase composition is yet to be determined [13],
- Deprotonation or dehydroxylation from the crystal lattice at a low temperature not losing the high SSA and without altering the optimum phase composition/distribution for the maximum PCA, and
- Introducing or incorporating VL absorbing chromophore in titania that extracts the entrapped protons at the same time.

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