

Current State Of Doped-TiO₂ Photocatalysts And Synthesis Methods To Prepare TiO₂ Films: A Review

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ABSTRACT: The aim of this paper is to review the effects of doping on the electronic structures and photocatalytic properties of TiO₂ including various types of dopants and doping methods currently available. It also discusses the detail of some selected preparation techniques of TiO₂ thin films such as Sol-gel method, Liquid phase deposition (LPD) method, Chemical vapor deposition (CVD) method

Key words: doping, Sol-gel method, Liquid phase deposition (LPD) method, Chemical vapor deposition (CVD) method, photocatalysts

1. INTRODUCTION

The world's ever increasing population and progressive adoption of an industrial based lifestyle led to an increased anthropogenic impact to the environment [1]. Environmental pollution, especially water pollution is one of the most feared problems to the modern societies. Since waste treatment needs high energy consumption and produces toxic liquid and solid side yields alternative treatment processes that consumes less energy and produces non-toxic side products has to be discovered [2]. Recent environmental regulations have led to the development of novel effective treatment technologies that are capable of removing the pollutants rather than transferring them from one phase to another [3]. One such technology is photochemical oxidation of organic contaminants that has received significant attention over the past few decades. Semiconductor-based photocatalysis is an advanced technology for removal of organic and inorganic pollutants in air or solution [4]. Many semiconductors, such as TiO₂, ZnO, Fe₂O₃, CdS, and WO₃ can act as catalysts for photo induced processes due to their electronic structure (filled valence band and empty conduction band [5]. But most of the studies have been focused on TiO₂ because of its high efficiency, long-time, photostability, low cost, reusable, and non-toxic and easily availability [6]. Despite those outstanding properties which TiO₂ displays, there are many shortcomings of TiO₂ as photocatalysts. The major drawback of TiO₂ is its wide band gap. This means that only a small portion of the solar light can be absorbed in the UV region, which occupies only 5% of the total solar spectrum. Thus, efficient absorption of the visible light which constitutes the major part of solar spectrum is prevented and the photocatalytic efficiency of TiO₂ is hindered [7]. The recombination rate of photogenerated electron-hole carriers is rapid. The lifespan of photogenerated electron-hole carriers are approximately 10 ns. The rapid recombination rate of photogenerated electron-hole carriers decreases photo quantum efficiency of TiO₂. Again at the initial stage of the study of photocatalysis, TiO₂ was used in the form of powders. After photocatalytic reaction, filtration step was requested to separate photocatalysts from slurry. This process adds extra cost to the development of commercial applications [7]. Therefore Considerable efforts/methods have been made/proposed to overcome those shortcomings and extend the photoresponse of

TiO₂ further into the visible light region [8]. Some of these methods are briefly introduced here.

Surface sensitization: If the sensitizers are absorbed (either chemi-sorbed or physic-sorbed) on the surface of TiO₂, they can be much more easily excited than TiO₂. Hence, the excitation process can be efficiently improved [9]. The sensitizers can extend the range of excitation energies of the TiO₂ into visible region. However, the sensitizers themselves can be degraded. Thereby, there is a need to add more sensitizers in reaction systems.

Metal and nonmetal-doping: Doping has been proven to be a great method to enhance the photocatalytic activity [10]. In recent years, nonmetal-doping has demonstrated great potential to be applied in the photocatalytic field [11].

Coupling with semiconductor having lower band gap energy: The benefits of this method are the absorption spectrum can be expanded and the carrier separation is effective, the wide band-gap semiconductor can be photoactivated by narrow band-gap semiconductors and in addition, the charge injection from the conduction band of the narrow band-gap semiconductor to that of TiO₂ can lead to efficient charge separation by reducing the electron-hole recombination rate [12].

Preparation of TiO₂ films: In order to solve the shortcoming of separating TiO₂ particles and avoid the filtration step, the techniques of immobilization of photocatalysts have been developed [13] Therefore the objective of this paper is to review:

- The effects of doping on the electronic structures and photocatalytic properties of TiO₂ including various types of dopants and doping methods currently available.
- Some selected preparation techniques of TiO₂ thin films. .

2. Doped-TiO₂ Photocatalysts and Synthesis Methods to Pre pare TiO₂ Films

2.1. Doped-TiO₂ Photocatalysts

Doped-TiO₂ photocatalysts (either with metal ions or non-metal ions) have been proven to enhance the photocatalytic

activity by red-shifting the absorption edge to lower energies direction [10]. Hence, these doped-TiO₂ photocatalysts have been widely prepared and discussed for years. However, it remains difficult to summarize the details of the mechanisms of the optical and photocatalytic properties of the doped-TiO₂ semiconductors due to the various experimental conditions, different kinds of preparation methods and the determination standards of photoreactivity [5]. It is well known that the band structure is one of the most important factors that evaluate the efficiency of TiO₂ based photocatalysts. In this section, experimental photocatalytic property of the visible-light reactive TiO₂ photocatalysts (doped) will be reviewed.

2.1.1. Doping TiO₂ with Metals and Their Preparation Methods

Metal-doping was dominant way at the initial stage of the study about doping effect on the photocatalytic properties of TiO₂. It was reported that the introduction of metal ions into the TiO₂ matrix could significantly influence photoactivity, charge carrier recombination rates, and interfacial electron-transfer rates [14]. Choi and co-workers systematically studied the role of metal-doping in quantum-sized TiO₂ photocatalysts. They explained the role of metal ion dopants of TiO₂ photocatalysts by experiments. The ionic radii of the dopant metal ions they choose were similar to that of Ti⁴⁺. Thus it would be much easier for the substitution of the metal ions into the lattice of TiO₂ matrix. All of the dopants showed that an optimum concentration existed in the degradation of CHCl₃. According to their work, doping with Fe³⁺, Mo⁵⁺, V⁴⁺ and Rh³⁺ could significantly increase the photoactivity. It was concluded that the relative efficiency of a metal ion dopant depended on whether it served as a mediator of interfacial charge transfer or as a recombination center [14]. They claimed that whether the dopant acted as an effective trap or not it depend on the dopant concentration, the energy level of dopants within the TiO₂ lattice, the distribution of dopants within the particles, the electron donor concentration, and the incident light intensity. The most important factor that influences the photoactivity of metal doped TiO₂ was the enhanced interfacial charge transfer in the presence of effective dopants. The iron-doped-TiO₂ was prepared by the hydrothermal method. Titanium (IV) tetratert-butoxide and FeCl₃ dissolved in n-octanol was heated at 230 °C for 2h in the presence of water. Resulting powders were rinsed, dried and calcined at 560 °C. Photocatalyst doped with FeCl₃ have better photoactivity for degradation of dye in aqueous solution under UV and visible light. It was found that the amount of doped iron ions plays a significant role in affecting its photocatalytic activity [15]. Sol-gel method was used to prepare Fe³⁺-doped TiO₂ with different Fe³⁺ concentrations [16]. According to their result, an optimal dopant concentration existed when the dopant content was less than 0.03 mol%; Fe³⁺ acted as the traps to capture the photoinduced electrons, which prohibited the recombination of photoinduced carriers and improved the photocatalytic activity of Fe³⁺ doped TiO₂; while when the dopant content exceeded 0.03 mol%, Fe₂O₃ formed and became the recombination centers of photoinduced carriers. Generally polycrystalline TiO₂ powders which were doped with transition metal ions such as Co, Cr, Cu, Fe, Mo, V and W were found to have strong absorption in visible light region.

2.1.2. Nonmetal-doped TiO₂ photocatalysts

The transition metal doping has been extensively studied to extend the optical absorption of TiO₂ to visible light. However, the metal-doping of TiO₂ photocatalysts also has some drawbacks, such as thermal instability and increase in the carrier-recombination centers [17], whereas, the nonmetal-doped TiO₂ seems to be more promising photocatalysts candidates. The vast research of nonmetal-doped TiO₂ photocatalysts was widely carried out since the early 1990s. Among all the nonmetal-doped TiO₂ photocatalysts, N-doped TiO₂ is the most studied system [18]. Subsequently, several other visible-light active materials, such as, C, F and S, doped TiO₂ were reported [19].

2.1.2.1. Nitrogen-doped TiO₂

Among all these nonmetal-doped TiO₂ systems, nitrogen-doping is the earliest studied system. Furthermore, it has attracted great attentions and becomes the most extensive studied system because of its relatively easier preparation method. N-doped TiO₂ not only improves absorption in the visible region but also demonstrates remarkable photocatalytic properties [17]. He attributed the photoresponse of visible light to the NO_x impurity introduced during preparation process. However, it was not until years later that researchers began to focus on the benign results which N-doped TiO₂ brought. Up to date, there have been several models which have been proposed to describe the origin of the visible-light photocatalytic activity of N-doped TiO₂. These models include:

- i. **Narrowing of the band gap of TiO₂.** Many researchers emphasized the importance of nitrogen-doped TiO₂. Based on the spin-restricted local density approximation calculation, they proposed that the substitutional doping of N for O in the anatase TiO₂ would lead the narrowing of the TiO₂ band gap by mixing N 2p with O 2p states. They emphasized the importance of the substitutional doping of N for O in the TiO₂ matrix in their experiment. Many other groups have also experimentally proved the band gap narrowing of nitrogen-doped TiO₂ [20].
- ii. **Mid-gap localized states of dopants.** It was found that the N 2p orbitals were localized above the O 2p valence bands, which explained the red shift of the optical absorption edge of N-doped. Excitation from the occupied high-energy states to the conduction band (CB) could account for the optical absorption edge shift to the lower energy of visible light region. They also found that N-doping in TiO₂ induced the decrease of the formation energy of an oxygen vacancy, and oxygen vacancy formation usually accompanied the nitrogen doping [21].
- iii. **Formation of color centers.** series of experiments were carried out to study nonmetal-doped TiO₂ (C-, N-, and S-doped) and proposed that the red-shift of the absorption edge of TiO₂ was due to the formation of oxygen vacancies and the formation of the color centers [19].

2.1.2.2. Sulfur-doped TiO₂

It was predicted that the doping of N or S would be most effective among several nonmetals for the mixing of their 2p states with O 2p states. However, they stated that the S ion

was hard to be introduced in TiO₂ matrix for the large ionic radius of S element. They successfully prepared S-doped TiO₂ by various methods. However, according to their experiment results, the S ions could either substitute lattice titanium atoms to form S-cation doped TiO₂ or substitute lattice oxygen atoms to form S-anion doped TiO₂ it depend on the preparation conditions. If the S-doped TiO₂ photocatalyst was prepared by chemically modified method, the S⁴⁺ could be detected from X-ray photoelectron spectra. Photocatalytic experimental results demonstrated that this S-cation doped TiO₂ showed strong visible light absorption and high degradation rate of methylene blue, and 2-propanol [22],

2.1.2.3. Carbon-doped TiO₂

By theoretically studying, the effects of C, N, and S-doping on TiO₂, [23] stated that the carbon-doped TiO₂ was the most promising photocatalyst. There were two reasons to support their conclusion. One was the significant overlap between the O 2p state and the carbon states near the valence band edge. The second was the large valence band red shift of carbon-doped TiO₂. It was also synthesized carbon-doped TiO₂ micro-nanospheres and nanotubes by using chemical vapor deposition method [24]. The percentage of carbon in TiO₂ microspheres and nanotubes was approximately 3% and 5%, respectively by compared to the pure TiO₂, band gap narrowing occurred (2.78 eV for the carbon-doped TiO₂ microspheres; 2.72 eV for the carbon-doped TiO₂ nanotubes). But many other researchers do not agree on the band gap narrowing of carbon-doped TiO₂ [25]. They conducted density functional theory calculation and concluded that the introduction of carbon into TiO₂ matrix could result in modest variations of the band gap and induce several localized occupied states in the gap. It was also stated that the visible light response of C-doped TiO₂ was attributed to the presence of isolated band-gap states rather than band-gap narrowing [26]

2.2. Preparation Methods of TiO₂ Films

TiO₂ thin films not only possess the virtues of photocatalysts, but also avoid the filtration process which accompanies the use of particles. Hence, it is a very economical way to develop TiO₂ thin films. Many methods have been used to prepare TiO₂ films, including wet chemical method, chemical vapor deposition, and physical vapor deposition method [27] some of the methods which are widely used to prepare TiO₂ films are:

2.2.1 Sol-gel method

Sol-gel method is a kind of wet chemical method. When sol-gel method is applied to synthesize oxide films, the precursors can be alkoxide or inorganic salts. Usually, the precursors dissolve in water or organic solution. Then, the solute undergoes hydrolysis reaction and sol is obtained. After the polymerization and loss of solvent process, the liquid sol turns into solid gel. Thin films can be prepared on the substrates by spin-coating, dip-coating or spray-coating. The advantages of sol-gel method for preparing TiO₂ films are:

- No special apparatuses are required, easy to operate
- Uniform films can be easily prepared, the purity of the films are high
- Phase structure of films can be controlled and
- Applied to the industrial production.

Transparent TiO₂ thin films via sol-gel method prepared from tetra-isopropyl titanium ethanol solution containing polyethylene glycol and diethylene glycoll. By decomposing gaseous acetaldehyde, they found that the quantum yield with the prepared TiO₂ films was comparable to the commercial p25. The photocatalytic activity of TiO₂ films depends on the pore size and number, the amount of OH, the surface area and transmittance of TiO₂ films [23]

2.2.2 Liquid phase deposition (LPD) method

According to [26], it was reported a novel method, which was called liquid phase deposition (LPD), to produce thin films. During the deposition process, metal oxide thin films can be deposited onto the immersed substrates via a ligand exchange equilibrium reaction of metal-fluoro-complex ions and F- consuming reaction by the addition of F-scavengers, such as boric acid or metal aluminum. The merits of LPD method are that it is very simple to operate and requires inexpensive equipment. The films prepared by LPD method possess dense structure and good chemical stability. Furthermore, LPD method can be applied to the preparation of films with large surface area, complex shapes, or on various kinds of substrates. The disadvantages of LPD method are:

- The films can only be prepared on the substrates with OH- radicle
- The growth rate of the films is slow.

2.2.3 Chemical vapor deposition (CVD) method

Chemical vapor deposition (CVD) method is widely used to prepare TiO₂ films with high quality, high uniformity and controlled properties. CVD technique has many benefits, such as high deposition rate and easy to deposit films on complex substrates. However, the drawbacks of CVD are also prominent. The biggest one is the call for high temperature (600°C or above) during the CVD deposition process. Hence, many kinds of substrates are not fit for the preparation of TiO₂ at this temperature. In order to lower the deposition temperature, plasma enhanced CVD (PECVD) and metal organic CVD (MOCVD) techniques have been developed. TiO₂ thin films on different substrates, such as stainless steel, titanium, barium borosilicate glass and alumina by MOCVD was deposited and Later, the PECVD was combined together with a metal organic precursor to develop a PEMOCVD method to deposit TiO₂ films [28]. The TiO₂ films were deposited at temperature between 393 and 523 K using titanium tetra iso-propoxide as a precursor. Thus, TiO₂ films could be deposited on some of the substrates which are very sensitive to temperature.

3. CONCLUSIONS

TiO₂ is a really wonderful material in photocatalysis field. It can decompose all the organic pollutants. However, the limits of this material are also obvious. Just as stated above, how to effectively utilize solar energy and effectively separate electrons and holes are still challenges. Scientists have already developed many ways to solve these problems [22] i.e

- (1) Combining different techniques to achieve higher activity.
- (2) Design and development of novel photocatalysts. Up to now, many kinds of new photocatalysts have already been invented. The expansion of photoca-

talyst family is a proof of the prosperity of photocatalysis science.

Based on the benign properties of TiO₂, every one should confidence that TiO₂ is and will continue to be a promising photocatalyst material in the future. Nowadays new patents on the surface of doped particles of TiO₂ are continuously innovated. This invention relates to metal-doped nanoparticles, which find utility as stabilizing ingredients within cosmetics to prevent degradation from sun light, for use in agriculture, horticulture and veterinary medicine, as coatings for plastics and for environmental protection [24]

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