



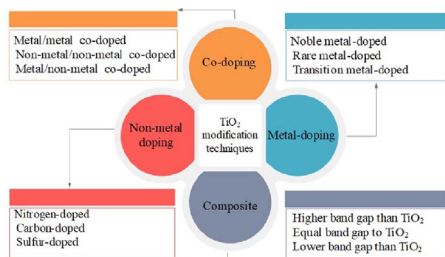
## Review

TiO<sub>2</sub> photocatalyst for removal of volatile organic compounds in gas phase – A review

Zahra Shayegan, Chang-Seo Lee, Fariborz Haghighat\*

Department of Building, Civil and Environmental Engineering, Concordia University, Montreal, Quebec H3G 1M8, Canada

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Keywords:

Volatile organic compounds (VOCs)  
 Photocatalytic oxidation (PCO)  
 Titanium dioxide (TiO<sub>2</sub>)  
 TiO<sub>2</sub> modification  
 Doping  
 Composite

## ABSTRACT

Heterogeneous photocatalytic oxidation process (PCO) is a promising technology for removing indoor volatile organic compounds (VOCs) contaminants. Titanium dioxide (TiO<sub>2</sub>) has been regarded as the most suitable photocatalyst for its cost effectiveness, high stability and great capability to degrade various VOCs. However, no TiO<sub>2</sub>-based photocatalysts completely satisfy all practical requirements given photoexcited charge carriers' short lifetime and a wide band gap requiring ultraviolet (UV) radiation. Strategies for improving TiO<sub>2</sub> photocatalyst activities by doping with different metal and/or non-metal ions and by coupling with other semiconductors have been examined and reported. These techniques can improve PCO performance through the following mechanisms: i) by introducing an electron capturing level in the band gap that would generate some defects in the TiO<sub>2</sub> lattice and help capture charge carriers; ii) by slowing down the charge carrier recombination rate and increasing VOCs degradation. This paper reports the outcomes of a comprehensive literature review of TiO<sub>2</sub> modification techniques that include approaches for overcoming the inherent TiO<sub>2</sub> limitations and improving the photocatalytic degradation of VOCs. Accordingly, it focuses on the recent development of modified-TiO<sub>2</sub> used for degrading gas phase pollutants in ambient conditions. Modification techniques, such as metal and non-metal doping, co-doping, and the heterojunction of TiO<sub>2</sub> with other semiconductors, are reviewed. A brief introduction on the basics of photocatalysis and the effects of controlling parameters is presented, followed by a discussion about TiO<sub>2</sub> photocatalyst modification for gas phase applications. The reported experimental results obtained with PCO for eliminating VOCs are also compiled and evaluated.

## 1. Introduction

Volatile organic compounds (VOCs) are a major group of biogenic/anthropogenic indoor air pollutants with several proven adverse health

effects [1]. VOCs are not only hazardous compounds, but also participate in undesirable mechanisms with harmful by-products, including organic compounds, ozone, and secondary organic aerosols [2]. To solve this problem, several air purification techniques have been

\* Corresponding author.

E-mail address: [Fariborz.Haghighat@Concordia.ca](mailto:Fariborz.Haghighat@Concordia.ca) (F. Haghighat).

proposed for VOCs removal [3,4]. Based on the literature, photocatalyst oxidation (PCO) is a promising VOCs removal method [5,6].

In PCO, VOCs destruction is conducted by using photocatalysts and UV light at ambient temperature [7,8]. Common photocatalysts (semiconductor materials) used in PCO are  $\text{TiO}_2$ , ZnO,  $\text{WO}_3$ , ZnS, and CdS [9,10]. Up to now, the application of titanium dioxide ( $\text{TiO}_2$ ) for photodegradation of organic contaminants [11–13] as well as batteries and solar cells [14–17] has generated significant attention due to its unique characteristics and environmental friendliness. Additionally, this option is attractive given  $\text{TiO}_2$  low cost, simple preparation, high stability, and great capability to degrade various VOCs pollutants [18–20]. Despite its merits, there are some drawbacks, including the large band gap and high charge carrier recombination rate, which restrict its application under visible light or natural solar light irradiation. Given the wide band gap, the electron from  $\text{TiO}_2$  valence band can only be activated under ultraviolet (UV) radiation. Furthermore, the quick recombination of photogenerated electrons and holes reduces photonic efficiency and consequently PCO efficiency as well. Therefore, it is imperative to develop highly efficient photocatalysts that separate charge carriers, slow down their recombination rate, and can also be excited under visible irradiation.

Moreover, to enhance the quantum yield of  $\text{TiO}_2$  under visible light irradiation, two obstacles must be overcome—the generation of photoexcited charge carriers must be enhanced, and the separation efficiency of these photogenerated charge carriers improved [21–24].

Significant efforts have been made to overcome the aforementioned disadvantages via various strategies such as metal or non-metal doping, co-doping, and coupling with other semiconductors. These techniques seem effective for increasing the lifetime of the photoexcited pairs of charge carriers and for shifting the band gap absorption edges to the visible range of irradiation light [22,25,26]. Based on our knowledge, despite considerable reported research on modifying  $\text{TiO}_2$ -based photocatalysts, there is a lack of a comprehensive review regarding the effect of modifying  $\text{TiO}_2$  by dopants on the removal performance of VOCs in PCO processes in the gas phase. Here, we have provided a comprehensive literature review of  $\text{TiO}_2$  modification to present the approaches required for overcoming the inherent  $\text{TiO}_2$  limitations and improving the photocatalytic degradation of VOCs. Accordingly, this paper discusses modification techniques. Such techniques include using metal and non-metal dopants, co-doped ions, and composite  $\text{TiO}_2$  with other semiconductors for photocatalytic degradation of pollutants in the gas phase. This paper also summarizes the effects of controlling parameters such as relative humidity, air flow rate, UV light, and initial contaminate concentration on VOCs decomposition with  $\text{TiO}_2$  photocatalysts.

## 2. Basic principles of photocatalytic oxidation process

Photocatalyst reactions begin when an electron is stimulated with light energy equal to or greater than the semiconductor's band gap (Fig. 1) [27]. Transferring a photoexcited electron from the valence band (VB) to the conduction band (CB) leaves a hole in the latter, which can be a powerful oxidizing agent. Consequently, electron and hole pairs ( $e^-/h^+$ ) are produced [28–30]. These pairs can be generated in femtoseconds (fs). Afterwards, photoexcited charge carriers can be trapped within picoseconds (ps) (shallow trap) or nanoseconds (ns) (deep trap) [31]. The hole and electron can recombine in a few tens of nanoseconds [32,33].

Environmental applications of semiconductor photocatalysts are directly related to the interfacial charge transfer mechanism between the semiconductor surface and organic compounds. Furthermore, the mechanism and time scale of interfacial charge transfers and recombination charge carriers could be affected by the interface structure [34,35]. Moreover, trapped photoexcited holes and electrons exist for nanoseconds and microseconds ( $\mu\text{s}$ ), respectively [32,33]. Interfacial charge transfers might oxidize or reduce pollutants directly or produce

reactive oxidants like hydroxyl radicals and superoxides [36,37]. For  $\text{TiO}_2$ , UV light (about 3% of solar radiation) is a common energy source for PCO because of its wide band gap [38].

The minimum band gap energy required for a photon to generate charge carriers over a  $\text{TiO}_2$  semiconductor (anatase phase) is 3.2 eV. This is equivalent to the absorption of a 388 nm wavelength photon. Therefore,  $\text{TiO}_2$  photoactivation occurs in  $\lambda < 388$  nm, near the UV region [9,28]. Recently, some researchers have modified  $\text{TiO}_2$  to enhance its photoactivity under visible light irradiation [39,40]. Several studies reported that  $\text{TiO}_2$  crystalline form affects its photocatalytic activity [41–43].  $\text{TiO}_2$  has three stable polymorphs—anatase ( $E_g = 3.2$  eV), rutile ( $E_g = 3.02$  eV), and brookite ( $E_g = 3.14$  eV) [10,44]. For PCO, the anatase performs better than the rutile because its conduction band location drives conjugate reactions involving electrons more efficiently [45]. Combining the rutile and anatase phases has been recommended for increasing  $\text{TiO}_2$  photocatalytic activity [27,43]. Given these facts, Degussa P25  $\text{TiO}_2$ , composed of 75% anatase and 25% rutile, is a commonly-used commercial catalyst [27].

To reduce the recombination rate, it is essential that electron acceptors and photogenerated electrons react [46]. When appropriate surface electron acceptors or a surface defect state are absent, and thus unavailable to trap these charge carriers, electrons and holes pair in a few nanoseconds, reducing the efficiency of photocatalytic degradation. It is reported that the anatase conduction band edge exceeds the rutile by 0.2 eV. This difference facilitates the electron transfer via an electron bridge [47]. As a result, the electron based on the anatase conduction band jumps to the less positive rutile part, thereby reducing the recombination rate of electrons and the formation of positive holes in the anatase site [41,48].

Using nanocatalysts helps produced electrons reach the surface and react with electron acceptors in a shorter transfer distance. Therefore, the nanostructure recombination rate is lower than the microstructure [46]. Different  $\text{TiO}_2$  nanostructure materials such as nanorods, nanofibers, nanospheres, nanosheets, and nanotubes have been produced in the nanostructure, which proves its efficiency [49]. It is proven that various parameters, such as crystallite size, specific surface area, pore structure, pore volume, and crystalline phases, have significant effects on photocatalytic performance [50]. The nano-sized catalyst high surface area and high surface density improves catalyst performance and photoactivity [49,51].

In general, several factors influence PCO efficiency, such as humidity, flow rate, the initial concentration of contaminant, the characteristics of the photocatalyst, light source, etc. [7,8]. The effects of above-mentioned parameters are reviewed briefly in Section 4.

## 3. Issues in VOCs photocatalytic oxidation

For key reactions involved in photocatalytic oxidation, see Table 1. Eq. 1 (Photoexcitation) explains  $\text{TiO}_2$  activation by UV light [10,52]. The  $\text{HOO}^\cdot$  in Eq. (5) is an electron acceptor that produces hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). This generates  $\text{H}_2\text{O}_2$  as an oxidizing agent and decreases the recombination rate of electrons and holes by capturing photo-induced electrons, thereby enhancing PCO efficiency (Eqs. 6 and 7). Reduction and oxidation reactions can both occur on the surface of the photoexcited semiconductor. The main oxidant species for degrading VOCs are hydroxyl radicals produced by oxidizing adsorbed water or adsorbed  $\text{OH}^-$ . The final results of total mineralization of hydrocarbon compounds by PCO are  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [10,40].

Photocatalytic oxidation of VOCs includes several processes such as the formation and recombination of electrons and holes, the adsorption of VOCs, chemical degradation, and the desorption of products or intermediates [20]. Moreover, photogenerated electrons and holes may take several pathways. They may recombine on the surface or in the bulk of the semiconductor; electron acceptors may be reduced by electrons; electron donors could be oxidized by holes. Photogenerated electrons and holes could react with  $\text{O}_2$  and  $\text{H}_2\text{O}$  to produce reactive

Download English Version:

<https://daneshyari.com/en/article/6580940>

Download Persian Version:

<https://daneshyari.com/article/6580940>

[Daneshyari.com](https://daneshyari.com)