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Original research article

## Photocatalytic oxidation of acetaminophen using carbon self-doped titanium dioxide

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## ABSTRACT

A new carbon self-doped (C-doped) TiO<sub>2</sub> photocatalyst was synthesized by sol–gel method, in which titanium butoxide was utilized because of its dual functions as a titanium precursor and a carbon source. The effects of calcination temperature from 200 to 600 °C on the photocatalytic activity towards acetaminophen (ACT, which was used as a model persistent organic pollutant) under visible light were examined. The effects of temperature on the structure and physicochemical properties of the C-doped TiO<sub>2</sub> were also investigated by X-ray diffraction, BET measurement, X-ray photoelectron spectroscopy, and scanning electron microscopy. The specific surface area of the as-doped TiO<sub>2</sub> declined as the crystal size increased with increasing calcination temperature. Only amorphous TiO<sub>2</sub> was present at 200 °C, while an anatase phase was observed between 300 and 500 °C. Both anatase and rutile phases were observed at 600 °C. Photocatalytic activity increased as the calcination temperature initially increased from 200 to 300 °C but it decreased as the calcination temperature further increased from 400 to 600 °C. The highest ACT removal of 94% with an apparent rate constant of  $5.0 \times 10^{-3} \text{ min}^{-1}$  was achieved using the new doped TiO<sub>2</sub> calcined at 300 °C, which had an atomic composition of 31.6% Ti<sub>2p3</sub>, 50.3% O<sub>1s</sub> and 18.2% C<sub>1s</sub>.

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## 1. Introduction

Acetaminophen (ACT also known as paracetamol) is a major active pharmaceutical ingredient of numerous commercial cold and flu medicines as it is effective in relieving pain and reducing fever. ACT inhibits prostaglandin synthesis and is heavily used globally in antipyretic, analgesic, and anti-inflammatory drugs for both humans and animals. It is the highest ranking marketed pharmaceutical in many European countries [1] and is one of the most detected pharmaceutical and emerging pollutants in various aqueous environments. It has been detected in European wastewater treatment effluents at concentrations of up to 11.3 mg L<sup>-1</sup> and at more than 65 mg L<sup>-1</sup> in the Tyne River in the UK [2]. The fate of ACT in aqueous environments is complicated and its

photochemical transformation pathways, kinetics and intermediates in surface waters have recently been addressed with great concern [3]. Therefore, global awareness of ACT as an emergent hazardous material and the requirements of technologies for its efficient control have been increasing rapidly [4].

Advanced oxidation processes are reported to be some of the most effective ACT removal approaches [5]. For example, Klammer et al. [6] used iron and H<sub>2</sub>O<sub>2</sub> to degrade real municipal wastewater that had been spiked with ACT (5 and 100 µg L<sup>-1</sup>) and 14 other organics by the solar photo-Fenton process. Titanium dioxide is the most popular photocatalyst in various deprecating techniques for emerging contaminants, owing to its highly stable chemical structure, relatively low cost, non-toxicity, and highly oxidizing photo-generated holes [7,8]. The photocatalytic degradation of ACT in aqueous solution under UV<sub>A</sub> and UV<sub>C</sub> has been studied [9]. TiO<sub>2</sub> can be directly suspended in aqueous solutions for degrading ACT because direct hole (h<sup>+</sup>) oxidation and *ipso*-substitution have been found to occur in the main initial step under UV irradiation [10]. Sarkar et al. [11] also provide a short review of process parameters of TiO<sub>2</sub> nanoparticles and various modes of the processes in

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heterogeneous photocatalysis of pharmaceutical wastes. However, a significant drawback of TiO<sub>2</sub> in photocatalysis is that its band-gap is rather large (3.0–3.2 eV) so it utilizes only a small fraction (approximately 5%) of the solar spectrum [12].

A number of works have been carried out to extend the absorption wavelengths of TiO<sub>2</sub> from UV to the visible region by doping with various elements [13,14]. Carbon and nitrogen are the most common species, as both effectively and economically reduce the band-gap of TiO<sub>2</sub> [15,16]. Chen et al. [17] compared the photocatalytic degradation of methylene blue by visible light using carbon (C-TiO<sub>2</sub>), nitrogen (N-TiO<sub>2</sub>), and co-doped (C-N-TiO<sub>2</sub>) nanoparticles that had been prepared by sol–gel methods. C-TiO<sub>2</sub> was more active than N-TiO<sub>2</sub> although both suppressed the crystal growth of TiO<sub>2</sub>, as revealed by their X-ray photoelectron spectroscopy (XPS), UV–Vis spectroscopy, and lattice parameter analysis. Additionally, doping with carbon may form carbonaceous species at the surface of TiO<sub>2</sub>, which facilitate further degradation under visible light. Park et al. [18] synthesized C-TiO<sub>2</sub> using sol–gel method, as a photocatalyst under visible light, and they found that carbon doping was maximal when the calcination temperature was 200–250 °C. The addition of dopants such as C, N, and S favors the transformation of anatase to rutile in TiO<sub>2</sub>, while a synergistic effect between the anatase and rutile forms reportedly increases the photocatalytic activity of such mixtures [19]. Bi<sub>2</sub>O<sub>3</sub>-co-doped TiO<sub>2</sub> can be synthesized on a large scale via a simple solvothermal-calcining route for the degradation of ACT under irradiation with visible light [20]. Sakatani et al. [21] extensively investigated the binary co-doping of TiO<sub>2</sub> with metal ions and nitrogen for the same purpose. Triple-elemental-co-doped TiO<sub>2</sub> (S-La<sub>2</sub>O<sub>3</sub>) was synthesized using an *in situ* hydrothermal method photocatalytically to degrade sulfosalicylic acid and methylene blue under visible light [22]. Other triple-elemental-doped TiO<sub>2</sub> catalysts (with K, Al, S) have been synthesized to oxidize 2-chlorophenol under visible light [23]. Phosphorous, nitrogen, and molybdenum ternary co-doped TiO<sub>2</sub> photocatalysts (P-N-Mo-TiO<sub>2</sub>) were prepared by sol–gel method to degrade methylene blue under visible light [24]. Quadruple-elemental-doped TiO<sub>2</sub> (C-S-N-Fe<sub>x</sub>) was synthesized to degrade Rhodamine B under irradiation by visible light [25]. Hence, in this work, potassium ferricyanide, K<sub>3</sub>[Fe(CN)<sub>6</sub>], was introduced as a new quadruple-elemental dopant into TiO<sub>2</sub>, through sol–gel method, and the compound thus formed was calcined at various temperatures to study the catalytic activity of ACT under visible light.

The calcination temperature in the synthesis process deeply influences the photocatalytic activity of TiO<sub>2</sub> under visible light [18]. Akpan and Hameed [26] reviewed parameters that affect the photocatalytic degradation of dyes using TiO<sub>2</sub>-based photocatalysts and reported the effects of calcination temperature on the surface areas, pore volumes and pore sizes of the photocatalysts. Tseng et al. [27] also reported that calcination temperature influences the particle size and lattice structure of TiO<sub>2</sub>. Wang et al. [28] examined the TiO<sub>2</sub> photocatalyst that was prepared using sol–gel method and calcined at 150, 200, 250, 270–300 °C. The results indicated that as calcination temperature increased, the photocatalytic activity of doped TiO<sub>2</sub> under visible light firstly increased then declined. This effect is attributable to the combined effect of two factors (carbon self-doping and groups that are photosensitive to visible light) in the synthesized TiO<sub>2</sub> [28]. The decline in the photocatalytic activity of photocatalysts that were calcined at elevated temperatures was also observed in another study of S-N-co-doped TiO<sub>2</sub> that was synthesized by sol–gel method. Mattle and Thampi [29] used the sol–gel method to generate C-doped TiO<sub>2</sub>, in which melamine borate was utilized as a complexing agent and titanium tetrachloride as a precursor for TiO<sub>2</sub>. Accordingly, the effects of calcination temperature (200–600 °C) on the photocatalytic activity of the as-

prepared photocatalyst on ACT degradation under visible light are studied herein.

Characterization of the modified TiO<sub>2</sub> is critical to understanding the relationships between the structure of these photocatalysts and their physicochemical properties. Hung et al. [30] characterized TiO<sub>2</sub> with and without ionic iron dopants using X ray diffraction (XRD), thermogravimetric analysis/differential thermal analysis, Fourier transform infrared spectroscopy, UV–Vis spectrometry, N<sub>2</sub> adsorption and scanning electron microscope (SEM) to elucidate the photocatalytic degradation of dichloromethane under visible light. McEvoy et al. [19] applied XRD, XPS, UV–Vis spectrometry, while Irie et al. [31] utilized XRD, XPS and UV–Vis diffuse reflectance spectroscopy (UV–Vis DRS) to characterize synthesized TiO<sub>2</sub>. Choi et al. [32] applied XRD, DRS, and XPS, and Shen et al. [33] used XRD, SEM, UV–Vis spectrometry and BET to characterize their modified TiO<sub>2</sub>. Therefore, in this study, the quadruple-elemental-doped TiO<sub>2</sub> was characterized by XRD, SEM, BET, and XPS, to elucidate the relationship between its structure and photocatalytic activity.

This study synthesized a new carbon self-doped (C-doped) TiO<sub>2</sub> in order to degrade ACT (which was used as a model compound) under visible light. Titanium butoxide was utilized because of its dual functions as a titanium precursor and a carbon source and potassium ferricyanide was doped by a sol–gel method. As calcination temperature is a critical parameter for synthesized photocatalysts, the effects of calcination temperature from 200 to 600 °C on the photocatalytic activity of ACT under five blue-light Light-Emitting Diodes (LEDs), serving as a visible light source, were examined. Meanwhile, the structure and physicochemical properties of the as-calcined TiO<sub>2</sub> were investigated by XRD, SEM, BET measurements and XPS. The aims of this study are: (1) to investigate the effectiveness of the new photocatalysts calcined at various temperatures in the degradation of the model compound under visible light; (2) to obtain the structural and physicochemical properties of the as-calcined TiO<sub>2</sub> with advanced surface characterization techniques; and (3) to enhance our understanding of the relationship between the structures of the as-calcined TiO<sub>2</sub> and visible-light active sites of the C-doped photocatalyst.

## 2. Materials and methods

All chemicals were used as received without further purification. Analytical-grade titanium butoxide (Ti[O(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>]<sub>4</sub>, 98%, Alfa Aesar), ethanol (EtOH, 99.5%, Merck), and acetaminophen (C<sub>8</sub>H<sub>9</sub>NO<sub>2</sub>, 99%, Merck) were used. All of the solutions were prepared using deionized water that was produced using Millipore system (18.2 MΩ cm).

The crystalline structures and properties were determined by the XRD method with a scanning range of 5–75° with a step size of 0.06°. The specific surface area was determined using the BET method (ASAP 2010, Micromeritics). The atomic composition and chemical states of the TiO<sub>2</sub>-300 (T2) sample were determined using an XPS (PHI 5000 Versa Probe ULVAC-PHI). The surface morphology and elemental analysis of the samples were recorded using a SEM equipped with EDS (QUANTA 200).

The C-doped TiO<sub>2</sub> catalyst was prepared using the sol–gel method, with Ti(OBu)<sub>4</sub> as the precursor. 10 mL Ti(OBu)<sub>4</sub> was mixed with 40 mL EtOH in a beaker with constant stirring at 400 rpm at ambient temperature. After 5 min, 10 mL deionized water was added to the mixture and stirred for 1 h until a homogeneous white sol was formed. 10 mL of EtOH was then added and the mixture was stirred for another 15 min. The mixture was allowed to age and precipitate at room temperature to complete the hydrolysis. The overall formation of the photocatalyst is described as follows:

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