



# Photocatalytic degradation of carbamazepine by tailored BiPO<sub>4</sub>: efficiency, intermediates and pathway

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## ABSTRACT

This study firstly explored the photodegradation of carbamazepine, one of the most frequently detected pharmaceuticals, with tailored BiPO<sub>4</sub> nanomaterials. BiPO<sub>4</sub> was synthesized with a hydrothermal method. The physicochemical properties of the obtained samples were characterized and the results indicated that both the hydrothermal temperature and reaction time influenced the phase, morphology and optical properties of the BiPO<sub>4</sub> catalysts, which may further determine their specific photocatalytic performances. The intrinsic microstructure and optical properties reflected the crystal properties of the catalysts to some extent. The BiPO<sub>4</sub> prepared at 180 °C for 72 h (BPO-180-72) displayed the best photocatalytic activity under UV irradiation, during which carbamazepine was nearly completely eliminated from ultrapure water after 60 min irradiation. The good photocatalytic activity was ascribed to the synergistic effect of monoclinic phase and relatively ordered morphology of the resulting BiPO<sub>4</sub>. Particularly, the monoclinic phase was firstly proved to be more active than the hexagonal phase for BiPO<sub>4</sub> samples. BPO-180-72 removed approximately 72.4% of carbamazepine from lab-prepared simulated wastewater after 60 min irradiation, suggesting the potential application of this material in wastewater treatment. Ten reaction intermediate products were observed and identified by HPLC–MS/MS, and a tentative reaction pathway was proposed. Results indicated that photogenerated holes and hydroxyl radicals were the main reactive species for the photodegradation of carbamazepine in the system.

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## 1. Introduction

The occurrence of pharmaceuticals and personal care products (PPCPs) in the environment is of increasing concern due to their high persistence during wastewater treatment processes [1–3]. Among various PPCPs, carbamazepine (5H-dibenzo[b,f]azepine-5-carboxamide) is one of the most frequently detected pharmaceuticals, which is prescribed for human medicine to control seizures. Carbamazepine is administered chronically to patients with a daily dosage of 100–2000 mg, resulting in high production around the world [4]. Approximately 50% of administered carbamazepine and its metabolites excreted in urine and feces are directly released to the municipal wastewater treatment plants (WWTPs) [5], however, the removal efficiencies of carbamazepine in conventional WWTPs are very low due to its biorefractory nature.

Numerous studies have reported the presence of carbamazepine in environmental samples at relatively high concentrations [1,6]. To

transform these compounds in to non-toxic and pharmaceutically inactive products, methods such as Fenton oxidation, ozonation, TiO<sub>2</sub> photocatalysis and other chemical oxidation processes are generally employed [2,3,7,8], of which photocatalytic oxidation by TiO<sub>2</sub> has become the most attractive clean alternative because of its economic and ecologically safe option for solving energy and pollution problems, and high degradation and mineralization efficiency [9–11]. However, there are some inherent drawbacks with traditional TiO<sub>2</sub> oxidation, such as the rapid recombination of charge carriers and the recovery of the reacted TiO<sub>2</sub> particles [11–13]. It was also reported that the relatively inefficient quantum yield and wide band gap of TiO<sub>2</sub> made it difficult for application at an industrial scale [13]. Bismuth-based nanostructured photocatalysts have been documented to show superior photocatalytic performances than traditional TiO<sub>2</sub> in both UV and visible light regions [14–16]. Bismuth phosphate (BiPO<sub>4</sub>) as one of the Bi salts has potential applications in ion sensing, separating radioactive elements as well as catalysis [17]. The photocatalytic efficiency of BiPO<sub>4</sub> was well verified by the degradation of dyes, such as methyl orange (MO), methyl blue (MB) and rhodamine B (RhB) [14,17,18]. Pan et al. reported the photocatalytic performance of synthesized BiPO<sub>4</sub> oxy-acid salt on dyes degradation, and found the inductive role of PO<sub>4</sub><sup>3-</sup> helped the e<sup>-</sup>/h<sup>+</sup> separation and enhanced its photocatalytic activity [14]. The

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photocatalytic performance of BiPO<sub>4</sub> has been proven to be closely related to its crystalline phase, band gap, surface area and morphologies [17,18]. However, controllably synthesizing the desired catalysts with best activity under different experimental conditions was not systemically studied. Besides, the main targets of photocatalysis by BiPO<sub>4</sub> were dyes, and its ability to degrade PPCPs is not well understood.

The purpose of this study was to investigate the photocatalytic degradation of carbamazepine by fabricated BiPO<sub>4</sub> as a catalyst under UV irradiation. BiPO<sub>4</sub> was synthesized by hydrothermal method, taking into account variables such as hydrothermal temperature and reaction time, since both factors play important roles in simultaneously controlling the size, morphology, and dispersivity of the nanocrystals [15]. The synthesized materials were comprehensively characterized by field emission scanning electron microscope (FESEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), ultraviolet–visible spectroscopy (UV–vis) and X-ray photoemission spectroscopy (XPS) techniques. Liquid chromatography–tandem mass spectrometry (LC–MS/MS) was used to identify the reaction intermediates of carbamazepine, and a tentative reaction pathway was proposed. Additionally, the removal efficiency of carbamazepine in simulated wastewater was also studied by BiPO<sub>4</sub> catalyst with the best catalytic performance, in the view of practical applications.

## 2. Experimental design

### 2.1. Materials

Carbamazepine standard (purity >99%) was purchased from Sigma–Aldrich (St. Louis, MO, USA). The chemicals used for the mobile phase for HPLC–MS analysis included Milli-Q ultrapure water and HPLC grade methanol (Dikma Chemical, China). Other chemicals and reagents, such as Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O, NaOH, and HNO<sub>3</sub>, were in analytical grade and used as received.

### 2.2. Synthesis and characterization of BiPO<sub>4</sub>

BiPO<sub>4</sub> was synthesized via a simple hydrothermal method. Briefly, 1.14 g of Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O was dissolved in 20 mL of ultrapure water, and 20 mL of 0.15 mol/L Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O stock solution was added drop-wise. The mixture (pH = 0.5) was magnetically stirred for 30 min at room temperature, and the obtained suspension was transferred to a 50 mL Teflon-lined autoclave. The influence of hydrothermal temperature and reaction time was investigated by putting the autoclave in the oven at different temperatures (140, 160, 180 and 200 °C) for different time courses (1, 4, 12, 24, 48, 72 and 96 h). After the autoclave naturally cooled down to room temperature, the products were collected and washed with distilled water and absolute ethanol several times, then air-dried at 60 °C for 12 h.

The phase composition of the obtained BiPO<sub>4</sub> catalysts was determined by a Rigaku D/Max-2500 diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). The morphology and size of the catalysts were obtained by FESEM (FEI nanosem 430) and TEM (JEM-100CX II). The specific surface area, total pore volume, and average pore diameter were determined using the surface area and pore-size analyzer (Quantachrome NOVA 2000e). The optical properties of the products were recorded by a diffuse-reflectance UV–vis spectrometer (Shimadzu UV-3600), which was equipped with integrating spheres using BaSO<sub>4</sub> as a reference. XPS analysis was performed by a Kratos Axia Ultra DLD spectrometer with a monochromated Al K $\alpha$  X-ray source ( $h\nu = 1489.6 \text{ eV}$ ).

### 2.3. Photocatalytic reaction

The photocatalytic degradation experiments were performed in a photochemical reactor (XPA-2, Nanjing Xujiang Machinery Factory, Nanjing, China). The UV irradiation was supplied by a 100 W mercury lamp (Institute of Electric Light Source, Beijing, China), which was positioned in the middle of a cylindrical quartz trap. A quantity of 0.2 g of BiPO<sub>4</sub> catalyst was added into 200 mL carbamazepine solution (5 mg/L). Prior to irradiation, the suspension was magnetically stirred in darkness for 30 min to achieve adsorption–desorption equilibrium of carbamazepine on BiPO<sub>4</sub> (a preliminary study indicated that 30 min was sufficient time to achieve adsorption equilibrium). With the light on, an aliquot of 4 mL reaction solution was sampled at given time intervals. The solution was centrifuged at 3000 rpm for 5 min, and filtered through 0.45  $\mu\text{m}$  nylon membrane prior to carbamazepine analysis. The removal efficiencies of carbamazepine were calculated by the following equation:

$$\text{Removal} = \frac{C_t}{C_0} \times 100\%$$

where  $C_0$  and  $C_t$  represent the initial equilibrium concentration of carbamazepine and the reaction concentration at time  $t$ , respectively.

For comparison, simulated wastewater spiked with certain amounts of carbamazepine was conducted under the identical experimental conditions. The chemical composition of the simulated wastewater was referenced to the work of Postigo and co-authors, which met the guidelines established by both the United States Environmental Protection Agency (USEPA) and the Organization for Economic Co-operation and Development (OECD) for moderately hard synthetic freshwater and synthetic sewage, respectively [19]. Solid-phase extraction (SPE) was applied to extract carbamazepine from the simulated wastewater, during which the reaction solution passed through Oasis HLB cartridges (200 mg, 6 mL, Waters Corp., Milford, MA, USA), and the final residues were eluted with methanol.

### 2.4. Analysis of carbamazepine and its intermediates

The HPLC separation was performed using an Agilent 1200 series (Palo Alto, CA, USA) equipped with an Agilent Zorbax Eclipse XDB-C18 column (2.1 mm  $\times$  100 mm, 3.5  $\mu\text{m}$ ). The column was maintained at 30 °C during the sample analysis. The mobile phase consisted of eluent A (methanol) and eluent B (0.1% formic acid in ultrapure water). The flow rate was kept at 0.2 mL/min, and the injection volume was 10  $\mu\text{L}$ . The separation of carbamazepine and its degradation intermediates were achieved with the following gradient program: 0–2 min: 30% A; 2–8 min: 30–70% A; 8–14 min: 70% A; 14–16 min: 70–30% A; 16–18 min: 30% A. The system was re-equilibrated for 10 min between runs. The concentration of carbamazepine was determined by HPLC–SIR–MS (Agilent 6410 triple quadrupole) equipped with an electrospray ionization source (ESI) in negative ionization mode for isolation of  $m/z$  at 237.1 ([M–H]<sup>–</sup>ion).

The identification of oxidative degradation intermediates in the solution was conducted by LC–MS and LC–SIR–MS equipped with electrospray ionization source, which was operated in the negative ionization mode. Selected ion recording (SIR) mode with a dwell time of 200 ms was used to acquire MS spectra of carbamazepine and its intermediates with a scan in the range of  $m/z$  100–500. The nebulizer pressure was set to 35 psi and the flow rate of drying gas was 7 L/min. The capillary and nozzle voltages were 4000 and 0 V, respectively. The flow rate and temperature of the sheath gas were 8 L/min and 350 °C, respectively.

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