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# Effective photocatalytic degradation of paracetamol using La-doped ZnO photocatalyst under visible light irradiation

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ABSTRACT

Visible light-driven photocatalysts of lanthanum (La) doped ZnO nanoparticles were successfully prepared by a facile precipitation method using various La doping concentrations (0.5, 1.0 and 1.5 wt%). La doping did not modify the crystallinity of ZnO significantly, but enhanced the optical absorption of visible light due to the reduction in particle size and band gap energy. La-doped ZnO photocatalysts were applied to treat 100 mg/L paracetamol in aqueous solution under visible light irradiation after 3 h. 1.0 wt% La-doped ZnO photocatalyst showed the highest photocatalytic activity for the degradation of paracetamol with a degradation efficiency of 99% and TOC removal of 85%. Based on the chemical analysis of photocatalytic products detected, proposed mechanism for paracetamol removal by La-doped ZnO nanoparticles under visible light illumination including radical generation with use of photocatalytic degradation and subsequent reaction pathways was proposed.

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## 1. Introduction

In recent decades, a huge number of prescription and non-prescription drugs such as antibiotics, anticonvulsants, antipyretics, cytostatic drugs, and hormones have been consumed around the world [1]. The occurrence and transformation of these pharmaceuticals in the environment has raised concerns about their negative effects on the environment and human health. A lot of unused, expired and residual pharmaceuticals have been discharged into the environment during and after treatment [2,3]. After metabolism in the human bodies, these pharmaceutical compounds are also discharged into the environment through exertion in human urine and manure. As a result, pharmaceutical have been found in sewage, surface water and ground water in many countries [1,4].

Paracetamol (also known as acetaminophen or APAP) is a very common analgesic and antipyretic drug that has been widely used all over the world [5]. The chemical structure and some physical chemical properties of APAP are shown in Table 1.

The presence of trace APAP in drinking water is a public concern since its potential chronic health effects from long-term ingestion have been discovered [6,7]. Acute overdoses of APAP can potentially cause fatal liver damage and the drug's toxicity is the foremost cause of acute liver failure in Western countries, accounting for most drug overdoses in the USA, UK, Austria and New Zealand [8,9]. On August 2013, the US Food and Drug Administration (FDA) issued a new warning that paracetamol could cause rare skin reactions such as Stevens-Johnson syndrome and toxic epidermal necrolysis, which can be fatal [10]. Some studies have suggested that kidney damage or stomach bleeding can occur when high doses of APAP are used [11,12]. In a study conducted in 2000, APAP was ranked as one of the top three drugs produced in England, and consumption of APAP alone totaled more than 400 tons in that year [6,13]. APAP has been found at concentrations of up to 6 μg/L in European countries' sewage [4], up to 10 μg/L in natural water of the USA [14], and at even more than 65 μg/L in the Tyne river in the UK [15].

Considering the potential impacts of pharmaceutical products, particularly APAP, on environment and human health, many management and treatment methods have to be applied to lower their concentrations to non-detectable levels. Some reported APAP treatment techniques include activated carbon adsorption [16,17] as well as advanced oxidation processes including ultrasound [18], Fenton oxidation [19,20] and ozonation [21,22]. Furthermore, a few studies were also reported on the use of photocatalysts for pharmaceutical removal. However, most of them were related to

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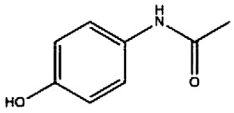
**Table 1**
Information and properties of APAP.

| Category | Detail | Category | Detail |
|---|---|---|---|
| Structure |  | IUPAC name<br>Trade names | N-(4-hydroxyphenyl)acetamide<br>Tylenon/Panadol |
| Molecular mass | 151.163 g/mol | Melting point | 169 °C |
| Density | 1.263 g/cm$^3$ | Water solubility | 12.87 mg/mL |
| log$K_{ow}$ | 0.46 | p$K_a$ | 9.38 |

the use of $TiO_2$ under UV light which requires high energy consumption and contains a UV exposure risk [23,24].

Semiconductor photocatalyst application is a promising technique for the removal poisonous and organic pollutants. Among the numerous semiconductors used, ZnO is one of the most common because of its outstanding properties of physical and chemical stability, low cost and non-toxicity. However, ZnO does have a few drawbacks such as wide band gap that means it absorbs only UV light, resulting in low quantum efficiency. Therefore, developing a visible light-responsive photocatalyst has become one of the greatest challenges in research into ZnO.

Rare earth elements are very important in advanced photocatalytic technologies due to their particular 4f–5d and 4f–4f electronic transitions which are different from the other elements [25,26]. Contrary to their name, rare earth metals are not so rare. There are 17 rare earth elements in the lanthanide series. The lanthanoids with f-orbitals are renowned for being able to form complexes with various Lewis bases such as amines, aldehydes, and alcohols. If lanthanoids are combined with a $TiO_2$ or ZnO matrix, this may provide means for pollutants to be absorbed onto the semiconductor surface [27]. In addition, it is noticeable that rare earth elements used as dopants could take an obviously active effect on cracking and ring-opening of hydrocarbons [28,29]. Thus, very recently, La doped $TiO_2$ nanoparticles have attracted much attention because of their high photocatalytic activity in the degradation of organic contaminants under UV light due to the suppression of electron-hole pairs recombination [6,30,31]. However, there has been no report on the degradation of pharmaceuticals in water using La-doped ZnO under visible light.

In this paper, we report for the first time on the photocatalytic degradation of APAP as a model pollutant. This study hypothesized that the photocatalytic activity of La-doped ZnO would be much higher as compared with pure ZnO. The major aim of this study is to investigate the APAP removal efficiency and photocatalytic removal mechanism under visible light irradiation after preparing La-doped ZnO nanoparticles by a facile synthesis method.

## 2. Experimental

### 2.1. Material preparation

All used chemicals in this study were ordered from Samchun Chemical Ltd., Republic of Korea. Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) (Extra pure) and lanthanum nitrate hexahydrate ($La(NO_3)_3{\cdot}6H_2O$) (Special grade) were used as zinc and lanthanum sources, respectively. Sodium carbonate anhydrous ($Na_2CO_3$) and 4-Acetamidophenol ($C_8H_9NO_2$) (Extra pure) were also purchased for the fabrication procedure. All the chemicals were used without any further purification. Stock solutions that were not used immediately were stored in glass containers for no longer than 2 days before use, while also wrapped with aluminum foil and kept in a cooler fridge to minimize potential photodegradation.

### 2.2. Preparation of photocatalyst

La-doped ZnO nano particles were prepared by a precipitation method using $Zn(NO_3)_2{\cdot}6H_2O$ and $La(NO_3)_3.6H_2O$. Firstly, $Zn(NO_3)_2{\cdot}6H_2O$ and $Na_2CO_3$ were dissolved separately in double distilled water to obtain 0.5 M solutions. Zinc nitrate solution was slowly added into vigorously stirred sodium carbonate anhydrous solution with the approximate addition rate of around 5 mL/min. Next, lanthanum nitrate 0.01 M was slowly added into the above mixture and a white precipitate was obtained. This precipitate was filtered and repeatedly rinsed with distilled water. The resultant solid product was dried at 70 °C for 24 h and calcined in an air oven at 400 °C for 3 h.

### 2.3. Photocatalytic reactor setup

The photocatalytic activity of synthesized materials was estimated by using an illumination system which consists of three 20 W compact fluorescent lamps as the irradiation sources. In a typical process, 0.1 g photocatalyst was suspended in 100 mL APAP with a concentration of 100 mg/L in a 500 mL cylinder glass reactor. Before starting the photocatalytic reaction, the suspension was stirred for 60 min in a dark condition to reach adsorption/desorption equilibrium in the aqueous solution. Photocatalytic reactions were carried out in stable conditions (at temperature 25 °C and shaking speed of 120 rpm). After 3 h irradiation, the suspensions were centrifuged at a speed of 5000 rpm for 15 min to obtain the final remaining solution used for characterization.

### 2.4. Analytical methods

#### 2.4.1. Microstructure characterization

The crystallinity of pure ZnO and La-doped ZnO were analyzed by X-ray powder diffraction using an X-ray diffractometer (XRD – Bruker Model AXS D8 ADVANCE) in the scan range $2\theta = 10^{00}$ to $80^{00}$ using a step size of $0.1^{00}$. Their surface morphologies and microstructures were examined using field emission scanning electron microscopy (FE-SEM – JEOL Model 6500F) and transmittance electron miscroscopy (TEM – JEOL TEM Model 2100). The presence of elements and chemical states of materials were examined using an X-Ray photoelectron spectrophotometer (XPS – Thermo Fisher Scientific Model ESCALAB 250 XI). Structure properties were further examined using Fourier transformation-infraction red spectra (FTIR – Varian Model 670) spectroscopy and all spectra obtained were in the range of 500–4000 cm$^{-1}$. To study the electronic interaction near the optical band gap resulting from the addition of dopant atoms, UV–vis diffuse reflectance spectra

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