

## **Sonochemical Deposition of the La and Ce Nanoparticles on the TiO<sub>2</sub> Photocatalyst for Degradation of Antibiotic**

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### **Abstract**

Novel La-Ce-TiO<sub>2</sub> photocatalysts were successfully synthesized via a facile sonochemical-assisted synthesis method. The photocatalytic degradation of the amoxicillin antibiotic was investigated via the addition of rare-earth metals, namely Lanthanum and Cerium nanoparticles as cocatalysts on the surface of TiO<sub>2</sub>. The synergistic interaction between La and Ce nanoparticles loaded on the TiO<sub>2</sub> shows a profound activity as the amoxicillin removal via La-Ce-TiO<sub>2</sub> photocatalyst was double than the pure TiO<sub>2</sub> sample. Obviously, the sonochemical-assisted method played an important role in minimizing the particles aggregation and thus improving the photocatalytic activity.

**Keywords:** Titanium Dioxide, Sonochemical, Photocatalyst, Degradation, Antibiotics

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## Introduction

The increasing demand and incomplete consumption of antibiotics among the community have led to water contamination due to the improper discharge to the aquatic environment. Among the antibiotics, amoxicillin is the most commonly detected antibiotic pollutants in the domestic wastewater and pharmaceutical industries [1]. This is because amoxicillin is recalcitrant to the conventional wastewater treatment processes owing to its low metabolic degradation. To date, the semiconductor photocatalysis system has garnered much attention as an alternative for conventional wastewater treatment technologies [2]. Among various photocatalyst, Titanium dioxide ( $\text{TiO}_2$ ) has been widely explored owing to its intrinsic features including cheap, abundant, and excellent photochemical stability [3,4]. Nevertheless, the wide bandgap ( $\sim 3.2$  eV) of  $\text{TiO}_2$  corresponds to the UV light activation has hindered its practical application [5]. As a result, extensive studies have been done to suppress the aforementioned limitation via various strategies such as doping, construction of heterostructure system, and surface defect morphology [6]. In addition, the conventional method for synthesizing  $\text{TiO}_2$  has many limitations such as low photocatalytic activity, complex process, and particles agglomeration [7].

With respect to the abovementioned limitations, this report aims to mitigate the limitations exist within the conventional approach in synthesizing the  $\text{TiO}_2$  photocatalyst. Herein, for the first time, we report the synthesizing method for preparing the composite  $\text{TiO}_2$  photocatalyst via a facile sonochemical-assisted synthesis method. Two rare-earth metals, namely Lanthanum and Cerium were chosen as cocatalysts for enhancing the photocatalytic performance of the  $\text{TiO}_2$  photocatalyst. Additionally, we examine the photocatalytic performance of the as-developed photocatalyst using the amoxicillin antibiotic.

## Materials and Methods

### *Preparation of La-Ce-TiO<sub>2</sub>*

The La-Ce- $\text{TiO}_2$  photocatalysts were synthesized using a facile sonochemical-assisted synthesis method. 1 wt. % of the La and Ce nanoparticles and 1 g of  $\text{TiO}_2$  were thoroughly mixed in 50 mL of deionized water. The mixture was continuously stirred for 60 minutes. Afterward, the solution was sonicated for 60 minutes at a frequency of 45 kHz and the temperature was maintained at 40 °C. Then, the heat was applied while the solution was stirred until the water has evaporated. The resultant slurry was then dried in the drying oven at 80 °C. The crystalline phase of the product was examined using X-ray diffraction (XRD; Model: X'Pert<sup>3</sup> powder and Empyrean, PANalytical) with scanning range from 10 – 20° of 2 $\theta$ . A scanning electron microscope (SEM, Zeiss Supra 55VP) was used to identify the morphology of the modified photocatalyst. The optical properties of the modified photocatalysts were examine using DR-UV-Vis Spectrophotometer (Cary 100s) to obtain the energy threshold of the structure. The wavelength was specified at the range of 400 to 700nm. The Kubelka-Munk method was used to determine the bandgap energy of the samples.

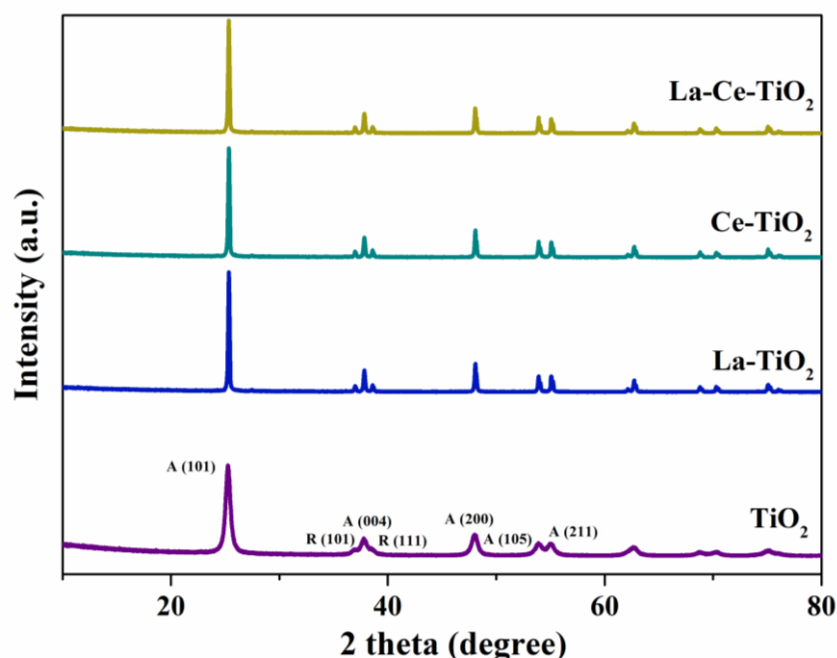
### *Photocatalytic Degradation of Expired Amoxicillin*

The photocatalytic degradation activity was carried out by using Amoxicillin as a mimicking antibiotic wastewater solution. A 500 W halogen lamp was used as a visible-light

source. Generally, an appropriate amount of the as-developed sample was added into 100 mL of 10 mg/L amoxicillin solution. The solution was stirred in a dark reaction condition for 60 minutes to achieve adsorption-desorption equilibrium [8,9]. Upon light illumination, 5 mL of aliquots solution was collected and analyzed using UV-Vis spectrophotometer (UV-1800, Shimadzu).

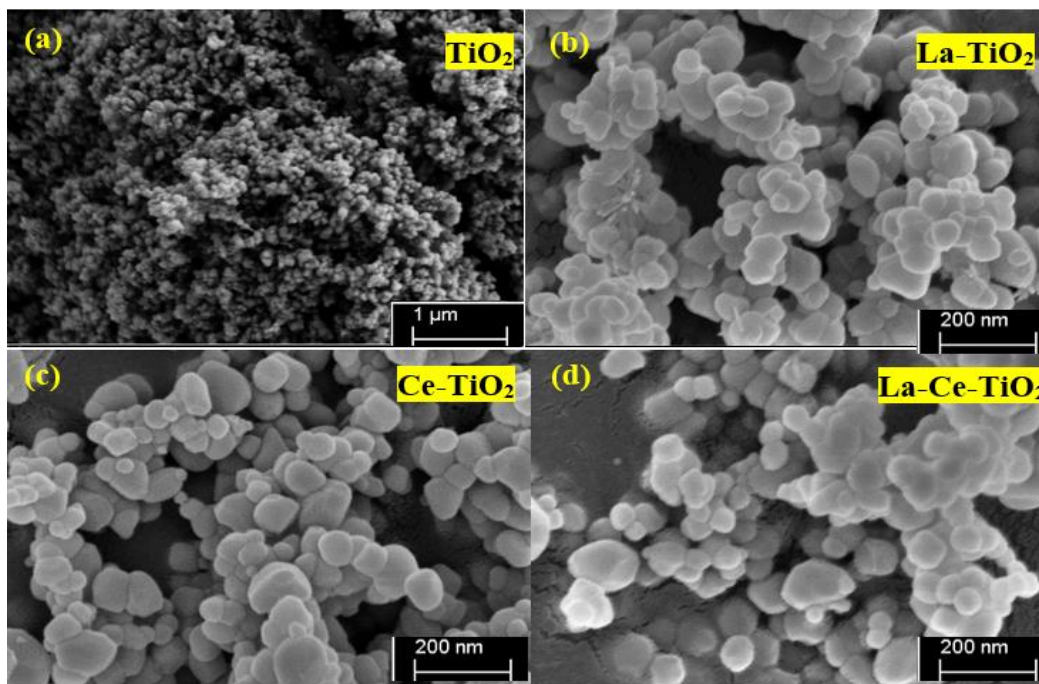
## Result and Discussion

**Figure 1** illustrates the XRD diffraction peaks of the La-Ce-TiO<sub>2</sub> photocatalyst along with the pure TiO<sub>2</sub> nanoparticles. The strong diffraction peaks monitored at 25.2, 37.7 48.0, 53.8 and 55.2 ° of 2θ corresponds to the (101), (004), (200), (105) and (211) crystal planes of the anatase phase of the TiO<sub>2</sub> (JCPDS No. 86-1157) [10]. Meanwhile, the weak diffraction peaks observed at 36.5 and 38.7° of 2θ were attributed to the rutile phase of crystallite TiO<sub>2</sub> (JCPDS No. 21-1276) [11]. It can be seen that the integration of both rare-earth metals onto TiO<sub>2</sub> nanoparticles promotes the anatase to rutile (A-R) transformation (see **Figure 1**) in which the rutile peaks were enhanced compared to the pure TiO<sub>2</sub>.



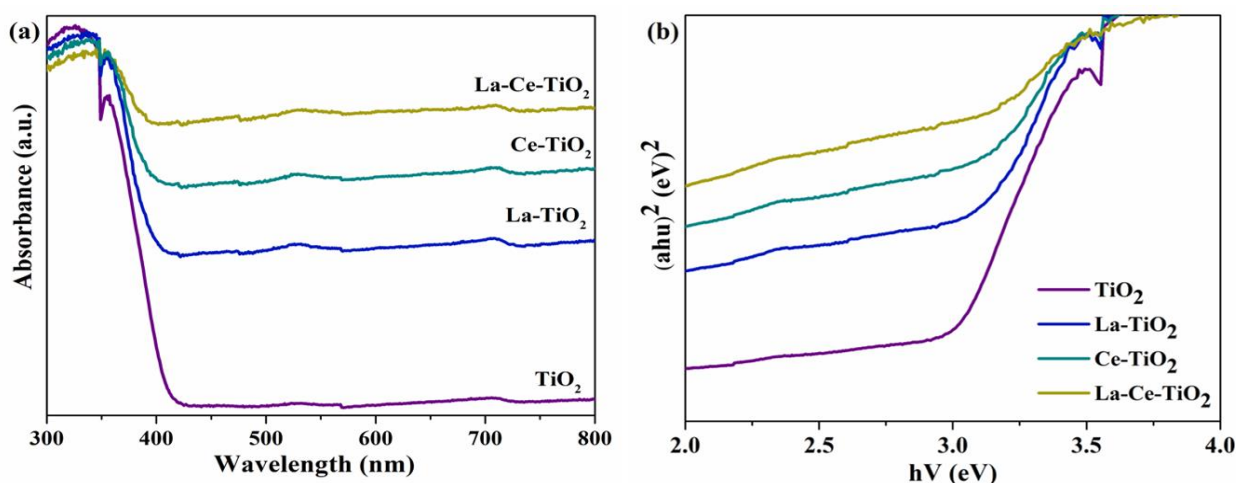
**Figure 1: XRD patterns of the as-developed photocatalyst.**

Although some of the studies claimed that the doping of the rare earth materials hinders this A-R transformation, but our findings show a contradictory result (**Figure 1**). This A-R transformation was presumably due to the formation of more defect center within the composite photocatalyst which results in the lattice imperfection and the micro-strain phenomenon [12]. On the other hand, the anatase phase of the Ce-TiO<sub>2</sub> sample was slightly deteriorated compared to the La-TiO<sub>2</sub>. This is due to the presence of CeO<sub>2</sub> species which preferentially nucleate on the oxygen vacancies within the anatase structure [13]. Nevertheless, the synergistic interaction between La and Ce on the TiO<sub>2</sub> sample along with the sonochemical-assisted synthesis method, results in enhancement on the crystallinity peaks which is known to be beneficial for the photocatalytic degradation performance.



**Figure 2: SEM micrograph images of the as-developed photocatalysts.**

**Figure 2** depicts the SEM morphological structure of the photocatalyst samples. The pure TiO<sub>2</sub> sample showed an agglomerate structure of nanospherical particles. Meanwhile, the composite sample prepared via the sonochemical-assisted method exhibit a typical nanospherical structure similar to the pure TiO<sub>2</sub> with less agglomeration. This signifies that the sonochemical-assisted synthesis approach helps to reduce the agglomeration issues. The agglomeration of particles tends to reduce the exposure of the active site to the targeted pollutants and hence abating the photocatalytic activity. All of the composite samples exhibit the nanospherical structure with a diameter range of 71 – 120 nm.

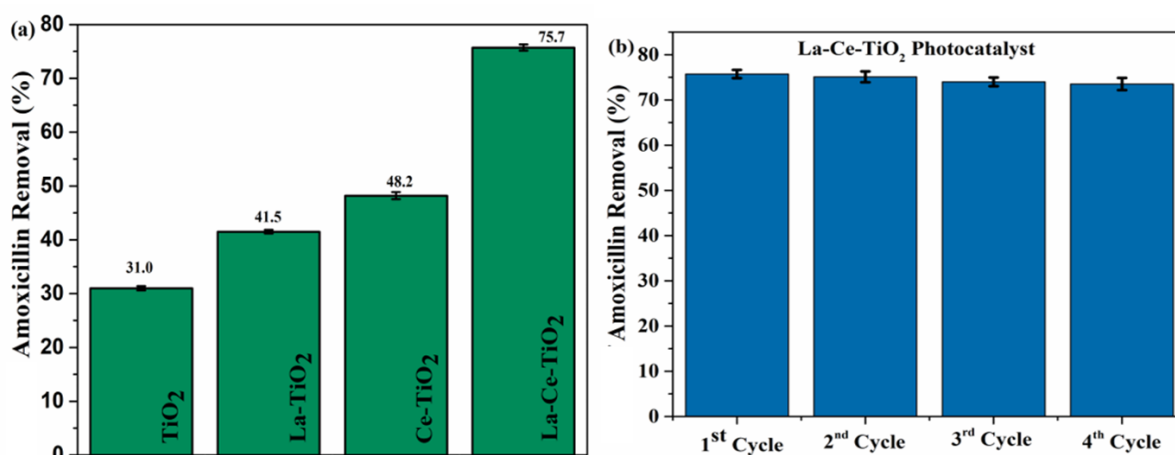


**Figure 3: (a) absorbance spectra and (b) Tauc plot of the as-developed photocatalysts.**

**Figure 3** exhibits the bandgap energy of the as-developed photocatalysts. The calculated bandgap energy for the pure TiO<sub>2</sub>, La-TiO<sub>2</sub>, Ce-TiO<sub>2</sub>, and La-Ce-TiO<sub>2</sub> were 3.12, 2.78, 2.65

and 2.50 eV, respectively. It was found that the addition of La narrows the bandgap energy of  $\text{TiO}_2$  and thus the composite sample was capable of absorbing the visible-light energy instead of UV irradiation only [14]. A similar observation was monitored for the composite Ce- $\text{TiO}_2$  as its bandgap energy falls within the visible-light region. The red-shifted observed indicates the presence of Ti–O–Ce bonds. Additionally, this red-shifted signify the photocharge carrier transfer transition between the Ce 4f orbital and the band edge position of the  $\text{TiO}_2$  [15]. Furthermore, the synergistic interaction between La and Ce loaded onto  $\text{TiO}_2$  nanoparticles further enhanced the light absorption capacity of the pure  $\text{TiO}_2$ .

The photodegradation performance of the photocatalyst via amoxicillin removal was illustrated in **Figure 4**. It was found that the addition of two rare-earth metals, namely La and Ce significantly improved the performance of pure  $\text{TiO}_2$  by more than two-fold. Additionally, the photodegradation performance of the La-Ce- $\text{TiO}_2$  sample remains outstanding with only a 2.2% reduction in the activity after 4 cyclic performance. The superior photocatalytic degradation performance as well as outstanding recyclability features signify the great synergistic interaction between La and Ce. The formation of electron trap and defects via the addition of Ce nanoparticles prolong the lifetime of the holes in the system which will further react to produce more active radicals to be used in the photocatalytic reaction [14].



**Figure 4: (a) Total amoxicillin removal via the as-developed photocatalysts and (b) the reusability test of La-Ce- $\text{TiO}_2$  sample under visible-light-irradiation.**

In addition, the differences between the reduction and oxidation potential of the  $\text{Ce}^{4+}/\text{Ce}^{3+}$  with respect to the band edge location of the  $\text{TiO}_2$  hinder the photocharge carrier recombination and enhanced the chemisorbed oxygen on the surface of the photocatalyst. Similarly, the addition of La onto  $\text{TiO}_2$  photocatalyst prolongs the photocharge carrier lifetime and hinder the photocharge carrier recombination. Generally, the ionic radius of La ion is bigger than the Ti ion, consequently prevent La ion from entering the lattice structure of the  $\text{TiO}_2$  [16]. Nevertheless, this limitation can be mitigated by employing a suitable approach. The use of the sonochemical-assisted synthesis approach in preparing the composite sample does facilitate the migration of the La ion into the  $\text{TiO}_2$  lattice structure which results in the formation of the Ti–O–La bond. The presence of a La ion in this bond formation would result in the imbalance of the photocharge carrier [17]. This phenomenon will allow the hydroxide ions to be adsorbed on the surface of the photocatalyst and producing the  $\bullet\text{OH}$  radicals. The formation of these  $\bullet\text{OH}$  radicals would be beneficial in the photodegradation activities. Furthermore, the  $\text{La}^{3+}$  ion could

act as a hole trap within the TiO<sub>2</sub> photocatalyst which can prevent the photocharge carrier from recombine and prolong their lifetime.

## Conclusions

In summation, a sonochemical-assisted synthesis method was proposed for the first time for synthesizing the La-Ce-TiO<sub>2</sub> photocatalyst. The characterization results revealed that the synergistic interaction between two rare earth metals helps to improve the activity of the pure sample via narrowing the bandgap energy within the visible-light region, prolong the photocharge carrier lifetime and minimize the rate of the photocharge carrier recombination.

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## Author Contributions

M.F.R. Samsudin: Writing – Original Draft and Editing, Formal Analysis, F. Maeght: Formal Analysis, N. Kamarudin: Formal Analysis, and S. Sufian: Supervision, Project administration, and Funding acquisition.

## Disclosure of Conflict of Interest

The authors have no disclosure to declare.

## Compliance with Ethical Standards

The work is compliant with ethical standards.

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