



# Active composite photocatalyst synthesized from inactive Rh & Sb doped TiO<sub>2</sub> nanorods: Enhanced degradation of organic pollutants & antibacterial activity under visible light irradiation

Su-Gyeong Kim<sup>a,1</sup>, Love Kumar Dhandole<sup>a,1</sup>, Young-Seok Seo<sup>a</sup>, Hee-Suk Chung<sup>b</sup>, Weon-Sik Chae<sup>c</sup>, Min Cho<sup>a</sup>, Jum Suk Jang<sup>a,\*</sup>

<sup>a</sup> Division of Biotechnology, College of Environmental and Bioresource Sciences, Chonbuk National University, Iksan 570 752, Republic of Korea

<sup>b</sup> Jeonju Center, Korea Basic Science Institute, Jeonju 54907, Republic of Korea

<sup>c</sup> Daegu Center, Korea Basic Science Institute, Daegu 41566, Republic of Korea

## ARTICLE INFO

### Keywords:

Composite photocatalyst  
Titanate nanotubes  
TiO<sub>2</sub> nanorod  
TiO<sub>2</sub> nanoparticle  
Organic pollutants decomposition  
Pathogens disinfection

## ABSTRACT

In this study, rhodium-antimony co-doped TiO<sub>2</sub> nanorods and titanate nanotube (RS-TONR/TNT) composite was hydrothermally synthesized from rhodium-antimony co-doped TiO<sub>2</sub> nanorod (RS-TONR). Initially, RS-TONR and RS-TONR/TNT samples were photocatalytic inactive under visible light irradiation ( $\lambda \geq 420$  nm). Catalytic performance of RS-TONR/TNT composite was improved by surface protonation and then post-calcination process. Calcination of protonated sample has transformed most titanate nanotubes of RS-TONR/TNT into anatase TiO<sub>2</sub> nanoparticle (TNP) in the composite. This composite contains admixture of both rutile phase of TiO<sub>2</sub> nanorods and TiO<sub>2</sub> nanoparticle (48/RS-TONR/TNP-400). The photocatalytic activity of 48/RS-TONR/TNP-400 composite was increased for decomposition of organic compounds under visible light irradiation. In the composite structure rutile phase of TiO<sub>2</sub> nanorods composed of rhodium-antimony co-doping is responsible for absorption of visible light irradiation and low band edge position of TNP facilitate the transport of conduction band charge carriers. At next step, 48/RS-TONR/TNP-400 sample was loaded with copper oxide as co-catalyst. The synergistic effect of calcination and co-catalyst was observed as Cu(3 wt%) 48/RS-TONR/TNP-400 sample showed the highest photocatalytic performance for degradation of organic pollutants. Also, Cu(3 wt%) 48/RS-TONR/TNP-400 photocatalyst was successfully applied for disinfection of both Gram-negative and Gram-positive bacterial pathogens such as *E. coli*, *S. typhimurium* and *L. monocytogenes*.

## 1. Introduction

TiO<sub>2</sub> is an important photocatalyst due to its strong oxidizing power, non-toxicity, and long-term photo stability [1]. Photocatalytic properties of TiO<sub>2</sub> have been extensively studied as a means to control hazardous pollutants such as aromatic and synthetic compounds with successful performances demonstrated in many cases [2]. Since the discovery of structural modified TiO<sub>2</sub> based materials, one-dimensional (1-D) nanostructure materials including titanate nanotubes (TNTs) have been demonstrated to be promising nanostructured adsorbent material for removing heavy and toxic contaminants [3–7].

Hydrothermally synthesized titanate nanotubes have large specific surface area and high pore volume. Such titanate nanotube synthesis is also a simple, cost-effective, and environment-friendly technology

[8,9]. To retain the photocatalytic activity of TNTs, a suitable and feasible strategy is by using post-thermal treatment to form well-crystallized TiO<sub>2</sub> while retaining tubular structures. Several studies have demonstrated enhanced photocatalytic activity of calcined TNT towards organic dye and organic pollutant photodegradation [10]. Murakami et al. have studied modified TNTs to obtain improved photocatalytic activity for acetaldehyde decomposition [11]. Xiong et al. have also studied adsorption and photocatalytic degradation of methylene blue by calcined TNTs [12]. However, rutile and anatase, the two common forms of TiO<sub>2</sub>, have band gaps of 3.00 eV and 3.20 eV respectively. They are active under ultraviolet radiation only [13].

Several researches have studied the co-doping effect of rhodium and antimony for visible light photocatalysis [13–15]. Niishiro et al. have studied photocatalytic activities of rutile-type TiO<sub>2</sub> doped with rhodium

\* Corresponding author.

E-mail address: [jangjs75@jbnu.ac.kr](mailto:jangjs75@jbnu.ac.kr) (J.S. Jang).

<sup>1</sup> These authors have equal contribution.

and co-dopants under visible light irradiation [14]. Their results have confirmed that rhodium and antimony co-doped TiO<sub>2</sub> has low band-gap energy and good photocatalytic performance under visible light irradiation. The present study is focused on the synthesis of material in order to find visible active materials.

Reduced band gap is sufficient to enhance the photoactivity of photocatalyst under visible light. Charge recombination factor is also a challenging task to harvest high photocatalytic activity. Several studies have shown various approaches to reduce charge recombination rate. Hou et al. have studied the effect of Cu<sub>2</sub>O nanoparticles loaded TiO<sub>2</sub> nanotube arrays and found that improved photoelectrocatalytic activity attributes to the synergism between Cu<sub>2</sub>O nanoparticles and TiO<sub>2</sub> nanotubes arrays [16]. This Cu<sub>2</sub>O nanoparticle at the conduction band of TiO<sub>2</sub> nanotubes facilitate the transport of charge carriers towards the band edge of TiO<sub>2</sub> nanotubes which enhance the decomposition of 4-chlorophenol by oxidization. Surface charge recombination also the key factor to design the proper heterojunction composite materials for photocatalysis applications [17–21]. There have been several approaches reported for improvement of photocatalytic performances of TiO<sub>2</sub> based nanostructured materials [22–26]. A similar approach of reduce electron-hole recombination rate has been well demonstrated by Liu et al. where Mn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> nanoparticles deposited TiO<sub>2</sub> nanotube arrays show high photoelectrocatalytic performance in the degradation of 2,4-DCP [27].

In this study, molten salt flux method was used to prepare Rh-Sb co-doped TiO<sub>2</sub> nanorods (RS-TONR). This manuscript mainly focused on synthesis of composite nanostructures by hydrothermal synthesis route at different hydrothermal reaction times (36, 48, and 60 h). The composite materials contains admixture of rutile phase of TiO<sub>2</sub> and titanate nanotubes (48/RS-TONR/TNT). The advantage of rutile phase of TiO<sub>2</sub> nanorods over titanate nanotubes is its visible light absorption property due to rhodium-antimony co-doping. Visible light absorption is a key factor for designing a visible-light-induces photocatalysts. Initially, RS-TONR and RS-TONR/TNT samples show very poor photocatalytic activity under visible light irradiation. Further, post-calcination (400 °C) process transformed titanate nanotubes of 48/RS-TONR/TNT into TiO<sub>2</sub> nanoparticles (TNP-400) and remained mixture of rutile phase of co-doped TiO<sub>2</sub> nanorods. In order to boost their photocatalytic performance, 48/RS-TONR/TNP-400 composite was loaded with different amounts of copper oxide. Among other as-prepared samples higher photocatalytic activity was observed for Cu(3 wt%) 48/RS-TONR/TNP-400 for degradation of Orange (II) dye and disinfections of bacteria. High photo-generated charge carrier lifetime was observed for Cu(3 wt%) 48/RS-TONR/TNP-400 sample. Composites Cu(3 wt%) 48/RS-TONR/TNP-400 and 48/RS-TONR/TNP-400 samples show 98% decomposition of bisphenol A (BPA) within 2 h under visible light irradiation.

## 2. Experimental procedure

### 2.1. Chemical reagents

All chemical reagents were used without further purification. Na<sub>2</sub>HPO<sub>4</sub> (Kanto chemicals, 99%), NaCl (JUNSEI Chemicals, 99.5%), P25 (Degussa), RhCl<sub>3</sub>·3H<sub>2</sub>O (Kojima, 99%), Sb<sub>2</sub>O<sub>3</sub> (Acros, 99%), NaOH (Samchun, 98%), Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (JUNSEI, 99%), and Orange (II) sodium salt (Aldrich, 85%) were purchased. HCl (Assay 35%, JUNSEI Japan) acid was diluted with deionized (DI) water (CBNU, pH 7) in 25% acid to water volume ratio.

### 2.2. Synthesis and modification of Rh and Sb co-doped titanate nanotubes

In our previous method, Rh-Sb co-doped TiO<sub>2</sub> nanorods (RS-TONR) were prepared by molten salt flux method. [28] RS-TONR/TiNT was synthesized by hydrothermal method. Briefly, 0.7 g of RS-TONR powder was stirred in 70 mL of 10 M NaOH. The mixture solution was

transferred to 125 mL Teflon hydrothermal reactor and placed inside a hot air oven at 160 °C. The same process was followed for different reaction time periods (36, 48, and 60 h). The colored pulp mixture was washed with DI water centrifugation and once its pH reached 7, it was dried at 80 °C in oven. These samples that were hydrothermally synthesized for 36 h, 48 h, and 60 h were a mixture of rhodium and antimony doped nanorod (RS-TONR) and titanate nanotube (TNT). They were denoted as 36/RS-TONR/TNT, 48/RS-TONR/TNT, and 60/RS-TONR/TNT, respectively.

For protonation of as-synthesized RS-TONR/TNT, 0.3 g of RS-TONR/TNT dry powder was dispersed in 40 mL of DI water and the mixture was stirred for 30 min. Then 24 mL of hydrochloric acid solution was added to the mixture under continuous stirring for 3 h. Hydrochloric acid was used as 1 M. The mixture was washed with DI water until its pH reached 7. It was then dried in a hot air oven at 60 °C overnight. Washed and dry RS-TONR/TNT was calcined inside a box furnace at different temperatures (300, 400, 500 °C) for 2 h. These samples were denoted as RS-TONR/TNP-300, RS-TONR/TNP-400, and RS-TONR/TNP-500, according to different temperatures used for calcination.

Further, prepared calcined samples were loaded with different amount of copper oxide nanoparticles. Briefly, Cu<sub>x</sub>O particles were deposited on the surface of titanate nanotubes by wet impregnation method. In a typical experiment procedure, 48/RS-TONR/TNP-400 sample and quantified amount of Cu<sub>x</sub>O precursor solution (2 wt%, 3 wt %, and 4 wt%) were grinded together in the presence of ethyl alcohol (3 mL). Thin paste of the mixture was allowed to dry and two times mixing ethyl alcohol again. Dried samples were calcined at 300 °C for 2 h inside a box furnace.

### 2.3. Photocatalytic performance

To determine the photocatalytic activity, reaction was carried out in a Pyrex glass vessel at atmospheric pressure and ambient temperature under visible light irradiation. In a typical experiment, 50 mg of TNTs was mixed with 45 mL of 25 μM aqueous Orange (II) dye or 10 μM (or 20 μM) Bisphenol A under continuous magnetic stirring. First, the solution was stirred for 30 min under dark condition to allow equilibrium adsorption between the catalyst and the solution. The reactor glass was exposed to a Xenon arc lamp (Abet, Japan) for 5 h using cutoff filter at 420 nm. The mixture of dye and titanate was filtered with a syringe filter system (pore size: 0.2 μm). Then 1.5 mL of the filtrate solution was subjected to UV-vis spectrophotometer (Shimadzu UV-2600 UV-vis-spectrophotometer) and HPLC analysis.

### 2.4. Culture and analysis of bacteria

Gram-negative bacterium *Escherichia coli* (*E. coli*, ATCC 8739) used in the inactivation experiment. It was cultured and counted following published procedures [29]. Briefly, *E. coli* was inoculated into a 500 mL baffled Erlenmeyer flask containing 300 mL of Tryptic Soy Broth (Difco Co., USA) and grown at 37 °C in a shaker-incubator for 18 h. Cultured *E. coli* were harvested by centrifugation in 50 mL conical tubes at 4000 rpm for 10 min (three times) with phosphate-buffered saline solution (PBS, pH 7.2, Sigma Co.). *Salmonella typhimurium* (*S. typhimurium*, pathogen SL1344, Gram-negative bacteria) [30] and *Listeria monocytogenes* (*L. monocytogenes*, pathogen BA00092, Gram-positive bacteria) [31] were cultivated in Luria-Bertani Broth (Difco Co., USA) and Brain-Heart Infusion Broth (Difco Co., USA), respectively. These three bacteria (*i.e.*, *E. coli*, *S. typhimurium*, and *L. monocytogenes*) stock solutions [about 1 · 10<sup>10</sup> colony forming unit (cfu)/ mL] were prepared by re-suspending washed cell pellets in 30 mL of PBS. The initial population of these bacteria was approximately 10<sup>5</sup> cfu/ mL after diluting the stock solution. Viable cell counts of these three bacteria were determined with a spread plate method (three replicate plates) with their specific agar after incubation at 37 °C for 24–48 h.

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