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# Bactericidal activity and mechanism of Ti-doped BiOI microspheres under visible light irradiation

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ABSTRACT

Ti doped BiOI microspheres were successfully synthesized through a solvothermal method. The photocatalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS) and UV–vis diffuse reflectance spectra (DRS) spectroscopy, respectively. The as-synthesized microspheres had 3D hierarchical structures, and the morphologies and visible-light-driven (VLD) disinfection performances were found to be determined by the amount of loaded Ti. The incorporation of Ti in the lattice of BiOI broadened the band gap of BiOI and enhanced the VLD disinfection activity. Ti doped BiOI microspheres with the optimal Ti content exhibited excellent antibacterial performances against both representative Gram-negative and Gram-positive strains, which completely inactivated $3.0 \times 10^7$ CFU $mL^{-1}$ *E. coli* in 24 min and $3.0 \times 10^6$ CFU $mL^{-1}$ *S. aureus* in 45 min, respectively. Active species including $h^+$, $e^-$, $^{\bullet}O_2^-$ and $H_2O_2$ were found to play important roles in disinfection system. Moreover, the damage of cell membrane and emission of cytoplasm directly led to the inactivation.



## 1. Introduction

To ensure the safety of drinking water, different techniques including chlorination, UV irradiation, ozonation, and advanced filtration have been commonly employed over past decades to eliminate pathogenic microorganisms in water [1]. Although they are demonstrated to be effective in inactivating microbes, these conventional chemical disinfection techniques yet have some drawbacks [2–5]. For example, carcinogenic and mutagenic disinfection byproducts would be generated throughout the chlorination process [2], while the regeneration of bacteria would occur after the disinfection via UV irradiation [3]. Great efforts thus have been devoted to develop innovative water purification technologies in recent years. Particularly, a variety of functionalized nanomaterials have been demonstrated to have great potentials to treat microbe polluted water via bacteria capture [6,7], photo-thermal disinfection [8,9], as well as photocatalytic inactivation mechanisms [1,10–20]. Among the different types of fabricated nanomaterials, visible-light-driven (VLD) photocatalyst has become one of the most attractive alternatives for bacteria inactivation in water due to their effective utilization of solar energy [14]. For example, $TiO_2$ particles doped with non-mental ions [15,16], modified with noble metals [1,17] or coupled with other materials [18–20] have been demonstrated to disinfect microbe efficiently under visible light irradiation.

With a narrow band gap (1.77 eV) [13], bismuth oxyiodide (BiOI) is able to absorb visible light within a wide spectrum range. Moreover, due to the unique structure of alternate $[Bi_2O_2]^{2+}$ sheets with the I-slabs and internal electric fields between positive and anionic slabs [21], photo-generated holes and electrons in BiOI can be efficiently separated. Thus, BiOI recently also attracted increasing attention in the field of water decontamination under visible light conditions [22–24]. To further improve the VLD disinfection activity of BiOI, strategies including surface deposition of elemental silver [25], heterojunction with silver iodide [13], and bromide doping [11] have been previously employed to modify BiOI. Comparing with BiOI without modification, the disinfection performance of modified composites could be greatly enhanced. For example, Zhu et al. [25] found that under visible light irradiation, 7.5 log *E. coli* could be inactivated to 4.5 log *E. coli* within 30 min using BiOI (0.5 g $L^{-1}$), while 7.7 log *E. coli* could be inactivated to 2.3 log *E. coli* within 10 min using 2.09% Ag/BiOI (Wt. Ag/Wt. BiOI). Due to the strong reductive capacity of $TiO_2$, appropriate amount of Ti doping, which might integrate $Tid_{xy}$ bands into the local conduction band

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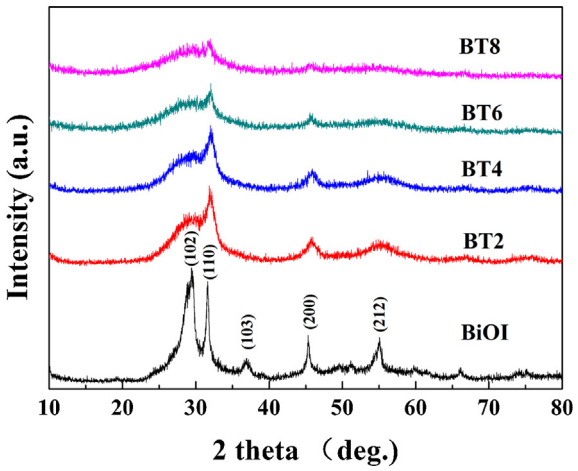


**Fig. 1.** XRD patterns of BiOI and Ti doped BiOI with different Ti content.

of BiOI, is also expected to improve the antibacterial performance under visible light irradiation. However, up to date, the bactericidal activity of Ti doped BiOI has not been explored. Moreover, the mechanisms involved in the photocatalytic disinfection processes Ti doped BiOI have not been elucidated.

Therefore, the objective of this study is to fabricate Ti doped BiOI microspheres and investigate their bactericidal performance as well as disinfection mechanisms. Ti doped BiOI microspheres were synthesized via a one pot solvothermal method using titanium (IV) isopropoxide as Ti source. The disinfection performances of Ti doped BiOI against both representative Gram-negative and Gram-positive strains were determined under visible light irradiation. Furthermore, the mechanisms involved in the photocatalytic disinfection system were systematically investigated.

## 2. Material and methods

### 2.1. Materials

Bismuth (III) nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), potassium iodide (KI), ethylene glycol (EG), terephthalic acid (TA), nitroblue tetrazolium (NBT), sodium oxalate ($Na_2C_2O_4$), ferrous sulfate ($FeSO_4{\cdot}7H_2O$), potassium chromate($K_2CrO_4$), ethylene diamine tetraacetic acid (EDTA), and NaCl were all of analytical grade and purchased from Sinopharm Corporation Ltd. (Shanghai, China). Isopropanol, titanium (IV) isopropoxide and 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPOL) were purchased from Sigma-Aldrich. Commercial-grade $TiO_2$ powder (P25) was purchased from Degussa Germany, with a crystalline structure of ca. 80% anatase and ca. 20% rutile. All the chemicals were analytical grade and used without further purification.

### 2.2. Material synthesis

Ti-doped BiOI microspheres were synthesized by a one-pot solvothermal process. In a typical procedure, $Bi(NO_3)_3{\cdot}5H_2O$ (2.0 mmol) was dissolved in 80 mL EG, after which stoichiometric amount of KI was added into the solution with magnetic stirring. Subsequently, after vigorously string for 30 min, appropriate amount of titanium (IV) isopropoxide was added into the transparent yellow solution. Following stirring for another 30 min, the mixture was transferred into a Teflon-lined autoclave to undergo a solvothermal process at temperature of 120 °C for 12 h. After cooling to room temperature, solids were collected by filtering through a 0.22 μm Millipore membrane, and washed with deionized water and absolute ethanol for at least 5 times, respectively. Finally, the purified materials were dried over night at 60 °C. Materials synthesized with the addition of 200, 400, 600 and 800 μL titanium (IV) isopropoxide were noted as BT2, BT4, BT6 and BT8, respectively. For comparison, single phase BiOI was also synthesized under the same conditions in the absence of titanium (IV) isopropoxide. In addition, commercial available P25 was chosen as the representative of $TiO_2$.

### 2.3. Catalysts characterization

The crystalline phases and constituents of the as-synthesized catalysts were examined by powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). XRD analysis was performed by DMAX-2400 (Rigaku, Japan) with Cu Kα ($\lambda$ = 0.154 nm) irradiation at 40 kV and 100 mA. The mean crystallite size can be roughly estimated using the full width at half maximum (FWHM) according to the Scherrer formula as shown in Eq. (1) [26]:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where $D$ is the crystallite size, $K$ refers to the Scherrer constant (herein assigned a value of 0.9), $\lambda$ (0.154 nm) stands for the Cu $K\alpha_1$ X-ray radiation wavelength, $\beta$ is the corrected FWHM (in radian) of the diffraction peak, and $\theta$ represents the Bragg diffraction angle.

XPS patterns were carried out on an Axis Ultra (Kratos Analytical Ltd) imaging photoelectron spectrometer using a monochromatized Al Kα anode. The C1s peak at 284.8 eV was utilized to calibrate the peak positions of the elements. The morphology of the as-synthesized catalysts were characterized by FEI Nova Nano scanning electron microscopic 430 (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) and FEI Tecnai F30 high resolution transmission electron microscope (HRTEM).

The UV–vis diffuse reflectance spectra were recorded for the dry pressed disk samples by a PerkinElmer Lambda 650S spectrophotometer, and $BaSO_4$ was used as a reference. The band gaps of the samples were calculated according to Eq. (2) [27]:

$$ah\nu = A\left(h\nu - E_g\right)^{\frac{n}{2}} \quad (2)$$

where $a$, $h$, $\nu$, $E_g$ and $A$ are adsorption coefficient, Planck constant, light frequency, band gap and a constant, respectively. $n$ was determined by the optical transition type of a semiconductor. BiOI is an indirect transition semiconductor [28], thus the value of $n$ is 4.

### 2.4. Bacteria preparation

*Escherichia coli* ATCC15597 (*E. coli*) and *Staphylococcus aureus* (*S. aureus*), which have been widely used as model bacteria of Gram-negative strain and Gram-positive strain in previous studies [15,18], were employed as model cells in the research. *E. coli* was cultured in 100 mL Luria Broth growth medium, which contained 10 g $L^{-1}$ tryptone, 5 g $L^{-1}$ bacto-yeast extract, and 10 g $L^{-1}$ NaCl, while *S. aureus* was cultured in 100 mL growth medium consisting of 15 g $L^{-1}$ tryptone, 5 g $L^{-1}$ bacto-yeast extract, and 5 g $L^{-1}$ NaCl. The flask containing the growth media were shaken at 200 rpm in an incubator until the early stationary phase was reached (37 °C and 16 h for *E. coli*, and 37 °C and 32 h for *S. aureus*). Bacterial cells were harvested by centrifugation at 5000 rpm for 8 min. After the centrifugation, the growth media were decanted, and the bacterial pellets were washed three times with sterilized physiological saline (0.9% of NaCl at pH 7.0) to remove the residual growth medium. The cell precipitates were then re-suspended in proper volumes of sterilized physiological saline to obtain the bacterial stock suspensions. The viable cell density of the as-prepared bacterial stock suspension was typically diluted to $3.0 \times 10^9$ colony forming unit per milliliter (CFU $mL^{-1}$) for *E. coli* and $3.0 \times 10^8$ CFU $mL^{-1}$ for *S. aureus*, respectively.