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# On structure and methylene blue degradation activity of an Aurivillius-type photocatalyst of $Bi_4V_2O_{11}$ nanoparticles

Yuting Lu [a], Yinfu Pu [a], Jing Wang [a], Chuangxiang Qin [a,*], Cuili Chen [b], Hyo Jin Seo [b,**]

[a] College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China
[b] Department of Physics and Interdisciplinary Program of Biomedical, Mechanical & Electrical Engineering, Pukyong National University, Busan 608-737, Republic of Korea

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ABSTRACT

Aurivillius-type photocatalyst of $Bi_4V_2O_{11}$ nanoparticles with an average particle size of 45 nm was prepared by the modified Pechini method. The sample was investigated by X-ray powder diffraction (XRD) and the structural refinement. The nanoparticles were characterized by scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopic (XPS) and UV–vis absorption spectrum. $Bi_4V_2O_{11}$ nanoparticles show an efficient absorption in the UV–vis light wavelength region with a narrowed band gap energy of 2.08 eV and an indirect allowed electronic transition. The photocatalytic activities of $Bi_4V_2O_{11}$ nanoparticles were evaluated by photodegradation of methylene blue (MB) under visible-light irradiation in air atmosphere. These results indicate that $Bi_4V_2O_{11}$ could be a potential photocatalyst driven by visible-light. Hybridization of the 6s and 6p orbitals of $Bi^{3+}$ and the resulting lone electron pair yields interesting properties. The effective photocatalytic activity was discussed on the base of the crystal structure characteristic such as polar $(VO_{3.5}\square_{0.5})^{2-}$ anionic groups, Aurivillius-type $(Bi_2O_2)^{2+}$ layers and long distance of the nearest V–V in the lattices, etc.



## 1. Introduction

Semiconductors with photocatalytic activities driven by UV–vis light have been widely investigated [1–10]. Optical absorption energy is decided by band gap, which is followed by the release of holes and electrons from valence (VB) and conduction (CB) bands, respectively. To get photocatalysts with effective response in visible light wavelength it is necessary to narrow band-gap of semiconductors. One of the methods is to construct VB utilizing O2p hybridized with Bi6s orbitals in host lattices [11]. This makes VB largely dispersed, which favors the mobility of photoinduced holes in VB and is beneficial to the oxidation reaction. For example, Oshikiri et al. [12] have confirmed that in $InMO_4$ (M = V, Nb, Ta), $BiVO_4$ and $TiO_2$ only the top of the VB of $BiVO_4$ shows a contribution from 6*s* orbitals of Bi as well as a dominant component due to 2*p* states of $O^{2-}$. This induces a narrower band-gap of $BiVO_4$ (1.3 eV) than those of $InTaO_4$ (3.7 eV), $InNbO_4$ (3.4 eV), $InVO_4$, (3.1 eV), and $TiO_2$ (3.0–3.2 eV).

Bismuth ($Bi^{3+}$) ion has an electronic configuration $[Xe]4f^{14}5d^{10}6s^2$ with a peculiar $6s^2$ lone pair (without bonding or sharing with other atoms). The repulsive force due to existence of lone pair in the lattices can apply to other bonding schemes generally causing a heavy distortion of the structure. $Bi^{3+}$-containing oxides have been widely developed for potential visible light active photocatalysts due to the peculiar electronic structure in these materials such as $BiVO_4$ [13], $Bi_2O_3$ [14], $Bi_2WO_6$ [15], $Bi_2MoO_6$ [16], $Bi_{20}TiO_{32}$ [17], $Bi_{12}MO_{20}$ (*M* = Ti, Ge, Si) [18], and so on. Among them $BiVO_4$-based photocatalysts have been intensively reported [11,13,19–24] which possess optical absorption and photocatalytic activities.

In this work, $Bi_4V_2O_{11}$ was developed as a photocatalyst driven by visible light. $Bi_4V_2O_{11}$ was reported by Venevtsev's group [25]. The Aurivillius layered-perovskite can be described as alternating layers of $Bi_2O_2^{2+}$ and $VO_{3.5}^{2-}$. With increasing of temperature, the room temperature orthorhombic α-$Bi_4V_2O_{11}$ phase transforms through β-$Bi_4V_2O_{11}$ (440 °C) to tetragonal γ-$Bi_4V_2O_{11}$ (560 °C), in which the oxygen vacancies are disordered [26]. The most attractive feature of this compound is its strong polar response [27], which is generally incompatible in most ferroelectrics. Up to now $Bi_4V_2O_{11}$ has been given extensive investigation as ionic conductors [28], solid-state electrolytes [29]. However, the non-bonding layered structure, providing the space large enough to

* Corresponding author.
** Corresponding author. Tel.: +82 51 629 5568; fax: +82 51 6295549.
*E-mail addresses:* qinchuanxiang@suda.edu.cn (C. Qin), hjseo@pknu.ac.kr (H.J. Seo).

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polarize the related atoms and orbitals, is very beneficial for the separation of electrons and holes, enhancing the photocatalytic activities in $Bi_4V_2O_{11}$ [30]. Thakral et al. [31] firstly investigated the visible-light photocatalytic performance of $Bi_4V_2O_{11}$ prepared by conventional solid state method. More recently, Chen et al. [32] reported $Bi_4V_2O_{11}$ hollow microspheres with hierarchical superstructures. It has been reported that the optical behavior of $Bi_4V_2O_{11}$ is highly sensitive to the synthetic conditions [31,33]. The synthesis method, the morphology and the size of crystals play a crucial role in determining the photocatalytic performance [32].

In this work, we introduced an easy modified Pechini method to prepare $Bi_4V_2O_{11}$, the rich oxygen stoichiometry vanadium. The sample was investigated by the crystal phase, morphologies, and UV–vis absorption. The efficient photocatalytic activity was confirmed by degradation of methylene blue (MB) under visible irradiation.

## 2. Experimental

$Bi_4V_2O_{11}$ was prepared by the Pechini method on the base of citrate-complexation route. The raw materials are stoichiometric amounts of $Bi(NO_3)_3{\cdot}5H_2O$ (99.99%), and $NH_4VO_3$ (99.99%). Firstly, the raw materials were dissolved in deionized water. The nitrate solution was then complexed by citric acid. The solution was neutralized by the ammonium hydroxide (30%wt). The obtained solutions were promoted by heat treatment at 85 °C for 3 h. Then, a certain amount of aqueous polyvinylalcohol was slowly added in the solutions to adjust the viscoelastic of the solution, which was stirred for 3 h to obtain a homogeneous viscous solution for the spin-coating on several clean glasses. The precursor thin film can be obtained by natural withering of the coated glasses. Finally, the spin-coated film was annealed to the desired temperature (800 °C) producing the $Bi_4V_2O_{11}$ powder with the heating rate of 3 °C/min, held there for 4 h and cooled to room temperature naturally.

XRD was obtained using a Rigaku D/Max diffractometer operating at 40 kV, 30 mA with Cu Kα as an incident radiation. The SEMs were used to study surface morphologies of the samples. Diffuse reflection spectra (DRS) were taken on a Cary 5000 UV–Vis–NIR spectrophotometer by using $BaSO_4$ powder as a standard reference. X-ray photo electron spectroscopy (XPS) analyses were performed using an XPS, Kratos analytical, ESCA-3400, Shimadzu.

The photocatalytic experiment was performed in a 0.5 L cylindrical glass photocatalytic reactor with a 500 W Xe lamp was selected as the visible light source. A cut filter (420 nm) was inserted between the xenon lamp and reactor to eliminate ultraviolet light. The flow rate of air was kept at 500 mL $min^{-1}$. Typically, 300 mL of methylene blue (10 mg $L^{-1}$) solution containing 0.05 g of photocatalyst was mixed in a beaker. Prior to the photocatalytic reaction, the suspension was allowed to reach adsorption/desorption equilibrium by maintaining the solutions in dark for 1 h. At a defined time interval, 5 mL of methylene blue was taken out from the reactor, and was analyzed using the UV–vis spectrophotometer.

## 3. Results and discussion

### 3.1. Phase formation and surface structure

The diffraction pattern of $Bi_4V_2O_{11}$ nanoparticles was investigated by structural refinement using the GSAS program as shown in Fig. 1. The XRD pattern reveals that the photocatalyst was well crystallized with a pure $Bi_4V_2O_{11}$ phase, and no impurity peaks were observed. The refined structural parameters and the atomic coordinates in the lattices of $Bi_4V_2O_{11}$ are given in Tables 1 and 2, respectively. The sample crystallizes in a monoclinic system with the space group of A112 (5). The unit parameters are $a = 16.589$ Å, $b = 5.62058$ Å, $c = 15.3581$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90.65°$, Z = 6 and $V = 1452.82(20)$ Å$^3$. The experimental data for the structure are in agreement the reports in references [34].

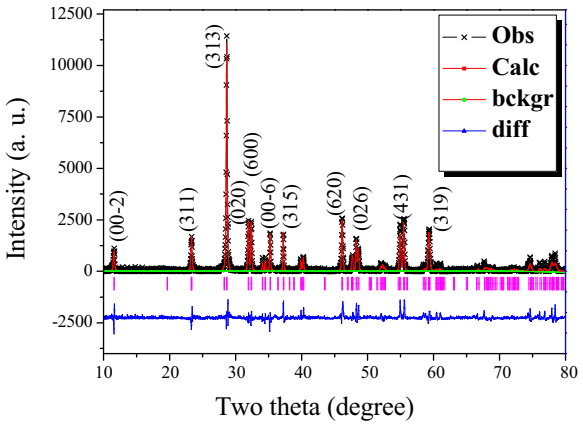


**Fig. 1.** A representative experimental (crossed) and calculated (red solid line) X-ray diffraction profiles of $Bi_4V_2O_{11}$. The difference profile is located at the bottom of the figure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

**Table 1**
Crystallographic refinement parameters of $Bi_4V_2O_{11}$.

| Formula | $Bi_4V_2O_{11}$ |
|---|---|
| Radiation | Cu Ka |
| $2\theta$ range (degree) | 10–80 |
| Symmetry | Monoclinic |
| Space group# | A112 (5) |
| $a$ (Å) | 16.5892(2) |
| $b$ (Å) | 5.62058(3) |
| $c$ (Å) | 15.3581(8) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 90 |
| $\gamma$ (°) | 90.65 |
| $Z$ | 6 |
| $R_p$ | 0.1241 |
| $R_{wp}$ | 0.1121 |
| $X^2$ | 1.7151 |
| $V$ (Å$^3$) | 1452.82(20) |

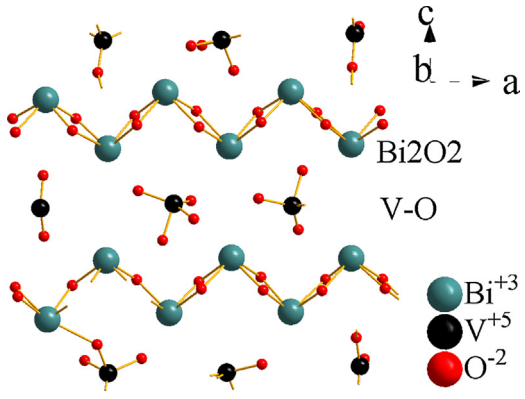


**Fig. 2.** Schematic structure views of $Bi_4V_2O_{11}$ along [010] direction.

Fig. 2 displays the structure sketch map of $Bi_4V_2O_{11}$ along [010], which was modeled using the Diamond Crystal and Molecular Structure Visualization software on the basis of the atomic coordinate's data from the XRD refinements in Table 2. The peculiar characteristic of $Bi_4V_2O_{11}$ is that the lattice has alternating $[Bi_2O_2]^{2+}$ layers and $(VO_{3.5}\square_{0.5})^{2-}$ oxygen deficient perovskite slabs. The structure can be regarded to be closely related to the Aurivillius form, which is built up from infinite $(Bi_2O_2)^{2+}$ layers