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Short communication

# The effects of Br dopant on the photo-catalytic properties of $Bi_2WO_6$

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ABSTRACT

We present an experimental study on photocatalysis of pure and Br-doped $Bi_2WO_6$ powders, including photo-degradation of Rhodamine B, UV–vis absorption spectra and photo-luminescence spectrum. The obtained results indicate that Br-doped $Bi_2WO_6$ powders exhibit preferable photocatalytic activity than pure $Bi_2WO_6$. Then, the structural stability and the electronic properties of Br-doped $Bi_2WO_6$ are studied by employing the first-principles method, and a promising improvement of photo-catalytic activity is found in the visible-light region after doping, which is consistent with the experimental results. The $Br_{II}$-doped structure is found to be more preferred, nevertheless all the three types of doping can narrow the band gap of $Bi_2WO_6$ pronouncedly, and thus the availability of solar energy increases consequently with the doping. On the other hand, the doping of Br results to smaller electron effective mass and induces impurity levels in gap, which is in favor of the carrier's transfer and the decrease of electron-hole recombination respectively.



## 1. Introduction

With the advancement of technology, the earth has been suffering from an astonishing decline in energy. This situation has led to a new focus on the development of clean and reproducible energy sources [1,2]. Ever since, $TiO_2$ has been demonstrated as a photo-catalysts and investigated comprehensively, it is also been widely studied because of its high reactivity, environment friendly and inexpensive features [3,4]. However, due to its intrinsic band gap (rutile 3.05 eV, anatase 3.26 eV) [5], $TiO_2$ can utilize only the ultraviolet part of the solar spectrum [6,7]. In order to improve the ability of $TiO_2$ to effectively utilize solar energy of the incoming solar light, many efforts have been devoted to modify the energy band structure of $TiO_2$ to shift its spectral response into the visible-light region and improve the photo-catalytic performance by doping elements [8–11]. On the other hand, new types of photo-catalysts are explored for better photo-catalytic efficiency. Due to the unique physical and chemical properties, $Bi_2WO_6$ has attracted significant attentions in recent years. The promising photocatalytic activity of $Bi_2WO_6$ is related to the special Aurivillius layered structure composing of $WO_6$ octahedron and Bi–O–Bi layers, which has been demonstrated remarkable photocatalytic activity [12–21]. The experimental band gap of pure $Bi_2WO_6$ has been evaluated to be about 2.79 eV [20], which is much narrow than that of $TiO_2$, but most visible-light is missed regrettably and the photocatalytic activity of pure $Bi_2WO_6$ is still somewhat low because of the fast recombination of photogenerated electron–hole pairs [22]. To meet the challenge of practical applications under visible-light, it is necessary to suppress the recombination of electrons and holes. It is known that photocatalytic activities can be influenced by many factors [23–25], of which doping has been evidenced to be an effective way in the semiconductor of $Bi_2WO_6$ [26,27].

In order to further understand the mechanism of enhanced photocatalytic efficiency, it is imperative to carry out systematic analysis on the ion-doping. It is noted that, halogen may be good dopant to improve the photoelectric properties of semiconductor such as $TiO_2$ [28]. So in the present work, the microstructure and electronic structures of Br-doped $Bi_2WO_6$ are studied by performing first-principles calculations in order to understand the improvement of photocatalytic activity. Meanwhile, $Bi_2WO_6$ powders doped with Br element are successfully synthesized by a hydrothermal method and the related properties of the $Bi_2WO_6$ powders are also conducted subsequently.

## 2. Experimental results

The pure and Br-doped $Bi_2WO_6$ powders are synthesized by hydrothermal method which has been described in detail in our paper before [29], and then the related experiments are conducted to investigate the photo-catalytic properties of the samples. (I) The

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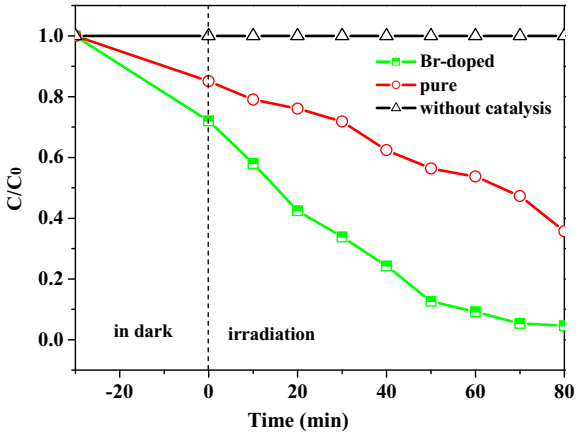


**Fig. 1.** Photodegradation efficiency for RhB.

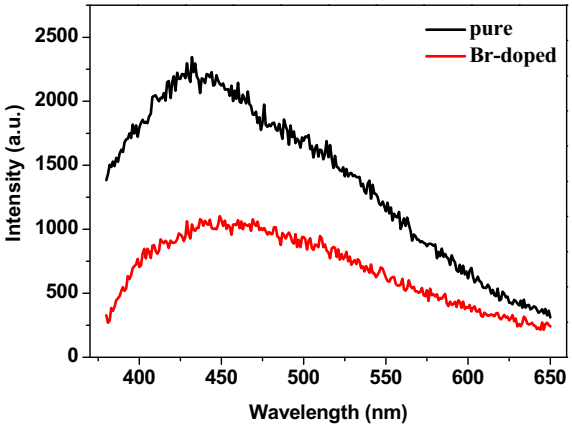


**Fig. 3.** The PL spectra of pure and Br-doped $Bi_2WO_6$ samples.

photo-catalytic activity of the Br-doped $Bi_2WO_6$ powders (with the concentration of 1.0 g/L) is evaluated by the photo-degradation of Rhodamine B (RhB) in aqueous solution (initial concentration of 20 mg/L) under visible light irradiation using 300 W Xe lamps with a 420 nm cut-off filter. The RhB concentration is analyzed by a U-3010 UV–vis spectrophotometer (Hitachi, Japan) and illustrated in Fig. 1. For the Br-doped $Bi_2WO_6$ powders, obvious higher photo-catalytic efficiency is observed during the degradation of RhB with much more rapid decrease especially within the first 50 min, while the total photo-degradation increased from 64% to 95% within 80 min compared with the pure powders. (II) The UV–vis absorption spectra of the samples are obtained using a Lambda 950 UV–vis-NIR spectrophotometer. Obvious red-shift is shown in Fig. 2(a) from the spectra. The result is similar to the calculated optical absorption spectra and it implies a smaller $E_g$ value by the well-known relation of the band gap energy and the optical absorption spectra ($(ah\nu = A(h\nu - Eg)^{n/2})$). The smaller $E_g$ value must be induced by the participation of Br and has been predicted by the theoretical calculation. The red-shift suggests that the Br-doped $Bi_2WO_6$ powders are more effectively absorbing visible-light. That is, we can apply the visible-light source more abundant and in a broadened range when the $Bi_2WO_6$ powders are used as catalyst. (III) In order to verify its photo-catalytic activity, the separation of the photo excited electron-hole pairs should be investigated. Fig. 3 shows photo-luminescence (PL) spectrum of the pure and Br-doped $Bi_2WO_6$ samples, which is measured with a HORIBA Fluoromax-4 spectrophotometer and the 325 nm excitation source. We can see from the result, the PL spectrum of pure $Bi_2WO_6$ shows strong emission intensity in the wavelength, whereas the PL spectrum of Br-doped $Bi_2WO_6$ exhibits lower emission intensity. It implies a lower recombination rate of the photo-excited electron–hole pairs, and thus enhances the photocatalytic activity of the Br-doped powders.

## 3. Theoretical section

### 3.1. Calculation detail and model

The calculations are performed using the Vienna ab-initio Simulation Package (VASP) [30,31] based on the density functional theory (DFT) [32,33]. The electron-ionic core interaction is represented by the projector augmented wave (PAW) [34] potentials which are more accurate than ultra-soft pseudopotentials. The $6s^26p^3$, $2s^22p^4$, $5d^46s^2$ and $4s^24p^5$ electrons are chosen as

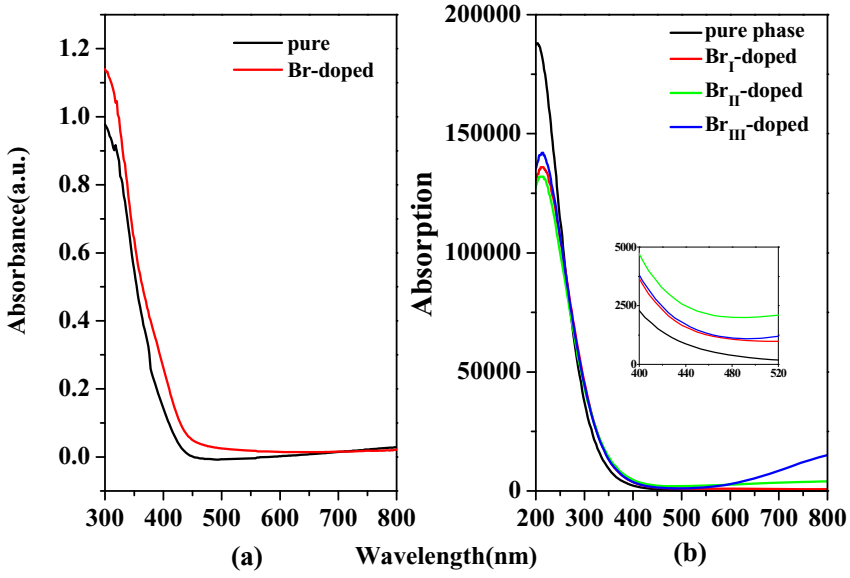


**Fig. 2.** (a) UV–vis spectra by experiment and (b) the absorption spectra of $Bi_2WO_6$ calculated by DFT.