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# Insights into structural properties of Cu species loaded on $Bi_2O_3$ hierarchical structures for highly enhanced photocatalysis

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ABSTRACT

Pristine $Bi_2O_3$ is known to possess poor photocatalytic activity due to its low conduction band potential. Here, we attempt to enhance the photocatalytic activity of $Bi_2O_3$ by loading Cu species through a very simple impregnation method. After Cu loading at the optimum amount, we observe significant enhancements of photocatalytic activity for degradation and mineralization of atrazine under visible light by maximum factors of 9.4 (0.2 wt.% Cu) and 11.7 (0.1 wt.% Cu), respectively. Microstructural properties of $Bi_2O_3$ are not altered upon Cu loading, yet its light absorption ability is greatly improved. On the basis of EXAFS and XANES analysis, we suggest that Cu species exists in the +2 oxidation state, coordinated with four O atoms with bond lengths of ~1.93 Å in the form of amorphous nanoclusters.



## 1. Introduction

Among various physicochemical methods, semiconductor photocatalysis appears to be a promising method for removal of organic pollutants from water environments. It has shown potential as an environmentally friendly, low-cost, solar-driven, and sustainable process [1,2]. For practical and commercial applications, searching for and optimizing visible-light-active photocatalysts with high performance is of great importance, since visible light accounts for about 44% of the total radiation emitted by the sun [3]. In this context, $Bi_2O_3$ seems to be a suitable material, as it possesses a small band gap of ~2.7 eV [4] and thus is able to harvest visible light. In addition, it features a high oxidation power of valence band (VB) hole, nontoxic properties, and resistance against photocorrosion [5]. However, $Bi_2O_3$ was found not to be as good as expected [4]. This is due to its low conduction band (CB) potential (+0.32 V vs. NHE), which cannot make one-electron transfer reactions through the reduction of $O_2$ to $^{\cdot}O_2^-$ ($E^\circ(O_2/^{\cdot}O_2^-) = -0.33$ V vs. NHE) thermodynamically favorable, leading to a high recombination rate of the photogenerated charge carriers. Therefore, achieving $Bi_2O_3$-based materials with appreciable photocatalytic performances under visible light remains a challenge. It was recently reported that loading Cu onto $Bi_2O_3$ results in significantly increased photocatalytic activity for decomposition of gaseous 2-propanol under visible light [4]. Unfortunately, the photocatalytic activity evaluation was made only on the selected photocatalyst, and therefore the effect of Cu loading on the photocatalytic activity has not yet been established. The issues regarding the structure and chemical state of the loaded Cu species have also not yet been fully addressed. It is not clear whether Cu exists solely as Cu(0), Cu(I), and Cu(II), or as Cu(0)/Cu(I), Cu(0)/Cu(II), Cu(I)/Cu(II), or Cu(0)/Cu(I)/Cu(II).

Having these concerns in mind, we perform an in-depth investigation into structural properties of Cu species loaded onto $Bi_2O_3$ in relation to the photocatalytic activity for degradation and mineralization of atrazine under visible light. Cu loading is aimed to enable multielectron transfer reactions for improvement of charge carrier separation [4,6,7]. To achieve satisfactory photocatalytic activity, the charge carrier separation and light harvesting ability should be improved simultaneously. Therefore, for the improvement of light harvesting ability, three-dimensional (3D) "flowerlike" nanostructures of $Bi_2O_3$ are constructed, as 3D structures typically exhibit higher light harvesting than 0D, 1D, or 2D structures [8].

## 2. Experimental

### 2.1. Synthesis

All chemical reagents were used as received. Pristine $Bi_2O_3$ was synthesized by dissolving 1 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ in $HNO_3$

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solution in the presence of $NH_4VO_3$. The solution was diluted using DI water until a final volume of 50 mL was achieved. After the solution was vigorously stirred for 30 min, NaOH was added until a final pH 12 was achieved. The suspension was then aged at 70 °C for 30 h in a closed system without stirring. The final product was collected through centrifugation, washed with DI water followed by ethanol, and subsequently dried in an oven at 100 °C for 24 h.

The loading of Cu onto $Bi_2O_3$ was done through impregnation of an aqueous solution of $CuCl_2$ [4,9]. The aqueous $Bi_2O_3$ suspension containing Cu was then heated at 90 °C under continuous stirring. After 1 h, the solid product was collected through centrifugation, washed with copious amounts of DI water, dried at 100 °C for 24 h, and denoted as *x*% Cu, where *x* represents Cu loading (0.1, 0.2, 0.4, 0.6, and 0.8 wt.%).

### 2.2. Characterization

The crystal structure was identified by X-ray diffraction (XRD) on a Bruker D8-Advance diffractometer. The topological and morphological properties were investigated by field emission scanning electron microscopy (FE-SEM) (JSM-7610F, Jeol) and transmission electron microscopy (TEM) (JEM 2010, Jeol), respectively. An inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima 8000, Perkin Elmer) was used to verify the actual amount of Cu loaded onto $Bi_2O_3$. The determination of band gap energy was performed by diffuse reflectance spectroscopy (DRS) using a UV–vis–NIR spectrophotometer (Lambda 950, Perkin Elmer). X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were performed at Beam Line 8 of the Synchrotron Light Research Institute (Public Organization), Thailand. The XANES and EXAFS spectra were recorded at ambient temperature in fluorescence mode due to low concentrations of Cu. The analysis of XANES and EXAFS spectra was done using Athena and Artemis software packages, respectively.

### 2.3. Photocatalytic activity evaluation

For photocatalytic activity evaluation, 50 mg of photocatalyst was added into 50 mL of atrazine solution with an atrazine concentration of 5 mg/L in a borosilicate glass reactor. The suspension was then stirred in the absence of light for 30 min to establish adsorption–desorption equilibrium. The photocatalytic experiments were performed under visible light using a 10 W light-emitting diode (LED) lamp (MASTER LEDbulb, Philips). No cutoff filter is used for removing UV light because the light spectrum of the lamp is entirely located in the visible region between 420 and 780 nm. All experiments were replicated three times under identical experimental conditions at 25 ± 2 °C and the results were presented as a mean of three experiments. The concentration of atrazine remaining in the suspension was determined by a HPLC system, and the degradation efficiency (DE) of atrazine was defined as

$$\mathrm{DE}\ (\%) = [(C_0 - C)/C_0] \times 100, \quad (1)$$

where $C_0$ and $C$ are the concentration of the atrazine solution after the establishment of equilibrium and the concentration after irradiation, respectively.

Moreover, the mineralization efficiency (ME) of atrazine was determined based on total organic carbon (TOC) measurement (TOC-LCPH/CPN, Shimadzu), defined as

$$\mathrm{ME}\ (\%) = [(\mathrm{TOC}_0 - \mathrm{TOC})/\mathrm{TOC}_0] \times 100, \quad (2)$$

where $TOC_0$ and TOC are the TOC of the atrazine solution after the establishment of equilibrium and the TOC after irradiation, respectively.

## 3. Results and discussion

### 3.1. Structural properties

Fig. 1 shows the XRD patterns of pristine $Bi_2O_3$ and a $Bi_2O_3$ sample loaded with the largest amount of Cu (0.8 wt.%) as representative. Both samples exhibit the typical diffraction patterns of cubic δ-phase $Bi_2O_3$ (JCPDS 52-1007). No additional crystalline phases belonging to the other $Bi_2O_3$ polymorphs or unwanted impurities are indicated, suggesting high purity of the samples. The XRD patterns remain unchanged upon Cu loading. The characteristic diffraction patterns of copper oxides, copper hydroxide, or coper metal are not observed in the 0.8% Cu sample. The unit cell parameter $a = b = c$ (5.527 Å) and the cell volume (168.84 $Å^3$) based on (1 1 1) diffraction peaks for pristine and 0.8% Cu samples are also the same, indicating that the lattice structure is essentially not affected by Cu loading. The unaffected lattice structure is likely due to the high degree of dispersion of Cu or to low concentrations of Cu. This result is in good agreement with a previously reported work for monoclinic α-$Bi_2O_3$ nanorods loaded with Cu using a similar impregnation method [4]. On the basis of all these discussions, we deduce the absence of substitutional doping through replacement of Bi by Cu. The Cu species seems to be loaded on the surface only.

The actual loadings of Cu estimated by ICP-OES for 0.1, 0.2, 0.4, 0.6, and 0.8% Cu are found to be 0.09 ± 0.01, 0.18 ± 0.01, 0.38 ± 0.02, 0.55 ± 0.04, and 0.75 ± 0.02 wt.%, respectively. Error represents the standard deviation of three individually prepared samples. It should be stressed that the actual loadings of Cu in all the samples are lower than the initial amounts introduced. Some Cu species in the reactants are not loaded and are washed away during the preparation. So a longer time is required to load all the Cu in the reactants.

Next, we inspect the morphology of the representative sample (0.8% Cu) by SEM and TEM. As seen in Fig. 2, the sample consists of microspheres with 3D "flowerlike" hierarchical structures. These "flowerlike" structures are constructed from nanosheets with a thickness of about 10 nm. Based on the TEM image shown in Fig. 2c, these nanosheets are composed of small nanoparticles with a size of about 5 nm. This unique hierarchical structure can be an excellent light harvester due to its multiple light reflections and scatterings [8]. Moreover, the inset of Fig. 2d shows the presence of amorphous Cu nanoclusters with a size of about 2 nm (indicated by the dotted lines) effectively attached to the $Bi_2O_3$ surface.

We subsequently investigate the light absorption capability of the samples using UV–vis DRS. Fig. 3 shows the absorption spectra

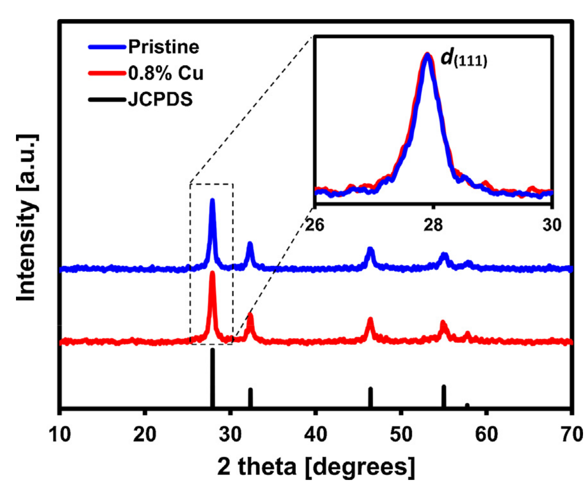


**Fig. 1.** XRD patterns of the as-synthesized samples.