Gamma Ray Radiation Effect on $\text{Bi}_2\text{WO}_6$ Photocatalyst

Qiang Zhang, Zhi-wen Jiang, Mo-zhen Wang*, Xue-wu Ge*

CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China

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The development of $\text{Bi}_2\text{WO}_6$-based materials has become one of research hotspots due to the increasing demands on high-efficient photocatalyst responding to visible light. In this work, the effect of high energy radiation ($\gamma$-ray) on the structure and the photocatalytic activity of $\text{Bi}_2\text{WO}_6$ nanocrystals was first studied. No morphological change of $\text{Bi}_2\text{WO}_6$ nanocrystals was observed by SEM under $\gamma$-ray radiation. However, the XRD spectra of the irradiated $\text{Bi}_2\text{WO}_6$ nanocrystals showed the characteristic 2θ of (113) plane shifts slightly from 28.37° to 28.45° with the increase of the absorbed dose, confirming the change in the crystal structure of $\text{Bi}_2\text{WO}_6$. The XPS results proved the crystal structure change was originated from the generation of oxygen vacancy defects under high-dose radiation. The photocatalytic activity of $\text{Bi}_2\text{WO}_6$ on the decomposition of methylene blue (MB) in water under visible light increases gradually with the increase of absorbed dose. Moreover, the improved photocatalytic performance of the irradiated $\text{Bi}_2\text{WO}_6$ nanocrystals remained after three cycles of photocatalysis, indicating a good stability of the created oxygen vacancy defects. This work gives a new simple way to improve photocatalytic performance of $\text{Bi}_2\text{WO}_6$ through creating oxygen vacancy defects in the crystal structure by $\gamma$-ray radiation.

**Key words:** $\text{Bi}_2\text{WO}_6$, Gamma ray, Oxygen vacancy, Visible-light photocatalyst

I. INTRODUCTION

$\text{Bi}_2\text{WO}_6$, the simplest Aurivillius-type oxide with a narrow band gap of about 2.8 eV [1, 2], is becoming more and more enthusiastic in view of their promising application in the photocatalytic degradation of organic pollutants [3-6]. However, the photocatalytic performance of $\text{Bi}_2\text{WO}_6$ remains to be improved due to its low light absorption efficiency and electron-hole separation efficiency [7-9]. Thus, many methods have been developed to improve the photocatalytic activity of $\text{Bi}_2\text{WO}_6$, including the regulation of morphology [10-13], doping [14-16], or the preparation of composite materials [17, 18]. For example, Zhou et al. [19] directly prepared three dimensional highly hierarchical flower-like $\text{Bi}_2\text{WO}_6$ microspheres which were formed by the self-aggregation of nanolites in a hydrothermal way at low temperature. Zhu et al. [20] prepared F− substituted $\text{Bi}_2\text{WO}_6$ ($\text{Bi}_2\text{WO}_6$–$_x\text{F}_{2x}$) photocatalysts with high activity by a two-step process. Sun et al. [21] synthesized hollow sphere shaped $\text{Bi}_2\text{WO}_6$/reduced graphene oxide (RGO) composites by a facile and cost-effective route and evaluated their photocatalytic activities by the degradation of five different kinds of pollutants under natural sunlight irradiation.

On the other hand, researches show that the oxygen vacancies in the $\text{Bi}_2\text{WO}_6$ crystals can also improve their photocatalytic performance due to the reduction of the recombination of photo-generated carriers [22-25]. For example, Zhu et al. [24] reported $\text{Bi}_2\text{WO}_6$–$_x$ nanolites with wide-range-visible photoresponse by introducing surface oxygen vacancies through the controllable hydrogen reduction method. Chai et al. [25] prepared $\text{Bi}_2\text{WO}_6$ with oxygen vacancies ($\text{Bi}_2\text{WO}_6$–$\text{O}_x$) by simple assisted solvothermal method using ethylene glycol as the reducing agent. However, as far as we know, there are no reports about the creation of oxygen vacancies in $\text{Bi}_2\text{WO}_6$ under high energy radiation, although it is well-known that high energy radiation such as $\gamma$-ray can interact with semiconductors and generate defects [26-29], and be widely used for the synthesis of various inorganic or polymeric materials [30-34].

Herein, in this work, the $\gamma$-radiation effect on the crystal structure and light absorption characteristics of $\text{Bi}_2\text{WO}_6$ was studied by using $^{60}\text{Co}$ as $\gamma$-ray source. The visible light photocatalytic degradation of MB in aqueous solution was also carried out to investigate the photocatalytic performance of the irradiated $\text{Bi}_2\text{WO}_6$. The results show that the oxygen vacancies can be created in $\text{Bi}_2\text{WO}_6$ nanocrystals under $\gamma$-ray radiation at a high absorbed dose, which improves the visible light photocatalytic performance of $\text{Bi}_2\text{WO}_6$. 

*Authors to whom correspondence should be addressed. E-mail: pstwmz@ustc.edu.cn, xwge@ustc.edu.cn, Tel: +86-551-63600843

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II. EXPERIMENTS

A. Materials

All reagents used in this work including Bi(NO$_3$)$_3$·5H$_2$O, Na$_2$WO$_4$·2H$_2$O, hexadecyl trimethyl ammonium bromide (CTAB), and methylene blue (MB) were purchased from Sinopharm Chemical Reagents Co., Ltd. (Shanghai, China). The reagents were all analytical grade except that MB was BS grade. Deionized water was used in all experiments.

B. Synthesis of Bi$_2$WO$_6$ nanosheets

The synthesis of Bi$_2$WO$_6$ nanosheets was via a simple hydrothermal method [35]. In a typical procedure, 0.48 g of Bi(NO$_3$)$_3$·5H$_2$O, 0.16 g of Na$_2$WO$_4$·2H$_2$O, and 0.025 g of CTAB were dissolved in 40 mL of deionized water with magnetic stirring for 30 min. Next, the mixed solution was transferred into a 50 mL Teflon-lined stainless steel autoclave and stood for 24 h in an oven at 120 °C. Then, the autoclave was cooled to room temperature naturally. The obtained product was collected by centrifugation, washed by water and absolute alcohol respectively for three times, and finally dried in an oven at 60 °C for 12 h. To remove the remaining surfactant CTAB, the dried sample was heated to 600 °C in air at a rate of 5 °C/min in a muffle furnace and calcinated for 5 h.

C. Gamma ray radiation on Bi$_2$WO$_6$ nanosheets

The as-prepared powder of Bi$_2$WO$_6$ nanosheets (100 mg) was put in a 10 mL of plastic centrifuge tube and irradiated by $^{60}$Co $\gamma$-ray (1.37×10$^{15}$ Bq, located in USTC, China) at a dose rate of 5.28 kGy/h for different total absorbed doses (127, 253, 380, and 507 kGy). The dose rate was calibrated using alanine/EPR standard dosimeter.

D. Characterization

X-ray diffraction (XRD) spectra were obtained on a TTHIII diffractometer (Rigaku, Japan) using Cu Kα radiation source ($\lambda$=1.5418 Å) at a scanning rate of 8°/min in the range of 10°–70°. The field-emission scanning electron microscopy (FESEM, JEOL JSM-6700F, 5 kV) was used to observe the morphologies of Bi$_2$WO$_6$ nanosheets. UV-Vis diffuse-reflectance spectroscopy was performed on Shimadzu SOLID 3700 UV-Vis spectrophotometer. The X-ray photoelectron spectroscopy (XPS) was carried out with Thermo ESCALAB 250 using monochromatic Al Kα radiation. Photoluminescence spectra were obtained using steady-state transient fluorescence spectrometer (Horiba JY Fluorolog-3-tau) with the excitation laser irradiation of 250 nm.

E. Photocatalytic performance of the irradiated Bi$_2$WO$_6$ nanosheets

The photocatalytic performance of the irradiated Bi$_2$WO$_6$ was evaluated using the decomposition of MB under the exposure of simulated visible light irradiation as the model reaction. A 300 W Xe lamp (Perfectlight PLS-SXE300/300UV) with a cut-off filter ($\lambda$>420 nm) was used as the light source. The powder of Bi$_2$WO$_6$ nanosheets (40 mg) was dispersed into 40 mL of the aqueous solution of MB (5 mg/L). The suspension was placed in the dark environment and stirred vigorously for 1 h to establish an adsorption-desorption equilibrium between Bi$_2$WO$_6$ and MB. Then, the system was exposed under the light. One milliliter of the suspension was sampled out at every 30 min, and Bi$_2$WO$_6$ particles were removed by centrifugation. The concentration of MB in the supernatant was measured by UV-Vis spectrometry (UV-2401 PC, Shimadzu). The light absorbance of MB at the wavelength of 664 nm was recorded. The decomposition rate of MB ($D_{\text{MB}}$) was calculated according to the following equation:

$$D_{\text{MB}} = \frac{C_0 - C_t}{C_0} \times 100\%$$

where $C_0$ is the concentration of MB at the adsorption-desorption equilibrium in dark environment, and $C_t$ is the concentration of MB after being irradiated by light for a time period of $t$. After the decomposition of MB, the irradiated Bi$_2$WO$_6$ nanosheets were recycled by centrifugation and washed by absolute alcohol to remove MB. After being dried at 60 °C, the recycled Bi$_2$WO$_6$ nanosheets were used for the next cycle of photocatalytic experiment.

III. RESULTS AND DISCUSSION

A. Effect of gamma ray radiation on the crystal structure of Bi$_2$WO$_6$ nanosheets

Disk-like Bi$_2$WO$_6$ nanosheets with a diameter of 400–800 nm and a thickness of about 100 nm can be facilely prepared by a solvothermal method [35], as shown in FIG. 1 (a). After being irradiated by $\gamma$-ray, the morphology of these disk-like Bi$_2$WO$_6$ nanosheets has little change when observed by SEM even at an absorbed dose as high as 507 kGy, as exhibited in FIG. 1 (b)–(e). However, the color of Bi$_2$WO$_6$ powders obviously changes from light yellow to light blue after $\gamma$-ray radiation with an absorbed dose above 380 kGy, as shown in the insets of FIG. 1 (a)–(e), which means that there are some changes occurring in the physical structure of Bi$_2$WO$_6$ nanocrystals after high-dose $\gamma$-ray radiation although the morphology has not been destroyed.

FIG. 2 displays the XRD spectra of Bi$_2$WO$_6$ nanosheets after being irradiated at different absorbed doses, compared with that of the unirradiated sample. Basically, the distinct peaks at 2θ values of 28.3°...
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FIG. 1 SEM images of Bi$_2$WO$_6$ before (a) and after being irradiated by γ-ray at different absorbed doses: (b) 127 kGy, (c) 253 kGy, (d) 380 kGy, and (e) 507 kGy. The insets are the corresponding digital photos of the appearance of the samples. The dose rate was 5.28 kGy/h.

FIG. 2 The XRD spectra (a) and the corresponding magnified views (b) of Bi$_2$WO$_6$ nanosheets before and after being irradiated by γ-ray at different absorbed doses.

In order to confirm the weak change in the crystal structure of Bi$_2$WO$_6$ nanosheets induced by γ-ray radiation, XPS spectra of the primary and irradiated Bi$_2$WO$_6$ nanosheets have been measured, as shown in FIG. 3. The peaks at 164.5 and 159.2 eV in FIG. 3(a) are ascribed to levels of Bi 4f$_{5/2}$ and Bi 4f$_{7/2}$ spin-orbit splitting photoelectrons in the Bi$^{3+}$ chemical state of unirradiated Bi$_2$WO$_6$, respectively. However, these two peaks have a 0.1 eV shift to a higher binding energy, which can be contributed to the formation of neighbouring oxygen vacancies with higher electron attracting ability [25]. The similar change also occurs for the peaks at 35.45 and 37.6 eV which are assigned respectively to W 4f$_{7/2}$ and W 4f$_{5/2}$ spin-orbit doublets in the W$^{6+}$ chemical state (FIG. 4(b)). There is a 0.15 eV shift to a higher binding energy for the irradiated Bi$_2$WO$_6$. Correspondingly, the binding energy of O 1s at 530.10 eV shifts to 530.25 eV after γ-ray irradiation, and splits into two peaks at 530.04 eV (Bi–O) and 530.66 eV (W–O) [24]. The decrease in the relative intensity of the peak for Bi–O to that for W–O reveals that oxygen vacancies are formed due to the removal of O atoms connected with Bi atoms.

The UV-Vis spectra of the primary and irradi-
FIG. 3 (a) Bi 4f, (b) W 4f, and (c) O 1s XPS spectra of primary and irradiated Bi$_2$WO$_6$ nanosheets (the absorbed dose: 507 kGy).

FIG. 4 (a) UV-Vis diffuse reflectance spectra (b) and the corresponding plots of $(\alpha h\nu)^2$ vs. $h\nu$ of primary and irradiated Bi$_2$WO$_6$ nanosheets.

Bi$_2$WO$_6$ nanosheets theoretically have a better visible light absorption efficiency and photocatalytic performance than primary Bi$_2$WO$_6$.

It is known that the intensity of the steady-state photoluminescence (PL) spectrum can reflect the recombination rate of photogenerated carriers in semiconductor materials [37]. FIG. 5 displays the PL spectra of the primary and irradiated Bi$_2$WO$_6$ nanosheets under the excitation of 250 nm laser. All of the Bi$_2$WO$_6$ samples present broad-band emission spectra. The emission intensity of Bi$_2$WO$_6$ has no change until the absorbed dose reaches 380 kGy, but it drops significantly when the absorbed dose rises up to 507 kGy. The results indicate that the oxygen vacancy defects in Bi$_2$WO$_6$ generated under high-dose $\gamma$-ray radiation will make the charge carriers transfer fast and retard their recombination [38]. This manifests that Bi$_2$WO$_6$ nanosheets should have an improved photocatalytic performance after the exposure under high-dose $\gamma$-ray radiation.

B. The photocatalytic performance of irradiated Bi$_2$WO$_6$ nanosheets

The photocatalytic performances of Bi$_2$WO$_6$ nanosheets irradiated by $\gamma$-ray at different absorbed dose have been investigated using the decomposition...
of MB in aqueous solution under simulated visible light irradiation (λ>420 nm) as the model reaction. FIG. 6(a) shows a typically time evolution of the UV-Vis spectra of the aqueous solution of MB (5 mg/L) at the presence of the irradiated Bi₂WO₆ nanosheets irradiated at an absorbed dose of 507 kGy. It is found that the absorbance of MB decreases gradually with the visible light exposure time. MB was decomposed mostly after 150 min. The similar decomposition behaviors of MB catalyzed by primary and other irradiated Bi₂WO₆ nanosheets under the same conditions are displayed in FIG. S1 in supplementary materials. The real-time relative concentration of MB (C/C₀) at the presence of different Bi₂WO₆ nanosheets under the exposure of visible light is presented in FIG. 6(b) according to FIG. 6(a) and FIG. S1. It shows that the photocatalytic activity of Bi₂WO₆ nanosheets is improved gradually with the increase of the absorbed doses, which is in accord with the above results, i.e., the generation of oxygen vacancy defects and the lowering of E₉ and the peak intensity of photo-induced fluorescence. The maximum DMB at the presence of Bi₂WO₆ nanosheets irradiated at an absorbed dose of 507 kGy can reach 99.2%.

The cyclic photocatalytic activity of Bi₂WO₆ nanosheets irradiated at an absorbed dose of 507 kGy on the decomposition of MB is shown in FIG. 7. The catalytic performance of the recycled irradiated Bi₂WO₆ nanosheets seems to be little changed after three cycles, indicating a good stability of the oxygen vacancy defects existing in the irradiated Bi₂WO₆ nanosheets.

IV. CONCLUSION

In this work, the effect of γ-ray radiation on the crystal structure of Bi₂WO₆ nanosheets was first studied. The color of Bi₂WO₆ nanosheets changed significantly after a high-dose γ-ray radiation up to 507 kGy. Although the morphologies of the irradiated Bi₂WO₆ nanosheets observed by SEM have no change, the XPS and XRD spectra confirm the generation of oxygen vacancy defects and the resulted shrinkage of the lattice spacing in the irradiated Bi₂WO₆ nanocrystals. The existence of oxygen vacancy defects lowered E₉ and the peak intensity of photo-induced fluorescence, which fa-
vors to improve the photocatalytic activity of the irradiated Bi$_2$WO$_6$ nanosheets. The decomposition ratio of MB in aqueous solution at the presence of the Bi$_2$WO$_6$ nanosheets irradiated at an absorbed dose of 507 kGy can reach 99.2% under the exposure of visible-light for 150 min. The recycled irradiated Bi$_2$WO$_6$ nanosheets also can retain the excellent photocatalytic activity, indicating a good stability of the generated oxygen vacancy defects under γ-ray radiation. This work provides a new simple way to improve photocatalytic performance of Bi$_2$WO$_6$ through creating oxygen vacancy defects in the crystal structure by γ-ray radiation.

**Supplementary materials**: The photocatalytic performance of irradiated Bi$_2$WO$_6$ nanosheets with different absorbed doses and the working curve for the determination of MB concentration are given.

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