Post-illumination activity of Bi₂WO₆ in the dark from the photocatalytic “memory” effect

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Received: April 22, 2020; Revised: December 17, 2020; Accepted: December 19, 2020

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Abstract: Photocatalysts with the photocatalytic “memory” effect could resolve the intrinsic activity loss of traditional photocatalysts when the light illumination is turned off. Due to the dual requirements of light absorption and energy storage/release functions, most previously reported photocatalysts with the photocatalytic “memory” effect were composite photocatalysts of two phase components, which may lose their performance due to gradually deteriorated interface conditions during their applications. In this work, a simple solvothermal process was developed to synthesize Bi₂WO₆ microspheres constructed by aggregated nanoflakes. The pure phase Bi₂WO₆ was found to possess the photocatalytic “memory” effect through the trapping and release of photogenerated electrons by the reversible chemical state change of W component in the (WO₄)²⁻ layers. When the illumination was switched off, Bi₂WO₆ microspheres continuously produced H₂O₂ in the dark as those trapped photogenerated electrons were gradually released to react with O₂ through the two-electron O₂ reduction process, resulting in the continuous disinfection of *Escherichia coli* bacteria in the dark through the photocatalytic “memory” effect. No deterioration of their cycling H₂O₂ production performance in the dark was observed, which verified their stable photocatalytic “memory” effect.

Keywords: Bi₂WO₆; photocatalytic “memory” effect; energy storage/release; activity in the dark; stability

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1 Introduction

Photocatalytic “memory” effect, whereby a photocatalyst could remain active for an extended period of time in the dark, is a recent development in photocatalysis [1–4]. It resolves the intrinsic loss of activity in traditional photocatalysts when the illumination is switched off due to their incapability for the production of reactive oxidation species (ROSs) in the dark continuously, and could find many potential applications where activity in the dark is needed for an extended period of time [1,3,5–7]. To obtain this interesting photocatalytic “memory” effect, a photocatalyst must possess both light absorption and energy storage/release functions at the same time. The light absorption function allows it to generate electron–hole pairs under proper illumination, while its energy release/storage function stores part of photogenerated charge carriers during the light illumination. After the light illumination is turned off, those stored photogenerated charge carriers are then released to generate ROSs continuously in the dark to maintain its activity [8–12].

Due to the dual function requirement above, most reported photocatalysts with the photocatalytic “memory” effect were composite photocatalysts composed of two phase components [1,3,4,10,12–14]. To allow photogenerated charge carriers to transfer from the light absorption component to the energy storage/release component, proper energy band matching is required and a good contact interface must exist between them [3,9]. Thus, their phases, compositions, and synthesis were usually complex. Even so, the interface contact between these two phases may be deteriorated during their applications, leading to the performance loss. Although pure phase Se nanorods [15] and Bi nanoparticles [16] had been reported to be active in the dark, their activities in the dark were derived from the very limited amount of charge carriers at their surfaces, with very short lives. As a result, the duration of their activity was short (< 0.5 h) after the illumination was off. Such a short-lived “memory” effect is very different from the charge storage/release process seen in the composite photocatalysts because the Se nanorods and Bi nanoparticles by themselves did not have the energy storage capability.

Bi_2WO_6 is a promising ferroelectric/multiferroic ceramic material with a structure composed of alternating fluorite-like $(\text{Bi}_2\text{O}_2)^{2+}$ layers and perovskite-like $(\text{WO}_4)^{2-}$ layers stacked together by the van der

Waals interaction [17]. It has been extensively investigated for photocatalysis in recent years due to its intrinsic internal polarization beneficial for the separation of photogenerated electron and hole pairs [18–26]. The structure of its $(\text{WO}_4)^{2-}$ layers is similar to that of WO_3 , which is well-known for the energy storage capability [5–9,13,27]. Thus, it may be postulated that a photocatalytic “memory” effect may be found in the pure phase Bi_2WO_6 , where its $(\text{WO}_4)^{2-}$ layers could act to store and release charge carriers, creating a post-illumination photocatalytic activity that may extend over a long period of time (hours). Such a unique “memory” effect would be very different from that observed in the composite photocatalyst and would overcome the very short lasting problem that pure phase Se nanorods and Bi nanoparticles demonstrated.

In this work, Bi_2WO_6 (BWO) microspheres were synthesized by self-assembly of nanoflakes (the BWO sample) through a simple solvothermal process. Due to the electronic band structure of the BWO, photogenerated electrons were trapped on W component when part of W^{6+} was reduced to W^{5+} under simulated solar illumination. When the illumination was switched off, these trapped photogenerated electrons were gradually released to react with O_2 in the dark through the two-electron O_2 reduction process to produce H_2O_2 . Consequently, post-illumination activity lasting for an extended period of time in the dark was observed in the pure phase Bi_2WO_6 microspheres from the photocatalytic “memory” effect. Such a unique photocatalytic “memory” effect was found to be stable over multiple cycles, with very little loss, unlike the “memory” effect found in previously reported composite photocatalysts, where the interfacial contact deteriorates over multiple cycles of light on/off. The stability was expected because the energy storage/release function in BWO came from the W component within its crystal structure. If the concept of the “memory” effect in BWO extends to other pure phase photocatalysts with similar energy storage/release function, the selection of photocatalytic materials may be largely expanded in search for continuous activity in the dark for a broad range of environmental applications.

2 Experimental

2.1 Chemicals and materials

Ethylene glycol (EG, 98%) and ethyl alcohol (EtOH, 99.7%) were used as solvents in the solvothermal

process. Sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 99%) and bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 99%) were used in the synthesis of Bi_2WO_6 as the sources for W and Bi, respectively. Acetone ($\text{C}_3\text{H}_6\text{O}$, 99.5%) and iodine (I_2 , 99.8%) were used as the solvent and accessory ingredient in the electrophoretic deposition process, respectively. Deionized (DI) water was obtained from a water purification system (Sichuan Wortel Water Treatment Equipment Co. Ltd., Chengdu, China) with the resistivity higher than $18 \text{ M}\Omega \cdot \text{cm}$. Sulfamethoxazole (SMX, 98%) and phenol ($\text{C}_6\text{H}_6\text{O}$, 99.5%) were used as the target organic pollutants in photocatalytic degradation experiments. Radical scavengers of sodium bromate (NaBrO_3 , 99.7%), isopropanol (IPA, 99.7%), ammonium oxalate ($\text{C}_2\text{H}_8\text{N}_2\text{O}_4 \cdot \text{H}_2\text{O}$, 99.5%), and Fe(II)-EDTA ($\geq 99\%$) were used to examine main ROSs produced in the photocatalytic process. EG, SMX, and phenol were obtained from Aladdin Industrial Corporation Co. Ltd. (Shanghai, China), EtOH was obtained from Beijing Yili Fine Chemicals Co. Ltd. (Beijing, China), and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{C}_3\text{H}_6\text{O}$, I_2 , NaBrO_3 , IPA, ammonium oxalate, and Fe(II)-EDTA were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All chemicals were of analytically pure grade and used without further purification.

2.2 Synthesis of the BWO sample

6 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (2.91 g) and 3 mmol $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.990 g) were dissolved in 10 mL ethylene glycol (EG) under magnetic stirring, respectively. Then, these two solutions were mixed, and 40 mL ethanol (EtOH) was slowly added into the mixture. After further stirring for 10 min, the reactant solution was transferred into a 100 mL Teflon-lined stainless steel autoclave. The autoclave was heated and maintained at 160°C for 20 h for solvothermal reaction, before it was cooled to room temperature naturally. After reaction, the precipitate was filtered, washed with ethanol for several times, and then dried at 80°C in air for 12 h to obtain the Bi_2WO_6 photocatalyst (named as the BWO sample).

2.3 Characterization of the BWO sample

The crystal structure of the BWO sample was analyzed by X-ray diffraction (XRD) on an X-ray powder diffractometer (D/MAX-2004, Rigaku Corporation, Japan) with Ni-filtered $\text{Cu K}\alpha$ ($\lambda = 1.54178 \text{ \AA}$) radiation at 56 kV and 182 mA, and a scanning step of

0.02° in 2θ was used to record the XRD pattern. The sample's morphology was observed by the emission scanning electron microscopy (SEM) on a field emission scanning electron microscope (SUPRA55, Zeiss, Germany) with the acceleration voltage of 20 kV. For a better imaging, the sample was sputtered with gold for 120 s before the observation (Cressington Sputter Coater 208 HR, Cressington Scientific Instrument Ltd., UK). Brunauer–Emmett–Teller (BET) measurement was conducted by N_2 adsorption–desorption isotherm on an Autosorb-1 Series Surface Area and Pore Size Analyzer (TriStar II 3020, Micromeritics Instrument Corporation, USA). X-ray photoelectron spectroscopy (XPS) measurements were conducted on an X-ray photoelectron spectrometer (ESCALAB 250, Thermo Fisher Scientific Inc., USA) with an Al K anode. The UV–vis spectra of samples were measured on a spectrophotometer (UV-2550, Shimadzu Corporation, Japan).

The electrophoretic deposition method was used to prepare the BWO electrode for electrochemical measurements [28]. Before the electrophoretic deposition process, 40 mg sample was suspended in 30 mL acetone solution under ultrasonic dispersion with 15 mg iodine as the accessory ingredient. To form a two-electrode system, two pieces of FTO glass substrates with $1 \text{ cm} \times 2 \text{ cm}$ area were immersed in this suspension. Then, a direct current (DC) power supply was used to provide a bias of 20 V to drive the deposition of the BWO samples onto the FTO substrate for 5 min. Subsequently, the BWO-deposited FTO substrate was heated to 200°C for 2 h in air to obtain the BWO electrode.

A conventional three-electrode configuration was used for the Mott–Schottky analysis of the BWO sample. A platinum wire was used as the counter electrode at a direct current (DC) potential range from -0.6 to $+0.7 \text{ V}$ vs. the reference Ag/AgCl electrode in a $0.2 \text{ M Na}_2\text{SO}_4$ solution with the alternating current (AC) potential frequency of 2 kHz and an amplitude of AC potential of 50 mV in the dark on an electrochemical workstation (CHI 660D, Shanghai Chenhua Instrument Ltd., China). The open circuit potential–time (OCPT) curves and capacitance of the BWO electrode were also measured by the CHI 660D electrochemical workstation in a $0.2 \text{ M Na}_2\text{SO}_4$ solution with the platinum wire counter electrode and the Ag/AgCl reference electrode. To simulate solar illumination, a 300 W xenon lamp (PLS-SXE300, Beijing Perfect Light Technology Co. Ltd., Beijing, China) was used as the light source with

a light intensity of $\sim 100 \text{ mW/cm}^2$ as measured by an optical radiometer (FZ-A, Photoelectric Instrument Factory of Beijing Normal University, China).

2.4 Detection of hydrogen peroxide (H_2O_2) concentration

To detect *in situ* photogenerated H_2O_2 in the post-illumination photocatalytic “memory” process, the colorimetric DPD method based on the horseradish peroxidase (POD) catalyzed oxidation of *N, N*-diethyl-*p*-phenylenediamine (DPD) was used [29]. In a typical experiment, 10 mg POD was dissolved in 10 mL water, and 0.1 g *N, N*-diethyl-*p*-phenylenediammonium (DPD) sulfate was dissolved in 10 mL H_2SO_4 solution (0.05 M), respectively. 5 mL reaction solution was firstly put into a 10 mL test tube, and 0.5 mL phosphate buffer solution (0.5 M KH_2PO_4 and 0.5 M K_2HPO_4) was then added into it to obtain a mixture solution with pH at ~ 6.0 . Next, 50 μL DPD sulfate solution was added into the mixture solution and shaken for 5 s, and 50 μL POD solution was added into the mixture solution, shaken for another 5 s, and settled for 20 s before the UV–vis spectrum measurement. The H_2O_2 concentration in the reaction solution was quantified by measuring the absorption maximum at λ_{max} of 551 nm with the UV-2550 spectrophotometer.

2.5 Photocatalytic disinfection of *E. coli* bacteria by the BWO sample under simulated solar illumination and its post-illumination photocatalytic “memory” disinfection of *E. coli* bacteria in the dark

To demonstrate the photocatalytic performance under simulated solar illumination and the post-illumination photocatalytic “memory” effect of the BWO sample, a wild type of *E. coli* bacteria (ATCC 15597, the American Type Culture Collection, VA, USA) was used as the model microorganism for the disinfection experiments. After overnight culture in the LB culture medium, *E. coli* cells were collected by centrifuging, washed several times by the buffer solution (0.05 M KH_2PO_4 and 0.05 M K_2HPO_4 , pH = 7.0) to remove residual LB culture medium, and then diluted in the buffer solution to a 10^7 cfu/mL concentration before the disinfection experiments. All solid or liquid materials were autoclaved for 30 min at 121°C before use. The light source was the same xenon lamp used in OCPT measurement, a fixed concentration of $\sim 1.0 \text{ mg}$

sample/mL *E. coli* solution was used, and analyses were in triplicate.

In a typical disinfection experiment, 10 mL *E. coli* cell solution was pipetted onto a sterile $50 \times 10 \text{ mm}$ petri dish with 10 mg BWO sample. At regular time intervals, 100 μL of aliquots of the treated cell solution were withdrawn in sequence. After appropriate dilutions in buffer solution, aliquot of 100 μL was spread onto an agar medium plate and incubated at 37°C for 30 h. The number of viable cells in terms of colony-forming units was counted, and the *E. coli* survival ratio could be determined by the ratio of N_t/N_0 , where N_0 and N_t were the numbers of colony-forming units at the initial and each following time interval, respectively. For the *E. coli* disinfection experiments in the dark, 10 mg BWO sample was firstly irradiated by simulated solar illumination for 5 h. Then, the illumination was turned off and the BWO sample was used for *E. coli* disinfection experiments in the dark with fresh *E. coli* cell solutions.

2.6 Photocatalytic degradation of SMX and phenol by the BWO sample under simulated solar illumination and its post-illumination photocatalytic “memory” degradation of SMX and phenol in the dark

To further demonstrate the post-illumination photocatalytic “memory” effect of the BWO sample, its degradation effects on model organic pollutants of SMX and phenol were explored both under simulated solar illumination and in the dark after the illumination was turned off. In a typical experiment, 50 mL SMX solution (25 ppm) was added into a 100 mL beaker, and 50 mg BWO sample was dispersed into it. At given time intervals, 3 mL aliquots were collected from the suspension and immediately centrifuged at 9700 rpm for 5 min to separate the BWO sample from the treated SMX solution. The light absorption of the clear solution was measured with the UV-2550 spectrophotometer. For comparison purpose, the SMX degradation experiments were conducted under different conditions, including under only simulated solar illumination, under simulated solar illumination with the BWO sample, in the dark with the BWO sample without prior illumination, and in the dark with the BWO sample with prior simulated solar illumination for 5 h. For the phenol degradation experiments, 50 mL phenol solution (10 ppm) was used and other experimental conditions were the same as that used in the SMX degradation experiments.

3 Results and discussion

3.1 Crystal structure, morphology, and chemical composition of the BWO sample

In the solvothermal process to synthesize the BWO sample, C_2H_5OH and ethylene glycol (EG) served as both the reaction solvents and the complexing agents. Figure 1(a) shows the XRD pattern of the BWO sample, where the diffraction peaks all belonged to the orthorhombic Bi_2WO_6 phase (JCPDS No. 39-0256). Thus, the synthesis process produced a pure phase of Bi_2WO_6 . Figure 1(b) shows the SEM image of the BWO sample, consisting of microspheres formed by self-assembly of nanoflakes. The TEM image in Fig.

1(c) confirmed its nanoflake-aggregated microsphere morphology. The inset selected area electron diffraction (SAED) pattern could be well indexed to the polycrystalline structure of orthorhombic Bi_2WO_6 phase. BET analysis gave a BET specific surface area of $\sim 73.2 \text{ m}^2 \cdot \text{g}^{-1}$, which was in accordance with its nanoflake-aggregated microsphere morphology.

X-ray photoelectron spectroscopy (XPS) analysis was used to examine the chemical composition and element valence states of the BWO sample. Figure 2(a) shows the XPS survey spectrum of the BWO sample, identifying the existence of Bi, W, and O. C 1s signal could also be observed due to the wide existence of carbon in the environment. Figures 2(b)–2(d) present the high resolution XPS scans over Bi 4f, W 4f, and

Fig. 1 (a) XRD pattern, (b) SEM image, and (c) TEM image of the BWO sample (the inset image in (c) shows the corresponding SAED pattern).

Fig. 2 (a) XPS survey spectra of the BWO sample. (b–d) High resolution XPS scans over Bi 4f, W 4f, and O 1s peaks of the BWO sample, respectively.

O 1s peaks of the BWO sample, respectively. For Bi 4f spectra, two XPS peaks at 158.8 and 164.2 eV were identified, which could be assigned to $\text{Bi}^{3+} 4f_{7/2}$ and $\text{Bi}^{3+} 4f_{5/2}$, respectively [18–22]. For W 4f spectra, two XPS peaks at 34.9 and 37.0 eV were assigned to $\text{W}^{6+} 4f_{7/2}$ and $\text{W}^{6+} 4f_{5/2}$, respectively [13,19–22,27]. For O 1s spectra, the asymmetric peak could be best fitted into the combination of three sub-peaks at 529.9, 530.9, and 532.2 eV, respectively, which corresponded to the Bi–O and W–O chemical bondings in the BWO sample and the coordination of oxygen in O–H or adsorbed oxygen [30,31]. XPS analysis results further confirmed that pure Bi_2WO_6 was synthesized by our approach.

3.2 Light absorbance and energy band structure of the BWO sample

The light absorbance spectrum of the BWO sample could be approximated by the Kubelka–Munk function from its UV–vis diffuse reflectance spectrum [32,33]. The light absorbance spectrum of the BWO sample is shown in Fig. 3(a), indicating a good light absorbance from the UV light region to the visible light region. The light absorbance spectrum had a steep dropping shape with the fundamental absorbance stopping edge at ~ 420 nm, which indicated that its main light absorption arose from the band-gap transition [21,34]. The Tauc plot $((F(R) \cdot hv)^n \text{ vs. } hv)$, which was constructed from the light absorbance data is given in the inset image in Fig. 3(a) [35]. From its Tauc plot, the band gap value was determined at ~ 3.15 eV. Note that the adsorption tail deeply entered into the visible light region, which may be attributed to the light scattering among the aggregated Bi_2WO_6 nanoflakes in the BWO sample [36]. Thus, the light absorbance of the BWO sample suggested that it could have a good

photocatalytic performance under solar illumination.

Mott–Schottky (M–S) analysis was conducted to determine the conduction band (CB) minimum of the BWO sample. As shown in Fig. 3(b), its M–S plot demonstrated that the flat band potential value of the BWO sample was at ~ 0.06 V (vs. Ag/AgCl) and the positive slope confirmed its n-type nature [35]. The flat band potential of an n-type semiconductor is generally 0.2 V more positive than its conduction band bottom [35], and $E(\text{Ag}/\text{AgCl})$ is 0.2224 V (vs. NHE, normal hydrogen electrode). So the conduction band (CB) minimum of the BWO sample (vs. NHE) was found to be ~ 0.08 V. Combined with its band gap value (~ 3.15 eV) determined from the Tauc plot, the valence band (VB) maximum of the BWO sample (vs. NHE) was determined at ~ 3.23 V. Thus, its band structure could be constructed as shown in the inset image in Fig. 3(b), which demonstrated that the BWO sample had a proper band structure to generate radicals for photocatalytic reactions. The photogenerated electrons could react with O_2 through the two-electron reduction to generate active H_2O_2 because its conduction band minimum (0.08 V vs. NHE) was more negative than the two-electron oxygen reduction potential (0.68 V vs. NHE) [4,37], while the photogenerated holes could react with H_2O to generate active hydroxyl radicals ($\cdot\text{OH}$) or themselves react with organic pollutants for their degradation and microorganism for their disinfection.

3.3 Trapping/release of photogenerated electrons in the BWO sample upon the on and off of simulated solar illumination

Previous studies on the photocatalytic “memory” effect suggested that the trapping and release of photogenerated electrons upon the on and off of illumination afforded

Fig. 3 (a) Light absorbance of the BWO sample (the inset image in (a) shows the Tauc plot $((F(R) \cdot hv)^n \text{ vs. } hv)$ constructed from its light absorbance data to determine its band gap value). (b) Mott–Schottky plot of the BWO sample (the inset image in (b) shows its band structure).

these photocatalysts the radical production capability in the dark so that the photocatalysts had activity even when the illumination was off [1–4]. Thus, the capability of trapping and release of photogenerated electrons of the BWO sample was investigated by electrochemical tests, which was critical for evaluating its potential photocatalytic “memory” effect. Figure 4(a) shows the open circuit potential–time (OCPT) curves of the BWO sample electrode vs. the Ag/AgCl electrode under different conditions. Without illumination, its OCPT curve was mostly constant at ~ 0.12 V in the dark. Under simulated solar illumination, however, its OCPT curve dropped immediately with the beginning of the illumination to ~ -0.075 V and then remained at ~ -0.065 V after 0.5 h. This observation could be attributed to the equilibrium state established between the generation/transfer of photogenerated electrons to the BWO sample electrode surface and their subsequent release through the reaction with the electron acceptor of O_2 . After the BWO sample electrode was firstly irradiated by simulated solar illumination for 5 h, its OCPT curve was measured in dark. Now, a similar beginning value as that under simulated solar illumination was firstly observed, and then a gradual increase towards its OCPT value in dark without prior illumination was observed with the increase of dark time. When simulated solar illumination was switched off, the established equilibrium state could not be kept because no more electrons could be photogenerated and transferred to the BWO sample electrode surface, while O_2 could continue to react with trapped electrons and prompt further release of the trapped electrons. Thus, its OCPT curve would show the observed increase behavior

towards its OCPT value in dark without prior simulated solar illumination. These OCPT curves clearly indicated that the BWO sample had the capability to trap photogenerated electrons under simulated solar illumination and then release them when the illumination was turned off. Figure S1 in the Electronic Supplementary Material (ESM) shows the open circuit potential–time (OCPT) curves of a TiO_2 electrode vs. the Ag/AgCl electrode for comparison purpose. No obvious difference was observed between its OCPT curves without illumination and in dark after prior illumination, which was different from that of the BWO sample. Thus, TiO_2 could not trap and subsequently release photogenerated electrons with the on and off of UV illumination, which was consistent with the known fact that TiO_2 does not possess the photocatalytic “memory” effect.

Due to its variable valences and reported energy storage function, W component in the BWO sample was expected to possess the electron trapping and release capability. Figure 4(b) shows the high resolution XPS scans over W 4f peaks of the BWO sample just after being irradiated with simulated solar illumination for 5 h and after 20 h in the dark since the irradiation was switched off, respectively. Just after being irradiated with simulated solar illumination for 5 h, a clear difference was observed on the W 4f spectrum of the BWO sample, compared with that without the prior irradiation (see Fig. 2(c)). Besides the two XPS peaks at 34.9 and 37.0 eV assigned to $W^{6+} 4f_{7/2}$ and $W^{6+} 4f_{5/2}$, respectively, two other peaks were found at 34.3 and 36.4 eV for the best fitting of the spectrum. They could be assigned to $W^{5+} 4f_{7/2}$ and $W^{5+} 4f_{5/2}$, respectively [13].

Fig. 4 (a) Open circuit potential–time (OCPT) curves of the BWO sample electrode vs. the Ag/AgCl electrode in the dark without prior illumination, under simulated solar illumination, and in the dark after being previously irradiated for 5 h under simulated solar illumination. (b) High resolution XPS scans over W 4f peaks of the BWO sample just after being irradiated with simulated solar illumination for 5 h and after 20 h in the dark since the irradiation was turned off. (c) Schematic diagram of the energy band structure and the post-illumination photocatalytic “memory” effect of the BWO sample in the dark.

Thus, part of W^{6+} in the BWO sample was reduced to W^{5+} under simulated solar illumination, which indicated the trapping of photogenerated electrons on W component in the BWO sample. This observation was in accordance with the electronic band structure of the BWO sample. The reduction potential of W^{6+} to W^{5+} is 0.26 V vs. NHE [38], while the conduction band minimum of the BWO sample was determined at 0.08 V vs. NHE. Thus, photogenerated electrons in the BWO sample under simulated solar illumination could have enough energy to reduce W^{6+} to W^{5+} .

After 20 h in the dark since the irradiation was switched off, these two W^{5+} 4f peaks could still be observed on the high resolution XPS scan over W 4f peaks of the BWO sample, while they became relatively weaker than that just after being irradiated with simulated solar illumination. This observation indicated that trapped photogenerated electrons could be continuously released for a relatively long time after simulated solar illumination was turned off, which was beneficial for the BWO sample to keep its activity in the dark for a long time from the photocatalytic “memory” effect. Figures S2(a) and S2(b) in the ESM show the high resolution XPS scans over Bi 4f and O 1s peaks of the BWO sample just after being irradiated with simulated solar illumination for 5 h and after 20 h in the dark since the irradiation was switched off, respectively. No chemical state changes were observed on both Bi and O components in the BWO sample, no matter it was illuminated or not. Thus, XPS analysis results clearly demonstrated the trapping and release of photogenerated electrons by the BWO sample upon the on and off of simulated solar illumination were directly related to the reversible chemical state changes of its W component between W^{6+} and W^{5+} , respectively.

Due to its trapping and release behavior of photogenerated electrons, the BWO sample electrode could be considered as a capacitor [37]. Thus, the trapped/released photogenerated electron amount by the BWO sample could be quantitatively analyzed based on its capacitance and OCPT curve [5,7,10–12,39,40] as detailed in the ESM. It was found that the percentage of W^{6+} in the BWO sample reduced to W^{5+} after being irradiated by simulated solar illumination for 5 h could be determined as 1.7%. These released electrons should react with O_2 in the dark through the two-electron reduction to produce H_2O_2 due to their more negative energy (0.26 V vs. NHE) than that of the two-electron oxygen reduction potential (0.68 V vs. NHE), which

could impart the BWO sample with the desired photocatalytic “memory” effect to keep it active in the dark after the illumination was turned off [4]. Figure S3(b) in the ESM shows the H_2O_2 concentrations in the test solution by the BWO sample in the dark after simulated solar illumination was turned off. The H_2O_2 concentration had a fast increase during the first 10 min in the dark with the maximum H_2O_2 concentration of $\sim 1.8 \mu\text{M}$, which was due to the quick release of trapped electrons from the BWO sample to react with O_2 and produce more H_2O_2 than that being consumed at the same time. After the initial increase period, it gradually decreased afterwards because fewer and fewer electrons could be released from the BWO sample with the increase of the time in dark to produce H_2O_2 for the compensation of H_2O_2 consumed at the same time. After 90 min in the dark, the H_2O_2 concentrations were still $\sim 0.8 \mu\text{M}$, much higher than that in the environment background [4]. Thus, the BWO sample could remain active in the dark after simulated solar illumination was turned off. For comparison purpose, the H_2O_2 production by the pre-illuminated BWO sample in the dark was also examined in an Ar-enriched atmosphere, and the result was shown in Fig. S4 in the ESM. It clearly demonstrated that the H_2O_2 production in an Ar-enriched atmosphere was suppressed, compared with that in the air as shown in Fig. S3(b) in the ESM.

Based on these analysis results, a schematic diagram of the energy band structure and the post-illumination photocatalytic “memory” effect of the BWO sample in the dark was proposed in Fig. 4(c). Under simulated solar illumination, part of photogenerated electrons could be trapped by reducing W^{6+} to W^{5+} in the BWO sample as determined by its energy band structure. When the illumination was switched off, these trapped electrons could be released and W^{5+} changed back to W^{6+} . In the meantime, the released electrons from the BWO sample reacted with O_2 in the dark through the two-electron reduction to produce active H_2O_2 , which was critical for the BWO sample to possess the photocatalytic “memory” effect.

3.4 Photocatalytic and photocatalytic “memory” disinfections of *E. coli* bacteria by the BWO sample

The photocatalytic performance of the BWO sample under simulated solar illumination and its post-illumination photocatalytic “memory” in the dark were

first demonstrated by its disinfection of *E. coli* bacteria. Figure 5(a) shows the *E. coli* cell survival ratios under different treatment conditions. When no photocatalyst was present in the *E. coli* cell solution, the survival ratio of *E. coli* cells only showed a very slight decrease to ~95% under simulated solar illumination for 2 h, indicating that simulated solar illumination had no obvious disinfection effect on them. When the BWO sample without prior illumination was present in the *E. coli* cell solution, the survival ratio of *E. coli* cells also showed a slight decrease to ~92% in the dark after 2 h, indicating that the BWO sample itself was not toxic to *E. coli* cells. Under simulated solar illumination, however, the BWO sample demonstrated a good disinfection effect on *E. coli* cells. The survival ratio of *E. coli* cells largely decreased to less than 30%, which could be attributed to the photocatalytic disinfection of *E. coli* cells by radicals produced by the BWO sample under simulated solar illumination.

To demonstrate its post-illumination photocatalytic “memory” effect, the BWO sample was firstly irradiated by simulated solar illumination for 5 h. Then, the illumination was turned off and the BWO sample was used for the disinfection experiment in the dark on a fresh *E. coli* cell solution (ca. 10^7 cfu/mL). The BWO sample demonstrated a clear disinfection on *E. coli* cells in the dark, and the survival ratio of *E. coli* cells continuously decreased with the increase of the dark time after simulated solar illumination was turned off. After 2 h treatment in the dark, it decreased to ~55%, far lower than that treated by the BWO sample without

prior illumination in the dark. The observed post-illumination disinfection capability of the BWO sample in the dark could be attributed to its “memory” of prior simulated solar illumination, which trapped photogenerated electrons. When the illumination was switched off, these trapped electrons could be released from the BWO sample and react with O_2 to produce active H_2O_2 in the dark as demonstrated in Fig. 4 and Fig. S3 in the ESM, and the disinfection of *E. coli* bacteria by H_2O_2 with similar concentrations had been reported in literature [41,42]. Thus, the BWO sample could continue to disinfect *E. coli* cells in the dark after the solar illumination was switched off from the photocatalytic “memory” effect. To further verify the role of H_2O_2 in the disinfection of *E. coli* bacteria through the photocatalytic “memory” effect, a H_2O_2 scavenger of Fe(II)-EDTA (0.1 mM/L) was added into the *E. coli* cell solution before the photocatalytic “memory” effect experiment was conducted. With the presence of Fe(II)-EDTA, the produced H_2O_2 could be quickly consumed, and the disinfection of *E. coli* in the dark by the pre-illuminated BWO sample was largely suppressed. This observation clearly demonstrated the critical role of active H_2O_2 in the photocatalytic “memory” disinfection of *E. coli* cells by the BWO sample.

For comparison purpose, the *E. coli* cell survival ratio treated in dark by Degussa P25 TiO_2 nanoparticles with prior simulated solar illumination for 5 h was shown in Fig. S5 in the ESM, which clearly demonstrated that no obvious disinfection of *E. coli* bacteria was

Fig. 5 (a) Survival ratio of *E. coli* (in N_t/N_0 form) vs. reaction time by the BWO sample in the dark after being irradiated under simulated solar illumination for 5 h (BWO Light + Dark), compared with that without the presence of the BWO sample under simulated solar illumination (only Light), by the BWO sample in the dark without prior illumination (BWO Dark), and by the BWO sample under simulated solar illumination (BWO Light), respectively. (b) Residue SMX concentrations (in C/C_0 form) vs. reaction time by the BWO sample in the dark after being irradiated under simulated solar illumination for 5 h (BWO Light + Dark), compared with that by only simulated solar illumination, the BWO sample in the dark without prior illumination (BWO Dark), and by the BWO sample under simulated solar illumination (BWO Light), respectively. (c) Residue phenol concentrations (in C/C_0 form) vs. reaction time by the BWO sample in the dark after being irradiated under simulated solar illumination for 5 h (BWO Light + Dark), compared with that by only simulated solar illumination, the BWO sample in the dark without prior illumination (BWO Dark), and by the BWO sample under simulated solar illumination (BWO Light), respectively.

observed. This observation was consistent with the OCPT curves of TiO_2 (see Fig. S1 in the ESM). Without the capability to trap and release photogenerated electrons, no photocatalytic “memory” effect could be possessed by TiO_2 .

3.5 Photocatalytic and photocatalytic “memory” degradations of SMX and phenol by the BWO sample

The photocatalytic performance of the BWO sample under simulated solar illumination and its post-illumination photocatalytic “memory” in the dark were further demonstrated by its degradation on model organic pollutants of SMX and phenol as shown in Fig. 5(b) and Fig. 5(c), respectively. The concentrations of both SMX and phenol showed a slight decrease under simulated solar illumination without the presence of photocatalyst, which may be attributed to the small portion of UV light within simulated solar illumination. The concentrations of both SMX and phenol continuously were decreased by the photocatalytic treatment of the BWO sample under simulated solar illumination, which suggested that the BWO sample demonstrated good photocatalytic degradation effects on both of them. The BWO sample was also effective in degrading the organics in the dark from the photocatalytic “memory” effect as shown in Fig. S6 in the ESM of the UV absorption spectra of SMX and phenol at different treatment time from 0 to 2 h by the BWO sample in the dark with prior simulated solar illumination for 5 h, respectively. Without prior illumination, the concentrations of both SMX and phenol showed almost no change when treated by the BWO sample in the dark, while moderate degradations on both SMX and phenol were observed in the dark by the BWO sample with prior illumination. The observed degradation behaviour difference in the dark by the BWO sample upon prior illumination suggested that the photocatalytic “memory” effect extended to organic pollutant degradation as well. However, the degradation effect in the dark from the photocatalytic “memory” effect of the BWO sample was not strong because only a relatively mild oxidant of H_2O_2 was produced through the reaction of released electrons with O_2 and its concentration was not high [43,44], while SMX and phenol are stable organic compounds with benzene rings. Thus, the photocatalytic “memory” effect of the BWO sample was more favorable for the disinfection of pathogenic microorganisms. For comparison purpose,

Fig. S5 in the ESM shows the concentrations of SMX and phenol treated in dark by Degussa P25 TiO_2 nanoparticles with prior simulated solar illumination for 5 h, respectively. As expected, no obvious concentration change was observed for both SMX and phenol because TiO_2 could not possess the photocatalytic “memory” effect due to its incapability to trap and release photogenerated electrons.

3.6 Major active species for the photocatalytic activity of the BWO sample

To verify the working mechanism of the BWO photocatalyst, major active species produced by the BWO sample under illumination were examined. Radical scavengers of isopropanol (IPA), Fe(II)-EDTA , NaBrO_3 , and ammonium oxalate were used to trap hydroxyl radicals ($\cdot\text{OH}$), H_2O_2 , electrons (e^-), and holes (h^+), respectively. Figure 6 shows the residue phenol concentrations treated by the BWO sample under simulated solar illumination with the presence of different radical scavengers at different treatment time. The presence of ammonium oxalate or Fe(II)-EDTA largely suppressed the photocatalytic phenol degradation by the BWO sample, while the presence of IPA and NaBrO_3 had no obvious affection on its photocatalytic performance. Thus, the major active species produced by the BWO sample were h^+ and H_2O_2 under simulated solar illumination, which was consistent with its energy band structure (see Fig. 3(b)). Photogenerated electrons of the BWO sample reacted with O_2 to produce H_2O_2 because its conduction band potential was more negative than the two-electron reduction potential of O_2 , while photogenerated holes directly reacted with pollutants.

Fig. 6 Residue phenol concentration vs. reaction time treated by the BWO sample under simulated solar illumination with the presence of different radical scavengers.

3.7 Stability and reusability of the BWO sample on its post-illumination photocatalytic “memory”

Figure 7(a) compares the XRD patterns of the BWO sample without prior simulated solar illumination and in the dark for 20 h after being irradiated with simulated solar illumination for 5 h. Both XRD patterns were identical. Figure S7 in the ESM shows the SEM image of the BWO sample in the dark for 20 h after being irradiated with simulated solar illumination for 5 h. No obvious change could be found from its original state without illumination (see Fig. 1(b)). Both comparisons indicated that the BWO sample had good structure stability after the on and off cycle of simulated solar illumination. Figure 7(b) compares the H_2O_2 production of the BWO sample in the dark after being pre-irradiated by simulated solar illumination for 5 h for five consecutive runs. The BWO sample was separated from the reaction solution after each run, washed, dried at 60 °C in air for 2 h, set aside at room temperature for 5 h under simulated solar illumination, and then reused in the next run. It is evident that the H_2O_2 production behaviour by the BWO sample in the dark from its photocatalytic “memory” effect was very similar in the five successive runs. These results

suggested that the photocatalytic “memory” effect of the BWO sample was stable and BWO could be reused to generate similar activity in the dark from the photocatalytic “memory” effect, which was beneficial for its potential applications in various environmental remediation cases.

4 Conclusions

In summary, post-illumination activity in the dark for an extended period of time was found in pure phase Bi_2WO_6 microspheres from the photocatalytic “memory” effect. Due to its electronic band structure, part of photogenerated electrons could be trapped on W component within Bi_2WO_6 through its valence change from W^{6+} to W^{5+} under simulated solar illumination as demonstrated by the electrochemical test and in-situ XPS analysis results. When the light illumination was off, these trapped electrons were gradually released to react with O_2 through the two-electron reduction to produce H_2O_2 in the dark continuously because they had higher energy than that of the two-electron oxygen reduction potential, which endowed Bi_2WO_6 microspheres the observed disinfection capability on *E. coli* cells in the dark for an extended period of time. The demonstrated activity in the dark of Bi_2WO_6 microspheres relied on the energy storage/release function of the W component within the Bi_2WO_6 crystal itself, which resulted in their stable photocatalytic “memory” effect during cycling experiments. It is expected that other pure phase photocatalysts could also possess the photocatalytic “memory” effect if themselves have the energy storage/release function similar as Bi_2WO_6 , which could largely expand the selection of photocatalytic materials for continuous activity in the dark for an extended period of time for a broad range of potential applications.

Acknowledgements

This study was supported by the National Natural Science Foundation of China (Grant Nos. 51672283, 51602316, and 51902271), the Fundamental Research Funds for the Central Universities (Grant Nos. A1920502051907-15, 2682020CX07, and 2682020CX08), Sichuan Science and Technology Program (Grant Nos. 2020YJ0259 and 2020YJ0072), Joint Fund between Shenyang National Laboratory for Materials Science and State Key Laboratory

Fig. 7 (a) XRD patterns of the BWO sample without prior simulated solar illumination and in the dark for 20 h after being irradiated with simulated solar illumination for 5 h. (b) H_2O_2 production of the BWO sample in the dark after being irradiated by simulated solar illumination for 5 h for five consecutive runs.

of Advanced Processing and Recycling of Nonferrous Metals (Grant No. 18LHPY009), Liaoning Baiqianwan Talents Program, Natural Science Foundation of Liaoning Province of China (Grant No. 20180510042), and the Natural Science Foundation of Shandong Province, China (Grant No. ZR2017MEM017).

Electronic Supplementary Material

Supplementary material is available in the online version of this article at <https://doi.org/10.1007/s40145-020-0448-8>.

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