Temperature-Program Assisted Synthesis of Novel Z-Scheme CuBi$_2$O$_4$/β-Bi$_2$O$_3$ Composite with Enhanced Visible Light Photocatalytic Performance

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Abstract: Novel Z-Scheme CuBi$_2$O$_4$/β-Bi$_2$O$_3$ composite photocatalysts with different mass ratios and calcination temperatures were firstly synthesized by the hydrothermal method following a temperature-programmed process. The morphology, crystal structure, and light absorption properties of the as-prepared samples were systematically characterized, and the composites exhibited enhanced photocatalytic activity toward diclofenac sodium (DS) degradation compared with CuBi$_2$O$_4$ and β-Bi$_2$O$_3$ under visible light irradiation. The optimal photocatalytic efficiency of the composite, achieved at the mass ratio of CuBi$_2$O$_4$ and β-Bi$_2$O$_3$ of 1:2.25 and the calcination temperature of 600°C is 92.17%. After the seventh recycling of the composite, the degradation of DS can still reach 82.95%. The enhanced photocatalytic activity of CuBi$_2$O$_4$/β-Bi$_2$O$_3$ is closely related to OH•, h+ and O$_2^{-}$•, and the photocatalytic mechanism of CuBi$_2$O$_4$/β-Bi$_2$O$_3$ can be explained by the Z-Scheme theory.

Keywords: CuBi$_2$O$_4$/β-Bi$_2$O$_3$; temperature programmed; semiconductors; Z-Scheme; visible light; organics

1. Introduction

Diclofenac sodium (DS) is a very effective anti-inflammatory drug widely used in many countries [1,2]. Due to the poor absorbability of organisms to DS, most of the DS will be released into the environment after it is taken [1]. However, long-term exposure to a DS-polluted environment will cause serious risk to ecosystems and human health [3,4]. Therefore, effective degradation technologies for DS should be explored to control its persistent contamination.

Semiconductor photocatalytic technology has aroused widespread interest in organic pollution control [5–8] due to its advantages of rich catalysts, mild reaction conditions, fast reaction speed, and no secondary pollution. In past decades, titanium dioxide (TiO$_2$) has attracted considerable attention for its low cost and chemical inertness [8–10]. However, the large band gap of TiO$_2$, which is approximately 3.2 eV, limits its absorption of sunlight to the ultraviolet (UV) region [10,11]. Because the visible light occupies 43% of sunlight, whereas UV light occupies only 4%, the development of visible-light responsive semiconductor photocatalysts is becoming a research hotspot [12–15].
CuBi₂O₄ possesses a strong visible light response, excellent chemical stability, high conduction band position, and strong reducing ability [16–18]. However, the single CuBi₂O₄ exhibits poor photocatalytic performance [17]. Some related studies suggest its activity could be improved through the synergistic effect with other metal oxide semiconductors [17,19,20]. Bi₂O₃, a visible light-responsive semiconductor material, is regarded as a promising photocatalyst for organic pollutant degradation [21,22]. This is mainly due to that the energy band gap (in the range from 2.4 to 3.2) of Bi₂O₃ can be tuned by employing different synthesis techniques, such as sol gel, hydrothermal/solvothermal and solid-state decomposition methods [21,23,24]. β-Bi₂O₃, as one of the six different polymorphs of Bi₂O₃ (i.e., α-, β-, γ-, δ-, ω- and ε-polymorph), exhibits a narrower band gap with the strongest light-absorption ability than other phases [23,25–27]. Yet the photocatalytic activity of pure β-Bi₂O₃ is still far from satisfactory for the fast recombination of photogenerated charges [26,28].

In theory, CuBi₂O₄ coupling with β-Bi₂O₃ could form the hybrid composite via matching the band structure of each other with significantly enhanced photocatalytic activity. Nevertheless, the research on the temperature-programmed synthesis and photocatalytic application of a CuBi₂O₄/β-Bi₂O₃ system has not been investigated in detail. In this study, novel CuBi₂O₄/β-Bi₂O₃ composite photocatalysts with different mass ratios and calcination temperatures were firstly synthesized by the hydrothermal method following a temperature-programmed process. The as-synthesized composites were systematically characterized and their photocatalytic performance was carefully investigated by the degradation of D5 under visible-light irradiation (λ > 400 nm). Moreover, the active species in the CuBi₂O₄/β-Bi₂O₃ photocatalytic system were discussed through the free radical capture experiments, and the photocatalytic mechanism of CuBi₂O₄/β-Bi₂O₃ was also put forward.

2. Materials and Methods

2.1. Materials

All reactants and solvents were analytical grade and used without further purification. Bi(NO₃)₃·5H₂O, Cu(NO₃)₂·3H₂O, Na₂CO₃, NaOH, HNO₃, gluconic acid, tert-butanol (t-BuOH), para-benzoquinone (BZQ), disodium ethylenediaminetetraacetate (Na₂-EDTA), ethanol, and diclofenac sodium were obtained from Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China). Ultrapure water was used throughout this study.

2.2. Synthesis of CuBi₂O₄/β-Bi₂O₃

The detailed synthesis pathway of CuBi₂O₄/β-Bi₂O₃ is illustrated in Figure 1. Firstly, CuBi₂O₄ was prepared through a simple hydrothermal method, and the detailed experiment processes are similar to that reported by our previous paper [16]. Secondly, a core-shell structural CuBi₂O₄@C was synthesized, that is, 0.1 g of CuBi₂O₄ was ultrasonically dispersed into 70 mL of aqueous solution (with 0.3 mL gluconic acid), and then the solution was transferred into a 100-mL sealed Teflon-lined stainless steel autoclave for 4 h at 180 °C. When the autoclave was cooled naturally to room temperature, the precipitate was isolated by centrifugation and washed several times with distilled water. Thirdly, a temperature-programmed method was used to synthesize the CuBi₂O₄/β-Bi₂O₃. Then 0.1 g of CuBi₂O₄@C obtained above was ultrasonically dispersed into 20 mL HNO₃ solution (1 mol/L) to obtain solution A; 0.39 mmol Bi(NO₃)₃·5H₂O was completely dissolved into another 20 mL HNO₃ solution (1 mol/L) under the acute agitation to obtain solution B; 2.34 mmol Na₂CO₃ was dissolved into 40 mL ultrapure water to obtain solution C. After solutions A and B were well mixed, solution C was added into the mixture drop by drop, and a large amount of white precipitate was produced. Then the washed precipitate by ethanol and ultrapure water was placed into a temperature-programmed furnace, and the reaction furnace was set to be heated to 600 °C within 30 min and kept at this temperature for 5 h. The CuBi₂O₄/β-Bi₂O₃ with mass ratio of 1:2.25 at different calcination temperatures of 400 °C, 600 °C and 800 °C was obtained through changing the temperature of the reaction furnace. In addition, the CuBi₂O₄/β-Bi₂O₃ with different mass ratios of 1:1, 1:2.25 and 1:4 was obtained through adjusting
the added amount of Bi(NO$_3$)$_3$, 5H$_2$O and Na$_2$CO$_3$. For composition, the pure CuBi$_2$O$_4$ and β-Bi$_2$O$_3$ were also prepared through the above synthesis process, and the detailed synthesis steps can also be seen from the Figure 1.

![Figure 1. The detailed synthesis pathway of CuBi$_2$O$_4$/β-Bi$_2$O$_3$.](image)

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were examined to study the crystal structure and phase composition of the materials using the D/max 2500 PC (Rigaku, Japan) instrument with Cu Ka radiation (40 kV, 100 mA) at a rate of 4.0°/min over a 2θ range of 20°–60°. Morphologies of the samples were characterized by scanning electron microscopy (SEM, JSM-6360LV, JEOL, Tokyo, Japan). Ultraviolet-visible (UV-Vis) diffusive reflectance spectra were obtained by a Shimadzu UV-2550 spectrophotometer (Shimadzu, Kyoto, Japan) over the analysis range from 200 to 800 nm. X-ray photoelectron spectra (XPS) were recorded using the ESCALAB 250 instrument (Thermo Scientific, Waltham, MA, USA) with Al Ka radiation.

2.4. Photocatalytic Performance Experiments

The photocatalytic performance experiments were conducted in photoreaction apparatus (BL-GHX-V, Bilang Biological Science and Technology Co., Ltd., Xi’an, China) using a 300 W Xe lamp with an ultraviolet cutoff filter (providing visible light ≥ 400 nm) as the light source. In each experiment, a 25 mg photocatalyst was added to 50 mL of DS solution (8 mg/L). Before irradiation, the solution was magnetically stirred in the dark for 30 min to reach the adsorption-desorption equilibrium. As the reaction time elapsed, the sample was taken out and filtered immediately with 0.45 μm membrane filters, the concentrations of DS and Total Organic Carbon (TOC) are measured by a high performance liquid chromatography (HPLC, Agilent 1260, Santa Clara, CA, USA) and TOC (Shimadzu TOC-VCPH, Kyoto, Japan) analyzer, respectively. In addition, repeated experiments for DS degradation were also conducted to study the stability of the as-prepared photocatalysts, and the operation processes were similar to the photocatalytic experiments. All experiments were repeated twice and the data shown in the article was averaged.

2.5. Analysis of Reactive Species

Free radical capture experiments were used to ascertain the reactive species of CuBi$_2$O$_4$/β-Bi$_2$O$_3$ photocatalytic system, and tert-butanol (t-BuOH) was chosen as the hydroxyl radical (OH$^*$).
scavenger, disodium ethylenediamine tetraacetate (EDTA-Na$_2$) was chosen as the hole ($h^+$) scavenger, benzoquinone (BZQ) was chosen as the superoxide radical ($O_2^{•-}$) scavenger. The detailed experiment processes were similar to the photocatalytic activity experiments.

3. Results and Discussion

Figure 2 depicts scanning electron microscope (SEM) images of the as-prepared materials. A well-distributed micro-sphere structure (~5 µm) with smooth surface for pure CuBi$_2$O$_4$ is shown in Figure 2a. The transition material of CuBi$_2$O$_4$@C, from Figure 2b, shows increased size and relatively rough surface compared with pure CuBi$_2$O$_4$. Moreover, some dispersed carbon microspheres exist as well. In the formation process of CuBi$_2$O$_4$/β-Bi$_2$O$_3$, the control of temperature is an important step. As shown from Figure 2c, the products exhibit a chain-connected spherical structure when the temperature is at 400 °C, and the connection matter is the incompletely burned carbon. That is because the complete combustion temperature of carbon is higher than 500 °C [29]. Therefore, the composition of calcined products just contain CuBi$_2$O$_4$ and β-Bi$_2$O$_3$ when the temperatures are at 600 °C and 800 °C. But the rising of calcination temperature will destroy sphere-structural CuBi$_2$O$_4$, which can be seen from the SEM images of Figure 2d,e.

**Figure 2.** Scanning electron microscope (SEM) images of (a) CuBi$_2$O$_4$; (b) CuBi$_2$O$_4$@C; (c) CuBi$_2$O$_4$/β-Bi$_2$O$_3$ (1:2.25, 400 °C); (d) CuBi$_2$O$_4$/β-Bi$_2$O$_3$ (1:2.25, 600 °C); (e) CuBi$_2$O$_4$/β-Bi$_2$O$_3$ (1:2.25, 800 °C).
The purity and crystallinity of CuBi$_2$O$_4$ and CuBi$_2$O$_4$/β-Bi$_2$O$_3$ calcined at 600 °C were examined with XRD, as depicted in Figure 3. From the XRD pattern of CuBi$_2$O$_4$, the diffraction peaks can be perfectly indexed to the phase of CuBi$_2$O$_4$ (JCPDS No. 84-1969) [30]. In the XRD pattern of CuBi$_2$O$_4$/β-Bi$_2$O$_3$ (600 °C), except for the peaks indicating CuBi$_2$O$_4$, the diffraction peaks located at the 2θ values of 27.66°, 32.86°, 46.32°, 55.44°, and 57.86°, can be indexed to the (201), (220), (222), (421), and (402) crystalline planes of tetragonal β-Bi$_2$O$_3$ (JCPDS No. 27-0050) [22,25]. Moreover, there are no obvious carbon peaks from the XRD pattern of CuBi$_2$O$_4$/β-Bi$_2$O$_3$ (600 °C), indicating the complete combustion of carbon in this calcination temperature [29].

![Figure 3. X-ray diffraction (XRD) patterns of CuBi$_2$O$_4$ and CuBi$_2$O$_4$/β-Bi$_2$O$_3$ (1:2.25, 600 °C).](image)

The UV-Vis absorption spectrum of CuBi$_2$O$_4$, β-Bi$_2$O$_3$ (600 °C) and CuBi$_2$O$_4$/β-Bi$_2$O$_3$ (600 °C) are displayed in Figure 4a. Both of the materials exhibit strong absorbance in the UV and visible light regions, and the maximum absorption boundary of CuBi$_2$O$_4$, β-Bi$_2$O$_3$ (600 °C) and CuBi$_2$O$_4$/β-Bi$_2$O$_3$ (600 °C) appear at approximately 800 nm, 500 nm and 725 nm, respectively. The band gap energy ($E_g$) of CuBi$_2$O$_4$ and β-Bi$_2$O$_3$ (600 °C) can be determined with the classic Tauc approach by using the following equation [31]:

$$a h v = A (h v - E_g)^{n/2},$$

where $a$, $h$, $v$, $E_g$ and $A$ are the absorption coefficient, the Planck constant, the light frequency, the band gap energy, and a constant, respectively. In the equation, $n$ is a number characteristic of the charge transition in a semiconductor, and $n = 1$ for a direct transition while $n = 4$ for an indirect transition [31]. As for CuBi$_2$O$_4$ and β-Bi$_2$O$_3$ (600 °C), $n = 4$ [32,33]. Therefore, their band gap energy could be elicited from the plot of light energy ($ahv$) versus energy ($hv$), shown in Figure 4b, which suggests that the band gap energy of CuBi$_2$O$_4$ and β-Bi$_2$O$_3$ (600 °C) are 1.72 eV and 2.70 eV, respectively, which are very close to previous literature [33–35]. In addition, the valence band (VB) and conduction band (CB) edge position of the semiconductors can be estimated according to the following empirical equation:

$$E_{VB} = X - E^c + 0.5E_g$$  \hspace{1cm} (1)

$$E_{CB} = E_{VB} - E_g$$  \hspace{1cm} (2)

where $E_{VB}$ and $E_{CB}$ are the valence band (VB) and conduction band (CB) edge potentials, respectively; $X$ is the electronegativity of the absolute electronegativity of the constituent atoms, that is 4.59 eV for CuBi$_2$O$_4$ and 6.24 eV for β-Bi$_2$O$_3$ [25,33]; $E^c$ is the energy of free electrons on the hydrogen scale (approximately 4.5 eV) [31]. Consequently, the $E_{VB}$ and $E_{CB}$ positions of CuBi$_2$O$_4$ are estimated to be 0.95 and −0.77 eV/NHE; the $E_{VB}$ and $E_{CB}$ positions of β-Bi$_2$O$_3$ (600 °C) are estimated to be 3.09 and 0.39 eV/NHE.
The degradation of DS in different photocatalytic systems was evaluated under visible light irradiation, and the results are described in Figure 5. It can be seen from Figure 5a, the degradation efficiency of DS in the blank irradiation system is 38.21% in 240 min reaction while the degradation efficiency of DS is 44.48% and 65.85% with the addition of pure $\beta$-Bi$_2$O$_3$ and CuBi$_2$O$_4$. As for the system of mechanically mixed CuBi$_2$O$_4$ and $\beta$-Bi$_2$O$_3$ with the mass ratio of 1:2.25, 70.11% of DS can be degraded in the same condition. Figure 5c shows the photodegradation efficiency of DS in the system of composites CuBi$_2$O$_4$/β-Bi$_2$O$_3$ with different mass ratios. The adsorption capacity of composites to DS is less than 10%, suggesting the removal of DS is closely related to photodegradation and photocatalysis. The degradation efficiency of DS is enhanced with increasing $\beta$-Bi$_2$O$_3$ in the composite as the mass ratio of CuBi$_2$O$_4$ and $\beta$-Bi$_2$O$_3$ changes from 1:0.5 to 1:2.25, but will decrease with a further increase of the content of $\beta$-Bi$_2$O$_3$, i.e., the mass ratio of 1:4. Figure 5e shows the degradation efficiency of DS using CuBi$_2$O$_4$/β-Bi$_2$O$_3$ calcined at different temperatures. It can be seen that the degradation efficiencies of DS are 84.37%, 92.17% and 76.80%, respectively, and the composites calcined at 400 °C, 600 °C and 800 °C. Figure 5b,d,f describe the degradation rate curves of DS in different photocatalytic systems which derive from the In(C$_0$/C) versus irradiation time and the values of degradation rates are listed in Table 1. The maximum degradation rate of DS can be obtained in the system of composite CuBi$_2$O$_4$/β-Bi$_2$O$_3$ with the mass ratio of 1:2.25 and the calcination temperature of 600 °C, which is 0.0099 min$^{-1}$.

**Table 1.** Kinetic analysis of DS degradation in different photocatalyst systems.

| Photocatalytic System | $K_{app}$ (min$^{-1}$) | $R^2$ |
|-----------------------|------------------------|-------|
| Blank irradiation     | 0.0027                 | 0.92  |
| $\beta$-Bi$_2$O$_3$   | 0.0030                 | 0.90  |
| CuBi$_2$O$_4$         | 0.0040                 | 0.94  |
| Mechanically mixed with CuBi$_2$O$_4$ and $\beta$-Bi$_2$O$_3$ | 0.0048 | 0.94 |
| CuBi$_2$O$_4$/$\beta$-Bi$_2$O$_3$ (1:0.5, 600 °C) | 0.0055 | 0.92 |
| CuBi$_2$O$_4$/$\beta$-Bi$_2$O$_3$ (1:1, 600 °C) | 0.0076 | 0.91 |
| CuBi$_2$O$_4$/$\beta$-Bi$_2$O$_3$ (1:2.25, 600 °C) | 0.0099 | 0.90 |
| CuBi$_2$O$_4$/$\beta$-Bi$_2$O$_3$ (1:4, 600 °C) | 0.0059 | 0.96 |
| CuBi$_2$O$_4$/$\beta$-Bi$_2$O$_3$ (1:2.25, 400 °C) | 0.0065 | 0.95 |
| CuBi$_2$O$_4$/$\beta$-Bi$_2$O$_3$ (1:2.25, 800 °C) | 0.0060 | 0.95 |
Figure 5. Diclofenac sodium (DS) degradation efficiency in the photocatalytic system of (a) blank irradiation, CuBi$_2$O$_4$, β-Bi$_2$O$_3$ and CuBi$_2$O$_4$ + β-Bi$_2$O$_3$; (c) CuBi$_2$O$_4$/β-Bi$_2$O$_3$ with different mass ratios; (e) CuBi$_2$O$_4$/β-Bi$_2$O$_3$ with different calcination temperatures; (b,d,f) plots of ln($C_0$/C) versus irradiation time over different photocatalytic systems.

To further evaluate the degradation efficiency of DS in the as-prepared catalyst’s system, the removal efficiencies of Total Organic Carbon (TOC) are also explored and the results are shown in Figure 6. In the blank irradiation system, only 18.01% of TOC can be removed. And in the pure β-Bi$_2$O$_3$ and CuBi$_2$O$_4$ photocatalytic systems, the TOC removal efficiencies are 22.52% and 30.59%, respectively. When CuBi$_2$O$_4$ and β-Bi$_2$O$_3$ with the mass ratio of 1:2.25 are mechanically mixed to add into the system, 35.96% of TOC are removed. But for the composites CuBi$_2$O$_4$/β-Bi$_2$O$_3$ with different mass ratios calcinated at various temperatures, the removal efficiencies of TOC can be greatly improved, and the maximum value reaches 57.37%, which is achieved in the photocatalytic system of CuBi$_2$O$_4$/β-Bi$_2$O$_3$ with the mass ratio of 1:2.25 and the calcination temperature of 600 °C.
Figure 6. Total Organic Carbon (TOC) removal efficiency of the DS photodegradation solutions in different photocatalytic systems.

Figure 7a describes the photodegradation efficiency of DS under different recycling runs using CuBi$_2$O$_4$/β-Bi$_2$O$_3$ (1:2.25, 600 °C) as the catalyst. When the catalyst was repeated for seven times, the degradation efficiency of DS is 82.95%. Figure 7b shows the degradation rate curves of DS over CuBi$_2$O$_4$/β-Bi$_2$O$_3$ (1:2.25, 600 °C) under different recycling runs, and the values of rate constants are described in the illustration. It can be seen that the degradation rate of DS decreases from 0.0099 min$^{-1}$ to 0.0071 min$^{-1}$ after the seventh recycle. To further understand the photocatalytic stability of the as-prepared CuBi$_2$O$_4$/β-Bi$_2$O$_3$, XRD and Bi 4f XPS spectrums of the recycled composites are conducted seven times and the results are shown in Figure 8. Compared with the XRD spectra of the fresh and reused CuBi$_2$O$_4$/β-Bi$_2$O$_3$ in Figure 8a, there are no obvious changes for the main peaks. But from the Figure 8b, a new peak occur in the composite after recycling expect for the two main peaks existing in both of the two samples. According to reports, the main 4f 7/2 peak at 158.32 eV for a fresh sample and 158.30 eV for a reused sample, and the other main 4f 5/2 peak at 163.60 eV for a fresh sample and 163.49 eV for a reused sample, correspond to the Bi$^{3+}$ oxidation state [36,37], which are in accordance to the presence of either CuBi$_2$O$_4$ or β-Bi$_2$O$_3$ phases. The extra peak at 156.63 eV in the reused sample is ascribed to Bi metal [38], indicating that some Bi$^{3+}$ in the substance was reduced to be Bi metal after the reaction.
The photocatalytic activity of the CuBi heterojunction energy band theory and Z-scheme theory were of concern [8]. Based on the analysis above, a possible Z-scheme photocatalytic mechanism was put forward to explain the enhanced photocatalytic activity of the CuBi composite, which is illustrated in Figure 10. That is, both CuBiO4 and β-Bi2O3 could generate the photoinduced electron-hole pairs under visible-light illumination owing to their good light absorption abilities. Then, the formed Bi metal becomes the recombination center of the photogenerated electron from CB of β-Bi2O3 and the holes from the VB of the CuBi2O4 in the photocatalytic reaction process, leading to the improved charge separation. Besides, the dissolved O2 in the solution can be captured by the photogenerated electrons in the CB of CuBi2O4 to form O2•− due to the more negative CB level of CuBi2O4 than the potential of O2/O2•−.
(E(O₂/Ο₂*) = 0.13 eV (vs. NHE) [39]; while the photogenerated holes in the VB of β-Bi₂O₃ can lead the H₂O/OH⁻ to be oxidized to OH⁺ for the higher energy of holes in the VB of β-Bi₂O₃ than the potential of OH⁻/OH⁺ E(OH⁻/OH⁺) = 1.99 eV (vs. NHE) [39]. Subsequently, the holes in the VB of β-Bi₂O₃, the formed OH⁺ and O₂•− participate in the DS photodegradation.

Figure 10. Supposed photocatalytic mechanism of CuBi₂O₄/β-Bi₂O₃ by the Z-scheme theory.

4. Conclusions

A combined hydrothermal and temperature-programmed method was employed to synthesize the CuBi₂O₄/β-Bi₂O₃ composite photocatalysts. The properties of the as-prepared materials were systematically characterized by SEM, XRD, XPS and UV-Vis. Moreover, the composites exhibit enhanced photocatalytic performance toward DS degradation under visible light irradiation, and the optimal photodegradation efficiency of DS is achieved in the catalytic system of CuBi₂O₄/β-Bi₂O₃ with the mass ratio of 1:2.25 and the calcination temperature of 600 °C. Besides, the active species in the CuBi₂O₄/β-Bi₂O₃ photocatalytic system were discussed through the free radical capture experiments, and the photocatalytic mechanism of CuBi₂O₄/β-Bi₂O₃ was also put forward.

Author Contributions: X.C. (Xiaojuan Chen) designed and performed the experiments, and drafted the manuscript. N.L. and R.Z. provided guidance for the general idea of the thesis. S.L., C.Y., W.X., S.X. and X.C. (Xin Chen) carried out the sample preparations, part of the material characterization analysis, and data collection. All authors read and approved the final manuscript.

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