Investigations on the Synthesis and Properties of Fe$_2$O$_3$ /Bi$_2$O$_2$CO$_3$ in the Photocatalytic and Fenton-like Process

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Abstract. Catalyst of Bi$_2$O$_2$CO$_3$ and Fe$_2$O$_3$ modified Bi$_2$O$_2$CO$_3$ (Fe$_2$O$_3$:Bi$_2$O$_2$CO$_3$) were prepared by hydrothermal method and characterized by X-ray diffractions (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM) and UV-vis DRS. The catalytic activity of Bi$_2$O$_2$CO$_3$ and Fe$_2$O$_3$:Bi$_2$O$_2$CO$_3$ were comparatively investigated in the photodegradation and Fento-like process. Rhodamine B (Rhb) was selected as the target pollutant under the irradiation of 300 W xenon lamp. The results indicated that Fe$_2$O$_3$ plays a great role in the enhancing the treatment efficiency and the and the maximum reaction rate was achieved at the Fe$_2$O$_3$ loading of 1.5%. The Fenton-like degradation rate constant of Rhb with bare Bi$_2$O$_2$CO$_3$ in dark is 0.4 min$^{-1}$, while that with 1.5 Fe$_2$O$_3$:Bi$_2$O$_2$CO$_3$ increases to 28.4 min$^{-1}$ under visible light irradiation, a 71-fold improvement. It is expected to shed a new light for the constructing novel composite photocatalyst and also provide a potential method for the removal of dyes in the aqueous system.

1. Introduction

Bi$_2$O$_2$CO$_3$ is a typical Sillén-phase compound, in which the Bi-O atoms layer and CO$_3^{2-}$ layer is orthogonal staggered symbiosis [1]. This structure can improve the separation efficiency of electron-hole pairs [2]. However, with a low absorption of UV light (about 5% of the solar light [3]), the application of Bi$_2$O$_2$CO$_3$ photocatalytic materials is limited. Recently, many methods have been employed to overcome its limitations, including heterojunction fabrication. Tian et al. [4] compounded Ag:Cs$_2$N$_4$ and Bi$_2$O$_2$CO$_3$ and studied its photocatalytic performance. Wang et al. [3] successfully prepared the composite catalyst of Bi$_2$O$_2$CO$_3$/g-C$_3$N$_4$ for the first time. This kind of catalyst exhibits high photocatalytic activity on NO in air degradation. Puttaswamy Madhusudan [5] compounded BiVO$_4$ and Bi$_2$O$_2$CO$_3$, which can significantly improve its performance. Lin et al. [6] synthesized Bi$_2$O$_2$CO$_3$ and Bi$_2$MoO$_6$ via a one-pot hydrothermal method. Good photocatalytic activity can be attributed to the heterojunction interface which facilitates the separation of photogenerated electron–hole pairs. Zai et al. [7] researched I-doped Bi$_2$O$_2$CO$_3$ and the catalyst exhibits high photocatalytic activity. Lv et al. [8] prepared Bi$_2$O$_2$CO$_3$/TiO$_2$ composite powders which showed that the composite powders have a high photocatalytic activity than TiO$_2$. Furthermore, Fe$_2$O$_3$ [9], a photocatalyst, has also been studied.

AOPs (advanced oxidation processes) has an efficient oxidization ability for organic pollutants, has become an important research task in the field of environmental protection [10], in which Fenton
reaction as a fast-growing AOPs technology[11]. Normal Fenton reaction uses the chain reaction between bivalent iron ion (Fe$^{2+}$) and hydrogen peroxide (H$_2$O$_2$) to generate strong oxidation ability and high electronegativity of hydroxyl radicals, most of the organic material in water can be oxidized. Its harsh conditions greatly limits the application in organic wastewater treatment (pH < 3). Studies found that photo-Fenton system generated active ferric iron ligand which can regenerate ferrous iron ion through the transfer between ligand-metal charge under visible light. Therefore, finding visible light response catalyst which can efficiently use the solar energy light becomes a new direction in visible light photo-Fenton research.

In this paper, composite catalyst Fe$_2$O$_3$/Bi$_2$O$_3$CO$_3$ was synthesized by a one-pot hydrothermal method. Especially, N, N-dimethylformamide (DMF) as a carbon source which was used for synthetic Bi$_2$O$_3$CO$_3$ was used for the first time. The prepared samples were characterized and utilized as a kind of catalyst for the degradation of organic dye under Fenton synergistic effect. The research shows that it is an alternative technology for organic pollutants in wastewater treatment and has broad application prospects.

2. Experimental section

2.1. Preparation of Bi$_2$O$_3$:CO$_3$ and Fe$_2$O$_3$/Bi$_2$O$_3$CO$_3$ photocatalysts

All the chemicals were used as received without any further purification. To obtain Bi$_2$O$_3$:CO$_3$/Fe$_2$O$_3$ samples, Bi(NO$_3$)$_3$:5H$_2$O (2 mmol) was dissolved in 30 mL diluted HNO$_3$ (2 M) and stirred for 30 minutes. Then Fe(NO$_3$)$_3$:9H$_2$O was added into the above solution. The mixed solution was also stirred for another 4 hours. Thirdly, the pH was adjusted to 7.0 using ammonia solution under stirring. The fixed solution should be stirred for another 2 hours. With the increasing of the quality of Fe(NO$_3$)$_3$:9H$_2$O, the color of the final precursor was brown deepen. Fourthly, 5 ml DMF was added to above solution. Then the precursor was transferred into a 60 mL Teflon autoclave and maintained at 200°C for 10 hours. Subsequently, after cooling to room temperature, the products was washed with absolute ethanol and distilled water for several times, then freeze-drying. Especially, The preparation of pure Bi$_2$O$_3$:CO$_3$ is also described as above, except that it is not necessary to add Fe(NO$_3$)$_3$:9H$_2$O. The final products were described according to the molar percent of Fe(NO$_3$)$_3$:9H$_2$O used, the as-prepared catalysts were marked as Bi$_2$O$_3$:CO$_3$, 0.1 Fe$_2$O$_3$/Bi$_2$O$_3$:CO$_3$, 0.5 Fe$_2$O$_3$/Bi$_2$O$_3$:CO$_3$, 1.0 Fe$_2$O$_3$/Bi$_2$O$_3$:CO$_3$, 1.5 Fe$_2$O$_3$/Bi$_2$O$_3$:CO$_3$, 2.0 Fe$_2$O$_3$/Bi$_2$O$_3$:CO$_3$.

2.2. Materials characterization

The catalyst was characterized via powder X-ray diffraction (XRD) with Cu Ka radiation (λ = 1.5404 Å) at a scan rate of 0.05° 2θ/s. The morphology of the samples were examined by scanning electron microscope (SEM: Hitach, Japan) and transmission electron microscope (TEM: JEOL, Japan). UV-Vis spectra was achieved by UV-Vis DRS spectrophotometer (U-3900H, Hitachi, Japan) over a range of 100–800 nm using BaSO$_4$ as a reference.

2.3. Photocatalytic activity measurements

The catalysts were evaluated by the degradation of RhB at room temperature. The visible light source was a 300 W Xenon lamp with a cutoff filter (λ < 420 nm). Before irradiation, the suspension was magnetically stirred in the dark for 30 min to achieve adsorption/desorption equilibrium. 0.075 g catalyst was mixed with 1 mmol/L of H$_2$O$_2$. 150 ml RhB solution (RhB of 50 mg/L, pH 3.0) was mixed with the above mixture of catalyst and hydrogen peroxide. 3 ml of solution was taken every five minutes to test. The degradation of RhB was monitored by UV-Vis spectrophotometer.
3. Results and discussion

3.1. Crystal structure analysis

![XRD pattern](image)

**Figure 1.** XRD patterns of Bi$_2$O$_2$CO$_3$(1), 0.1 Fe$_2$O$_3$/Bi$_2$O$_2$CO$_3$(2), 1.0 Fe$_2$O$_3$/Bi$_2$O$_2$CO$_3$(3), 1.5 Fe$_2$O$_3$/Bi$_2$O$_2$CO$_3$(4), 2.0 Fe$_2$O$_3$/Bi$_2$O$_2$CO$_3$(5) samples.

Figure 1 shows the composites of Bi$_2$O$_2$CO$_3$(JCPDS card no.41-1488) and Fe$_2$O$_3$(JCPDS card no.88-2359). It is clear that the prepared catalyst is tetragonal structure. No other diffraction peaks were observed, and the sharp and intense peaks indicate a good crystalline nature. The lattice fringes of the composite catalysts match well, which can be confirmed by the overlapped peaks between Fe$_2$O$_3$ at 23.85°(012), 32.86°(104), 35.08°(110), 39.08°(006), 40.32°(113), 42.87°(202), 48.83°(024), 53.51°(116), 55.25°(211), 56.54°(122) and Bi$_2$O$_2$CO$_3$ at 23.90°(011), 32.73°(110), 35.31°(112), 39.51°(006), 40.36°(015), 42.30°(114), 48.93°(022), 53.41°(121), 54.51°(024), 56.90°(123). This is good for the Fe$_2$O$_3$ modification on the surface of Bi$_2$O$_2$CO$_3$. Furthermore, the lattice fringe of Bi$_2$O$_2$CO$_3$ and Fe$_2$O$_3$ matches so well that it could be ascribed to mixture of the characteristic peak of Bi$_2$O$_2$CO$_3$ and Fe$_2$O$_3$. However, the new occurred impurity peak should be confirmed by the following characterization ways.

3.2. Morphology characterization

It was found that Bi$_2$O$_2$CO$_3$ (Figure 2a) and Fe$_2$O$_3$/Bi$_2$O$_2$CO$_3$ (Figure 2b) showed the similar morphological structure as nano-chips, which could be accounted for the limited doping amount of Fe$_2$O$_3$. The SEM further indicated that the catalyst powder was uniformly dispersed without large-scale agglomeration. In addition, the results of TEM indicate that the catalyst has a length of about 250 nm and the thickness is about 20 nm. This is consistent with existing literature reports [12].
3.3. UV-Vis-DRS analysis

![Figure 3. UV-Vis-DRS absorption spectra of Bi$_2$O$_2$CO$_3$ (1), 0.1 Fe$_2$O$_3$/Bi$_2$O$_2$CO$_3$ (2), 1.0 Fe$_2$O$_3$/Bi$_2$O$_2$CO$_3$ (3), 1.5 Fe$_2$O$_3$/Bi$_2$O$_2$CO$_3$ (4), 2.0 Fe$_2$O$_3$/Bi$_2$O$_2$CO$_3$ (5) and the forbidden band width of Bi$_2$O$_2$CO$_3$ and Fe$_2$O$_3$/Bi$_2$O$_2$CO$_3$.]

It is very important to study the UV-vis absorption spectra as the semiconductor band structure is an important factor in determining the photocatalytic activity. Figure 3 shows the absorption spectra of different ratios of Fe$_2$O$_3$ in the composite catalyst. As can be seen from the figure, the pure Bi$_2$O$_2$CO$_3$ can only absorb UV light (lambda is about 360 nm), and with the increase of Fe$_2$O$_3$ deposition, the absorption peak of Fe$_2$O$_3$ is seen at lambda equals to 380 nm. The co-existence of Fe$_2$O$_3$ and Bi$_2$O$_2$CO$_3$ also indicates that the final composite catalyst has Fe$_2$O$_3$. In addition, the band width $E_g$ follows the formula.

$$(\alpha h\nu)^{1/n} = C(h\nu - E_g)$$

Where $\alpha$ is the absorption coefficient, $h$ is the Planck constant, $\nu$ is the frequency, $C$ is constant. The index $n$ is directly related to the type of semiconductor, direct band-gap semiconductor $n=1/2$, indirect band-gap semiconductor $n=2$ [12]. It is known by the lambert-beer law that $A$ is proportional to $\alpha$, and $A$ is the absorbance in the visible diffuse reflection. $H\nu$ (denoted by 1240/wavelength) is the $x$-coordinate. The tangent line of $(\alpha h\nu)^{1/n}$ is the graph of the vertical coordinate, and the tangent
line of the curve is equal to E_g. Figure 3 shows that the forbidden band width of the composite catalyst after doping was less than that of the pure Bi_2O_3. The electrons are more easily excited to produce the luminous carrier [4].

3.4. Effect of Fe_3O_4 loading on the Fenton-like reactivity of Bi_2O_3

![Figure 4](image)

Figure 4. Fenton-like degradation of RhB with Bi_2O_3CO_3(1), 0.1 Fe_2O_3/Bi_2O_3CO_3(2), 1.0 Fe_2O_3/Bi_2O_3CO_3(3), 1.5 Fe_2O_3/Bi_2O_3CO_3(4), 2.0 Fe_2O_3/Bi_2O_3CO_3(5).

Table 1. Degradation rate constants of RhB of the Bi_2O_3CO_3 and Fe_2O_3/Bi_2O_3CO_3 catalysts.

| Samples             | In the dark | Under visible light |
|---------------------|-------------|---------------------|
| Bi_2O_3CO_3         | 0.4         | 15.9                |
| 0.1 Fe_2O_3/Bi_2O_3CO_3 | 0.5       | 17.4                |
| 1.0 Fe_2O_3/Bi_2O_3CO_3 | 0.8       | 26.3                |
| 1.5 Fe_2O_3/Bi_2O_3CO_3 | 1.0       | 28.4                |
| 2.0 Fe_2O_3/Bi_2O_3CO_3 | 0.5       | 25.6                |

Figure 4 investigates the degradation effect of RhB with various Fe_2O_3/Bi_2O_3CO_3 catalytic systems. The Fenton-like response in the dark condition was achieved in Figure 4a, and the photo-Fenton-like reactivity under visible light irradiation was concluded in Figure 4b. The corresponding degradation rate constants of RhB of the Bi_2O_3CO_3 and Bi_2O_3CO_3-Fe_2O_3 catalysts are listed in Table 1.

In Figure 4a, the Fenton-like response conforms to the first order dynamic equation. With the increase of Fe_2O_3 loading, the catalytic performance of the catalyst gradually increased, the maximum removal efficiency occurred in the system of 1.5 Fe_2O_3/Bi_2O_3CO_3. The reaction rate of 1.5 Fe_2O_3/Bi_2O_3CO_3 is 2.5 times that of Bi_2O_3CO_3. This indicates that a small amount of Fe_2O_3 doping is beneficial to the enhancement of Fenton-like effect due to the Fe^{3+} components in the complex Fe_2O_3/Bi_2O_3CO_3, the Fenton reaction is bound to occur with the addition of H_2O_2 as a catalytic agent. The RhB is partially oxidized and degraded.

Figure 4b shows the degradation effect of RhB under photo-Fenton-like degradation of pure Bi_2O_3CO_3 and Fe_2O_3/Bi_2O_3CO_3. It was found that pure Bi_2O_3CO_3 shows a good photo-Fenton catalytic effect on RhB. Moreover, the addition of Fe_2O_3 enhances the photo-Fenton catalytic effect of the catalyst. Among them, the catalytic effect of 1.5 Fe_2O_3/Bi_2O_3CO_3 achieved the highest treatment efficiency, and the catalytic effect is 1.8 times that of pure Bi_2O_3CO_3. Notably, the photo-Fenton-like degradation effect of composite catalyst 1.5 Fe_2O_3/Bi_2O_3CO_3 under visible light is 71 times that of pure Bi_2O_3CO_3 under Fenton-like system in the dark.

Because of the response capacity of Bi_2O_3CO_3 to visible light, and its microstructure can increase the catalytic activity point, the synergistic effect of these advantages and Fenton reaction make photocatalytic activity and degradation ability growing rapidly. This may be due to the fact that the photoelectric electron generated by Fe_2O_3 is more likely to be transferred from its guide band to the guide band of Bi_2O_3CO_3 [12]. The electron in the guide band of Bi_2O_3CO_3 can react with the
adsorption of O₂ in the dye solution through a series of reactions to generate H₂O₂, the accumulation of holes in the Fe₂O₃ price band can react with the OH⁻ in the dye solution, then it produces ·OH with strong oxidation which is highly oxidized, while H₂O₂ can also quickly obtained an electron which also produces the strong oxidizing of ·OH [11].

4. Conclusions
In this paper, Bi₂O₃CO₃ and Fe₂O₃/Bi₂O₃CO₃ composite photocatalyst were successfully prepared by hydrothermal method. The final composite catalysts have a tetragonal phase with a nano-chip structure. The length of the composite catalysts is about 250 nm and the width of the thickness is about 20 nm. The addition of Fe₂O₃ can accelerates the degradation efficiency of RhB dramatically. The results further reveals that Fe₂O₃/Bi₂O₃CO₃ acts as a photo and a Fenton-like catalyst as well. It is expected to shed a new idea for the constructing novel composite photocatalyst and also provide a potential method for the removal of dyes in the aqueous system.

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