Preparation and Property Characterization of In$_2$YSbO$_7$/BiSnSbO$_6$ Heterojunction Photocatalyst toward Photocatalytic Degradation of Indigo Carmine within Dye Wastewater under Visible-Light Irradiation

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Abstract: In$_2$YSbO$_7$ and In$_2$YSbO$_7$/BiSnSbO$_6$ heterojunction photocatalyst were prepared by a solvothermal method for the first time. The structural characteristics of In$_2$YSbO$_7$ had been represented. The outcomes showed that In$_2$YSbO$_7$ crystallized well and possessed pyrochlore constitution, a stable cubic crystal system and space group Fd3m. The lattice parameter of In$_2$YSbO$_7$ was discovered to be a = 11.102698 Å and the band gap energy of In$_2$YSbO$_7$ was discovered to be 2.68 eV, separately. After visible-light irradiation of 120 minutes (VLGI-120M), the removal rate (ROR) of indigo carmine (IC) reached 99.42% with In$_2$YSbO$_7$/BiSnSbO$_6$ heterojunction (IBH) as a photocatalyst. The ROR of total organic carbon (TOC) reached 93.10% with IBH as a photocatalyst after VLGI-120M. Additionally, the dynamics constant k which was taken from the dynamic curve toward (DCT) IC density and VLGI time with IBH as a catalyst reached 0.02950 min$^{-1}$. The dynamics constant k which came from the DCT TOC density and VLGI time with IBH as a photocatalyst reached 0.01783 min$^{-1}$.

The photocatalytic degradation of IC in dye wastewater (DW) with IBH as a photocatalyst under VLGI was in accordance with the first-order kinetic curves. IBH was used to degrade IC in DW for three cycles of experiments under VLGI, and the removal rate (ROR) of indigo carmine (IC) reached 99.42% with In$_2$YSbO$_7$/BiSnSbO$_6$ heterojunction (IBH) as a photocatalyst. The ROR of total organic carbon (TOC) reached 93.10% with IBH as a photocatalyst after VLGI-120M. Additionally, the dynamics constant k which was taken from the dynamic curve toward (DCT) IC density and VLGI time with IBH as a catalyst reached 0.02950 min$^{-1}$. The dynamics constant k which came from the DCT TOC density and VLGI time with IBH as a photocatalyst reached 0.01783 min$^{-1}$.

The photocatalytic degradation of IC in dye wastewater (DW) with IBH as a photocatalyst under VLGI was in accordance with the first-order kinetic curves. IBH was used to degrade IC in DW for three cycles of experiments under VLGI, and the removal rate (ROR) of IC reached 99.42%, 96.89% and 94.88%, respectively, after VLGI-120M, indicating that IBH had high stability. Compared with superoxide anions or holes, hydroxyl radicals possessed the largest oxidative ability for removing IC in DW, as demonstrated by experiments with the addition of trapping agents. Lastly, the probable degradation mechanism and degradation pathway of IC were revealed in detail. The results showed that a visible-light-responsive heterojunction photocatalyst which possessed high catalytic activity and a photocatalytic reaction system which could effectively remove IC in DW were obtained. This work provided a fresh scientific research idea for improving the performance of a single catalyst.

Keywords: In$_2$YSbO$_7$; In$_2$YSbO$_7$/BiSnSbO$_6$ heterojunction photocatalyst; indigo carmine; photocatalytic degradation; visible-light irradiation; N-doped TiO$_2$

1. Introduction

In the last few years, the water pollution problem had drawn worldwide attention. Among the number of pollutants, organic pollutants derived from dye wastewater (DW) from textile and photography industries became an acute environmental problem due to its unacceptable color, high-chemical oxygen demand, toxicity and biodegradation. Indigo carmine (IC) could be detected in dyes, and IC was widely used in food, medicine, clothing and other fields. Moreover, IC was carcinogenic in nature and could cause serious health problems in human beings, including reproduction, neurons, acute toxicity, eye or skin exposure, hypertension, cardiovascular or respiratory problems [1]. The organic
pollutants from DW could be removed by coagulation–flocculation, adsorption and membrane filtration. However, because of the disadvantages of toxicity and high price [2,3], many macromolecular organic pollutants could not be biodegraded. The photocatalysis technique which possesses the strengths of environmental conservation, low cost and high treatment efficiency [4,5] is widely used in treating sewerage. From the perspective of energy, photocatalytic technology is more scientific and promising because photocatalytic technology only requires the use of sunlight for activating catalysts. [6]. Photocatalysts can effectively decompose organic pollutants because of the production of the oxidation free radicals. This is a new interdisciplinary research field. Catalysts can be regenerated and recycled, which is of great significance for the research work of photocatalysis technology in the future.

By analyzing previous reports, it was found that a large number of metal oxides such as TiO$_2$ and ZnO [7,8] have been developed as photocatalysts. However, the application of a single photocatalyst was limited because of intrinsic properties such as photo-etching and wide band gaps [9,10]. TiO$_2$ could only absorb ultraviolet rays effectively, but ultraviolet light energy only occupies 5% account of solar energy; as a result, light energy was not fully utilized. There was a great breakthrough when Zou found that Ni-doped InTaO$_4$ compounds were responsive to wavelengths in the visible-light region in 2001 [11]. Zou demonstrated that the development of visible-light-responsive photocatalysts for optimal use of visible-light energy, which occupied 43% of sunlight energy, was possible. Researchers were inspired to explore new photocatalysts, which is reflected in the extensive efforts of former scholars toward achieving degradation of pollutants under visible-light irradiation (VLGI). Therefore, the key to photocatalytic technology was the development of the photocatalysts that possess high catalytic efficiency [12–16]. There are many methods which have been proven to be effective, for example, ion doping methods such as N-doped TiO$_2$, the heterojunction construction method [17–23] and the photosensitization method [24,25]. The higher light utilization efficiency of the composite material system [22–28] reflected that the composite material system contained various functions of a single photocatalyst [29–33], higher photocatalytic performance, longer carrier life and higher chemical stability [34–40].

It is common knowledge within the field that slight changes in the internal structure of the photocatalyst can affect the photocatalytic activity. Luckily, A$_2$B$_2$O$_7$ compounds are known for their photocatalytic performance under VLGI. Xing et al. [41,42] prepared Bi$_2$Sn$_2$O$_7$ compound and Y$_2$Ti$_2$O$_7$ compound with a A$_2$B$_2$O$_7$ structure, which possessed good photocatalytic performance under VLGI. Based on our previous work [43], we found that Sm$_2$FeSbO$_7$ had a pyrochlore structure. As a catalyst under VLGI, the structural metamorphosis of Sm$_2$FeSbO$_7$ could hold potential for improving photocatalytic activity. According to the above analysis, we suppose that stead of Sm$^{3+}$ by In$^{3+}$, and stead of Fe$^{3+}$ by Y$^{3+}$ in Sm$_2$FeSbO$_7$ might increase carrier concentration. According to the above analysis, we may conclude that the structure and properties of the new In$_2$YSbO$_7$ compound can be changed and improved, and more advanced photocatalytic properties can be obtained.

During the process of photocatalysis, heterojunction catalysts have excellent performance [44–46]. The heterojunction could greatly improve the electron transfer rate and redox performance of the catalyst by inhibiting electron–hole recombination within two semiconductors [47]. Sabzehparvar et al. [48–51] prepared a battery of heterojunction catalysts with excellent properties, such as TiO$_2$/NiO–Ag heterojunction catalyst, Mn$^+$TiO$_2$/TiO$_2$ heterojunction catalyst, AgBr/BiPO$_4$ heterojunction catalyst and Bi$_2$MoO$_6$/Bi$_4$V$_2$O$_11$ heterojunction catalyst. Subsequently, these catalysts showed better performance during the degradation of organic pollutants in DW. The heterojunction catalysts which were prepared by Chanrai et al. all showed good effects on the degradation of indigo in DW; the heterojunction catalysts used were WO$_3$/CeO$_2$ catalyst, MoS$_2$/Cu$_2$O catalyst and ZnBi$_2$O$_4$/ZnS catalyst [52–54]. Analysis indicated that the synthesis of heterojunction photocatalysts could improve the redox performance of photocatalysts [55] and improved the total se-
lectivity and reactivity. In conclusion, the heterojunction structure of the catalysts is a promising research direction.

The structural properties of pure-phase BiSnSbO$_6$ and In$_2$YSbO$_7$ prepared by a solvothermal method were analyzed. The transmission electron microscopy (TEM) was utilized for analyzing the structural properties of nitrogen-doped TiO$_2$ (N-TiO$_2$). Moreover, the removal rate (ROR) of indigo carmine (IC) under VLGI with In$_2$YSbO$_7$ as a catalyst or with BiSnSbO$_6$ as a catalyst with high photocatalytic activity was acquired, and could degrade IC efficiently. Degradation of organic pollutants in DW with IBH as a catalyst showed higher efficiency and stronger security.

2. Results and Discussion

2.1. XRD Analysis

Structure of the prepared In$_2$YSbO$_7$ uses X-ray diffraction technology for detection and the results are shown in Figure 1. By analyzing the results, it was shown that In$_2$YSbO$_7$ was a single phase and the lattice parameter of the new catalyst In$_2$YSbO$_7$ was 11.102698 Å. Additionally, the whole of the diffraction peaks for In$_2$YSbO$_7$ could be indexed smoothly on the principle of the lattice constant and the above space group $Fd3m$. Table 1 shows the atomic coordinates and structural parameters of In$_2$YSbO$_7$. Figure 2 shows the atomic structure of In$_2$YSbO$_7$. It could be concluded from Figure 1 that In$_2$YSbO$_7$ crystallized into a pyrochlore-type structure. The structure of In$_2$YSbO$_7$ was refined, and the results showed that the unweighted R-factor $R_p$ was 44.31% and the obtained space group was $Fd3m$.

![XRD pattern and Rietveld refinement of In$_2$YSbO$_7$](image)

Figure 1. XRD pattern and Rietveld refinement of In$_2$YSbO$_7$ (red dotted line represents experimental XRD data for In$_2$YSbO$_7$; blue solid line represents simulated XRD data for In$_2$YSbO$_7$; black solid line represents the difference between experimental and simulated XRD data for In$_2$YSbO$_7$; green vertical lines indicate the observed reflection locations).

Table 1. Structural parameters of In$_2$YSbO$_7$ synthesized by solvothermal method.

| Atom  | x    | y    | z    | Occupation Factor |
|-------|------|------|------|-------------------|
| In    | 0    | 0    | 0    | 1                 |
| Y     | 0.5  | 0.5  | 0.5  | 0.5               |
| Sb    | 0.5  | 0.5  | 0.5  | 0.5               |
| O(1)  | $-0.185$ | 0.125 | 0.125 | 1               |
| O(2)  | 0.125 | 0.125 | 0.125 | 1               |
The x-coordinate of the known O (1) atom could be used as an indicator of the crystal structure change of pyrochlore-type $A_2B_2O_7$ compound (cubic system, space group $Fd3m$) and if six $A$–O (1) bonds were the same length as two $A$–O (2) bonds, both equal to 0.375 [56]. The value of $x$ for MO$_6$ ($M = Y^{3+}$ and Sb$^{5+}$) deviated from $x = 0.375$ [56]; thus, the distortion of the MO$_6$ ($M = Y^{3+}$ and Sb$^{5+}$) octahedron was evident in the crystal structure of In$_2$YSbO$_7$. Charge separation was required for photocatalytic degradation (PCD) of IC under VLGI to prevent the recombination of photoinduced electrons (PE) and photoinduced holes (PH). Inoue [57] and Kudo [58] showed that the local distortion of the MO$_6$ octahedron, which came from catalysts such as BaTi$_4$O$_9$ and Sr$_2$M$_2$O$_7$ ($M = Nb^{5+}$ and Ta$^{5+}$), was necessary in preventing recombination between charges and contributed to the amelioration of photocatalytic activity. Similarly, in the crystal structure of In$_2$YSbO$_7$, the ($M = Y^{3+}$ and Sb$^{5+}$) octahedral distortion of MO$_6$ was also considered to contribute to the enhanced photocatalytic activity. In$_2$YSbO$_7$ consisted of a three-dimensional network of octahedra with a corner sharing MO$_6$ ($M = Y^{3+}$ and Sb$^{5+}$). The MO$_6$ ($M = Y^{3+}$ and Sb$^{5+}$) octahedra were linked into chains by In$^{3+}$ ion. Two kinds of In–O bond lengths (BL) coexist: six In–O (1) BL (2.636 Å) were significantly longer than 2 In–O (2) BL (2.230 Å). The six M–O (1) ($M = Y^{3+}$ and Sb$^{5+}$) BL were 1.939 Å and the M–In ($M = Y^{3+}$ and Sb$^{5+}$) BL were 3.642 Å. The M–O–M ($M = Y^{3+}$ and Sb$^{5+}$) bond angle (BA) was 139.624° in the crystal structure of In$_2$YSbO$_7$. The In–M–In ($M = Y^{3+}$ and Sb$^{5+}$) BA was 135.505° in the crystal structure of In$_2$YSbO$_7$. The In–M–O ($M = Y^{3+}$ and Sb$^{5+}$) BA was 135.000° in the crystal structure of In$_2$YSbO$_7$. The study of luminescent properties showed that the angle between MO$_6$ ($M = Y^{3+}$ and Sb$^{5+}$) octahedra, such as the M–O–M BA of In$_2$YSbO$_7$, had an important influence on the photocatalytic activity of In$_2$YSbO$_7$. The closer the M–O–M BA was to 180°, the greater the mobility of PE and PH was; as a result, the photocatalytic activity was stronger because the mobility of PE and PH affected the probability of electrons and holes reaching the reaction sites on the catalyst surface [59].

Furthermore, the Sb–O–Sb BA of In$_2$YSbO$_7$ was larger, which led to an increase in photocatalytic activity of In$_2$YSbO$_7$. By analyzing the above results, under VLGI conditions with In$_2$YSbO$_7$ as a catalyst, the effect of IC degradation was mainly attributed to the crystal structure and electronic structure of In$_2$YSbO$_7$.

Figure 3 shows the XRD pattern of BiSnSbO$_6$ and marks the individual diffraction peaks. The structure of BiSnSbO$_6$ was tested by the XRD technique. From the analysis of the results, we might conclude that BiSnSbO$_6$ was a single phase and the building block parameters could be equivalently $a = b = c = 10.234594$ Å. By analyzing the above results, it is shown that BiSnSbO$_6$ possesses a pyrochlore structure and the cubic system; simultaneously, the space group was $Fd3m$ and the crystallization of BiSnSbO$_6$ was good.
Figure 3. The XRD pattern of BiSnSbO$_6$.

Figure 4 shows the XRD spectrum of IBHP. As can be seen from Figure 4, there were pure single-crystal In$_2$YSbO$_7$ photocatalyst and pure single-crystal BiSnSbO$_6$ photocatalyst. The diffraction peaks of In$_2$YSbO$_7$ and BiSnSbO$_6$ were marked successfully, and no other impurities were found.

Figure 4. The XRD spectrum of In$_2$YSbO$_7$/BiSnSbO$_6$ heterojunction.

Figure 5 shows the X-ray diffraction patterns of N-TiO$_2$ and pure TiO$_2$. The structure of N-TiO$_2$ and pure TiO$_2$ was tested by XRD technology. N-TiO$_2$-500 was calcined at 500 ºC and N-TiO$_2$-400 was calcined at 400 ºC. It can be seen from Figure 5 that N-TiO$_2$ or pure TiO$_2$ was mainly composed of anatase phase.
2.2. UV–Vis Diffuse Reflectance Spectra

The UV–vis diffuse reflectance spectra (U–V DRS) of the In$_7$YSbO$_7$ sample are listed in Figure 6a,b. The absorption edge of the novel photocatalyst In$_7$YSbO$_7$ was located in the visible-light region of 503 nm in the spectrum. The band gap energy (BGE) of a semiconductor could be indicated by the intersection between the $hv$ axis representing the photon energy and a conjectural line which was described in accordance with the linear part of the absorption edge of the Kubelka–Munk function (1) [59,60].

$$\frac{(1 - R_d(hv))^2}{2R_d(hv)} = \frac{\alpha(hv)}{S}$$

where $S$ is the scattering factor, $R_d$ is the diffuse reflectance and $\alpha$ is the radiation absorption coefficient.

The light absorption near the band edges of crystalline semiconductors fitted Equation (2) [61,62]:

$$ahv = A (hv - E_g)^n$$

$A$ was the proportionality constant, $\alpha$ was the absorption coefficient, $E_g$ was the band gap and $v$ was the optical frequency. In this equation, $n$ determined the properties of transitions in semiconductors. $E_g$ and $n$ could be calculated by the following steps: (1) plot $\ln (ahv)$ versus $\ln (hv - E_g)$ supposed an approximation value of $E_g$; (2) derive the value of $n$ from the slope in this graph; (3) refine the value of $E_g$ by plotting $(ahv)^{1/n}$ versus $hv$ and extrapolating the plot to $(ahv)^{1/n} = 0$. According to above methods, the value of $E_g$ for In$_7$YSbO$_7$ was computed to be 2.68 eV. The reckoning value of $n$ was about 0.5 and the optical transition of In$_7$YSbO$_7$ was a direct transition.

The BGE of In$_7$YSbO$_7$ was 2.68 eV, the BGE of Bi$_2$O$_3$I$_2$ was 2.02 eV [63] and the BGE of Co-doped ZnO was 2.39 eV [64]. The BGE of every catalyst derived from the above three catalysts was less than 2.69 eV, indicating that above three photocatalysts had strong visible-light catalytic activity.

Figure 7a,b shows the U–V DRS of BiSnSbO$_6$. According to the results analysis which was based on Figure 7a,b, the Eg value of BiSnSbO$_6$ is estimated to be 2.75 eV. The reckoning value of $n$ was about 2, and the optical transition of BiSnSbO$_6$ was an indirect transition.

Figure 8a,b shows the U–V DRS of IBHP. According to the above methods, the value of $E_g$ for IBHP was estimated to be 2.73 eV. The reckoning value of $n$ was about 0.5; as a result, the optical transition of IBHP was a direct transition.
Figure 6. (a) UV–vis diffuse reflectance spectra of In$_2$YSbO$_7$; (b) Plot of $(\alpha h\nu)^2$ versus $h\nu$ for In$_2$YSbO$_7$.

Figure 7. (a) The diffused reflection spectrum of BiSnSbO$_6$; (b) Correlative diagram of $(\alpha h\nu)^{1/2}$ and $h\nu$ for BiSnSbO$_6$.

Figure 8a,b shows the U–V DRS of IBHP. According to the above methods, the value of $E_g$ for IBHP was estimated to be 2.73 eV. The reckoning value of $n$ was about 0.5; as a result, the optical transition of IBHP was a direct transition.
Figure 7. (a) The diffused reflection spectrum of BiSnSbO$_6$; (b) Correlative diagram of $(\alpha h\nu)^{1/2}$ and $h\nu$ for BiSnSbO$_6$.

Figure 8. (a) The diffused reflection spectrum of In$_2$YSbO$_7$/BiSnSbO$_6$ heterojunction; (b) Correlative diagram of $(\alpha h\nu)^2$ and $h\nu$ for In$_2$YSbO$_7$/BiSnSbO$_6$ heterojunction.
The U–V DRS of TiO₂ and N-TiO₂ under different calcination temperatures are shown in Figure 9. In accordance with above procedures and Figure 9, the numerical value of Eg for pure TiO₂ or N-TiO₂ was calculated to be 3.13 eV or 2.95 eV.

![Figure 9. UV–vis absorption spectra of pure TiO₂ and N-TiO₂ with different calcination temperatures.](image)

2.3. Property Characterization of In₂Y:SbO₇/BiSn:SbO₆ Heterojunction Photocatalyst

Figure 10 shows the X-ray photoelectron spectroscopy (XPS) survey spectrum of IBHP. Figure 11 shows the XPS spectra of O₂⁻, In³⁺, Y³⁺, Bi⁵⁺, Sn⁴⁺ and Sb⁵⁺, which derive from IBHP. According to the XPS survey spectrum, the synthetical IBHP comprised the elements of In, Y, Sb, Bi, Sn and O. On the basis of XPS research results, which were shown in Figures 10 and 11, the oxidation state of In, Y, Sb, Bi, Sn and O ions was +3, +3, +5, +3, +4 and −2, respectively. On the basis of research results, the chemical formula of the new sample could be concluded as In₂Y:SbO₇/BiSn:SbO₆. In Figure 11, the O1s peak of O was situated at 530.35 eV. In3d₃/2 and In3d₅/₂ peaks of In were situated at 451.9 eV and 444.4 eV, respectively. The Y3p₃/2 peak of Y was situated at 301.05 eV. The position of the Bi5d₃/2 peak of Bi was situated at 26.85 eV. Sn3d₃/2 and Sn3d₅/₂ peaks of Sn were situated at 494.95 eV and 486.45 eV. The Sb4d₃/2 peak of Sb was 35.35 eV. The results of surface elemental analysis showed that the average atomic ratio In:Y:Bi:Sb:Sn:O was 382:193:379:179:186:3681. The atomic ratio of In:Y and Bi:Sn in the sample of IBHP was 1.98:1 and 0.96:1, respectively. The reason that the oxygen value was higher might be due to the large amount of oxygen adsorption on the surface of IBHP. Obviously, the XPS peaks of IBHP did not have shoulder and broadening, which meant that there were no other phases within IBHP.

As can be seen from Figures 12 and 13, the larger particles belonged to BiSn:SbO₆ and the smaller particles belonged to In₂Y:SbO₇. It is shown in Figures 12 and 13 that the particles of BiSn:SbO₆ were encircled by small particles of In₂Y:SbO₇; two kinds of particles were tightly combined, indicating the successful synthesis of IBHP.

The SEM–EDS results shown in Figures 12–14 express that there were no other doped elements in the IBHP compound. Meanwhile, the pure phase of In₂Y:SbO₇ was unanimous with the XRD analysis results, as shown in Figure 1. On the basis of Figure 14, the atomic ratio of In:Y:Bi:Sb:Sn:O was 802:397:905:504:512:6880. Above results were unanimous with XPS results of IBHP, which are expressed in Figures 10 and 11. The atomic ratio of In₂Y:SbO₇:BiSn:SbO₆ was close to 397:512. According to the above results, under our preparation conditions, we could conclude that IBHP possesses high purity.
Figure 10. XPS survey spectrum of the IBHP.

Figure 11. Cont.
According to the above results, under our prep-
with the XRD analysis results, as shown in Figure 1. On the basis of Figure 14, the atomic
ratio of 

Figure 11. (a) XPS spectra of O$^{2-}$ derived from the IBHP; (b) XPS spectra of In$^{3+}$ derived from the
IBHP; (c) XPS spectra of Y$^{3+}$ derived from the IBHP; (d) XPS spectra of Bi$^{3+}$ derived from the IBHP;
(e) XPS spectra of Sn$^{4+}$ derived from the IBHP; (f) XPS spectra of Sb$^{5+}$ derived from the IBHP.

Figure 12. SEM photograph of IBHP.

Figure 13. EDS elemental mapping of IBHP (In, Y, Sb, O from In$_2$YSbO$_7$ and Bi, Sn, Sb, O from BiSnSbO$_6$).
Figure 16 showed that the experiments followed the same VLGI time. When we used In$_2$O$_3$ as a catalyst, the ROR of IC reached 90.14% and the rate of reaction was 3.668 $\times 10^{-9}$ mol·L$^{-1}$·s$^{-1}$ and the PEY was 0.077% after VLGI-120M. Moreover, the ROR of IC within DW reached 85.18% and the rate of reaction was 3.467 $\times 10^{-9}$ mol·L$^{-1}$·s$^{-1}$ and the PEY was 0.073% with BiSnSbO$_7$ as a catalyst. The results show that the photodegradation efficiency (PDE) of IC in the case of using IBHP was the best; the PDE of IC with In$_2$YSbO$_7$ as a catalyst was better than that with In$_2$YSbO$_7$, BiSnSbO$_6$ or N-TiO$_2$ as a catalyst after VLGI.

Figure 14. EDS spectrum of IBHP.

Figure 15 displays the TEM morphology image and the selected-area electron diffraction (SAED) of N-TiO$_2$. Figure 15 shows that the mean diameter size of the particles of N-TiO$_2$ was 10 nm. The limitation of the SAED region was 50 nm; thus, the SAED image of N-TiO$_2$ particles is shown as a concentric circle.

Figure 15. (a) The TEM morphology image of N-TiO$_2$; (b) The selected-area electron diffraction of N-TiO$_2$.

2.4. Photocatalytic Activity

Figure 16 shows the concentration change curve (CCC) of IC during photocatalytic degradation (PCD) with IBHP or In$_2$YSbO$_7$, BiSnSbO$_6$ or N-TiO$_2$ as a catalyst, respectively, under VLGI. In the process of degradation, the concentration of IC in DW gradually decreased with increasing VLGI time. Analysis of the results in Figure 16 showed that the removal rate (ROR) of IC in DW reached 99.42% with a reaction rate of $4.046 \times 10^{-9}$ mol·L$^{-1}$·s$^{-1}$ and the photonic efficiency (PEY) was 0.085% with IBHP after visible-light irradiation of 120 min (VLGI-120M). Other experiments followed the same VLGI time. When we used In$_2$YSbO$_7$ as a catalyst, the ROR of IC reached 90.14% and the rate of reaction was $3.668 \times 10^{-9}$ mol·L$^{-1}$·s$^{-1}$ and the PEY was 0.077% after VLGI-120M. The ROR of IC within DW reached 85.18% and the rate of reaction was $3.467 \times 10^{-9}$ mol·L$^{-1}$·s$^{-1}$ and the PEY was 0.073% with BiSnSbO$_6$ as a catalyst after VLGI-120M. Moreover, the ROR of IC reached 41.57% and the rate of reaction was $1.692 \times 10^{-9}$ mol·L$^{-1}$·s$^{-1}$ and the PEY was 0.036% with N-TiO$_2$ as a catalyst after VLGI-120M. In addition, we could summarize from the analysis of the results that the photodegradation efficiency (PDE) of IC in the case of using IBHP was the best; the PDE of IC with In$_2$YSbO$_7$ as
a catalyst was better than that with BiSnSbO₆ as a catalyst or with N-TiO₂ as a catalyst. The results show that the photocatalytic activity of IBHP under VLGI was the highest compared with In₂YSbO₇, BiSnSbO₆, and N-TiO₂. Above results indicate that after VLGI-120M, the ROR of IC, which was degraded with IBHP as a catalyst, was 1.103 times, 1.167 times and 2.392 times higher than that with In₂YSbO₇, BiSnSbO₆ and N-TiO₂ as a catalyst, respectively.

Figure 16. Concentration variation curves of IC during PCD of IC with IBH as a catalyst or with In₂YSbO₇ as a catalyst or with BiSnSbO₆ as a catalyst or with N-TiO₂ as a catalyst under VLGI.

Figure 17 shows the concentration variation curves of IC during PCD of IC in DW with IBH as a catalyst or with In₂YSbO₇ as a catalyst or with BiSnSbO₆ as a catalyst or with N-TiO₂ as a catalyst under VLGI. Figure 17 shows that the ROR of TOC within DW reached 93.10%, 84.26%, 80.02% and 35.50%, respectively, after VLGI-120M when IBHP, In₂YSbO₇, BiSnSbO₆ and N-TiO₂ were used for degrading IC. Finally, by analyzing the results regarding the ROR of TOC at the time of IC degradation, the ROR of TOC with IBHP was the best among the above four catalysts. The obtained results also showed that the ROR of TOC during IC degradation using In₂YSbO₇ was much higher than that using BiSnSbO₆ or N-TiO₂, implying that IBHP possessed the highest mineralization rate during IC degradation compared with In₂YSbO₇ or BiSnSbO₆ or N-TiO₂.

Figure 17. Concentration variation curves of TOC during PCD of IC in DW with IBH as a catalyst or with In₂YSbO₇ as a catalyst or with BiSnSbO₆ as a catalyst or with N-TiO₂ as a catalyst under VLGI.
Figure 18 shows the CCC of IC during PCD with IBHP under VLGI for three cycle degradation tests (TCDT). As can be seen from Figure 18, the ROR of IC reached 98.74%, 96.89% and 94.88%, respectively, after VLGI-120M with IBH as a catalyst. Three cycle experiments were completed for degrading the IC. Figure 19 shows the CCC of TOC during PCD of IC with IBHP under VLGI for TCDT. The experimental data in Figure 19 show that the ROR of TOC was 92.64%, 90.26% and 89.19%, respectively, after VLGI-120M with IBH when three cycle experiments were completed for degrading IC. The test results shown in Figures 18 and 19 show that IBHP possesses strong stability.

![Figure 18](image1.png)  
**Figure 18.** CCC of IC during PCD of IC in DW with IBHP under VLGI for TCDT.

![Figure 19](image2.png)  
**Figure 19.** CCC of TOC during PCD of IC in DW with IBHP under VLGI for TCDT.

Figure 20 shows the analysis of first-order kinetic (FOK) plots for the PCD of IC with IBH as catalyst or with In$_2$YSbO$_7$ as a catalyst or with BiSnSbO$_6$ as a catalyst or with N-TiO$_2$ as a catalyst under VLGI. It can be seen from Figure 20 that the kinetic constant k (KCK), which was from the DCT IC concentration and VLGI time, with IBH, In$_2$YSbO$_7$, BiSnSbO$_6$ or N-TiO$_2$ as the catalyst, reached 0.0295 min$^{-1}$, 0.01603 min$^{-1}$, 0.01181 min$^{-1}$ and 0.00337 min$^{-1}$, respectively. The KCK which came from the DCT TOC concentration and VLGI time reached 0.0178 min$^{-1}$, 0.0136 min$^{-1}$, 0.0103 min$^{-1}$ and 0.0026 min$^{-1}$ with IBH, In$_2$YSbO$_7$, BiSnSbO$_6$ or N-TiO$_2$ as the catalyst. The $K_{TOC}$ value obtained during IC degradation was lower than the $K_C$ value obtained when the same catalyst was utilized.
to degrade IC. At the same time, compared with In$_2$YSbO$_7$ or BiSnSbO$_6$ or N-TiO$_2$, IBHP possessed the highest degradation mineralization efficiency for degrading IC.

![Figure 20](image-url)

**Figure 20.** (a) Observed FOK plots for the PCD of IC with IBH or In$_2$YSbO$_7$ or BiSnSbO$_6$ or N-TiO$_2$ as photocatalyst under VLGI. (b) Observed FOK plots for TOC during PCD of IC in DW with IBH or In$_2$YSbO$_7$ or BiSnSbO$_6$ or N-TiO$_2$ as photocatalyst under VLGI.

Figure 21 shows the FOK for the PCD of IC when IBH is used as a catalyst for TCDT under VLGI conditions. According to the results shown in Figure 21, the KCK derived from the DCT IC concentration and VLGI time with IBHP for TCDT achieved 0.02602 min$^{-1}$, 0.02119 min$^{-1}$ and 0.01877 min$^{-1}$. In addition, the KCK which came from the DCT TOC concentration and VLGI time with IBH as a photocatalyst for TCDT reached 0.01717 min$^{-1}$, 0.01569 min$^{-1}$ and 0.01491 min$^{-1}$. The results of the analysis are shown in Figures 20 and 21; the PCD of IC in DW with IBH as a photocatalyst under VLGI conformed to first-order reaction kinetics.
The analysis results in Figure 21 show that after TCDT, under VLGI, with IBHP, the ROR of IC was reduced by 3.86%, and the ROR of TOC was reduced by 3.45%. Above results indicate that there was no significant difference in the degradation efficiency of TCDT, and the catalyst structure of IBHP was stable.

Figure 22 shows the effect of adding different radical scavengers (RS) such as benzoquinone (BQ) or isopropanol (IPA) or ethylenediamine tetra-acetic acid (EDTA), respectively, on the ROR of IC with IBHP under VLGI. The experiments first mixed different RS in IC solution to determine the active species during IC degradation. IPA was utilized for capturing hydroxyl radicals (\(\cdot\)OH), and BQ was utilized for capturing superoxide anions (\(\cdot\)O\(_2\)\(^-\)), and ethylenediamine tetra-acetic acid (EDTA) was utilized for capturing holes (h\(^+\)). The planned concentration of IPA or EDTA or BQ was 0.15 mmol L\(^-1\), and the addition amount of EDTA or IPA or BQ was 1 mL. As shown in Figure 22, when the BQ, IPA or EDTA was mixed in the IC solution, the ROR of IC decreased by 73.41%, 34.27% and 31.4%, respectively, compared with the ROR of IC derived from the control group. Therefore, we can draw the conclusion that \(\cdot\)OH, \(\cdot\)O\(_2\)\(^-\) and h\(^+\) were all active radicals during IC degradation. As shown in Figure 22, \(\cdot\)OH in IC solution showed a key role in the degradation of IC with IBHP under VLGI. Through experiments, compared with superoxide anions or
holes, hydroxyl radicals possessed the largest oxidative removal capacity for IC in DW. The oxidizing ability of the three types of oxidative radical for degrading IC was, from high to low: hydroxyl radicals > superoxide anions > holes.

Figure 22. (a) Effect of different RS on ROR of IC with IBH as catalyst under VLGI; (b) Effect of different RS such as BQ, IPA or EDTA on the removal efficiency of IC with IBHP under VLGI.

Figure 23 shows the Nyquist impedance plots of IBHP or In$_2$YSbO$_7$ photocatalyst or BiSnSbO$_6$ photocatalyst. The Nyquist impedance map shows the PE transport processes and PH transport processes between the solid and the electrolyte for the synthetical photocatalyst. The smaller the radius of the arc is, the higher the transmission efficiency of the photocatalyst is. Figure 23 indicates that the arc radius is in the order: BiSnSbO$_6$ > In$_2$YSbO$_7$ > IBHP. Above results show that the preparative IBHP possesses high separation efficiency of PE and PH and fast interface charge transfer capability. The charge transfer resistance ($R_{CT}$, which was calculated according to the diameter of a semicircle) of BiSnSbO$_6$, In$_2$YSbO$_7$ and IBHP was $4.8 \times 10^5$ ohm, $4.5 \times 10^5$ ohm or $4.0 \times 10^5$ ohm, based on the Nyquist plot displayed in Figure 23.

2.5. Degradation Mechanism Analysis

Figure 24 displays the presumed photocatalytic degradation (PCD) mechanism of IC with IBH as a catalyst under VLGI. The potentials of the conductor band (CB) and valence
The band (VB) of the semiconductor can be computed according to the following Formulas (3) and (4) [65]:

\[ E_{CB} = X - E^c - 0.5E_g \]  

(3)

\[ E_{VB} = E_{CB} + E_g \]  

(4)

\[ E_{d}, E_{s}, E_{m}, E_{g}, E_{0}, E_{f}, E_{x}, E_{y}, E_{z}, E_{t}, E_{p}, E_{q}, E_{r}, E_{s}, E_{t}, E_{u}, E_{v}, E_{w}, E_{x}, E_{y}, E_{z}, E_{t}, E_{u}, E_{v}, E_{w}, E_{x}, E_{y}, E_{z}, E_{t}, E_{u}, E_{v}, E_{w}, E_{x}, E_{y}, E_{z}, E_{t}, E_{u}, E_{v}, E_{w}, E_{x}, E_{y}, E_{z}, E_{t}, E_{u}, E_{v}, E_{w}, E_{x}, E_{y}, E_{z}, E_{t}, E_{u}, E_{v}, E_{w}, E_{x} \]

**Figure 23.** Nyquist impedance plots of IBHP or In\(_2\)YSbO\(_7\) photocatalyst or BiSnSbO\(_6\) photocatalyst.

**Figure 24.** Possible PCD mechanism of IC with IBHP under VLGI.

In the formulas, X is the electronegativity of the semiconductor, \(E^c\) is the energy of free electrons on the hydrogen scale and \(E_g\) is the band gap. Based on above formulas, it can be seen that the VB potential and CB potential of In\(_2\)YSbO\(_7\) are about 1.95 eV and −0.73 eV, respectively. For BiSnSbO\(_6\), the VB potential and CB potential are about 3.06 eV and 0.31 eV, separately. It was observed that both In\(_2\)YSbO\(_7\) and BiSnSbO\(_6\) could absorb visible light; simultaneously, PE and PH could be generated when the IBHP was under the condition of VLGI. Due to the fact that the redox potential position of CB for
In$_2$YSbO$_7$ ($-0.73$ eV) was more negative than that of BiSnSbO$_6$ (0.31 eV), the PE on the CB of In$_2$YSbO$_7$ was diverted to the CB of BiSnSbO$_6$. Moreover, the redox potential position of VB for BiSnSbO$_6$ (3.06 eV) was more positive than that of In$_2$YSbO$_7$ (1.95 eV), so the PH on the VB of BiSnSbO$_6$ was transferred to the VB of In$_2$YSbO$_7$. Therefore, IBHP produced by the coupling of In$_2$YSbO$_7$ and BiSnSbO$_6$ can efficiently decrease the recombination rate of PE and PH, thereby reducing the internal resistance, extending the lifetime of the PE and the PH; as a result, the interfacial charge metastasis efficiency is improved [66].

In addition, the CB potential of In$_2$YSbO$_7$ was $-0.73$ eV, which was more nonpositive than that of O$_2$/*O$_2^-$ ($-0.33$ V), demonstrating that the electrons in the CB of In$_2$YSbO$_7$ could assimilate subaqueous soluble oxygen for producing $^*$O$_2^-$, which can degrade IC efficiently, as shown in Path 1. Meanwhile, the VB potential of BiSnSbO$_6$ was 3.06 eV, which was more nonnegative than OH$^-$/*OH (2.38 V), illustrating that the PH in the VB of BiSnSbO$_6$ could oxidize H$_2$O or OH$^-$ into $^*$OH, which can degrade IC effectively; this is displayed in Path 2. The PH in the VB of In$_2$YSbO$_7$ or BiSnSbO$_6$ could immediately oxidize IC for degradation of IC due to their powerful oxidizing capability, as shown in Path 3. To sum up, the excellent photocatalytic activity of IBHP toward IC degradation is mainly attributed to the higher separation efficiency of the PE and the PH, which was induced by IBHP.

In order to research the degradation mechanism of IC, LC–MS was used to analyze the intermediate products during the IC degradation process. The intermediate products were isatin ($m/z = 219$), 5′,6′-dihydroxy-3,3′-dioxo-[2,2′-biindolinylidene]-5-sulfonic acid ($m/z = 375$), diethyl oxalate ($m/z = 146$), ethyl oxamate ($m/z = 117$), 4-hydroxy-3,3′-dioxo-[2,2′-biindolinylidene]-5,5′-disulfonic acid ($m/z = 439$), C$_8$H$_4$NO$_6$S ($m/z = 242$), 2,3-dioxoindoline-5-sulfonic acid ($m/z = 228$), 2-(2-amino-5-sulfophenyl)-2-oxoacetic acid ($m/z = 246$), 2-amino-5-sulfobenzoic acid ($m/z = 217$), 6-amino-2,3,4-trihydroxybenzoic acid ($m/z = 186$), oxalic acid, aniline and acetic acid. The analysis of detected intermediate products showed possible PCD paths of the IC. Figure 25 shows a possible PCD pathway scheme with IBHP for IC degradation under the condition of VLGI. As shown in Figure 25, the hydroxylation reaction, oxidation reaction, methylation reaction, decarboxylation reaction and desulfonation reaction were achieved.
3. Experimental Section

3.1. Materials and Reagents

P-benzoquinone (BQ, C₆H₄O₂, purity ≥ 98.0%) was chemical grade (Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China). Ethylenediaminetetraacetic acid (EDTA, C₅H₈N₂O₈, purity = 99.5%) and isopropyl alcohol (IPA, C₆H₁₄O, purity > 99.7%) were analytical grade. Absolute ethanol (C₂H₅OH, purity ≥ 99.5%) was compliant with American Chemical Society Specifications (Aladdin Group Chemical Reagent Co., Ltd., Shanghai, China). IC (C₁₆H₁₆N₂Na₂O₆S₂, purity ≥ 98%) was gas chromatography grade (Tianjin Bodi Chemical Co., Ltd., Tianjin, China). Ultra-pure water (18.25 MU cm) was used throughout the work.

3.2. Synthesis of N-Doped TiO₂

Using tetrabutyl titanate as a precursor and ethanol as a solvent, nitrogen-doped titanium dioxide catalyst was synthesized and the sol-gel method was used for preparation. The work sequence was as following: Firstly, 17 mL tetrabutyl titanate and 40 mL anhydrous ethanol were combined as solution A; 40 mL of absolute ethanol, 10 mL of glacial acetic acid and 5 mL of double-distilled water were mixed as solution B; subsequently, ammonia water with a N/Ti ratio of 8 mol% was put into the clear colloidal suspension, which was formed by adding solution A dropwise to solution B under strong magnetic stirring and continuous magnetic stirring for 1 h. Xerogel was produced after 2 days of aging. The xerogel was ground into a powder and calcined at 500 °C for 2 h; finally, the mixed powder was sieved with a vibrating sieve after pulverization to obtain N-TiO₂ powder.

3.3. Synthesis of In₂YSb₂O₇/BiSnSbO₄ Heterojunction Photocatalyst

First, 0.30 mol/L In(NO₃)₃·5H₂O, 0.15 mol/L Y(NO₃)₃·6H₂O and 0.15 mol/L SbCl₅ were blended and continuously stirred for 20 h. The solution was then put into an autoclave and heated at 200 °C for 15 h. Hereafter, under the condition of N₂ ambience, the mixed compounds were calcined at 800 °C for 10 h in a tube furnace with a ramp rate of
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8 °C/min. In$_2$YSbO$_7$ powder was then obtained. After the above operation, 0.15 mol/L Bi(NO$_3$)$_3$·5H$_2$O, 0.15 mol/L SnCl$_4$·5H$_2$O and 0.15 mol/L SbCl$_5$ were blended and continuously stirred for 20 h and heated at 200 °C for 15 h. Then, the resulting powder was calcined at 780 °C for 10 h at 8 °C/min under an ambience of N$_2$. Thus, BiSnSbO$_6$ powder was obtained.

IBHP was made by mixing 800 mg of In$_2$YSbO$_7$ with 30 wt% (240 mg) of BiSnSbO$_6$ in 200 mL of octanol (C$_8$H$_{18}$O) and then the above mixed compounds were dispersed in an ultrasonic bath for 1 h with a simple solvothermal method [67]. Subsequently, the admixture was heated and refilled at 140 °C for 2 h under the condition of intense agitation to improve the adhesion of BiSnSbO$_6$ to the surface of In$_2$YSbO$_7$ nanoparticles to form IBHP. After cooling to room temperature, the outcomes were gathered by centrifugation and washed several times with an n-hexane/ethanol mixture. The refined powders were kept arid in a vacuity dryer at 60 °C for 6 h and then deposited into a dry container. Thus, IBHP was obtained.

3.4. Characterizations

The prepared pure crystal samples were tested by an X-ray diffractometer (XRD, Shimadzu, XRD-6000, Cu Kα radiation, Kyoto, Japan). The microstructure and morphology of the prepared products were represented by scanning electron microscopy (SEM, FEI, Quanta250, Lincoln, NE, USA), and the component content of the products was detected by energy-dispersive spectroscopy. Diffuse reflectance spectra of the synthetic substance were acquired using a UV–vis spectrophotometer (UV–vis DRS, Shimadzu, UV-3600). The surface chemical composition content and the elemental valence of the synthetic substance were detected by an X-ray photoelectron spectrograph (XPS, Ultravac-PHI, PHI 5000 VersaProbe, Kyoto, Japan). TEM (JEM-200CX, JEOL Corporation, Akishima, Japan) was used for detecting the morphology image and the SAED of N-TiO$_2$.

3.5. Photoelectrochemical Experiments

For electrochemical impedance spectroscopy (EIS) experiments, the practical instrument was a CHI660D electrochemical station with three standard electrodes (Shanghai Chenhua Instrument Co., Ltd., Shanghai, China). In this system, the working electrode was the prepared catalyst, the counter electrode was a platinum plate and the reference electrode was the commercial Ag/AgCl electrode. The electrolyte was Na$_2$SO$_4$ aqueous solution (0.5 mol/L), and photochemical measurements were performed using a 500 W Xe lamp with a UV cut-off filter as the visible-light source. The working electrode was prepared as following: after ultrasonic treatment for 1 h, 0.03 g sample and 0.01 g chitosan were dissolved in 0.45 mL dimethylformamide to form a solution. Subsequently, it was dropped onto a 10 mm × 20 mm indium tin oxide conductive glass. Finally, the working electrode was dried at 80 °C for 10 min. The frequency range for the EIS was from 0.01 Hz to 100 kHz.

3.6. Experimental Setup and Procedure

The working temperature was kept at 20 °C by using circulating cooling water and a photocatalytic reactor (XPA-7, Xujiang Power Plant, Nanjing, China). Imitation of sunlight was achieved by using a 500 W xenon lamp with a 420 nm cut-off filter. Twelve quartz tubes containing 480 mL of the experimental solution were used. The content of In$_2$YSbO$_7$ or BiSnSbO$_6$ or IBHP was 0.75 g/L; moreover, the concentration of IC was 0.0293 mmol/L. The IC concentration of 1.2 mmol/L was the residual concentration of DW after biodegradation. During the experiment, a UV–vis spectrophotometer (Shimadzu, UV-2450) was used to detect the residual concentration of IC by using 3 mL of the catalyst-filtered suspension solution, which was extracted periodically. Prior to VLGI, the suspension that contained the photocatalyst and IC was stirred magnetically in the dark for 30 min to ensure sufficient adsorption of IC and atmospheric oxygen within the photocatalyst; as a result, the adsorp-
tive saturated suspension was established. Under visible-light illumination, the suspension was stirred at 500 rpm.

Degradation data of IC in the experimental procedure were detected by the TOC analyzer. For testing the concentration of TOC during PCD of IC, potassium acid phthalate (KHC$_8$H$_4$O$_4$) or anhydrous sodium carbonate was used as the standard reagent. Potassium hydrogen phthalate standard solutions with defined carbon concentrations were prepared for calibration. TOC concentration was determined with six samples and every sample contained 45 mL of reaction solution.

Determination of IC and intermediate products were carried out by liquid chromatography–mass spectrometry (LC-MS, Thermo Quest LCQ Duo, Thermo Fisher Scientific Corporation, MA, USA. Beta Basic-C18 HPLC column: 150 × 2.1 mm, ID of 5 µm). A total of 20 µL of the reaction solution was injected into the LC–MS system. The reaction solution contained 60% methanol and 40% ultrapure water at a flow rate of 0.2 mL/min. The mass spectrometry conditions included a capillary temperature of 27 °C, a voltage of 19.00 V, a spray voltage of 5000 V and a constant sheath gas flow. Spectra were acquired over the m/z range of 50 to 600.

The incident photon flux after VLGI measured with a radiometer was 4.76 × 10$^{-6}$ Einstein L$^{-1}$ s$^{-1}$. By regulating the distance between the photoreactor and the xenon arc lamp, the incident photon flux on the photoreactor was altered.

The calculation method of photon efficiency was described by the following Formula (5):

$$\phi = \frac{R}{I_o}$$

where $\phi$ is the photonic efficiency (%) and $R$ is the degradation rate of IC (mol L$^{-1}$ s$^{-1}$) and $I_o$ is the incident photon flux (Einstein L$^{-1}$ s$^{-1}$).

4. Conclusions

Firstly, In$_2$YSbO$_7$ showing intense photocatalytic activity was manufactured by a solvothermal method. IBHP was synthesized by a solvothermal method for the first time. SEM–EDS, XRD, an UV–vis spectrophotometer and XPS were used to investigate the photophysical properties and photocatalytic properties of the prepared photocatalysts. The experimental results displayed that In$_2$YSbO$_7$ was a pure phase with a pyrochlore structure and a cubic crystal system by the space group Fd3m. The lattice parameter and the band gap of In$_2$YSbO$_7$ were $a = 11.102698$ Å and 2.68 eV, respectively. IBHP was certified to be an effective catalyst for the removal of IC in the DW. After VLGI-120M, the ROR of IC and TOC reached 99.42% and 93.10%, respectively. The removal rate of IC with IBHP was 1.103 times or 1.167 times or 2.392 times higher than that with In$_2$YSbO$_7$ as a catalyst or with BiSnSbO$_6$ as a catalyst or with N-TiO$_2$ as a catalyst after VLGI-120M. Therefore, IBHP was an efficient photocatalyst for treating DW or surface water which was contaminated by IC. In the end, the possible PCD pathways for IC were speculated.

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