Article

Synthesis, Property Characterization and Photocatalytic Activity of the $\text{Ag}_3\text{PO}_4/\text{Gd}_2\text{BiTaO}_7$ Heterojunction Catalyst under Visible Light Irradiation

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Abstract: A new type of $\text{Gd}_2\text{BiTaO}_7$ nanocatalyst (GBT) was synthesized by a high-temperature solid-phase method, and a heterojunction photocatalyst, which was composed of GBT and silver phosphate (AP), was prepared by the facile in-situ precipitation method for the first time. The photocatalytic property of GBT or the $\text{Ag}_3\text{PO}_4/\text{Gd}_2\text{BiTaO}_7$ heterojunction photocatalyst (AGHP) was reported. The structural properties of GBT and AGHP were characterized by an X-ray diffractometer, scanning electron microscope–X-ray energy dispersive spectra, an X-ray photoelectron spectrograph, a synchrotron-based ultraviolet photoelectron spectroscopy, a Fourier transform infrared spectrometer, an UV-Vis diffuse reflectance spectrophotometer and an electron paramagnetic resonance spectrometer. The results displayed that GBT was well crystallized with a stable cubic crystal system and space group $Fd3m$. The lattice parameter or band gap energy of GBT was found to be $a = 10.740051 \text{ \AA}$ or 2.35 eV, respectively. After visible light irradiation of 30 min, the removal rate of bisphenol A (BPA) reached 99.52%, 95.53% or 37.00% with AGHP as the photocatalyst, with Ag_3PO_4 and potassium persulfate (AP-PS) as photocatalysts or with N-doped TiO_2 (NT) as a photocatalyst, respectively. According to the experimental data, it could be found that the removal rate of BPA with AGHP as a photocatalyst was 2.69 times higher than that with NT as a photocatalyst. AGHP showed higher photocatalytic activity for photocatalytic degradation of BPA under visible light irradiation compared with GBT or AP-PS or NT. The removal rate of total organic carbon (TOC) was 96.21%, 88.10% or 30.55% with AGHP as a photocatalyst, with AP-PS as photocatalysts or with NT as a photocatalyst after visible light irradiation of 30 min. The above results indicated that AGHP possessed the maximal mineralization percentage ratio during the process of degrading BPA compared with GBT or AP-PS or NT. The results indicated that the main oxidation radical was $\bullet\text{OH}$ during the process of degrading BPA. The photocatalytic degradation of BPA with AGHP as a photocatalyst conformed to the first-order reaction kinetics. This study provided inspiration for obtaining visible light-responsive heterojunction photocatalysts with high catalytic activity and efficient removal technologies for organic pollutants and toxic pollutants, and as a result, the potential practical applications of visible light-responsive heterojunction photocatalysts were widened. The subsequent research of thin-film plating of the heterojunction catalysts and the construction of complete photoluminescent thin-film catalytic reaction systems, which utilized visible light irradiation, could provide new technologies and perspectives for the pharmaceutical wastewater treatment industry.

Keywords: $\text{Gd}_2\text{BiTaO}_7$; $\text{Ag}_3\text{PO}_4/\text{Gd}_2\text{BiTaO}_7$ heterojunction; potassium persulfate; bisphenol A; photocatalytic degradation; visible light irradiation; N-doped TiO_2

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1. Introduction

The treatment of toxic and refractory organic pollutants in water has always been a difficult hot spot in the field of water treatment. The residues of the treatment for toxic and

refractory organic pollutants in the environment has had a certain degree of persistence, and even if they contained very low concentrations, they might be extremely toxic. Bisphenol A (BPA) was 4-dihydroxydiphenylpropane ($C_{15}H_{16}O_2$) [1], which was mainly utilized in the organic synthesis of manifold polymer materials such as polycarbonate, epoxy resin, polyphenylene ether resin and unsaturated polyester resin. BPA was also widely utilized in the production of polyvinyl chloride heat stabilizers, rubber antioxidants, agricultural pesticides, plasticizers, antioxidants, coatings and other fine chemical products, as well as building materials floors, food packaging materials, tooth sealants and fungicides. BPA was a phenol representative environmental pollutant in the class of compounds. In the process of production or usage or related waste disposal, BPA was released into the environment; moreover, the human body ingested BPA by means of diet, breathing or direct contact. In 1993, Krishnan discovered that BPA had estrogenic activity and could interfere with the body's endocrine system [2]. Existing studies had confirmed that it could have an adverse effect on the reproductive system of gastropod males when the concentration of BPA in the water body reached $1 \mu\text{g/L}$. Thus, a method to efficiently degrade BPA needed to be resolved urgently [1–3].

Photocatalysis technology had the advantages of environmental protection, high treatment efficiency and low cost [4,5]. Photocatalysis technology used sunlight as an energy source for activating photocatalysts, which could produce oxidation groups under light irradiation and effectively remove organic pollutants and be utilized circularly. The research work of photocatalysis technology was of great importance in the future because it was scientifically attractive due to its high efficiency, energy saving and pollution-free characteristics. The crux of photocatalytic technology was the development of highly efficient photocatalysts [3–8]. In accordance with previous reports, many metal oxides such as TiO_2 and ZnO_2 [9,10] had been developed as photocatalysts. Because single photocatalysts had some inherent characteristics, such as photo-etching and wide band gaps, their applications were limited [11,12]. It was important for improving the photocatalytic property of photocatalysts [13–16]. Many methods have been proven to be effective, such as ion doping methods, the construction of heterojunctions [17–22] and photosensitization [23,24]. Among these methods, the construction of composite materials was an active research area in the field of photocatalysts [21–27]. A composite photocatalyst concentrated the effects of a single photocatalyst, which endowed the composite system with higher light utilization efficiency [28–32], longer carrier life, higher photocatalytic property and higher chemical stability [33–39].

Several scientists [40–43] have shown that the use of nitrogen-doped titanium dioxide for degrading other pollutants under visible light irradiation (VLI) was also effective. For instance, some photocatalytic experiments [40–43] had confirmed that nitrogen-doped titanium dioxide was effective for removing spiramycin in pharmaceutical wastewater (PW), removing methylene blue or removing oxalic acid [44–47]. The above research provided us with inspiration for designing visible light response photocatalysts with high catalytic activity.

Fortunately, $A_2B_2O_7$ compounds were often considered to possess photocatalytic properties under VLI. In our previous work [48], we had found that $\text{Bi}_2\text{InTaO}_7$ was crystallized with the pyrochlore-type structure and acted as a photocatalyst under VLI and seemed to have potential in the improvement of photocatalytic activity upon modification of its structure. In accordance with the above analysis, we could assume that substitution of Bi^{3+} by Gd^{3+} , and substitution of In^{3+} by Bi^{3+} in $\text{Bi}_2\text{InTaO}_7$ might increase the carriers' concentration. As a result, a change and improvement of the electrical transportation and photophysical properties could be found in the novel $\text{Gd}_2\text{BiTaO}_7$ (GBT) compound, which might possess advanced photocatalytic properties.

In photocatalysis, the Z-scheme heterojunction catalysts had excellent properties which were not found in ordinary photocatalysts and common type II catalysts [49–51]. The Z-scheme heterojunction greatly improved the redox property and electron transport rate of the catalyst by generating effective electron–hole recombination within the

two semiconductors [52]. Li et al. [53–56] discovered and prepared a series of doped perovskite catalysts with excellent low-temperature redox properties, such as direct Z-scheme $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3/\text{ATP}$ and indirect Z-scheme $\text{LaCoO}_3/\text{RGO}/\text{ATP}$. Subsequently, these catalysts were applied to photo-SCR, light nitrogen and other fields, and as a result, these catalysts showed excellent activity. Luo et al. [57] also rationally constructed a direct Z-scheme $\text{LaMnO}_3/\text{g-C}_3\text{N}_4$ hybrid for improving the photocatalytic degradation efficiency of tetracycline under VLI. The above findings confirmed that the construction of the photocatalyst with the Z-scheme could significantly improve the redox property of the photocatalyst [58] and enhance the overall selectivity and activity of the reaction. In summary, the construction of the catalyst with the Z-scheme was a promising application direction.

In this paper, an X-ray diffractometer, scanning electron microscope–X-ray energy dispersive spectra (SEM-EDS), X-ray photoelectron spectrograph (XPS), synchrotron-based ultraviolet photoelectron spectroscopy (UPS), Fourier transform infrared spectrometer (FT-IR), UV-Vis diffuse reflectance spectrophotometer (DRS) and electron paramagnetic resonance spectrometer (EPR) were used for analyzing the structural properties of pure-phase Ag_3PO_4 (AP) and single-phase GBT prepared by the kinetic control method and the high-temperature solid-phase sintering method. Moreover, the removal rate of BPA under VLI with pure-phase Ag_3PO_4 and potassium persulfate (AP-PS) as photocatalysts or with a $\text{Ag}_3\text{PO}_4/\text{Gd}_2\text{BiTaO}_7$ heterojunction photocatalyst (AGHP) as a photocatalyst was detected. In this study, our purpose was to prepare novel heterojunction photocatalysts that could remove BPA within pharmaceutical wastewater under VLI. The innovative research content of our work was that a new type of $\text{Gd}_2\text{BiTaO}_7$ nanocatalyst (GBT) was synthesized by the high-temperature solid-phase method and AGHP was prepared by the facile in-situ precipitation method for the first time. Furthermore, our aim was to obtain a visible light-responsive photocatalyst that could remove BPA effectively. The removal of organic pollutants within pharmaceutical wastewater with AGHP as a photocatalyst was more efficient and safe.

2. Result and Discussion

2.1. XRD Analysis

The structure with full-profile refinements of the as-prepared product GBT was examined by the X-ray diffraction technique and the results were shown in Figure 1. The collected data were obtained by the Materials Studio program, which was based on Rietveld analysis. According to Figure 1, it could be concluded that GBT was single phase and the lattice parameter of the new photocatalyst GBT was 10.740051 Å. Simultaneously, the final refinement for GBT showed good agreement between the observed and calculated intensities for the pyrochlore-type structure, a cubic crystal system and a space group $Fd\bar{3}m$ (O atoms were included in the model). In addition (Moreover), all of the diffraction peaks for GBT could be indexed successfully according to the lattice constant and above space group. Table 1 shows the atomic coordinates and structural parameters of GBT. Figure S1 shows the atomic structure of GBT. As could be seen from Figure 1, it could be concluded that GBT crystallized into a pyrochlore-type structure. The results of full-profile structure refinements for GBT generated the unweighted R factors, $R_p = 13.01\%$ with the space group $Fd\bar{3}m$.

All of the reflection peaks of GBT could be successfully indexed according to the lattice parameter and the space group. It was known that the x coordinate of the O(1) atom could be considered to be an index of the change of the crystal structure on the pyrochlore-type $\text{A}_2\text{B}_2\text{O}_7$ compounds (Cubic, space group $Fd\bar{3}m$) and was equal to 0.375 when the six A–O(1) bond lengths were the same as that of the two A–O(2) bond lengths [59]. Therefore, information on the distortion of the MO_6 ($\text{M} = \text{Bi}^{3+}$ and Ta^{5+}) octahedra could be gained from the x value [59]. The x value was shifted off $x = 0.375$ [59], thus the distortion of the MO_6 ($\text{M} = \text{Bi}^{3+}$ and Ta^{5+}) octahedra existed clearly in the crystal structure of GBT. Charge separation was required for photocatalytic degradation of BPA (PDB) under VLI for the sake of preventing recombination of the photoinduced electrons and photoinduced holes.

Inoue [60] and Kudo [61] had pointed out that the local distortion of the MO_6 octahedra, which derived from certain photocatalysts such as BaTi_4O_9 and $\text{Sr}_2\text{M}_2\text{O}_7$ ($\text{M} = \text{Nb}^{5+}$ and Ta^{5+}), was important for preventing the charge recombination and contributed to the improvement of the photocatalytic activity. Thus, the distortion of the MO_6 ($\text{M} = \text{Bi}^{3+}$ and Ta^{5+}) octahedra in the crystal structure of GBT could also be considered to be useful for enhancing the photocatalytic activity. GBT consisted of a three-dimensional network structure of corner-sharing MO_6 ($\text{M} = \text{Bi}^{3+}$ and Ta^{5+}) octahedra. The MO_6 ($\text{M} = \text{Bi}^{3+}$ and Ta^{5+}) octahedra were connected to form chains by Gd^{3+} ion. Two kinds of Gd-O bond lengths existed: The six Gd-O(1) bond lengths (2.748 Å) were clearly longer than that of the two Gd-O(2) bond lengths (2.325 Å). The six M-O(1) ($\text{M} = \text{Bi}^{3+}$ and Ta^{5+}) bond lengths were 2.023 Å and the M-Gd ($\text{M} = \text{Bi}^{3+}$ and Ta^{5+}) bond lengths were 3.797 Å. The M-O-M ($\text{M} = \text{Bi}^{3+}$ and Ta^{5+}) bond angles were 139.624° in the crystal structure of GBT. The Gd-M-Gd ($\text{M} = \text{Bi}^{3+}$ and Ta^{5+}) bond angles were 135° in the crystal structure of GBT. The Gd-M-O ($\text{M} = \text{Bi}^{3+}$ and Ta^{5+}) bond angles were 131.580° in the crystal structure of GBT. The study on the luminescent properties had concluded that the closer the M-O-M bond angle was to 180° , the more the excited state was delocalized [59]. It showed that the angles between the corner-sharing MO_6 ($\text{M} = \text{Bi}^{3+}$ and Ta^{5+}) octahedra, for example, the M-O-M bond angles for GBT, were important for affecting the photocatalytic activity of GBT. The closer the M-O-M bond angles were to 180° , the larger the mobilities of the photoinduced electrons and photoinduced holes were [59]. The mobilities of the photoinduced electrons and photoinduced holes affected the photocatalytic activity because they affected the probability of electrons and holes of reaching reaction sites on the catalyst surface [59].

Figure 1. X-ray powder diffraction patterns and Rietveld refinements of $\text{Gd}_2\text{BiTaO}_7$ (red dotted line represented experimental XRD data of $\text{Gd}_2\text{BiTaO}_7$; blue solid line represented simulative XRD data of $\text{Gd}_2\text{BiTaO}_7$; black solid line represented a difference between experimental XRD data of $\text{Gd}_2\text{BiTaO}_7$ and simulative XRD data of $\text{Gd}_2\text{BiTaO}_7$; green vertical line represented observed reflection positions).

Table 1. Structural parameters of $\text{Gd}_2\text{BiTaO}_7$ prepared by solid-state reaction method.

Atom	x	y	z	Occupation Factor
Gd	0	0	0	1
Bi	0.5	0.5	0.5	0.5
Ta	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

In addition, the Ta–O–Ta bond angle of GBT was larger, which resulted in an increase in the photocatalytic activity of GBT. As for GBT, Gd was a 5d-block rare earth metal element, Bi was a 6p-block metal element and Ta was a 5d-block metal element. According to the above analysis, the effect of degrading bisphenol A (BPA) under VLI with GBT as photocatalyst could be attributed mainly to the crystalline structure and electronic structure.

2.2. UV-Vis Diffuse Reflectance Spectra

The absorption spectra of GBT sample are listed in Figures 2 and S2. The absorption edge of this new photocatalyst GBT was found to be at 528 nm, which was in the visible region of the spectrum.

Figure 2. UV-Vis diffuse reflectance spectra of $\text{Gd}_2\text{BiTaO}_7$.

The band gap energies of the crystalline semiconductors could be determined by the intersection point between the photon energy $h\nu$ axis and the line extrapolated from the linear portion of the absorption edge of so-called Kubelka–Munk function (known as the re-emission function) [62,63].

$$\frac{[1 - R_d(h\nu)]^2}{2R_d(h\nu)} = \frac{\alpha(h\nu)}{S} \quad (1)$$

where S is the scattering factor, R_d is the diffuse reflectance and α represents the absorption coefficient of radiation.

The optical absorption near the band edge of the crystalline semiconductors obeyed the equation [64,65]:

$$\alpha h\nu = A (h\nu - E_g)^n \quad (2)$$

here, A , α , E_g and ν represent the proportional constant, absorption coefficient, band gap and light frequency, respectively. Within this equation, n determined the character of the transition in a semiconductor. E_g and n could be calculated by the following steps: (1) Plotting $\ln(\alpha h\nu)$ versus $\ln(h\nu - E_g)$ assuming an approximate value of E_g , (2) deducing the value of n in accordance with the slope in this graph, (iii) refining the value of E_g by plotting $(\alpha h\nu)^{1/n}$ versus $h\nu$ and extrapolating the plot to $(\alpha h\nu)^{1/n} = 0$. In accordance with the above method, the values of E_g for GBT were calculated to be 2.35 eV, respectively. The estimated value of n was approximately 2 and the optical transition for these photocatalysts was allowed indirectly.

The band gap energy of GBT was 2.35 eV, the band gap energy of $\text{Bi}_3\text{O}_5\text{I}_2$ was 2.02 eV [66] and the band gap energy of Co-doped ZnO was 2.39 eV [67]. The band gap energies of GBT or $\text{Bi}_3\text{O}_5\text{I}_2$ or Co-doped ZnO were all less than 2.40 eV, which meant the above three catalysts possessed visible light response characteristics and tremendous potential for displaying high catalytic activity under VLI.

2.3. Characterization of Ag_3PO_4 , $\text{Ag}_3\text{PO}_4/\text{Gd}_2\text{BiTaO}_7$ Heterojunction

The phase structure and crystal structure of the samples were analyzed by XRD. Figure S3 displays the XRD spectrum and PDF standard card of Ag_3PO_4 (AP). It could be seen from Figure S3 that sample AP was consistent with the corresponding PDF card of AP, indicating sample AP was successfully synthesized, and AP was pure single phase. The sample AP was a cubic crystal system, and the cell parameters were $a = b = c = 6.013 \text{ \AA}$.

Figure S4 shows the scanning electron microscope morphology pattern of the synthesized AP. Figure S5 displays the composition of the product AP, which was analyzed by the SEM-EDS method. The result shown in Figure S5 was consistent with the XRD pattern of AP, and AP was proven to be pure phase without any impurity. It could be concluded from Figure S4 AP contained silver, phosphorus and oxygen elements and the average atomic ratio of Ag: P: O was 3:1:4. The detected carbon and aluminum elements came from the detection process, which indicated the AP catalyst that was prepared was a pure phase. It could be found from Figure S4 that AP particles had regular morphology and uniform particle size. The particle size of AP was measured to be 970 nm.

Figure 3 shows the ultraviolet-visible diffuse reflectance spectrum of the prepared AP. It could be observed from Figure 3 that the absorbance edge of AP was 530 nm, which meant that AP had the ability to become a visible light-responsive photocatalyst. We utilized the Kubelka–Munk transformation method to analyze the band gap of AP. The optical absorption near the band edge of AP conformed to the above formula (1). According to the above formula (1), the forbidden band width of AP was 2.45 eV, as shown in the inset of Figure 3. The low band gap width for AP was beneficial to improve the photocatalytic activity under VLI.

Figure 3. UV-Vis diffuse reflectance spectra and band gap of Ag_3PO_4 .

Figure 4 displays the ultraviolet photoelectron spectrogram (UPS) of AP. According to the UPS results, which derived from Figure 4, the absolute electrochemical potential of the valence band value of AP was calculated to be 2.72 eV, which was related to the Fermi energy. Combined with the band gap value 2.45 eV of AP, the absolute electrochemical potential of the conduction band value of AP was 0.27 eV.

Figure 5 shows the Fourier transform infrared spectrum analysis of AP particles. It could be seen from Figure 5 that the absorption bands of the prepared AP were at 534 cm^{-1} and 929 cm^{-1} , respectively. The absorption band of AP at 534 cm^{-1} was attributed to the P=O-P bond. The absorption band of AP at 929 cm^{-1} was attributed to the P-O-P bond.

Figure 4. Ultraviolet photoelectron spectroscopy of Ag_3PO_4 .

Figure 5. Fourier transform infrared spectra of Ag_3PO_4 .

Figure S6a shows the absorbance standard curve of BPA at different concentrations when the AP dosage was 1.25 mg/L, 2.5 mg/L, 5 mg/L, 10 mg/L or 20 mg/L under ultraviolet light irradiation in the range of 220–320 nm using an ultraviolet-visible spectrophotometer at pH = 7. It could be seen from the inset of Figure S6a that the maximal absorption wavelength of BPA was 273 nm. The relationship between the concentration of BPA and the absorbance value at 273 nm was shown in Figure S6a. A linear regression method was used to obtain the equation: $Y = 0.01238X - 0.00377$, where Y was the absorbance value of BPA at 273 nm, and X was the concentration of BPA. The correlation coefficient R^2 was 0.9993, indicating that the linear regression results were good.

Figure S6b shows the absorption standard curve of BPA at pH = 11. It could be found from Figure S6b that the absorbance value of BPA was achieved when the AP dosage were 1.25 mg/L, 2.5 mg/L, 5 mg/L, 10 mg/L and 20 mg/L under ultraviolet light irradiation in the range of 180–330 nm. It could be seen from the inset of Figure S6b that one absorption wavelength of BPA was 293 nm.

Zhuang [68] obtained UV–visible absorption spectra of BPA and found that BPA had absorption peaks at 224 nm and 278 nm. Zhuang [68] summarized that 224 nm was the maximum absorbing peak, which was susceptible to the influence of the solvent absorption, and the 278 nm absorption peak was chosen as the detection wavelength for HPLC with UV detection. Similarly, we found from Figure S6b that BPA possessed absorption peaks at 208 nm, 242 nm and 293 nm when the pH value was 11. According to the results from Zhuang [68], we used the absorbance peak at 242 nm to detect the concentration of BPA.

The relationship between the concentration of BPA and the absorbance value at 242 nm was shown in Figure S6b. A linear regression method was utilized to obtain the equation

$Y = 0.01786X + 0.0024$, where Y was the absorbance value of BPA at 242 nm and X was the concentration of BPA. The correlation coefficient R^2 was 0.9996, indicating that the linear regression results were perfect.

Figure S7 shows the XRD patterns of AP under different reaction conditions. The black line derived from Figure S7 represents the XRD pattern of AP without a photocatalytic reaction. The red line derived from Figure S7 represents the XRD pattern of AP after photocatalytic degradation of BPA (PDB) for 30 min with AP as a photocatalyst under VLI. The blue line displayed the XRD pattern of AP after the adsorption of BPA for 30 min with AP-PS as the adsorbent under dark conditions. The pink line displayed the XRD pattern of AP after PDB for 30 min with Ag_3PO_4 and AP-PS as photocatalysts under VLI. Under different reaction conditions, all diffraction peak data of our prepared AP were in complete accordance with the diffraction peaks data of AP, which derived from the corresponding standard card of AP, indicating that the structure of the synthesized catalyst AP was stable. The intensity of the XRD peaks of AP indicated that the catalyst AP had good crystallinity, which exerted an important influence on the photocatalytic performance of the catalyst AP. In addition, the exposed crystal planes of the main peaks of AP were (210), (211) and (200), respectively. Optimizing these exposed crystal faces of AP was one of the ways to improve the photocatalytic performance of the photocatalyst AP.

2.4. Photocatalytic Activity

For further comparison, Figure S8a depicts the BPA concentration changes with AP and PS as catalysts under different reaction conditions. It could be seen from Figure S8a that after 30 min of VLI, the degradation efficiency of BPA with AP and PS as catalysts reached 95.53%. Figure S8a indicated that the removal rate of BPA without any catalyst after VLI of 30 min was estimated to be 0%. After 30 min of VLI without any catalyst, the concentration of BPA did not change. Using potassium persulfate as a catalyst, the concentration of BPA changed slightly after 30 min in darkness, and the removal rate of BPA was 0.44%. With potassium persulfate as a catalyst, the degradation removal rate of BPA changed slightly after VLI for 30 min, and the removal rate of BPA was 0.70%. AP was used as a catalyst to degrade BPA under VLI, and as a result, the concentration of BPA decreased gradually with an increasing VLI duration, and the removal rate of BPA was 28.10% when the VLI duration reached 30 min. Using silver phosphate and potassium persulfate as catalysts, BPA was degraded under dark conditions and the removal rate of BPA was 56.10% after VLI for 30 min. Silver phosphate and potassium persulfate were used as catalysts for removing BPA under VLI, and as a result, the concentration of BPA decreased gradually with the increase in light time, and the removal rate of BPA was 95.53% when the VLI duration reached 30 min. The above results showed that the degradation efficiency of BPA with silver phosphate and potassium persulfate as catalysts was higher than that with AP as catalyst after VLI for 30 min. The removal rate of BPA with silver phosphate and potassium persulfate as catalysts was 3.40 times that with AP as a catalyst after VLI for 30 min. In addition, according to the change of the absorption spectrum of BPA with the irradiation time, the degradation kinetics of BPA with AP as a catalyst or with AP and PS as catalysts under VLI was calculated. Figure S8b shows the degradation kinetics of BPA with AP as a photocatalyst or with AP-PS as photocatalysts under VLI. The above results showed that the photocatalytic kinetics curve of BPA with AP as a photocatalyst to degrade BPA conformed to first-order kinetics. The first-order rate constant for the degradation of BPA under VLI with AP as a catalyst was 0.01117 min^{-1} , the first-order rate constant for the degradation of BPA under dark conditions with AP and PS as catalysts was 0.02644 min^{-1} and the first-order rate constant for the degradation of BPA with AP and PS as photocatalysts under VLI was examined to be 0.09461 min^{-1} . Figure 6 shows the UV-Vis absorption spectrum changes of BPA under VLI when AP-PS are present. It could be clearly seen from Figure 6 that the characteristic peak of BPA was located at 276 nm. A significant decrease in the absorbency value intensity could be observed within 30 min.

Figure 6. UV-visible absorption spectra of time-dependent bisphenol A with Ag_3PO_4 and potassium persulfate as photocatalysts under visible light irradiation.

Figure 7 shows the effect of different concentrations of AP on the photocatalytic removal efficiency of BPA with AP as a photocatalyst under VLI. It could be seen from Figure 7 that the degradation efficiency of BPA with 1.0 g/L AP as a catalyst was higher and the degradation rate was 92.39% within 30 min of VLI, while the degradation efficiency of BPA with 0.25 g/L AP as a catalyst was 36.97%, which was the lowest. The results derived from Figure 7 indicate that the removal rate of BPA gradually increased in the same illumination time when increasing the AP concentration. It could be seen from Figure 7 that the degradation rate of BPA with 1.25 g/L AP as a photocatalyst was 93.20%, which was basically the same as the degradation rate of BPA with 1.0 g/L AP as a photocatalyst within 30 min of VLI. Figure S9 shows the observed kinetic plots for the PDB with AP as a photocatalyst under VLI. It could be found from Figure S9 that the first-order rate constant for PDB under VLI with 0.25 g/L AP as a catalyst was 0.01522 min^{-1} ; moreover, the first-order rate constant for PDB under VLI with 0.50 g/L AP as a catalyst was 0.02055 min^{-1} . Figure S9 also depicted that the first-order rate constant for PDB under VLI with 0.75 g/L AP as a catalyst was 0.09461 min^{-1} . Furthermore, the first-order rate constant for PDB under VLI with 1.00 g/L AP as a catalyst was 0.09338 min^{-1} . The above results proved that the removal rate of organic pollutants increased gradually with the increase in the catalyst concentration under the same VLI duration. When the concentration of AP increased from 0.25 g/L to 0.75 g/L, the removal rate of BPA increased rapidly. When the concentration of AP increased from 0.75 g/L to 1.0 g/L, the removal rate of BPA increased slowly. When the AP concentration was higher than 1.0 g/L, the removal rate of BPA could not be improved, thus 1.0 g/L of the AP concentration was saturated. When the concentration of the AP dosage reached 1.0 g/L, the removal rate of BPA was close to saturation, thus the best dosage of AP was 1.0 g/L.

Figure 8 shows the effect of different anions on the degradation efficiency of BPA with AP-PS as photocatalysts under VLI. AP-PS were used as catalysts for degrading BPA in PW under VLI. In order to investigate the effect of anions on the photocatalytic reaction, ultrapure water that contained anions was added to the photocatalytic reaction system to simulate the wastewater environment. As can be seen from Figure 8, the concentration of BPA in PW gradually decreased with the gradual increase in illumination time. The results derived from Figure 8 indicate that the removal rate of BPA in PW was 95.54% with AP-PS as photocatalysts after 30 min of illumination under VLI. Moreover, the removal rate of BPA in PW was 43.40% when adding 1 mM Cl^- within the PW with AP-PS as photocatalysts after 30 min of illumination under VLI, while the removal rate of BPA in PW was 90.94% when adding 1 mM NO_3^- within the PW with AP-PS as photocatalysts after 30 min of illumination under VLI. The removal rate of BPA in PW was 58.10% when adding 1 mM CO_3^{2-} and the removal rate of BPA in PW was 91.33% when adding 1 mM SO_4^{2-} with

AP-PS as photocatalysts after 30 min of illumination under VLI. It could be found from Figure 8 that the NO_3^- anion showed a weak promoting effect on the PDB during the VLI duration from 15 min to 20 min. The above results indicated that the most potent inhibitor for BPA degradation was found to be a Cl^- anion, and the removal rate of BPA without adding any anions was 2.2 times the removal rate of BPA when adding 1 mM Cl^- with AP-PS as photocatalysts after 30 min of illumination under VLI. The reason was that Cl^- consumed the $\bullet\text{OH}$ and the photogenerated holes in the reaction system, and as a result, the amount of $\bullet\text{OH}$ and the photogenerated holes within the system was reduced, and the above results caused the greatest negative effect on the degradation of BPA [69–71]. The reason for the higher inhibitory effect of NO_3^- or SO_4^{2-} on the degradation of BPA was that NO_3^- or SO_4^{2-} consumed the photogenerated holes within the reaction system [70–72].

Figure 7. The effect of different concentration of Ag_3PO_4 on the photocatalytic removal efficiency of bisphenol A with Ag_3PO_4 as a photocatalyst under visible light irradiation.

Figure 8. The effect of different anions on the degradation efficiency of bisphenol A with Ag_3PO_4 and potassium persulfate as photocatalysts under visible light irradiation.

Figure 9 shows the effect of different cations on the degradation efficiency of BPA with AP-PS as photocatalysts under VLI. In order to investigate the effect of cations on the photocatalytic reaction, ultrapure water that contained cations was added to the photocatalytic reaction system to simulate the wastewater environment. The results in Figure 9 indicate that AP-PS were used as catalysts to degrade BPA in PW under VLI. As can be found in Figure 9, the concentration of BPA in PW gradually decreased with the gradual increase in VLI duration. Figure 9 indicated that the removal rate of BPA in PW was 95.54% after VLI of 30 min with AP-PS as photocatalysts under VLI. Moreover, the removal rate of BPA in PW was 93.20% by adding 1 mM Mg^{2+} , the removal rate of BPA in PW was 95.10% by adding 1 mM Zn^{2+} and the removal rate of BPA in PW was 93.60% by adding 1 mM Ba^{2+} with AP-PS as photocatalysts under VLI. Cations did not significantly inhibit the PDB

compared with the removal rate of BPA, without adding any additional cations and with AP-PS as photocatalysts under VLI.

Figure 9. The effect of different cations on the degradation efficiency of bisphenol A with Ag_3PO_4 and potassium persulfate as photocatalysts under visible light irradiation.

Figure 10a shows the DMPO spin trapping EPR spectra with AP as a catalyst in an aqueous dispersion for $\text{DMPO}/\bullet\text{OH}$ and $\text{DMPO}/\bullet\text{O}_2^-$ under VLI or under conditions of darkness. In order to further confirm the presence of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ in the procedure of PDB, EPR characterization was performed, and DMPO spin-trapping EPR spectra with AP as a photocatalyst under VLI were shown in Figure 10a. During the EPR characterization process, 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was utilized to spin trap the active radicals in the system for detection. As can be found in Figure 10a, when in darkness, EPR signals that were relevant to DMPO adducts were not detected for AP. However, after VLI for 30 min, there were apparent signals in Figure 10a, which correspond with $\text{DMPO}/\bullet\text{OH}$ adducts [62]. Figure 10b shows the DMPO spin trapping EPR spectra with AP-PS as catalysts or with AP as a catalyst in an aqueous dispersion for $\text{DMPO}-\text{SO}_4^{\bullet-}$, $\text{DMPO}-\bullet\text{OH}$ and $\text{DMPO}-\bullet\text{O}_2^-$ under VLI. In order to further confirm the presence of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ in the procedure of PDB, EPR characterization was performed, and DMPO spin-trapping EPR spectra with AP-PS as catalysts under VLI were shown in Figure 10b. During the EPR characterization process, DMPO was utilized to spin trap the active radicals in the system for detection. As can be seen from Figure 10b, when AP was utilized as a catalyst to degrade BPA, only the signal of $\bullet\text{OH}$ was detected after 1.0 mM EDTA was used to capture h^+ under VLI. After VLI for 30 min with AP-PS as photocatalysts, there were apparent signals as shown in Figure 10b, which corresponded with $\text{DMPO}/\bullet\text{OH}$ adducts and $\text{DMPO}/\text{SO}_4^{\bullet-}$ adducts, respectively [73]. The above results indicated that the main oxidation radical was $\bullet\text{OH}$ during the process of degrading BPA with AP-PS as photocatalysts under VLI.

Figure 11a shows the effect of different pH values on the removal efficiency of BPA with AP-PS as catalysts under VLI or with potassium persulfate as a catalyst under conditions of darkness. As can be seen from Figure 11a, AP-PS possessed the best degradation effect on BPA under VLI when $\text{pH} = 3.5, 5.4, 7.4$ and 8.4 . The results derived from Figure 11a indicate that the degradation rate of BPA was 98.16%, 97.20%, 99.53%, 99.57% or 99.10% after 30 min of VLI when $\text{pH} = 3.5, 5.4, 7.4, 8.4$ or 10.9 , respectively. Figure 11b shows the temporal spectral changes of aqueous solutions of BPA with AP-PS as catalysts under VLI at $\text{pH} = 10.9$. The results derived from Figure 11b indicate that the typical absorbance peak of BPA at 293 nm decreased with an increasing VLI duration.

Figure 10. (a) DMPO spin trapping EPR spectra with Ag_3PO_4 as catalyst in aqueous dispersion for $\text{DMPO-}\bullet\text{OH}$ and $\text{DMPO-}\bullet\text{O}_2^-$ under visible light irradiation or under the condition of darkness; (b) DMPO spin trapping EPR spectra with Ag_3PO_4 and potassium persulfate as catalysts or with Ag_3PO_4 as catalyst in aqueous dispersion for $\text{DMPO-SO}_4^{\bullet-}$, $\text{DMPO-}\bullet\text{OH}$ and $\text{DMPO-}\bullet\text{O}_2^-$ under visible light irradiation.

Figure 11. (a) The effect of different pH values on removal efficiency of bisphenol A with Ag_3PO_4 and potassium persulfate as catalysts under visible light irradiation or with potassium persulfate as catalyst under conditions of darkness; (b) temporal spectral changes of aqueous solutions of bisphenol A with Ag_3PO_4 and potassium persulfate as catalysts under visible light irradiation at $\text{pH} = 10.9$.

Figure 12 shows the effects of different radical scavengers on the removal rate of BPA with AP-PS as catalysts under VLI. The different radical scavengers were separately added to the BPA solution at the beginning of the photocatalytic experiment to determine the active species during the process of degrading BPA. Isopropanol (IPA) was utilized to capture hydroxyl radicals ($\bullet\text{OH}$), benzoquinone (BQ) was used to capture superoxide anions ($\bullet\text{O}_2^-$) and ethylenediaminetetraacetic acid (EDTA) was utilized to capture holes (h^+). The scheming IPA concentration, BQ concentration or EDTA concentration was 0.15 mmol L^{-1} , and the added amount of IPA, BQ or EDTA was 1 mL. Based on Figure 12, while IPA, BQ or EDTA were added to the BPA solution, the removal rate of BPA decreased by 71.90%, 32.86% or 85.26%, respectively, compared with the removal rate of BPA, which was derived from the control group. Thus, it could be concluded that $\bullet\text{OH}$, h^+ and $\bullet\text{O}_2^-$ were all active radicals during the degrading BPA process. It could be seen from Figure 12 that h^+ in the BPA solution played a leading role when BPA was degraded with AP-PS as catalysts under VLI.

Figure 12. (a) Effect of different radical scavengers on removal rate of bisphenol A with Ag_3PO_4 and potassium persulfate as catalysts under visible light irradiation; (b) effect of different radical scavengers such as benzoquinone and isopropanol on removal efficiency of bisphenol A with Ag_3PO_4 and potassium persulfate as catalysts under visible light irradiation.

Figure 13 shows the concentration variation curves of BPA with AP-PS as catalysts under VLI for three cycles of degradation tests. According to Figure 13, AP-PS were utilized as catalysts to degrade BPA in PW under VLI. As can be seen from Figure 13, the concentration of BPA in PW gradually decreased with the gradual increase in VLI duration. The results derived from Figure 13 indicate that the removal rate of BPA for three cycles in PW was 92.80%, 89.20% and 88.40%, respectively, after 30 min of VLI. It could be found in Figure 13 that the removal rate of BPA decreased by 4.40% after three cycles of degradation tests. There was no significant difference for the degradation efficiency of BPA among the above three cycles of experiments, and the catalyst structure of AP or potassium persulfate was stable.

Figure 13. Concentration variation curves of bisphenol A with Ag_3PO_4 and potassium persulfate as catalysts under visible light irradiation for three cycles of degradation tests.

Figure 14 shows the concentration variation curves of total organic carbon during PDB with AP-PS as catalysts under VLI for three cycles of degradation tests. As can be seen from Figure 14, AP-PS were utilized as catalysts to degrade BPA in PW under VLI, and the concentration of the total organic carbon in PW decreased gradually with the gradual increase in VLI duration. The results in Figure 14 indicate that the removal rate of the total organic carbon in PW was 87.39%, 84.63% or 82.91%, respectively, after 30 min of VLI for three cycles of experiments. It could be found in Figure 14 that the removal rate of total

organic carbon decreased by 4.48% with AP-PS as catalysts under VLI after three cycles of degradation tests.

Figure 14. Concentration variation curves of total organic carbon during photocatalytic degradation of bisphenol A with Ag_3PO_4 and potassium persulfate as catalysts under visible light irradiation for three cycles of degradation tests.

Figure 15 shows the concentration variation curves of BPA during PDB with AGHP as a photocatalyst, with NT as a photocatalyst or with AP-PS as catalysts under VLI. As can be found in Figure 15, AP-PS were used as catalysts to degrade BPA in PW under VLI, and the concentration of BPA in PW gradually decreased with an increasing VLI duration. The results derived from Figure 15 indicate that the removal rate of BPA in PW reached 95.53%, the rate of reaction was $4.650 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ and the photonic efficiency was 0.977% with AP-PS as catalysts after VLI of 30 min. As can be seen in Figure 15, when AGHP was utilized to degrade BPA in PW under VLI, the concentration of BPA in PW gradually decreased with the gradual increase in VLI duration. The results in Figure 15 indicate that the removal rate of BPA in PW reached 99.52%, the rate of reaction was $4.844 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ and the photonic efficiency was 1.018% after VLI of 30 min with AGHP as a photocatalyst. It could be found from Figure 15 that the concentration of BPA in PW gradually decreased with an increasing VLI duration after NT was used as a photocatalyst. The results derived from Figure 15 showed that the removal rate of BPA in PW with N-TiO₂ as a photocatalyst was 37.00%, the rate of reaction was $1.801 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ and the photonic efficiency was 0.378% after VLI of 30 min. Moreover, we could observe from above results that the photodegradation efficiency of BPA in the presence of AGHP was higher than that in the presence of silver phosphate and potassium persulfate. The results shown in Figure 15 indicate that the removal rate of BPA in PW reached 91.13% after VLI of 30 min with a $\text{ZnFe}_2\text{O}_4\text{-TiO}_2$ nanocomposite as a photocatalyst, and the removal rate of BPA in PW reached 87.20% after VLI of 30 min with a ZnO/CdS hierarchical heterojunction as a photocatalyst. The above results also indicate that the photodegradation efficiency of BPA in the presence of AP-PS was much higher than that in the presence of NT, meaning that the visible-light photocatalytic activity of AGHP was maximal compared with that of silver phosphate and potassium persulfate or that of NT.

Figure 15. Concentration variation curves of bisphenol A during photocatalytic degradation of bisphenol A with $\text{Ag}_3\text{PO}_4/\text{Gd}_2\text{BiTaO}_7$ heterojunction photocatalyst as photocatalyst, with N-doped TiO_2 as photocatalyst, with Ag_3PO_4 and potassium persulfate as catalysts, with $\text{ZnFe}_2\text{O}_4\text{-TiO}_2$ nanocomposite as photocatalyst or with ZnO/CdS hierarchical heterojunction as photocatalyst under visible light irradiation.

Figure 16 shows the concentration variation curves of the total organic carbon during PDB in PW with AGHP as a photocatalyst, with NT as a photocatalyst or with AP-PS as catalysts under VLI. As can be seen from Figure 16, when silver phosphate and potassium persulfate were used as catalysts to degrade BPA in PW, the concentration of the total organic carbon in PW decreased gradually with the gradual increase in VLI duration. The results in Figure 15 indicate that the removal rate of total organic carbon in PW reached 88.10% with AP-PS as catalysts after VLI of 30 min. As can be found in Figure 16, when AGHP was utilized to degrade BPA in PW, the concentration of the total organic carbon in PW gradually decreased with the gradual increase in VLI duration. It could be concluded from Figure 16 that the removal rate of total organic carbon in PW reached 96.21% with AGHP as a photocatalyst after VLI of 30 min. Figure 16 indicated that the concentration of total organic carbon in PW gradually decreased with an increasing VLI duration when NT was used as a photocatalyst, and the removal rate of total organic carbon with NT as a photocatalyst in PW reached 30.55% after VLI of 30 min. It could be concluded from Figure 16 that the removal rate of total organic carbon in PW reached 83.68% with a $\text{ZnFe}_2\text{O}_4\text{-TiO}_2$ nanocomposite as the photocatalyst after VLI of 30 min, and the removal rate of total organic carbon in PW reached 80.63% with a ZnO/CdS hierarchical heterojunction as the photocatalyst after VLI of 30 min. Moreover, we could observe from the above results that the removal rate of total organic carbon during the degradation of BPA in the presence of AGHP was higher than that in the presence of silver phosphate and potassium persulfate. The above results also indicate that the removal rate of total organic carbon during the degradation of BPA in the presence of silver phosphate and potassium persulfate was much higher than that in the presence of NT, which meant that AGHP possessed the maximal mineralization percentage ratio during the process of degrading BPA compared with silver phosphate and potassium persulfate or NT.

Figure 17 shows the concentration variation curves of total organic carbon during PDB in PW with AGHP as a photocatalyst under VLI for three cycles of degradation tests. As can be seen in Figure 17, when AGHP was used to degrade BPA in PW, the concentration of total organic carbon in PW gradually decreased with the gradual increase in VLI duration. We could observe from Figure 17 that the removal rate of total organic carbon during PDB in PW was 99.10%, 99.01% or 98.99% in three cycles with AGHP as the photocatalyst after VLI of 30 min. It could be found in Figure 17 that the removal rate of total organic carbon decreased by 0.11% with AGHP as a photocatalyst under VLI after three cycles of degradation tests.

Figure 16. Concentration variation curves of total organic carbon during photocatalytic degradation of bisphenol A in pharmaceutical wastewater with $\text{Ag}_3\text{PO}_4/\text{Gd}_2\text{BiTaO}_7$ heterojunction as photocatalyst, with N-doped TiO_2 as photocatalyst, with Ag_3PO_4 and potassium persulfate as catalysts, with $\text{ZnFe}_2\text{O}_4\text{-TiO}_2$ nanocomposites as photocatalyst or with ZnO/CdS hierarchical heterojunction as photocatalyst under visible light irradiation.

Figure 17. Concentration variation curves of total organic carbon during photocatalytic degradation of bisphenol A in pharmaceutical wastewater with $\text{Ag}_3\text{PO}_4/\text{Gd}_2\text{BiTaO}_7$ heterojunction as photocatalyst under visible light irradiation for three cycle degradation tests.

Figure 18 shows the concentration variation curves of BPA during PDB in PW with AGHP as a photocatalyst under VLI for three cycles of degradation tests. As can be found in Figure 18, when AGHP was utilized to degrade BPA in PW under VLI, the concentration of BPA in PW gradually decreased with the gradual increase in VLI duration. We could draw the conclusion that the removal rate of BPA in PW was 99.60%, 99.59% or 99.50%, respectively, with AGHP as a photocatalyst after VLI of 30 min. We could also draw the conclusion from Figure 18 that the removal rate of BPA decreased by 0.10% with AGHP as a photocatalyst under VLI after three cycles of degradation tests. There was no significant difference for the degradation efficiency among the above three cycles of experiments, and the catalyst structure of AGHP was stable.

Figure 18. Concentration variation curves of bisphenol A during photocatalytic degradation of bisphenol A in pharmaceutical wastewater with $\text{Ag}_3\text{PO}_4/\text{Gd}_2\text{BiTaO}_7$ heterojunction as photocatalyst under visible light irradiation for three cycle degradation tests.

Figure 19 shows the observed first-order kinetic plots for the PDB with AGHP as a photocatalyst, with NT as a photocatalyst or with AP-PS as catalysts under VLI. A linear correlation between $\ln(C/C_0)$ (or $\ln(\text{TOC}/\text{TOC}_0)$) and the irradiation time for the PDB under VLI with AP-PS as catalysts, with AGHP as a photocatalyst or with NT as a photocatalyst could be clearly seen in Figure 19. According to Figure 19, the first-order rate constant k_C for the BPA concentration was estimated to be 0.09392 min^{-1} with AP-PS as catalysts, the first-order rate constant k_C for the BPA concentration was estimated to be 0.15647 min^{-1} with AGHP as a catalyst and the first-order rate constant k_C for the BPA concentration was estimated to be 0.01480 min^{-1} with NT as a catalyst, which demonstrated that AGHP was more suitable for PDB under VLI compared with NT or with AP-PS. The above results indicated that AGHP possessed the maximal photocatalytic activity compared with AP-PS or with NT. Meanwhile, the first-order rate constant K_{TOC} of total organic carbon was estimated to be 0.06374 min^{-1} with AP-PS as catalysts under VLI, and the first-order rate constant K_{TOC} of total organic carbon was estimated to be 0.10197 min^{-1} with AGHP as a catalyst under VLI. Moreover, the first-order rate constant K_{TOC} of total organic carbon was estimated to be 0.01179 min^{-1} with NT as a catalyst under VLI. The fact that the value of K_{TOC} for degrading BPA was lower than the value of K_C for degrading BPA using the same catalyst illustrated that the photodegradation intermediate products of BPA probably appeared during PDB under VLI. At the same time, AGHP showed a higher mineralization efficiency for BPA degradation compared with NT or with AP-PS. With the same VLI duration, the K_C value for BPA degradation and the removal rate of BPA with AGHP as a photocatalyst was higher than that with AP-PS as catalysts and was higher than that with NT as catalyst. With the same VLI duration, the K_{TOC} value for BPA degradation and the removal rate of total organic carbon with AGHP as a photocatalyst was higher than that with potassium persulfate and AP as catalysts and was higher than that with NT as a catalyst.

Figure 19. Observed first-order kinetic plots for the photocatalytic degradation of bisphenol A with $\text{Ag}_3\text{PO}_4/\text{Gd}_2\text{BiTaO}_7$ heterojunction as photocatalyst, with N-doped TiO_2 as photocatalyst or with Ag_3PO_4 and potassium persulfate as catalysts under visible light irradiation.

2.5. Possible Degradation Mechanism Analysis

Figure 20 shows the possible photocatalytic degradation mechanism of BPA with AGHP as a photocatalyst under VLI. The potential of the valence band (VB) and conductor band (CB) for a semiconductor catalyst could be calculated in accordance with the following Equations (3) and (4) [74]:

$$E_{\text{CB}} = X - E^e - 0.5E_g \quad (3)$$

$$E_{\text{VB}} = E_{\text{CB}} + E_g \quad (4)$$

where E_g is the band gap of semiconductor, X is the electronegativity of the semiconductor and E^e is the energy of free electrons on the hydrogen scale (about 4.5 eV). According to the above equations, the VB potential or CB potential for GBT was estimated to be 1.72 eV or -0.63 eV, respectively. The VB potential or the CB potential for AP was estimated to be 2.72 eV or 0.27 eV, respectively. It could be found in Figure 20 that both GBT and AP could absorb visible light and internally generated electron–holes pairs when the AGHP was irradiated by visible light. Since the redox potential position of CB of GBT at -0.63 eV was more negative than that of AP at 0.27 eV, the photo-induced electrons on the CB of GBT could transfer to the CB of AP. Since the redox potential position of VB of AP at 2.72 eV was more positive than that of GBT at 1.72 eV, the photo-induced holes on the VB of AP could transfer to the VB of GBT.

Figure 20. Possible photocatalytic degradation mechanism of bisphenol A with $\text{Ag}_3\text{PO}_4/\text{Gd}_2\text{BiTaO}_7$ heterojunction as photocatalyst under visible light irradiation.

Therefore, the coupling of GBT and AP to produce AGHP effectively reduced the recombination rate of photo-induced electrons and photo-induced holes, subsequently decreased the internal resistance, prolonged the lifetime of photo-induced electrons and photo-induced holes and also enhanced the interfacial charge transfer efficiency [75]. As a result, more oxidative radicals such as $\bullet\text{OH}$ or $\bullet\text{O}_2^-$ could be produced to improve the degradation efficiency of BPA. Moreover, the CB potential of GBT was -0.63 eV, which was more negative than that of $\text{O}_2/\bullet\text{O}_2^-$ (-0.33 V), suggesting that the electrons in the CB of GBT could absorb oxygen to produce $\bullet\text{O}_2^-$ to degrade BPA, which was shown as path 1 in Figure 20. Meanwhile, the VB potential of AP was 2.72 eV, which was more positive than that of $\text{OH}^-/\bullet\text{OH}$ (2.38 V), suggesting that the holes in the VB of AP could oxidize H_2O or OH^- into $\bullet\text{OH}$ to degrade BPA, which was shown as path 2 in Figure 20. Ultimately, the photo-induced holes in the VB of AP and GBT could directly oxidize and degrade BPA owing to the strong oxidizing ability, and this was shown as path 3 in Figure 20. In brief, the excellent photocatalytic activity of AGHP toward BPA degradation was mainly contributed by the high efficiency of electron–hole separation, which was induced by AGHP.

For the sake of investigating the degradation mechanism of BPA, LC–MS was utilized to assess the degradation intermediate products of BPA.

The intermediate products obtained during PDB were identified as 4-hydroxyacetophenone (A) ($m/z = 135$), 4-hydroxyacetophenone (B) ($m/z = 135$), maleic acid ($m/z = 112$), 2,2-dimethyl (-3-hexanone) ($m/z = 128$), 2,4-di-tert-butylphenol ($m/z = 206$), 4-ethyl-2,2,6, 6-tetramethyl heptane ($m/z = 184$), 4,4'-(4-hydroxy-1,3-phenylene) bis (propane-2,2-diyl) diphenol ($m/z = 355$), quinone of MH BPA ($m/z = 242$), quinone of dihydroxylated BPA ($m/z = 257$), formic acid ($m/z = 116$), biphenyldiol ($m/z = 186$), benzaldehyde ($m/z = 106$), p-hydroxyacetophenone ($m/z = 136$), benzophenone ($m/z = 182$), 4-isopropyl-1-phenoxy-2-isopropyl-4-phenol ($m/z = 270$), hydroxylated (4-isopropyl-1-phenoxy-2-isopropyl)-4-phenol ($m/z = 286$), hydroperoxide derivative ($m/z = 227$), phenol, oxalic acid, succinic acid, fumaric acid, glutaric acid, acetic acid and propanoic acid.

BPA molecules were diffused across the surface of AGHP, and subsequently, oxidative reactive radicals such as $\bullet\text{OH}$, $\bullet\text{O}_2^-$ or h^+ would attack BPA and the C–C bond between the two aromatic rings, and as a result, two aromatic rings could separate from each other and form isopropyl phenol [76]. Simultaneously, the position of oxidative reactive radicals that attacked the aromatic ring was the bond between ortho- and para-orientation positions [76], due to the ortho- and para-orientation tendency of the phenolic hydroxyl group [76,77]. Thus, multihydroxylated BPA could be produced, and as a result, hydroxylated BPA would dehydrate and turn into quinone compounds [76]. Moreover, because of the H-abstraction, some intermediate products could combine with each other to form coupling compounds

that had higher molecular weight than BPA [76,77], and these coupling compounds could be attacked by oxidative reactive radicals and were decomposed into smaller molecules again. Ultimately, the above intermediate products would be transformed to ring-opened compounds and were subsequently mineralized by oxidative reactive radicals. In a word, the possible degradation mechanism of BPA could be credited to hydroxylation, oxidative skeletal rearrangement, demethylation, dehydration and ring opening [78].

Figure 21 shows the XPS survey spectrum of AGHP before the reaction of photocatalytic degradation of bisphenol A and that of AGHP after the reaction of photocatalytic degradation of bisphenol A. Figure 22 shows the XPS spectra of O^{2-} , Ag^+ , P^{5+} , Gd^{3+} , Bi^{3+} and Ta^{5+} derived from AGHP before the reaction of the photocatalytic degradation of bisphenol A. Figure 23 shows the XPS spectra of O^{2-} , Ag^+ , P^{5+} , Gd^{3+} , Bi^{3+} and Ta^{5+} derived from AGHP after the reaction of the photocatalytic degradation of bisphenol A. According to the XPS analysis displayed in Figures 21–23, the oxidation state of Ag, P, Gd, Bi, Ta or O ion was +1, +5, +3, +3, +5 or −2, respectively. Based on the above analysis, it could be concluded that the chemical formula of the novel compound was Ag_3PO_4/Gd_2BiTaO_7 .

Figure 21. (a) XPS survey spectrum of the Ag_3PO_4/Gd_2BiTaO_7 heterojunction photocatalyst before the reaction of photocatalytic degradation of bisphenol A; (b) XPS survey spectrum of the Ag_3PO_4/Gd_2BiTaO_7 heterojunction photocatalyst after the reaction of photocatalytic degradation of bisphenol A.

Figure 24 shows a SEM image of AGHP. Figure 25 shows EDS spectra of AGHP. Figure 26 shows the EDS elemental mapping of AGHP (Ag, P, O from Ag_3PO_4 and Gd, Bi, Ta, O from Gd_2BiTaO_7).

It could be seen from Figure 24 that AP possessed rhombic dodecahedron-like morphology. It was well-known that the different surface energies of crystallite facets control the structural growth of AP. Previously, researchers suggested the order of increasing surface energy for different facets of AP $g(111) < g(100) < g(110)$. Among them, the AP (110) facet showed higher surface energy than the (111) facet, which was why irregularly shaped AP structures became accumulated along the (110) crystallographic direction, which led to the formation of rhombic dodecahedron-like morphology for AP [79,80].

The SEM-EDS analysis displayed in Figures 24–26 reveals that AGHP did not possess other impure elements. At the same time, the powder X-ray diffraction analysis showed that AGHP was a pure phase, which was consistent with the results in Figures 24–26. It could be concluded from Figures 25 and 26 that AGHP contained silver, phosphorus, oxygen, gadolinium, tantalum and bismuth elements.

Figure 22. XPS spectra of O^{2-} , Ag^+ , P^{5+} , Gd^{3+} , Bi^{3+} and Ta^{5+} from the Ag_3PO_4/Gd_2BiTaO_7 heterojunction photocatalyst before the reaction of photocatalytic degradation of bisphenol A.

In the experimental results shown in Figure 24, the larger particles were AP, which possessed a regular sphere-like morphology and a homogeneous structure. The particle size of AP was measured to be 970 nm, while other smaller particles were GBT, of which the particle size was measured to be 480 nm.

In accordance with the XPS spectra of AGHP (Figure 22) and the EDS spectrum of AGHP (Figure 25), the atomic ratio of O:P:Ag:Gd:Ta:Bi was 87:13:39:10:5:4.8. The atomic ratio of AP:GBT was close to 13:5. According to the above results, we could conclude that the resulting materials for AGHP were of high purity under our preparation conditions.

Figure 23. XPS spectra of O^{2-} , Ag^+ , P^{5+} , Gd^{3+} , Bi^{3+} and Ta^{5+} from the $\text{Ag}_3\text{PO}_4/\text{Gd}_2\text{BiTaO}_7$ heterojunction photocatalyst after the reaction of photocatalytic degradation of bisphenol A.

Figure 24. SEM photograph of $\text{Ag}_3\text{PO}_4/\text{Gd}_2\text{BiTaO}_7$ heterojunction photocatalyst.

Figure 25. EDS spectrum of $\text{Ag}_3\text{PO}_4/\text{Gd}_2\text{BiTaO}_7$ heterojunction photocatalyst.

Figure 26. EDS elemental mapping of $\text{Ag}_3\text{PO}_4/\text{Gd}_2\text{BiTaO}_7$ heterojunction photocatalyst (Ag, P, O from Ag_3PO_4 and Gd, Bi, Ta, O from $\text{Gd}_2\text{BiTaO}_7$).

3. Experimental Section

3.1. Materials and Reagents

Silver nitrate (AN, AgNO_3 , purity = 99.8%), phosphoric acid (H_3PO_4 , mass concentration ≥ 85 wt% in H_2O), potassium persulfate (PS, $\text{K}_2\text{S}_2\text{O}_8$, purity $\geq 99.5\%$), ethylenediaminetetraacetic acid (EDTA, $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$, purity = 99.5%), isopropyl alcohol (IPA, $\text{C}_3\text{H}_8\text{O}$, purity $\geq 99.7\%$) and manganese acetate (MA, $\text{MnC}_4\text{H}_6\text{O}_4$, purity = 99.0%) were analytical grade. P-benzoquinone (BQ, $\text{C}_6\text{H}_4\text{O}_2$, purity $\geq 98.0\%$) was chemical grade. Moreover, the above chemical reagents were all purchased (Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China). Absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$, purity $\geq 99.5\%$) conformed to American Chemical Society Specifications (Aladdin Group Chemical Reagent Co., Ltd., Shanghai, China). BPA ($\text{C}_{15}\text{H}_{16}\text{O}_2$, purity $\geq 98\%$) was gas chromatography grade (Tianjin kwangfu Fine Chemical Industry Research Institute, Tianjin, China). Ultra-pure water (18.25 MU cm) was utilized throughout this work.

3.2. Synthesis of Tetrahedral Ag_3PO_4

Tetrahedral Ag_3PO_4 (AP) was prepared by a kinetic control method [32]. In a typical procedure, 6 mmol of AgNO_3 was dissolved in 40 mL of absolute ethanol under magnetic stirring conditions and transparent solution A was formed. Simultaneously, 10 mL of H_3PO_4 , of which the mass concentration was 85 wt%, was mixed thoroughly with 40 mL of absolute ethanol under magnetic stirring conditions and transparent solution B was formed. Solution A was subsequently added dropwise to solution B under magnetic stirring conditions. After 1 h of vigorous stirring in darkness, a sample with a bright green color was obtained when the centrifuge was utilized and the sample with a bright green color was subsequently washed with absolute ethanol, which was ultimately dried at 70°C for 12 h. The achieved sample AP was denoted as AP.

3.3. Preparation Method of $\text{Gd}_2\text{BiTaO}_7$

The novel photocatalyst $\text{Gd}_2\text{BiTaO}_7$ (GBT) had been synthesized by the solid-state reaction method. Gd_2O_3 , Bi_2O_3 and Ta_2O_5 with a purity of 99.99% (Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China) were utilized as starting materials without further purification. Due to the volatility of Bi_2O_3 , we finally decided to add 120% quantities of Bi_2O_3 after 5 experiments. All powders ($n(\text{Gd}_2\text{O}_3):n(\text{Bi}_2\text{O}_3):n(\text{Ta}_2\text{O}_5) = 2:1.2:1$) were dried at 200°C for 4 h before synthesis. In order to synthesize GBT, the precursors were stoichiometrically mixed, then pressed into small columns and put into an alumina crucible (Shenyang Crucible Co., LTD, Shenyang, China). After calcining at 400°C for 2 h, then at 750°C for 10 h, the raw materials and the small columns were taken out of the electric furnace. The mixed materials should be ground and subsequently be put into the electric furnace (KSL 1700X, Hefei Kejing Materials Technology CO., LTD, Hefei, China). Ultimately, the calcination process was separately carried out at 1120°C for 30 h in an electric furnace with the color of light yellow.

3.4. Synthesis of N-Doped TiO_2

The nitrogen-doped titania (N-doped TiO_2) catalyst was prepared by the sol-gel method with tetrabutyl titanate as a precursor and ethanol as solvent. The procedure was as follows: Firstly, 17 mL tetrabutyl titanate and 40 mL absolute ethyl alcohol were combined to serve as solution A; 40 mL absolute ethyl alcohol, 10 mL glacial acetic acid and 5 mL double distilled water were blended to be solution B; subsequently, solution A was added dropwise into the solution under vigorous magnetic stirring conditions, and then a transparent colloidal suspension was formed. Subsequently, aqua ammonia, within which N/Ti proportion was 8 mol%, was placed into the resulting transparent colloidal suspension under magnetic stirring conditions for 1 h. Next the xerogel was generated after being aged for 2 days. The xerogel was ground into powder, which was calcined at 500°C for 2 h. Subsequently, the above powder was ground in an agate mortar and screened by a shaker to gain N-doped TiO_2 (NT) powders.

3.5. Synthesis of $\text{Ag}_3\text{PO}_4/\text{Gd}_2\text{BiTaO}_7$ Heterojunction Photocatalyst, $\text{ZnFe}_2\text{O}_4\text{-TiO}_2$ Nanocomposite and ZnO/CdS Hierarchical Heterojunction

First, 0.30 mol/L $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.15 mol/L $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.15 mol/L TaCl_5 were mixed and kept stirred for 20 h. The above solution was transferred into a Teflon-lined autoclave and was heated at 200 °C for 15 h. Subsequently, the achieved powder was calcined at 800 °C for 10 h in a tube furnace at a rate of 8 °C/min under an atmosphere of N_2 . A $\text{Gd}_2\text{BiTaO}_7$ powder was finally gained and denoted as GBT. The facile in-situ precipitation method was utilized for preparing the $\text{Gd}_2\text{BiTaO}_7/\text{Ag}_3\text{PO}_4$ heterojunction photocatalyst. In a typical process, a certain amount (0.05 mol) of $\text{Gd}_2\text{BiTaO}_7$ powder was added to 200 mL of $\text{C}_2\text{H}_6\text{O}_2$ and sonicated for 30 min. Subsequently, 100 mL of AgNO_3 (0.39 mol) was added and kept stirred for 15 h to ensure Ag^+ combined with $\text{Gd}_2\text{BiTaO}_7$ sufficiently. In succession, another 100 mL of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (0.13 mol) was added dropwise to the above mixed solution and then stirred for one hour. The above mixture was washed several times with ultrapure water, and subsequently, this mixture was collected for use. Finally, the $\text{Ag}_3\text{PO}_4/\text{Gd}_2\text{BiTaO}_7$ heterojunction photocatalyst was prepared successfully.

The $\text{ZnFe}_2\text{O}_4\text{-TiO}_2$ nanocomposite was prepared by mixing 80 mg of ST01 TiO_2 with 1 wt% (0.808 mg) of ZnFe_2O_4 in 20 mL of octanol ($\text{C}_8\text{H}_{18}\text{O}$) and then dispersed in an ultrasonic bath for 1 h [81]. The mixture was then heated and refluxed at 140 °C for 2 h under vigorous stirring conditions to improve the attachment of ZnFe_2O_4 on the surface of TiO_2 nanoparticles to form a $\text{ZnFe}_2\text{O}_4\text{-TiO}_2$ heterojunction [81]. After cooling to room temperature, the products were harvested by centrifugation and washed with the mixture of n-hexane/ethanol several times [81]. The purified powders were dried in a vacuum oven at 60 °C for 6 h and stored in a desiccator for further use [81].

ZnO/CdS hierarchical heterojunction was prepared by chemical bath deposition [82]. The method was as follows: Firstly, 20 mL of deionized water was measured and 0.1 mmol $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was added, then 1 mmol of ZnO nanofibers was added after dissolving, and the solution was stirred for 30 min, which was recorded as solution A [82]. Meanwhile, 20 mL of deionized water was measured and 0.1 mmol of $\text{C}_2\text{H}_5\text{NS}$ was dissolved into it, which was recorded as solution B [82]. Subsequently, solutions A and B were blended and stirred consistently for 30 min [82]. Then, the mixed solution was centrifuged to separate, absolute ethanol and deionized water were utilized to wash the powder for several times, and it was ultimately dried at 60 °C in a vacuum oven for 12 h [82]. The dried product was the ZnO/CdS hierarchical heterojunction [82].

3.6. Characterizations

The pure crystals of the prepared samples were examined by the powder X-ray diffractometer (XRD, Shimadzu Corporation, Kyoto, Japan, XRD-6000, Cu K α radiation, $\lambda = 1.54184 \text{ \AA}$, sampling pitch of 0.02°, preset time of 0.3 s step⁻¹). The morphology and microstructure of the prepared samples were characterized using a scanning electron microscope (SEM, Sigma 300, ZEISS, Germany), and the elementary composition, which was derived from the above prepared samples, was captured by energy dispersive spectroscopy (EDS). The diffuse reflectance spectrum of the above prepared sample was obtained using an UV-Vis spectrophotometer (UV-Vis DRS, UV-3600, Shimadzu Corporation, Kyoto, Japan). The surface chemical composition and states of the prepared sample were analyzed by an X-ray photoelectron spectrograph (XPS, UIVAC-PHI, PHI 5000 VersaProbe, Japan) with an Al-K α X-ray source. The band structures of the prepared sample were performed by a synchrotron-based ultraviolet photoelectron spectroscopy (UPS), which was mainly utilized for the measurement of the valence band spectrum of the prepared sample.

3.7. Experimental Setup and Procedure

The experiments were performed in a photocatalytic reactor (XPA-7, Xujiang Electromechanical Plant, Nanjing, China) and the temperature of the reaction system was 20 °C, which was controlled by circulating cooling water. Simulated sunlight irradiation was

provided by a 500 W xenon with a 420 nm cut-off filter. There were 12 quartz tubes among which the volume of a single reaction solution was 40 mL, and the total reaction volume for pharmaceutical wastewater was 480 mL. The dosage of AP was 0.75 g/L; moreover, the concentrations of potassium persulfate and BPA were 1.0 mM and 20 mg/L, respectively. The concentration of bisphenol A (BPA) was the residual concentration after biodegradation for practical pharmaceutical wastewater, which contained BPA of 160 mg/L. During the reaction, a 3 mL suspension was withdrawn periodically, and subsequently, the filtration (0.22 µm PES polyethersulfone filter membrane) was realized for removing the catalyst; finally, the residual concentration of BPA in the solution was determined by the UV-Vis spectrophotometer (Shimadzu Corporation, UV-2450, Kyoto, Japan). The absorption wavelength of BPA was 273 nm. The absorbance standard curve of BPA at different concentrations was accomplished and the Ag_3PO_4 (AP) dosage ranged from 1.25 mg/L to 20 mg/L under ultraviolet light irradiation in the range of 220–320 nm with an ultraviolet-visible spectrophotometer. The relationship between the concentration of BPA and the absorbance value at 273 nm should be calculated. The absorbance of BPA in the solution was measured at the maximum absorption wavelength, and the calibration curve of BPA was drawn according to the absorbance at the maximum absorption wavelength of different concentrations of BPA. A linear regression method was used for the quantification of BPA.

The mineralization experimental data of BPA within the reaction solution were measured using a total organic carbon analyzer (TOC-5000 A, Shimadzu Corporation, Kyoto, Japan). In order to examine the concentration of total organic carbon during photocatalytic degradation of BPA (PDB), potassium acid phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$) or anhydrous sodium carbonate were utilized as the standard reagent. Standard solutions of potassium acid phthalate with a known carbon concentration (in the range of 0–100 mg/L) were prepared for calibration purposes. Six samples that contained a 45 mL reaction solution were used to measure the TOC concentration every time.

The signals of the radicals were measured by an electron paramagnetic resonance spectrometer (EPR, Bruker, EMX-10/12, Germany) with the spin trap of 5,5-dimethyl-1-pyrroline-N-oxide (DMPO).

The identification and measurement of BPA and its intermediate degradation products were carried out by liquid chromatography–mass spectrometry (Thermo Fisher Scientific Corporation, MA, USA. Beta Basic-C18 HPLC column: 150 mm × 2.1 mm, ID of 5 µm, (Thermo Fisher Scientific Corporation, MA, USA). Here, 20 µL of the solution obtained after the photocatalytic reaction was injected automatically into the LC–MS system. The mobile phase contained 60% methanol and 40% ultrapure water, and the flow rate was 0.2 mL/min. MS conditions included an electrospray ionization interface, a capillary temperature of 27 °C with a voltage of 19.00 V, a spray voltage of 5000 V and a constant sheath gas flow rate. The spectrum was acquired in the negative ion scan mode and the m/z range swept from 50 to 600.

The incident photon flux I_0 measured by a radiometer (Photoelectric Instrument Factory Beijing Normal University, Beijing, China) was determined to be 4.76×10^{-6} Einstein $\text{L}^{-1} \text{s}^{-1}$ under VLI (wavelength range of 400–700 nm). The incident photon flux on the photoreactor was changed by adjusting the distance between the photoreactor and the Xe arc lamp.

The photonic efficiency was calculated in accordance with the following equation:

$$\phi = R/I_0$$

where ϕ was the photonic efficiency (%), R was the degradation rate of BPA ($\text{mol L}^{-1} \text{s}^{-1}$) and I_0 was the incident photon flux ($\text{Einstein L}^{-1} \text{s}^{-1}$).

4. Conclusions

In this study, a new type of GBT was synthesized by a high-temperature solid-phase method and AGHP was prepared by the facile in-situ precipitation method for the first time. The photocatalytic property of GBT or AGHP was reported. The structural properties of AP-PS, GBT or AGHP were characterized by different material characterization methods.

The results showed that GBT was a well-crystallized, stable, cubic crystal system by the space group $Fd3m$. The lattice parameter and band gap energy of GBT was found to be $a = 10.740051 \text{ \AA}$ and 2.35 eV, respectively. The band gap of AP was about 2.45 eV. After VLI of 30 min, the removal rate of BPA reached 99.52%, 95.53% and 37.00% with AGHP as a photocatalyst, with AP-PS as photocatalysts or with NT as a photocatalyst. The removal rate of BPA with AGHP as a photocatalyst was 2.69 times higher than that with NT as a photocatalyst. The removal rate of BPA with AP-PS as photocatalysts was 2.58 times that with N-TiO₂ as a photocatalyst. Compared with AP-PS or NT, AGHP displayed higher photocatalytic activity for PDB under VLI. The removal rate of total organic carbon reached 96.21%, 88.10% and 30.55% with AGHP as a photocatalyst, with AP-PS as photocatalysts and with NT as a photocatalyst after VLI of 30 min. The above results indicated that AGHP possessed the maximal mineralization percentage ratio during the process of degrading BPA compared with AP-PS or NT. The results indicated that the main oxidation radical was $\bullet\text{OH}$ during the process of degrading BPA. The PDB with AGHP conformed to first-order reaction kinetics.

The first-order rate constant k_C for the BPA concentration was estimated to be 0.15647 min^{-1} , 0.09392 min^{-1} and 0.01480 min^{-1} with AGHP as a photocatalyst, with AP-PS as photocatalysts or with NT as a photocatalyst under VLI. Meanwhile, the first-order rate constant K_{TOC} of the total organic carbon was estimated to be 0.10197 min^{-1} , 0.06374 min^{-1} and 0.01179 min^{-1} with AGHP as a photocatalyst, with AP-PS as photocatalysts and with NT as a catalyst under VLI. AGHP displayed a higher mineralization efficiency for BPA degradation compared with NT or AP-PS.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal12010022/s1>, Figure S1: Atomic structure of Gd₂BiTaO₇. (Red atom: O, cyan atom: Gd, purple atom: Bi or Ta.), Figure S2: (a) Plot of $\ln(\alpha h\nu)$ versus $\ln(h\nu - E_g)$ for Gd₂BiTaO₇; (b) Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for Gd₂BiTaO₇, Figure S3: X ray diffraction pattern of Ag₃PO₄, Figure S4: Scanning electronic microscope photograph of Ag₃PO₄, Figure S5: EDS spectrum of Ag₃PO₄ and EDS elemental mapping of Ag₃PO₄ (Ag, P, O from Ag₃PO₄), Figure S6: (a) The absorbance standard curve of bisphenol A; (b) The absorption standard curve of bisphenol A at pH=11, Figure S7: X ray diffraction patterns of Ag₃PO₄ under different reaction conditions, Figure S8: (a) Removal rates of bisphenol A under different reaction conditions; (b) Degradation kinetics of bisphenol A with Ag₃PO₄ as a photocatalyst or with Ag₃PO₄ and potassium persulfate as photocatalysts under visible light irradiation, Figure S9: Observed kinetic plots for the photocatalytic degradation of bisphenol A with Ag₃PO₄ as photocatalyst under visible light irradiation.

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