



Article In-Situ Hydrothermal Synthesis of Ag₃PO₄/g-C₃N₄ Nanocomposites and Their Photocatalytic Decomposition of Sulfapyridine under Visible Light

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Abstract: Highly efficient visible-light-driven heterogeneous photocatalyst $Ag_3PO_4/g-C_3N_4$ with different weight ratios from Ag_3PO_4 to $g-C_3N_4$ were synthesized by a facile in situ hydrothermal method and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectrometry (FTIR), photoluminescence spectra (PL), UV–vis diffuse reflectance spectra (UV-Vis), and electrochemical impedance spectra (EIS). Under visible light irradiation, $Ag_3PO_4/g-C_3N_4$ showed very excellent photocatalytic activity for sulfapyridine (SP) which is one of the widely used sulfonamide antibiotics. When the ratio from Ag_3PO_4 to $g-C_3N_4$ was 1:2, the degradation rate of SP at 120 min was found to be 94.1%, which was superior to that of pure Ag_3PO_4 and pure $g-C_3N_4$ was proposed.

Keywords: visible light; photocatalysis; Ag₃PO₄; g-C₃N₄; sulfapyridine

1. Introduction

Over the past decades, with rapid economic development, water pollution has become more and more serious, threatening the health of human beings in the world. Among pollutants, antibiotics are usually used to treat or prevent bacterial infections in humans and animals. In particular, the continuous and long-term abuse of antibiotics has attracted widespread attention because various antibiotics are detected in natural water bodies, including surface water and groundwater, which has resulted in drug resistance to pathogenic microorganisms and has led to cross-resistance and multi-drug resistance even at very low concentrations [1–5]. However, conventional wastewater biological treatment technologies cannot remove antibiotics effectively from water due to antibiotics' complex composition, toxicity, and recalcitrant. It was found that the effluent from a wastewater treatment plant with conventional biological treatment technology, which is responsible for treating wastewater from 90 antibiotic drug manufacturers in India, contains 31 mg/L ciprofloxacin, which is about over 1000 times toxic to certain bacteria [6]. There were three kinds of antibiotics, including tetracycline, sulfonamide, and quinolone, detected at 195, 2001, and 3866 ng/L in the effluent from a wastewater treatment plant adopting activated sludge in Beijing, and the concentration of these antibiotics was much higher than that of the ambient river water [7]. Al Maadheed et al. found that two conventional wastewater treatment plants in Doha, built in 1990 and 2010, respectively, received hospital sewage, and even if the sewage passed the ultrafiltration stage, two antibiotics (clavulanic acid and ciprofloxacin) could not be removed [8]. Wang et al. selected 37 antibiotics from four classes of sulfonamides, macrolides, tetracyclines, and fluoroquinolones to be detected and observed that 19-33 of these antibiotics were discovered



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). in the effluent of conventional wastewater treatment plants ranging from ng/L to μ g/L [9]. Hendricks et al. took fluoroquinolones and sulfamethoxazole as model antibiotics to study the removal efficiency of wastewater treatment plants employing biological technologies, and the result showed that the removal efficiency of fluoroquinolone and sulfamethoxazole was only 21% and 34%, respectively [10].

Hence, it is imperative to develop an effective technology to remove antibiotics from the water environment [5,11,12]. During the past few decades, it was found that advanced oxidation processes (AOPs) could efficiently remove antibiotics by generating reactive species [13–16]. Dehghani et al. applied the Fenton oxidation process to the degradation of sulfamethoxazole, and antibiotic removal was achieved for up to 99.99% in 15 min [17]. Nasseh et al. used the FeNi₃/SiO₂ nanocomposite with the presence of H₂O₂ as a heterogeneous Fenton-like catalytic process for oxidating metronidazole, and the result showed that the removal efficiency of metronidazole reached 80.29% in 180 min with the presence of 150 mg/L H₂O₂, 0.1 g/L nanocomposite and Ph = 7 [18]. Feng et al. utilized ozonation to degrade flumequine in an aquatic environment, and the result showed that ozonation could remove flumequine fast and efficiently from water [19]. As one of the AOPs, or photocatalysts, photocatalysis has attracted widespread attention due to its properties such as effective, cost, environmentally friendly, and safe qualities [20–23].

In the past years, photocatalysis using semiconductors as photocatalysts has been widely studied and applied in the removal of antibiotics. TiO₂ was first reported for use in decomposing water under UV light irradiation [24] and then became one of the most common photocatalysts. However, the band gap of TiO_2 is about 3.2 eV, which means that only Ultra-Violet (UV) light energy, which accounts for <5% of sunlight energy, could be utilized. Additionally, a serious of photocatalysts that could utilize visible light has been discovered by many researchers. Over the last few decades, graphitic carbon nitride $(g-C_3N_4)$, as a metal-free polymeric photocatalyst, has become a promising photocatalyst for photocatalysis since it is abundant, has low cost, is non-toxic, and demonstrates chemical and thermal stability and simple synthesis. Nevertheless, the application of $g-C_3N_4$ is limited by its relatively insufficient light capture and rapid charge carrier recombination rate [25,26]. Therefore, many researchers have made a lot of effort to improve the photocatalytic performance of $g-C_3N_4$, such as nonmetal doping [27], metal doping [28,29], the morphology and structure modification [30,31], and constructing a heterojunction composite coupling of two or more semiconductors [32,33]. Liu et al. reported that $g-C_3N_4$ could be doped by sulfur to enhance the nanocomposite photoactivity, and the result showed that the photoactivity of synthesized nanocomposite for H_2 evolution is about eight times higher than that pure $g-C_3N_4$ under UV [34]. Han et al. found that chlorine-doped $g-C_3N_4$ had a stronger oxidation capability, more active sites, and more efficient charge transfer compared to pure g-C₃N₄ [35]. Xu et al. doped Mn and O to g-C₃N₄ to enhance g-C₃N₄ photocatalytic performance and found that the photodegradation rate was constant to that of the synthesis nanocomposites for Malachite green, which was about 5.09 times more than that of pure g- C_3N_4 [36]. Niu et al. successfully synthesized g- C_3N_4 with highly anisotropic 2D nanosheets through a thermal oxidation etching method and found that the modified $g-C_3N_4$ had higher photocatalytic activity due to the modification of morphology and construction [37]. The study of Du et al. showed that g-C₃N₄ coupled with Bi₂WO₆ and black phosphorus quantum dots had much higher photocatalytic activity for bisphenol A than for that of $g-C_3N_4$, Bi_2WO_6 , and phosphorus quantum dots [38]. The hybrid photocatalyst is widely used because it can not only improve the photogenerated electron-hole pairs separation efficiency but also extend the photocatalyst's response to light. Hence, there are a lot of scientists focusing on the enhancement of the photocatalytic performance of g-C₃N₄, constructing it with other semiconductors. Ye et al. found that $CoTiO_3/g-C_3N_4$ photocatalyst could enhance the H₂ evolution under visible light, accounting for efficient charge carrier separation and strong reduction ability [39]. Tao et al. investigated that $TiO_2/g-C_3N_4$ with a multi-layered porous structure had a superior photocatalytic performance for the photodegradation of Rhodamine B due to its low recombination rate of the

photogenerated electron-hole [40]. Maminozhi et al. synthesized $g-C_3N_4/ZnO$ photocatalyst through a hydrothermal method and found that it had very excellent degradation for organic dye driven by visible light [41].

After that, Ye et al. first reported that silver nitrate (Ag_3PO_4) had excellent photocatalytic activity under visible light irradiation, and more and more studies have revealed its excellent photocatalytic performance in water oxidation and the photodegradation of organic pollutants. It has been reported that Ag₃PO₄ would have quantum efficiencies as high as 90%, even at wavelengths greater than 420 nm, which is much higher than previously reported by other semiconductors. Despite the great advantages of Ag₃PO₄based photocatalysts, there are still many issues hindering their practical applications in the degradation of organic pollutants, such as the rapid recombination rate of photogenerated carriers and stability. To overcome these problems, a lot of researchers coupled Ag₃PO₄ with various semiconductors, and it has been proven to be an effective method for promoting the photoactivity of the photocatalyst since Ag_3PO_4 could significantly enhance the visible-light absorption of the photocatalyst and suppress the separation of electron–hole pairs [42–44]. Recently, photocatalysts hybridized with π -conjugated structure materials have been proven to be effective in improving the nanocomposite photocatalytic activity under visible light irradiation [45]. $g-C_3N_4$ can be easily decorated on the surface of nanocomposites since it is a soft polymer with a π -conjugated structure [46]. Thus, the heterogeneous photocatalyst $g-C_3N_4/Ag_3PO_4$ was desired to have prominent photocatalytic activity.

Sulfapyridine (SP), one of the most commonly used sulfonamide antibiotics, has been widely employed as a veterinary drug for disease treatment in humans and added to animal feed, which is frequently detected in the aquatic environment [47]. According to much research, there are various deleterious effects of SP, such as bio-toxicity and endocrine disruption for both aquatic wildlife and human beings [47–50]. Meanwhile, SP cannot be removed efficiently by the chlorination method, which is the most common way to disinfect the water [51]. In the meantime, there would be an assortment of disinfection by-products formed during chlorination [52]. Hence, it is strongly desired for an efficient way to remove SP from the aquatic environment.

In this work, $Ag_3PO_4/g-C_3N_4$ hybrid photocatalysts with different weight ratios of Ag_3PO_4 to $g-C_3N_4$ were prepared through an in situ hydrothermal method and were characterized. The photocatalytic activity of $Ag_3PO_4/g-C_3N_4$ was evaluated by the photodegradation of SP under visible light irradiation, and the optimal weight ratio of Ag_3PO_4 to $g-C_3N_4$ was determined. Finally, the possible photocatalytic mechanism of $Ag_3PO_4/g-C_3N_4$ was proposed.

2. Materials and Methods

2.1. Materials

Urea, AgNO₃, disodium hydrogen phosphate (Na₂HPO₄·12H₂O), and ethanol for this experiment were obtained from Tianjin Xintong Fine Chemicals Company Limited, Tianjin, China. SP were obtained from Shanghai McLean Biochemical Technology Co., Ltd., Shanghai, China. All reagents used in this work were of an analytical grade and used as received without any further purification. All solutions were prepared using deionized water.

2.2. Preparation of Photocatalyst

2.2.1. Synthesis $g-C_3N_4$

A total of 10 g of urea was weighed and placed in a covered crucible and heated at 550 °C for 4 h with a heating rate of 2 °C min⁻¹ in a muffle furnace. The obtained yellow-colored powder was collected and cooled to room temperature, washed several times with deionized water and ethanol thoroughly, and then dried at 60 °C for 12 h. After that, the obtained powder was calcined at 500 °C for 330 min with a heating rate of 5 °C min⁻¹ in a muffle furnace, and the resulting products were g-C₃N₄.

The Ag₃PO₄/g-C₃N₄ were prepared according to the literature [53] with slight modifications. Briefly, g-C₃N₄ was sonicated in 20 mL of water for 2 h. Then, 0.312 g of AgNO₃ was put into the above solution, and then the solution was sonicated continually at room temperature for 1 h. Thenceforth, 0.238 g of Na₂HPO₄·12H₂O was put into the solution at 60 °C for 1 h with continuous stirring. The obtained yellow powder was collected through a centrifuge, then washed thoroughly with water and ethanol, and dried at 60 °C for 24 h. For comparison purposes, we prepared different weight ratios of Ag₃PO₄ to Ag₃PO₄/g-C₃N₄ (50%, 33%, 25%, and 20%), which were chosen in the nanocomposite photocatalysts and denoted as 1:1 Ag₃PO₄/g-C₃N₄, 1:2 Ag₃PO₄/g-C₃N₄, 1:3 Ag₃PO₄/g-C₃N₄, and 1:4 Ag₃PO₄/g-C₃N₄, respectively.

2.3. Characterization

Power X-ray diffraction (XRD) was investigated by an X-ray diffractometer (Rigaku UltimaIV) using Cu K α irradiation with the 2 θ range from 10 to 90°. The scanning electron microscope images were collected by an FEI Quanta-PEG 450 microscope. The photoluminescence spectra (PL) were investigated with an F-98 system (Shanghai, China). The FTIR spectrum was recorded with a PerkinElmer Spectrum Two spectrometer. The UV–vis diffuse reflectance spectra (UV-vis) were carried out via a TU-1901 with a wavelength range from 200 to 800 nm. The electrochemical impedance spectra (EIS) were carried out via the electrochemical workstation (Ivium Technologies BV, Ivium, Eindhoven, The Netherlands) with a standard three-electrode configuration using a working electrode, a platinum plate as a counter electrode, and a standard Ag/AgCl in saturated KCl solution as a reference electrode. A total of 0.5 M Na₂SO₄ solution was used as the electrolyte.

2.4. Photocatalytic Experiments

The photocatalytic performance of $Ag_3PO_4/g-C_3N_4$ samples was evaluated by the photocatalytic degradation of the SP under the irradiation of a 500 W xenon lamp with a 420 nm cut-off filter. A total of 100 mg of the prepared samples was dispersed into the SP solution (3 mg/L), and the solution was 50 mL. Before irradiation, the suspensions were magnetically stirred for 30 min in the dark to reach an adsorption/desorption equilibrium between the SP and the photocatalysts. A 1.5 mL suspension was withdrawn and filtered through a 0.22 µm filter (Millipore) at regular intervals for testing the residual SP concentration. The SP concentration was recorded by HPLC (Agilent Technologies 1200-Series).

3. Results and Discussion

3.1. Characterization

Figure 1 depicts the XRD patterns of g-C₃N₄, Ag₃PO₄, and 1:2 Ag₃PO₄/g-C₃N₄ samples. There are two typical diffraction peaks at 13.0° and 27.4° in the XRD patterns of g-C₃N₄, which were ascribed to the (100) and (002) crystal planes of g-C₃N₄, respectively. The XRD pattern of Ag₃PO₄ can be originated from the cubic structure of Ag₃PO₄ (JCPDS No. 06–0505). The peaks at 20.9°, 29.7°, 33.3°, 36.5°, 42.5°, 47.8°, 52.7°, 55.0°, 57.2°, 61.6°, 69.9°, 71.9°, 73.8°, and 87.2°, correspond to (110), (200), (210), (211), (220), (310), (222), (320), (321), (400), (420), (421), (332), and (520) diffraction plane, respectively. The XRD patterns also further affirmed Ag₃PO₄ and g-C₃N₄ purity. The characteristic peaks of crystalline g-C₃N₄ can be indexed in the patterns of 1:2 Ag₃PO₄/g-C₃N₄, and the peak intensity is weaker than pure g-C₃N₄ owing to the presence of Ag₃PO₄, which is in good agreement with the literature [54].

The morphology and microstructure of $g-C_3N_4$, Ag_3PO_4 , and 1:2 $Ag_3PO_4/g-C_3N_4$ were investigated by SEM and are shown in Figure 2. As shown in Figure 2a, $g-C_3N_4$ had a large number of randomly stacked sheet structures. From Figure 2b, it can be seen that Ag_3PO_4 particles are spherical in shape without any aggregation. Figure 2c displays the SEM images of 1:2 $Ag_3PO_4/g-C_3N_4$, and it can obviously be seen that the Ag_3PO_4 was well dispersed on the thin and smooth sheets, along with the porous morphology of $g-C_3N_4$. The nanocomposite nanoparticles are also similar in size and shape to those of the Ag_3PO_4 particles. This further confirmed that $g-C_3N_4$ and Ag_3PO_4 had been combined successfully.



Figure 1. XRD patterns of g-C₃N₄, Ag₃PO₄, and 1:2 Ag₃PO₄/g-C₃N₄.



Figure 2. SEM images of $g-C_3N_4$ (a), Ag_3PO_4 (b) and 1:2 $Ag_3PO_4/g-C_3N_4$ (c).

FTIR could be recorded to investigate the detailed structural composition of nanocomposites. Figure 3 shows the FTIR spectra of the $Ag_3PO_4/g-C_3N_4$ composites prepared in this paper. There are three main strong characteristic peaks of $g-C_3N_4$ at about 810, 1200–1700, and 3200–3400 cm⁻¹, which could be assigned to the breathing mode of triazine unites, the typical stretching vibration of CN heterocycles, and the O–H stretches, respectively [55–61]. The peak at 1010 cm⁻¹ could be associated with the P-O stretching vibration in PO₄ [62–64], and the broad bands at 1300–1450 cm⁻¹ which originated from phosphoryl (P = O), which also found another characteristic frequency of PO₄ [54]. It further confirmed that $Ag_3PO_4/g-C_3N_4$ had been successfully prepared.



Figure 3. FTIR spectra of $Ag_3PO_4/g-C_3N_4$ with different ratios between Ag_3PO_4 and $g-C_3N_4$ prepared in this paper.

The Photoluminescence (PL) emission spectra of pure g-C₃N₄, pure Ag₃PO₄, and 1:2 Ag_3PO_4/g - C_3N_4 are exhibited in Figure 4. Generally, PL emission spectra can reveal the migration, transfer, and recombination of photogenerated charge carriers in semiconductors. Hence, there is a strong correlation between PL intensity and photodegradation performance. Generally, a higher PL peak would suggest higher recombination rates of electron-hole pairs, leading to lower photodegradation activity. In opposition to this, a lower intensity of PL means lower recombination rates of electron-hole pairs, resulting in higher photodegradation activity. The main emission peak centered at about 460 nm, and a broad PL peak in the range of 445–475 nm for the g-C₃N₄. Ag₃PO₄ exhibits the strongest peak at around 462nm, and 1:2 $Ag_3PO_4/g-C_3N_4$ presents a strong PL emission intensity at 460 nm, which is in line with the literature [65]. The PL emission intensity of $g-C_3N_4$ has the highest PL intensity, which means that $g-C_3N_4$ has the most efficiency in photogenerated charge recombination. The PL emission intensity of Ag_3PO_4 is much lower than that of g- C_3N_4 . Among these nanocomposites, the PL emission intensity of 1:2 Ag_3PO_4/g - C_3N_4 PL emission is the lowest. It definitely proves that 1:2 $Ag_3PO_4/g-C_3N_4$ processes a higher efficiency in separating the electron-hole pair and would have good photodegradation performance.



Figure 4. Photoluminescence emission spectra of $g-C_3N_4$, Ag_3PO_4 , and $1:2 Ag_3PO_4/g-C_3N_4$.

The optical properties of pure $g-C_3N_4$, pure Ag_3PO_4 , and $1:2 Ag_3PO_4/g-C_3N_4$ were investigated by the UV–vis DRS technique. As shown in Figure 5, the absorption edge of pure $g-C_3N_4$ and Ag_3PO_4 were approximately 438 nm and 510 nm, suggesting both nanocomposites could absorb visible light energy. The light-absorbance ranging from 200 to 420 nm was much higher for $1:2 Ag_3PO_4/g-C_3N_4$ than that for pure $g-C_3N_4$ and pure Ag_3PO_4 . This revealed that there was a small shift in the band edge position to a higher wavelength in the $g-C_3N_4$ coupling with Ag_3PO_4 compared to pure $g-C_3N_4$. The above results suggest that the $1:2 Ag_3PO_4/g-C_3N_4$ would have more efficient utilization of solar energy and higher photocatalytic activities compared to pure $g-C_3N_4$ and pure Ag_3PO_4 .



Figure 5. UV-vis spectra a of g-C₃N₄, Ag₃PO₄, and 1:2 Ag₃PO₄/g-C₃N₄.

The electrochemical impedance spectra (EIS) technique is an effective method to evaluate the charge carrier separation and transportation ability during the photocatalytic reaction [66]. The detected semicircles in the EIS are ascribed to the charge transfer resistance on the electrode material surface [67]. Usually, the small arc radius in an EIS Nyquist plot indicates a low recombination rate of electron-hole pairs, and the large arc radius in an EIS Nyquist plot indicates a high recombination rate of electron-hole pairs [68–70]. Figure 6 shows typical Nyquist plots of the EIS results over pure g-C₃N₄ and 1:2 Ag₃PO₄/g-C₃N₄. As shown in Figure 6, 1:2 Ag₃PO₄/g-C₃N₄ has a smaller arc radius than pure g-C₃N₄, suggesting that Ag₃PO₄ can improve g-C₃N₄'s efficiency in the separation of electron-hole pairs. The result is in good agreement with PL. To be brief, it proves that 1:2 Ag₃PO₄/g-C₃N₄ would be a favorable photocatalyst.



Figure 6. Electrochemical impedance spectra over $g-C_3N_4$, Ag_3PO_4 , and $1:2 Ag_3PO_4/g-C_3N_4$ as a working electrode.

3.2. Photocatalyst Performance Analysis

The photocatalytic degradation activity of Ag₃PO₄/g-C₃N₄ prepared in this study has been evaluated in terms of the removal of SP under simulated visible light irritation. Because SP is very stable, it is very difficult to be degraded under visible light without a photocatalyst. After visible light irradiation for 120 min, very limited removal efficiency (<5%) was observed for SP by photocatalysts in the dark condition, suggesting that the adsorption by photocatalysts could be neglected. However, there was obvious degradation with photocatalysts and visible light irritation. As shown in Figure 7a, the $g-C_3N_4$ with Ag_3PO_4 content exhibited a substantially increased SP degradation compared to g- C_3N_4 under visible light. Additionally, the photodegradation of SP by $Ag_3PO_4/g-C_3N_4$ increased with the ratio of Ag_3PO_4 to $g_2C_3N_4$ from 1:4 to 1:2. When the ratio of Ag_3PO_4 to g_2PO_4 C_3N_4 increased to 1:1, a lower photodegradation of SP was observed compared to 1:2 Ag_3PO_4/g - C_3N_4 . The photodegradation efficiencies of g- C_3N_4 , 1:1 Ag_3PO_4/g - C_3N_4 , 1:2 Ag₃PO₄/g-C₃N₄, 1:3 Ag₃PO₄/g-C₃N₄, and 1:4 Ag₃PO₄/g-C₃N₄ were 73.1%, 89.9%, 94.1%, and 89.5% at 120 min, respectively. The relationships between $\ln(C_0/C_t)$ (C_0 , the initial concentration of SP and C_t , the concentration of SP after t min visible light irritation) and visible light irritation time were recorded in Figure 7b. From Figure 7b, it can be seen that the photodegradation processes of SP by $Ag_3PO_4/g-C_3N_4$ fit the first-order kinetics model very well. Additionally, the slopes of these lines are the SP photocatalytic degradation kinetic constants with Ag_3PO_4/g - C_3N_4 under visible light irritation. The photodegradation kinetic constants of 1:1 Ag₃PO₄/g-C₃N₄, 1:2 Ag₃PO₄/g-C₃N₄, 1:3 Ag₃PO₄/g-C₃N₄, and 1:4 $Ag_3PO_4/g-C_3N_4$ were 0.01936 min⁻¹, 0.02335 min⁻¹, 0.0202 min⁻¹, and 0.01856 min⁻¹, which were 1.72, 2.08, 1.79, and 1.65 times that of pure $g-C_3N_4$, respectively. Among these photocatalysts, 1:2 Ag_3PO_4/g - C_3N_4 exhibited the highest photocatalytic degradation of SP under the present experiment.



Figure 7. Photocatalytic efficiencies (**a**) and Kinetics (**b**) of SP by $Ag_3PO_4/g-C_3N_4$ with different ratios between Ag_3PO_4 and $g-C_3N_4$ under visible light irradiation.

3.3. Possible Photocatalytic Mechanism

It is well-known that both g-C₃N₄ and Ag₃PO₄ can be irradiated by visible light to generate electrons and holes because they belong to the scope of the narrow band gap energy [71–73]. On the basis of the above results and analysis, a possible photocatalytic mechanism for the photocatalytic performance of Ag₃PO₄/g-C₃N₄ for SP is proposed and illustrated in Figure 8. In order to analyze the photocatalytic reaction activity of the nanocomposite, the valence bands (VBs) and conduction bands (CBs) positions for g-C₃N₄ and Ag₃PO₄ were evaluated by the Mulliken electronegativity theory [74]:

$$E_{VB} = X - E_c + 0.5E_g$$
(1)

$$E_{CB} = E_{VB} - E_g \tag{2}$$

where X is the absolute electronegativity of the semiconductor, expressed as the geometric mean of the absolute electronegativity of the constituent atoms, which is defined as the arithmetic mean of the atomic electron affinity and the first ionization energy (g-C₃N₄ = 4.72 eV and Ag₃PO₄ = 5.93 eV) [75,76]; E_c is the energy of free electrons on the hydrogen (4.5 eV); E_g is the band gap of the semiconductor. According to the results from Figure 5b, the E_g values of g-C₃N₄ and Ag₃PO₄ can be calculated through the following equation:

$$\alpha hv = A \left(hv - E_g \right)^n \tag{3}$$

where α , h, ν , A, and n are absorption index, plank constant, optical frequency, constant, and a configurable parameter, respectively. Based on Equation (3), the direct band gap of $g-C_3N_4$ and Ag_3PO_4 are about 2.96 and 2.27 eV, which is consistent with examples in the literature [77,78]. The indirect band gap of $g-C_3N_4$ and Ag_3PO_4 are 2.64 and 2.48 eV, respectively (Figure S1). According to Equations (1) and (2), the CB (E_{CB}) and VB (E_{VB}) values for $g-C_3N_4$ are calculated to be -1.26 eV and +1.7 eV, respectively. The values of CB and VB for Ag_3PO_4 are +0.16 eV and +2.64 eV, respectively. Because the CB of $g-C_3N_4$ is more negative than that of Ag₃PO₄, the photoexcited electrons from $g-C_3N_4$ tend to migrate toward the CB of Ag_3PO_4 through the well-defined interface. In the meantime, the photoexcited holes generated from Ag_3PO_4 are transferred in the composite. Thermodynamically, the photoexcited electrons are noble reductants, which can diffuse to the photocatalyst surface and react with the adsorbed O_2 molecules on the photocatalyst surface, hence inhibiting the recombination of the charge carriers. Therefore, accumulated electrons in the CB of Ag₃PO₄ can enhance the production of radical OH efficiently, highlighting the role of the charge separation process. Meanwhile, a reduction reaction takes place in $g-C_3N_4$, thus forming O_2^{--} radicals, which can directly oxidize the target organic pollutant subsequently. The high photocatalytic performance of $Ag_3PO_4/g-C_3N_4$ is ascribed to the rapid charge transfer and efficient separation processes, which can inhibit the recombination of the photogenerated holes.



Figure 8. Plausible photocatalytic mechanism of Ag₃PO₄/g-C₃N₄ under visible light.

4. Conclusions

In summary, a facile chemical precipitation method was employed to synthesize hybrid $Ag_3PO_4/g-C_3N_4$ nanocomposites with enhanced photocatalytic performance. The physical and chemical characterizations were investigated by XRD SEM, FTIR, DRS, PL, and EIS analysis. Compared to pure g-C₃N₄, the introduction of Ag_3PO_4 can significantly enhance the visible light-responsive photocatalytic activity for the degradation of the SP solution. In the meantime, the ratio of Ag_3PO_4 and g-C₃N₄ was found to be 1:2. The SP photodegradation efficiency reached 94.1% with the presence of the 1:2 $Ag_3PO_4/g-C_3N_4$ under 120 min visible light, which is 1.28 times that of pure g-C₃N₄. Meanwhile, the observed rate constant for the photodegradation of SP by 1:2 $Ag_3PO_4/g-C_3N_4$ was found to be about 0.02335 min⁻¹, which is 2.08 times that of pure g-C₃N₄. In conclusion, this study provides the possible application of the $Ag_3PO_4/g-C_3N_4$ composite for the photodegradation of sulfonamides in aquatic environments.

Supplementary Materials: The following supporting information can be downloaded at: https://www. mdpi.com/article/10.3390/pr11020375/s1, Figure S1. (a) and (b) band gap energies of g-C₃N₄, Ag₃PO₄.

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