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Construction of a CQDs/Ag₃PO₄/BiPO₄ Heterostructure Photocatalyst with Enhanced Photocatalytic Degradation of Rhodamine B under Simulated Solar Irradiation

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Abstract: A carbon quantum dot (CQDs)/Ag₃PO₄/BiPO₄ heterostructure photocatalyst was constructed by a simple hydrothermal synthesis method. The as-prepared CQDs/Ag₃PO₄/BiPO₄ photocatalyst has been characterized in detail by X-ray diffraction, field-emission scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, ultraviolet–visible spectroscopy, and photoelectrochemical measurements. It is demonstrated that the CQDs/Ag₃PO₄/BiPO₄ composite is constructed by assembling Ag₃PO₄ fine particles and CQDs on the surface of irregular BiPO₄ granules. The CQDs/Ag₃PO₄/BiPO₄ heterostructure photocatalyst exhibits a higher photocatalytic activity for the degradation of the rhodamine B dye than that of Ag₃PO₄, BiPO₄, and Ag₃PO₄/BiPO₄. The synergistic effects of light absorption capacity, band edge position, separation, and utilization efficiency of photogenerated carriers play the key role for the enhanced photodegradation of the rhodamine B dye.

Keywords: carbon quantum dots; CQDs/Ag₃PO₄/BiPO₄; photodegradation activity; synergistic effect; photocatalytic mechanism

1. Introduction

The photocatalytic degradation of organic pollutants in wastewater is an attractive, environmentally friendly and green method that offers a way to harness solar power efficiently and convert them into non-toxic degradation products [1–8]. Recently, although great progress has been made in the field of photocatalysis, only few photocatalysts can effectively use visible light in the degradation of organic pollutants. Therefore, it is desirable to develop novel photocatalysts with high visible-light utilization for degradation of organic pollutants in wastewater. In recent years, silver phosphate (Ag₃PO₄) based composite photocatalysts, such as Bi₄Ti₃O₁₂/Ag₃PO₄ [9], Ag₃PO₄/NaTaO₃ [10], MoS₂/Ag₃S/Ag₃PO₄ [11], Ag₃PO₄/Bi₂WO₆ [12], Ag₃PO₄/Cu₂O [13], TiO₂/Ag₃PO₄/bentonite [14], Co₃(PO₄)₂/Ag₃PO₄ [15], and Ag₃PO₄/BiFeO₃ [16] have been extensively studied due to their excellent photocatalytic activity for photocatalytic degradation of the organic pollutants under visible light irradiation.

Bismuth phosphate (BiPO₄) as a photocatalyst has been widely studied because of its good photoelectric performance, low cost, low toxicity, excellent photocatalytic activity, and high...
stability [1]. However, the large optical bandgap ($E_g = 4.5$ eV) of BiPO$_4$ limits the transmission efficiency of photon-generated carriers and light-response range to sunlight [17,18]. To expand the photosresponse range of BiPO$_4$, constructing composite photocatalysts with Ag$_3$PO$_4$ ($E_g = 2.43$ eV) can effectively improve the photocatalytic activity of the composite photocatalysts [19–24]. However, the Ag$_3$PO$_4$/BiPO$_4$ photocatalysts have a high recombination rate of photogenerated electrons ($e^-$) and holes ($h^+$) in the degradation of organic pollutions in wastewater [25]. To achieve excellent photocatalytic performances of the photocatalysts, the photoexcited electrons and holes must be efficiently separated [26–29].

Noble metal nanoparticles (NPs) and carbon nanomaterials including carbon quantum dots (CQDs), carbon nanotubes (CNTs) and graphene manifest many intriguing physicochemical characteristics and offer a wide scope of technological applications in electronic devices, biomedicine, sensors, and wave absorption [30–37]. These nanomaterials are good carrier transport materials and also exhibit interesting localized surface plasmon resonance (LSPR) effect or photoluminescence (PL) up-conversion effect [38–40]. Due to these outstanding properties, noble metal NPs, CQDs, CNTs, and graphene have been demonstrated to be excellent modifiers or co-catalysts to enhance the photocatalytic performances of semiconductor photocatalysts [41–46].

Herein, we report a hydrothermal synthesis of unique CQDs/Ag$_3$PO$_4$/BiPO$_4$ heterostructure photocatalyst. The composite photocatalyst with the CQDs, Ag$_3$PO$_4$, and BiPO$_4$ three phase junction structure has not been reported previously and may be commonly applicable to other composite photocatalyst systems. The as-obtained CQDs/Ag$_3$PO$_4$/BiPO$_4$ heterostructure photocatalyst possesses a high light absorption capacity, high utilization and separation efficiency of photogenerated carriers, and exhibits a high photocatalytic activity for photocatalytic degradation of the rhodamine B (RhB) dye. The present CQDs/Ag$_3$PO$_4$/BiPO$_4$ heterostructure photocatalysts can be used for the design of micro/nano-photocatalytic devices for the wastewater treatment.

2. Materials and Methods

2.1. Synthesis of the Ag$_3$PO$_4$ Photocatalyst

According to the formula Ag$_3$PO$_4$, an amount of silver nitrate (AgNO$_3$) was mixed with a stoichiometric amount of sodium dihydrogen phosphate (NaH$_2$PO$_4$) powder with Ag/P = 3:1 and added into 60 mL distilled water. After that, a stoichiometric amount of ammonium hydroxide (NH$_3$·H$_2$O) was added to the mixture. The whole process was accompanied by magnetic stirring. Subsequently, the above mixture was transferred to a 100 mL high-pressure autoclave and heated to 160 °C for 6 h. After finishing the hydrothermal reaction, the content was taken out and washed with distilled water several times to remove excess alkali ions. The slurry was centrifuged and dried for 12 h at 80 °C to obtain the Ag$_3$PO$_4$ photocatalyst. The flow-chart for the synthesis of Ag$_3$PO$_4$ photocatalyst via the hydrothermal synthesis method is shown schematically in Figure 1(I).

2.2. Synthesis of the BiPO$_4$ Photocatalyst

According to the formula BiPO$_4$, stoichiometric amounts of bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O), NaH$_2$PO$_4$ and NH$_3$·H$_2$O were successively added in 20 mL of dilute nitric acid solution (2 mL HNO$_3$ + 18 mL distilled water). The role of HNO$_3$ is to dissolve Bi(NO$_3$)$_3$·5H$_2$O. The mixture was filled up to 60 mL by adding distilled water. The remaining experimental steps are consistent with Section 2.1. The flow-chart for the synthesis of BiPO$_4$ photocatalyst via the hydrothermal method is shown schematically in Figure 1(II).
2.3. Synthesis of Ag$_3$PO$_4$/BiPO$_4$ Photocatalyst

To prepare Ag$_3$PO$_4$/BiPO$_4$ photocatalyst, stoichiometric amounts of Bi(NO$_3$)$_3$, AgNO$_3$, NaH$_2$PO$_4$ and NH$_3$H$_2$O ($n_{AgNO_3}/n_{BiNO_3}=1.011$) were successively added in 20 mL of dilute HNO$_3$ solution, and then filled up to 60 mL by adding distilled water. The assembly of Ag$_3$PO$_4$ on BiPO$_4$ followed the procedure as described in Section 2.1. The flow-chart for the synthesis of the Ag$_3$PO$_4$/BiPO$_4$ photocatalyst is schematically shown in Figure 1(III).

2.4. Synthesis of CQDs/Ag$_3$PO$_4$/BiPO$_4$ Photocatalyst

To obtain the CQDs/Ag$_3$PO$_4$/BiPO$_4$ photocatalyst, stoichiometric amounts of Bi(NO$_3$)$_3$, AgNO$_3$, NaH$_2$PO$_4$ and NH$_3$H$_2$O and 6 mL of the CQDs suspension derived according the literature [45] were successively 20 mL of dilute HNO$_3$ solution, and then filled up to 60 mL by adding distilled water. The subsequent preparation process is consistent with Section 2.1. The flow-chart for the synthesis of the CQDs/Ag$_3$PO$_4$/BiPO$_4$ photocatalyst is shown in Figure 1(IV).

2.5. Sample Characterization

The phase purity of the Ag$_3$PO$_4$, BiPO$_4$, Ag$_3$PO$_4$/BiPO$_4$ and CQDs/Ag$_3$PO$_4$/BiPO$_4$ photocatalysts was analyzed by means of D8 advanced X-ray diffractometer with Cu K$_\alpha$ radiation at a wavelength of 1.5406 Å. The surface morphology of the samples was characterized by JSM-6701F field-emission scanning electron microscopy (SEM, JEOL Ltd., Tokyo, Japan) and JEM-1200EX field-emission transmission electron microscopy (TEM, JEOL Ltd., Tokyo, Japan). Ultraviolet–visible (UV–VIS) diffuse reflectance spectra of the samples were examined on a UV–VIS spectrophotometer with...
an integrating sphere attachment using BaSO4 as the reference. To determine the bonding states, chemical composition, and electron levels of the samples, X-ray photoelectron spectroscopy (XPS) measurements were carried out by using a PHI-5702 X-ray photoelectron spectrometer (Physical Electronics, Hanhassen, MN, USA).

The electrochemical properties of the samples were investigated according to the method reported in the literature [45]. A CST 350 electrochemical workstation (Wuhan Corrtest Instruments Co., Ltd., Wuhan, China) equipped with a three-electrode cell configuration was used to study the electrochemical impedance spectroscopy (EIS) and photocurrent response of the samples. The working electrode was prepared as follows: 15 mg of the photocatalyst, 0.75 mg of polyvinylidene fluoride (PVDF), 0.75 mg of carbon black, and 1 mL of 1-methyl-2-pyrrolidione (NMP) were mixed together to form uniform slurry. The slurry mixture was homogeneously coated on the surface of fluorine-doped tin oxide (FTO) thin film (effective area: 1 × 1 cm²), and subjected to drying 60 °C for 5 h. The used electrolyte was 0.1 mol L⁻¹ Na₂SO₄ aqueous solution. The used light source was a 200 W xenon lamp emitting simulated sunlight. A 0.2 V bias voltage was used during the transient photocurrent measurement. The sinusoidal voltage pulse was used for the EIS measurement (amplitude: 5 mV; frequency range: 10⁻²⁻¹₀⁵ Hz).

2.6. Photocatalytic Testing

The photocatalytic activities of the samples were investigated by removing RhB from aqueous solution according to the procedure as described in the literature [45]. A 200-W xenon lamp (sunlight simulator) was used as the light source. The photocatalytic system was composed of 0.1 g photocatalyst and 100 mL RhB solution (C_{photocatalyst} = 1 g L⁻¹, C_{RhB} = 5 mg L⁻¹). Based on the initial RhB concentration (C₀) and residual RhB concentration (C₁), the degradation percentage (DP) of RhB was given as: DP = (C₀ − C₁)/C₀ × 100%.

3. Results and Discussion

3.1. Phase Structural Analysis

Figure 2a,b show the XRD patterns of Ag₃PO₄ and BiPO₄, respectively. For the Ag₃PO₄ and BiPO₄ samples, the XRD curves were fitted using the Jade 6.0 package. The black curves, red curves, vertical olive lines, and blue lines represent the observed XRD peaks, theoretically estimated curves, Bragg peaks, and difference between the observed values, and theoretically estimated values of XRD diffraction peaks, respectively. The result indicates that the theoretically simulated values are in good agreement with the observed XRD diffraction peaks. The XRd diffraction peaks of Ag₃PO₄ and BiPO₄ can be ascribed to JCPDF#06-0505 and JCPDF#15-0767, respectively. Figure 2c shows the XRD patterns of Ag₃PO₄/BiPO₄ and CQDs/Ag₃PO₄/BiPO₄. The main XRD diffraction peaks of the Ag₃PO₄/BiPO₄ and CQDs/Ag₃PO₄/BiPO₄ composites are similar to those of pure Ag₃PO₄, indicating that the host lattice of Ag₃PO₄ in these composites undergoes no change. In addition to the XRD characteristic peaks of the Ag₃PO₄ phase, the XRD characteristic peaks of BiPO₄ are also observed in these composites. For the CQDs/Ag₃PO₄/BiPO₄ composite, the intensity of the diffraction peaks is sharper than that for Ag₃PO₄/BiPO₄. The structure analysis shows that the introduction of CQDs in the Ag₃PO₄/BiPO₄ composites obviously accelerate the formation of Ag₃PO₄ and BiPO₄. In our previous study, the carbon can suppress the formation of M-ferrite [47] and α-Al₂O₃ [48] phase prepared by a polycrylamide gel method. In this case, this phenomenon may be due to the fact that CQDs do not react with oxygen in the reactor to form carbon dioxide. Figure 2d,e show the crystal structures of BiPO₄ and Ag₃PO₄, respectively. The BiPO₄ and Ag₃PO₄ are monoclinic phase with space group P21/n (14) and cubic phase with space group P-43n (218), respectively. For the BiPO₄, the Bi atom and the P atom are surrounded by eight oxygen atoms and four oxygen atoms, respectively. The wide Bi–O and P–O bond length of BiPO₄ exhibits a high photocatalytic activity for photocatalytic degradation of organic pollutants [49]. For the Ag₃PO₄, the Ag atom, P atom and O atom experience four-fold coordination by four O atoms.
four-fold coordination by four O atoms, and 4-fold coordination by one P atom and three Ag atoms, respectively [50].

Figure 2. XRD patterns of (a) BiPO$_4$, (b) Ag$_3$PO$_4$, (c) Ag$_3$PO$_4$/BiPO$_4$ and CQDs/Ag$_3$PO$_4$/BiPO$_4$, and crystal structures of (d) BiPO$_4$ and (e) Ag$_3$PO$_4$.

3.2. Surface Morphology and Elemental Component Analysis

Figure 3a,b show the SEM images of Ag$_3$PO$_4$/BiPO$_4$ and CQDs/Ag$_3$PO$_4$/BiPO$_4$, respectively. For the Ag$_3$PO$_4$/BiPO$_4$ composite, the sample is composed of fine spherical particles and rice-like granules, as shown in Figure 3a. Figure 3b represents the SEM image of the CQDs/Ag$_3$PO$_4$/BiPO$_4$ composite, revealing that its morphology is very similar to that of the Ag$_3$PO$_4$/BiPO$_4$ composite. The insets in Figure 3a,b show the real photos of Ag$_3$PO$_4$/BiPO$_4$ and CQDs/Ag$_3$PO$_4$/BiPO$_4$, respectively. The results show that the introduction of CQDs to the Ag$_3$PO$_4$/BiPO$_4$ composite deepens the color of the sample. The detailed analysis will be done in the optical properties section. Figure 3c shows the SEM image of pure CQDs, from which it is seen that the prepared CQDs have a narrow size distribution of 7–10 nm.

The microstructure and elemental composition of the CQDs/Ag$_3$PO$_4$/BiPO$_4$ composite was characterized by TEM, as shown in Figure 4. Figure 4a displays the TEM image of the composite. Spherical fine particles (Ag$_3$PO$_4$) are seen to be assembled on the surface of rice-like granules (BiPO$_4$). The high-resolution TEM (HRTEM) image further confirms the assembly of Ag$_3$PO$_4$ fine particles on the surface of BiPO$_4$ rice-like granules, as depicted in Figure 4b. The rice-like granules manifest obvious lattice fringes with an interlayer spacing of 0.347 nm, which correspond to the (222) facet of the cubic Ag$_3$PO$_4$ phase. The attached spherical particles exhibit the lattice fringes with a d-spacing of 0.407 nm, which correspond to the (101) facet of the monoclinic Ag$_3$PO$_4$ phase. The decorated ultrafine particles with no lattice fringes could be CQDs. The energy-dispersive X-ray spectroscopy (EDS) spectrum (Figure 4c) demonstrates that the elemental composition of the CQDs/Ag$_3$PO$_4$/BiPO$_4$ composite is Ag, Bi, P, O, and C. Additional Cu signal observed on the EDS spectrum can be ascribed to the TEM microgrid holder [51]. To further elucidate the spatial distribution of elements, Figure 4b shows the dark-field scanning TEM (DF-STEM) image of the CQDs/Ag$_3$PO$_4$/BiPO$_4$ composite and Figure 4e–i...
display the corresponding elemental maps. Ag, P, O, Bi, and C elementals are homogenously distributed throughout the rice-like granules, implying the uniform decoration of Ag$_3$PO$_4$ nanoparticles and CQDs on the surface of rice-like BiPO$_4$ granules. The observed C element in the blank area without the sample could come from the TEM microgrid holder.

Figure 3. SEM images of (a) Ag$_3$PO$_4$/BiPO$_4$, (b) CQDs/Ag$_3$PO$_4$/BiPO$_4$, and (c) pure CQDs. The insets represent the real photos of Ag$_3$PO$_4$/BiPO$_4$ and CQDs/Ag$_3$PO$_4$/BiPO$_4$.

3.3. XPS Analysis

To understand the chemical composition and electronic core levels of the Ag$_3$PO$_4$/BiPO$_4$ and CQDs/Ag$_3$PO$_4$/BiPO$_4$ composites, Figure 5 shows the XPS results of the two composites. In Figure 5a, the XPS survey scan spectra for the Ag$_3$PO$_4$/BiPO$_4$ and CQDs/Ag$_3$PO$_4$/BiPO$_4$ composites clearly contain the P, Bi, Ag, O, and C elements. The electronic core levels of Bi 4f, P 2p, Ag 3d, O 1s, and C 1s in the composites are further characterized using the high-resolution XPS spectra. Figure 5b shows the Bi 4f core-level XPS spectra. Two obvious characteristic peaks at 161.02/160.29 and 166.26/165.63 eV are observed on the spectra, which are assigned to Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$ binding energies of Bi$^{3+}$ in BiPO$_4$, respectively [52].
3.3. XPS Analysis

To understand the chemical composition and electronic core levels of the Ag₃PO₄/BiPO₄ and CQDs/Ag₃PO₄/BiPO₄ composites, Figure 5 shows the XPS results of the two composites. In Figure 5a, the XPS survey scan spectra for the Ag₃PO₄/BiPO₄ and CQDs/Ag₃PO₄/BiPO₄ composites clearly contain the P, Bi, Ag, O, and C elements. The electronic core levels of Bi 4f, P 2p, Ag 3d, O 1s, and C 1s in the composites are further characterized using the high-resolution XPS spectra. Figure 5b shows the Bi 4f core-level XPS spectra. Two obvious characteristic peaks at 161.02/160.29 and 166.26/165.63 eV are observed on the spectra, which are assigned to Bi 4f 7/2 and Bi 4f 5/2 binding energies of Bi³⁺ in BiPO₄, respectively [52].

The XPS spectra of P 2p core level shown in Figure 5c present a broad peak at 134.36 (or 133.69) eV, suggesting that P species exhibits +5 oxidation state [52]. Figure 5d shows the Ag 3d core level XPS spectra. The peaks at 369.59/368.86 and 375.58/374.79 eV can be assigned to Ag 3d₅/₂ and Ag 3d₃/₂ of Ag₃PO₄, respectively [53]. For the O 1s core-level XPS spectra, the peak at 531.63/532.28 eV can be ascribed to the lattice oxygen, while the peak at 532.92/533.53 eV is related to the adsorbed oxygen [54,55], as shown in Figure 5e. The C 1s core-level XPS spectra are shown in Figure 5f. For the Ag₃PO₄/BiPO₄ composite, the peak at 284.77 eV can be assigned to the adventitious hydrocarbon for the XPS instruments [56]. For the CQDs/Ag₃PO₄/BiPO₄ composite, the C 1s peak can be divided into three separate peaks at 283.75, 284.77 and 286.38 eV, corresponding to CQDs [57], adventitious hydrocarbon [56] and impurity structure of carbon [58]. It is noted that the electronic core levels of Bi 4f, P 2p, Ag 3d and O 1s for the CQDs/Ag₃PO₄/BiPO₄ composite are smaller (about 0.61–0.73 eV) than those for the Ag₃PO₄/BiPO₄ composite, which could be due to the fact that the CQDs facilitate the formation of CQDs/Ag₃PO₄/BiPO₄ heterostructures.
It is noted that the optical properties of semiconductors have an important effect on their photocatalytic performances, which can be determined by UV–vis DRS measurements [59]. Figure 6a shows the UV–VIS diffuse reflectance spectra of the Ag$_3$PO$_4$/BiPO$_4$ and CQDs/Ag$_3$PO$_4$/BiPO$_4$ photocatalysts. For both the samples, the reflectance first increases and then decreases with the increase in the wavelength, and finally increases again. The two samples present higher reflectance in the wavelength range from 550 to 850 nm. When CQDs are introduced to Ag$_3$PO$_4$/BiPO$_4$, a decrease in the reflectance of the resultant CQDs/Ag$_3$PO$_4$/BiPO$_4$ composite in the wavelength range from 300 to 850 nm is observed. According to the literatures [60], the color parameters (L*, a*, b*), chroma parameter (c*), hue angle (H*), and total color difference (E$_{CIE}$) of Ag$_3$PO$_4$/BiPO$_4$ and CQDs/Ag$_3$PO$_4$/BiPO$_4$ are evaluated, as shown in Table 1. The Ag$_3$PO$_4$/BiPO$_4$ composite shows a negative a* value, indicating that it displays a reseda, as shown in the inset of Figure 3a. The CQDs/Ag$_3$PO$_4$/BiPO$_4$ composite exhibits the smaller L* and b* values and positive a* value, which means it exhibits yellowish black, as shown in the inset of Figure 3b. The first derivative curves of UV-vis diffuse reflectance spectra are useful to determine the optical bandgaps ($E_g$) of semiconductors [61]. As shown in Figure 6b, the Ag$_3$PO$_4$/BiPO$_4$
composite shows two absorption edges at 276.1 and 502.3 nm, whereas the CQDs/Ag₃PO₄/BiPO₄ composite exhibits an absorption edge at 271.9 nm. The absorption edges at 276.1/271.9 and 502.3 nm can be assigned to BiPO₄ and Ag₃PO₄, respectively. The disappearance of the Ag₃PO₄ absorption peak on the spectrum of the CQDs/Ag₃PO₄/BiPO₄ composite is ascribed to the enhanced optical absorption caused by CQDs. The \( E_g \) values of Ag₃PO₄ and BiPO₄ in the samples (see Table 1) can be derived on the basis of Equation (1):

\[
E_g (eV) = \frac{hc}{\lambda_0 (nm)} \approx \frac{1240}{\lambda_0 (nm)}
\]

where \( \lambda_0 \), \( h \), and \( c \) is the maximum absorption wavelength, Plank constant, and velocity of light, respectively.

![Figure 6. UV-VIS diffuse reflectance spectra (a) and the corresponding first derivative curves of the UV-VIS diffuse reflectance spectra (b) of the Ag₃PO₄/BiPO₄ and CQDs/Ag₃PO₄/BiPO₄ composites.](image)

Table 1. Color coordinates and \( E_g \) values of Ag₃PO₄/BiPO₄ and CQDs/Ag₃PO₄/BiPO₄.

| Sample                  | \( L^* \)  | \( a^* \) | \( b^* \) | \( c^* \) | \( H^* \) | \( E_{CIE}^* \) | \( E_g \) of Ag₃PO₄ (eV) | \( E_g \) of BiPO₄ (eV) |
|-------------------------|------------|-----------|-----------|-----------|-----------|----------------|---------------------|---------------------|
| Ag₃PO₄/BiPO₄            | 87.110     | -3.666    | 30.235    | 30.456    | -83.087   | 92.281         | 2.469               | 4.491               |
| CQDs/Ag₃PO₄/BiPO₄       | 63.817     | 4.286     | 15.421    | 16.006    | 74.468    | 65.794         | -                   | 4.561               |

3.5. Photoelectrochemical Properties

Figure 7a shows the EIS spectra of the Ag₃PO₄/BiPO₄ and CQDs/Ag₃PO₄/BiPO₄ composites. For the two samples, the EIS spectra show a semicircle and a straight line, which can be ascribed to the charge transfer and the Warburg impedance, respectively [62,63]. The CQDs/Ag₃PO₄/BiPO₄ photocatalyst has a smaller semicircle than that for the Ag₃PO₄/BiPO₄ photocatalyst, which means the former exhibits a higher photocatalytic activity. Photocurrent response curves can also be used to predict the photocatalytic activity of semiconductor materials [64]. Figure 7b shows the photocurrent response curves of the Ag₃PO₄/BiPO₄ and CQDs/Ag₃PO₄/BiPO₄ photocatalysts. The photocurrent response of Ag₃PO₄/BiPO₄ can be attributed to the electron transfer between Ag₃PO₄ and BiPO₄. The CQDs/Ag₃PO₄/BiPO₄ photocatalyst exhibits a higher photocurrent intensity than that of Ag₃PO₄/BiPO₄, indicating that it possesses a higher photocatalytic activity because of its higher electron transfer and separation efficiency.
where Ag has the highest photocatalytic activity. It should be noted out that photosensitized degradation of RhB could occur in the present photocatalytic system. However, the photosensitization effect is not the dominant degradation mechanism since Ag$_3$PO$_4$ based photocatalysts have also been demonstrated to exhibit pronounced degradation of non-biodegradable at ambient conditions. The dye degradation rate over the samples increases with increasing the irradiation time. The photocatalytic activity of these photocatalysts follows the order: CQDs/Ag$_3$PO$_4$/BiPO$_4$ > Ag$_3$PO$_4$/BiPO$_4$ > Ag$_3$PO$_4$ > BiPO$_4$. The result indicates that the CQDs/Ag$_3$PO$_4$/BiPO$_4$ composite has the highest photocatalytic activity. It should be noted out that photosensitized degradation of RhB could occur in the present photocatalytic system. However, the photosensitization effect is not the dominant degradation mechanism since Ag$_3$PO$_4$ based composite photocatalysts have also been demonstrated to exhibit pronounced degradation of colorless phenol [65].

The first order kinetic rate of the dye degradation photocatalyzed by the samples can be evaluated by Equation (2) [66]:

$$\ln(C_t/C_0) = -kt$$

where $C_0$, $C_t$, $k$, and $t$ is the initial concentration of RhB, apparent concentration of RhB after degradation, kinetic rate constant, and irradiation time, respectively. Figure 8b shows the plots of $\ln(C_t/C_0)$ vs. $t$. The rate constant ($k$) for the photocatalysts is found to be $k_{\text{BiPO}_4} = 0.00261, k_{\text{Ag}_3\text{PO}_4} = 0.00261, k_{\text{Ag}_3\text{PO}_4/\text{BiPO}_4} = 0.00261, k_{\text{CQDs/Ag}_3\text{PO}_4/\text{BiPO}_4} = 0.00261$. 

Figure 7. EIS spectra (a) and photocurrent response curves (b) of the Ag$_3$PO$_4$/BiPO$_4$ and CQDs/Ag$_3$PO$_4$/BiPO$_4$ composites.

3.6. Photocatalytic Activity

To study the photocatalytic activity of the BiPO$_4$, Ag$_3$PO$_4$, Ag$_3$PO$_4$/BiPO$_4$, and CQDs/Ag$_3$PO$_4$/BiPO$_4$ photocatalysts, RhB dye was used as a degradation dye. Figure 8a shows the time-dependent photodegradation of RhB in the presence of the samples under simulated sunlight irradiation. Based on the blank experiment, the RhB dye exhibits a high stability and is non-biodegradable at ambient conditions. The dye degradation rate over the samples increases with increasing the irradiation time. The photocatalytic activity of these photocatalysts follows the order: CQDs/Ag$_3$PO$_4$/BiPO$_4$ > Ag$_3$PO$_4$/BiPO$_4$ > Ag$_3$PO$_4$ > BiPO$_4$. The result indicates that the CQDs/Ag$_3$PO$_4$/BiPO$_4$ composite has the highest photocatalytic activity.
We compare the photodegradation performance of CQDs with Ag which indicates that the CQDs photocatalytic activity for the degradation of RhB.

A possible photocatalytic mechanism of the CQDs/Ag3PO4/BiPO4 composite photocatalysts, as shown in Table 2. It is seen that the CQDs/Ag3PO4/BiPO4 composite photocatalyst prepared in this work manifests a photodegradation performance superior to most of other photocatalysts.

Table 2. Comparison of the photocatalytic performance of CQDs/Ag3PO4/BiPO4 with that of other typical composite photocatalysts toward the degradation of RhB.

| Samples          | Light Source | Cphotocatalyst (g L⁻¹) | CRhB (mg L⁻¹) | Irradiation Time (min) | D%  | Reference |
|------------------|--------------|------------------------|---------------|------------------------|-----|-----------|
| CQDs/Ag3PO4/BiPO4| 200 W Xe lamp| 1                      | 5             | 50                     | 98.7| This work |
| 20wt%Ag3PO4/Bi2WO6| 200 W Xe lamp| 0.5                    | 5             | 120                    | 94  | [9]       |
| 10% Bi4Ti3O12/Ag3PO4| 200 W Xe lamp| 0.2                    | 5             | 30                     | 99.5| [6]       |
| Ag3PO4          | 30 W fluorescent light lamp (λ ≥ 420 nm) | 0.75              | 10            | 60                     | 70  | [67]      |
| Fe2O3/ZnO/Ag3PO4| 50 W LED lamp | 0.4                    | 12 (10⁻⁵ mol/L) | 100                    | 75  | [68]      |
| Ag3PO4-Bi2MoO5  | 400-nm cutoff filter | 1                    | 10            | 100                    | 39  | [69]      |
| Ag3PO4-ZnO (1:40)| 300 W Xe lamp with a 400-nm cutoff filter | 0.67              | 12 (10⁻⁵ mol/L) | 30                     | 93  | [70]      |
| Ag3PO4          | 15 W four fluorescent lamp | 0.3                  | 15            | 60                     | 75  | [71]      |
| Agl/BiPO4       | 500 W Xe lamp with a 420-nm cutoff filter | 1.67              | 10            | 60                     | 92.2| [72]      |
| Ag3S(C)CQDs/CuBi2O4| 200 W Xe lamp | 0.1                   | 20            | 120                    | 65  | [45]      |
| BiPO4/Ag3PO4    | 420-nm cutoff filter | 0.1                  | 20            | 120                    | 65  | [73]      |

The stability and reusability of the CQDs/Ag3PO4/BiPO4 photocatalyst was performed by repeating the experiments for the degradation of the RhB dye under simulated sunlight irradiation, as shown in Figure 9. It is seen that, after five cycles, no obvious decrease in the dye degradation is observed, which indicates that the CQDs/Ag3PO4/BiPO4 photocatalyst has a high stability and maintains a high photocatalytic activity for the degradation of RhB.

Figure 9. Recyclability of the CQDs/Ag3PO4/BiPO4 photocatalyst for the photocatalytic degradation of RhB under simulated sunlight irradiation.

3.7. Photocatalytic Mechanism

Figure 10a schematically shows the assembly structure of the CQDs/Ag3PO4/BiPO4 composite with Ag3PO4 fine particles and CQDs homogeneously decorated on the surface of rice-like BiPO4 granules. A possible photocatalytic mechanism of the CQDs/Ag3PO4/BiPO4 composite toward the degradation of RhB is described as follows.
degradation of RhB under simulated sunlight irradiation is schematically depicted in Figure 10b. The conduction band (CB) and valence band (VB) potentials of BiPO$_4$ and Ag$_3$PO$_4$ can be calculated by using Equations (3) and (4) [74,75]:

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

$$E_{VB} = X - E^e + 0.5E_g$$  
(4)

where $E^e$ is 4.5 eV, being the free electron energy on the hydrogen scale. $X_{Ag3PO4}$ and $X_{BiPO4}$ are estimated as 5.959 and 6.633 eV, respectively, according to Equations (5) and (6):

$$X(Ag_3PO_4) = \sqrt{X(Ag)^3X(P)X(O)^4}$$  
(5)

$$X(BiPO_4) = \sqrt{X(Bi)X(P)X(O)^4}$$  
(6)

where $X(Ag) = 4.44$, $X(P) = 5.62$, $X(Bi) = 4.69$, and $X(O) = 7.54$ eV. The CB potentials of BiPO$_4$ and Ag$_3$PO$_4$ are estimated as $-0.127$, and $+0.222$ V, respectively, and their corresponding VB potentials are $+4.434$, and $+2.691$ V. For the Ag$_3$PO$_4$/BiPO$_4$ composite, the energy band of Ag$_3$PO$_4$ is completely located within the energy band of BiPO$_4$. Therefore, the Ag$_3$PO$_4$/BiPO$_4$ composite obeys the type-I band alignment. When CQDs are introduced to the Ag$_3$PO$_4$/BiPO$_4$ composite, it promotes the change transfer between the two kinds of semiconductors. When the CQDs/Ag$_3$PO$_4$/BiPO$_4$ photocatalyst is irradiated by simulated sunlight, the electron transition occurs from the VB to the CB of Ag$_3$PO$_4$, thus producing electron-hole pairs. Subsequently, the holes in the VB of Ag$_3$PO$_4$ react with the RhB dye to form degradation products. Simultaneously, CQDs can be also excited by absorbing visible light, i.e., the $\pi$ electrons or $\sigma$ electrons are excited to the lowest unoccupied molecular orbital (LUMO) [76,77]. The excited CQDs can be acted as excellent electron donors and acceptors. However, BiPO$_4$ could not be photoexcited to generate electron-hole pairs under simulated sunlight irradiation due to its large bandgap energy (4.561 eV). Consequently, the CB electrons in Ag$_3$PO$_4$ will transfer to CQDs ($\pi$ or $\sigma$ orbitals), and the photoexcited electrons in CQDs will transfer to the CB of BiPO$_4$. Due to this interesting electron transfer process, the recombination of the photoexcited electron-hole pairs in Ag$_3$PO$_4$ are efficiently suppressed. Furthermore, the up-conversion photoluminescence emitted from CQDs could excite Ag$_3$PO$_4$ to generate additional electron-hole pairs. The photoexcited electrons in the LUMO of CQDs and those relaxed to the CB of BiPO$_4$ react with oxygen in the photocatalytic system to form superoxide (•O$_2^-$) radicals. The produced •O$_2^-$ radicals react with dye molecules adsorbed on the surface of the photocatalyst to produce degradation products.

Figure 10. Schematic illustration of the assembly structure (a) and a possible photodegradation mechanism (b) of the CQDs/Ag$_3$PO$_4$/BiPO$_4$ composite.
4. Conclusions

A simple hydrothermal method has been used to synthesize the CQDs/Ag$_3$PO$_4$/BiPO$_4$ heterostructure photocatalyst. The carbon quantum dots are anchored at the interfaces between Ag$_3$PO$_4$ and BiPO$_4$, thus forming the CQDs/Ag$_3$PO$_4$/BiPO$_4$ three-phase junction structure. The three-phase junction structure results in an efficient charge separation and utilization, high light absorption capacity and low photoluminescence intensity. The CQDs/Ag$_3$PO$_4$/BiPO$_4$ composite exhibits significantly enhanced photocatalytic activity for the degradation of RhB, which can be explained as the result of efficient charge separation and increased visible-light absorption.

Author Contributions: H.Y. conceived the idea of experiment; H.G. and C.Z. performed the experiments; H.Y., H.G., C.Z., X.N. and S.W. discussed the results; S.W. wrote the manuscript; and all authors read and approved the final manuscript.

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