A novel Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ heterojunction photocatalyst with enhanced photocatalytic performance

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Abstract

In this work, we integrated Ag$_3$PO$_4$ with Bi$_4$Ti$_3$O$_{12}$ to form Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ heterojunction nanocomposites by an ion-exchange method. The as-prepared Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ composites were systematically characterized by means of XRD, SEM, TEM, BET, XPS, UV-vis DRS, EIS, PL spectroscopy, and photocurrent response. SEM, TEM, and XPS results demonstrate the creation of Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ heterojunction with obvious interfacial interaction between Bi$_4$Ti$_3$O$_{12}$ and Ag$_3$PO$_4$. PL spectra, EIS spectra, and photocurrent responses reveal that the composites display an enhanced separation efficiency of photogenerated electron-hole pairs, which is due to the charge transfer between Bi$_4$Ti$_3$O$_{12}$ and Ag$_3$PO$_4$. Rhodamine B (RhB) was chosen as the target organic pollutant to evaluate its degradation behavior over Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ composites under simulated sunlight irradiation. Compared to bare Bi$_4$Ti$_3$O$_{12}$ and Ag$_3$PO$_4$ nanoparticles, the composites exhibit a significantly enhanced photocatalytic activity. The highest photocatalytic activity is observed for the 10% Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ composite with 10% Bi$_4$Ti$_3$O$_{12}$ content, which is about 2.6 times higher than that of bare Ag$_3$PO$_4$. The photocatalytic mechanism involved was investigated and discussed in detail.

Keywords: Bi$_4$Ti$_3$O$_{12}$ nanoparticles, Ag$_3$PO$_4$ nanoparticles, Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ heterojunction, Photocatalytic performance, Photocatalytic mechanism

Background

With the rapid development of economy, environmental pollution has become one of the most serious problems for human. Particularly, a huge amount of wastewater containing various organic dyes and pigments has been generated annually from chemical industries like paper, textile, paint, and cosmetic manufacturers all over the world. Before releasing the wastewater into the river, those organic pollutants must be removed since most of them are non-biodegradable and carcinogenic and pose an immense threat to the environment and human health. Semiconductor photocatalysis has been received as one of the most promising wastewater treatment technologies [1–9]. This technology can utilize solar energy as the power source for the organic pollutant decomposition. To utilize the solar energy more effectively in the photocatalysis, it is highly desirable to develop visible-light-responsive photocatalysts since visible light accounts for 45% of the solar energy. Moreover, to achieve a good photocatalytic activity of the photocatalyst, the photogenerated electron-hole (e$^-$-h$^+$) pairs must be effectively separated because the photocatalytic reaction is associated with the photogenerated electrons and holes [10, 11].

Recently, silver orthophosphate (Ag$_3$PO$_4$) with a bandgap energy of ~ 2.4 eV has been extensively studied as a promising visible light photocatalyst [12–31]. First principle calculations based on the density functional theory suggested that Ag$_3$PO$_4$ has a highly dispersive band structure of the conduction band minimum resulting from Ag s-Ag s hybridization without localized d states [32], which is advantageous for the separation of electron hole pairs as well as the electron transfer. Furthermore, Ag$_3$PO$_4$ has a quantum efficiency much higher than the values reported for other semiconductors (~ 90% at $\lambda > 420$ nm) [12, 13]. These make Ag$_3$PO$_4$ an excellent photocatalytic activity for the decomposition of organic pollutants as well as O$_2$ evolution from water splitting under visible light irradiation.
However, there are still some limitations in the Ag$_3$PO$_4$ photocatalyst. It is noted that the conduction band potential of Ag$_3$PO$_4$ is more positive than that of the hydrogen electrode [12]. This means that if there are no sacrificial electron acceptors involved in the photocatalytic system, the photogenerated electrons could reduce the lattice Ag$^+$ in Ag$_3$PO$_4$ into metallic Ag during the photocatalytic process. This self-photocorrosive phenomenon leads to a decrease in the photocatalytic stability of Ag$_3$PO$_4$. Moreover, Ag$_3$PO$_4$ is slightly soluble in aqueous solution, which could also decrease its structural stability during the photocatalytic process. To further improve the photocatalytic performance as well as the photocatalytic stability of Ag$_3$PO$_4$, much recent work has been devoted to the heterojunction composites constructed from Ag$_3$PO$_4$ and other semiconductors, such as Ag$_x$/Ag$_3$PO$_4$ (X = Cl, Br, I), Fe$_2$O$_3$/Ag$_3$PO$_4$, Ag$_3$PO$_4$/SnO$_2$, Ag$_3$PO$_4$/TiO$_2$, Ag$_3$PO$_4$/Bi$_2$MoO$_6$, g-C$_3$N$_4$/Ag$_3$PO$_4$, Ag$_3$PO$_4$/CeO$_2$, Ag$_3$PO$_4$/SrTiO$_3$, Ag$_3$PO$_4$/BiPO$_3$, Ag$_3$PO$_4$/MoS$_2$, and Ag$_3$PO$_4$/g-C$_3$N$_4$ [33–46]. In these composite photocatalysts, photogenerated electrons and holes tend to migrate from one semiconductor to another, leading to an efficient separation of electron hole pairs. As a result, more photogenerated electrons and/or holes are available for participating in photocatalytic reactions. It has been shown that the heterojunction composites exhibit enhanced photocatalytic performance compared to individual semiconductors. Furthermore, the photocorrosion and solubility behaviors of Ag$_3$PO$_4$ can be inhibited to some extent by the construction of heterojunction composites.

In this work, we report the integration of Ag$_3$PO$_4$ with Bi$_4$Ti$_3$O$_12$ to form Ag$_3$PO$_4$/Bi$_4$Ti$_3$O$_12$ heterojunction composites. Bi$_4$Ti$_3$O$_12$ has a layered structure composed of alternate (Bi$_2$O$_2$)$^2+$ blocks and (Bi$_6$O$_8$)$^{2+}$ layers along the c-axis orientation [47]. Density functional theory calculation has shown that the conduction band (CB) and valence band (VB) of Bi$_4$Ti$_3$O$_12$ consist of Ti 3d + Bi 6p orbitals and O 2p + Bi 6s hybrid orbitals, respectively [48]. Due to its unique layered crystal structure and electronic band structure, Bi$_4$Ti$_3$O$_12$ exhibits pronounced photocatalytic activity toward the degradation of organic pollutants [49–53]. It is known that Ag$_3$PO$_4$ is a p-type semiconductor and Bi$_4$Ti$_3$O$_12$ is an n-type semiconductor. The well-matched overlapping band-structures suggest that Ag$_3$PO$_4$ and Bi$_4$Ti$_3$O$_12$ can be used to construct an excellent p-n heterojunction composite photocatalyst with super photocatalytic performance.

**Methods**

**Synthesis of Bi$_4$Ti$_3$O$_12$ and Ag$_3$PO$_4$ nanoparticles**

Bi$_4$Ti$_3$O$_12$ nanoparticles were synthesized via a polyacrylamide gel route as described in the literature [54]. All raw materials and chemical reagents were of analytical grade and were used without further purification. Five milligrams of HNO$_3$ was added to 20 mL distilled water to make a dilute nitric acid solution. 0.00857 mol of Bi(NO$_3$)$_3$·5H$_2$O was dissolved in the above dilute nitric acid solution (designated as solution A). 0.00643 mol of C$_6$H$_{12}$O$_2$Ti was dissolved in 25 mL ethanol (designated as solution B). The solution B was added slowly into the solution A to obtain a mixture solution. Then, the mixture solution were successively added with 0.0225 mol of citric acid, 20 g of glucose, and 0.135 mol of acrylamide. During the addition of chemical reagents, the solution was agitated by magnetic stirring to make the additives dissolve fully. The resultant solution was heated in a water bath at 80 °C to initiate the polymerization reaction. After dried at 120 °C for 24 h in a thermostat drier, the formed xerogel was ground into powder and submitted to calcination in a tubular furnace at 300 °C for 3 h and then at 500 °C for 8 h. After the tubular furnace was naturally cooled down to room temperature, Bi$_4$Ti$_3$O$_12$ nanoparticles were obtained.

Ag$_3$PO$_4$ nanoparticles were synthesized by an ion exchange method. 0.003 mol of AgNO$_3$ and 0.001 mol of Na$_2$HPO$_4$ were dissolved in 30 and 20 mL distilled water with the aid of magnetic stirring, respectively. The Na$_2$HPO$_4$ solution was added drop by drop to the AgNO$_3$ solution under continuous stirring. The mixture solution was then continuously stirred by a magnetic stirrer for 5 h, during which time Ag$_3$PO$_4$ nanoparticles were formed. The produced particles were collected and washed several times with distilled water and absolute ethanol, followed by drying at 60 °C for 10 h.

**Preparation of Bi$_4$Ti$_3$O$_12$/Ag$_3$PO$_4$ nanocomposites**

A stoichiometric amount of the as-prepared Bi$_4$Ti$_3$O$_12$ nanoparticles was added to 30 mL distilled water and was submitted to ultrasonic treatment for 1 h to make the particles disperse uniformly. To the suspension was dissolved 0.003 mol of AgNO$_3$. 0.001 mol of Na$_2$HPO$_4$ was dissolved in 20 mL distilled water, which was then added drop by drop to the above suspension. The resultant mixture solution was magnetically stirred for 5 h, during which time Ag$_3$PO$_4$ nanoparticles were grown and integrated with Bi$_4$Ti$_3$O$_12$ nanoparticles to form Bi$_4$Ti$_3$O$_12$/Ag$_3$PO$_4$ composites. The produced composites were collected, washed several times with distilled water and absolute ethanol, and dried at 60 °C for 10 h. By varying the Bi$_4$Ti$_3$O$_12$ content from 5 to 15%, several composite samples of 5% Bi$_4$Ti$_3$O$_12$/Ag$_3$PO$_4$, 10% Bi$_4$Ti$_3$O$_12$/Ag$_3$PO$_4$, and 15% Bi$_4$Ti$_3$O$_12$/Ag$_3$PO$_4$ were prepared.

**Sample characterization**

X-ray powder diffraction (XRD) with Cu Kα radiation was used to determine the crystal structure of the samples. Field emission scanning electron microscopy (SEM) and field emission transmission electron microscopy (TEM)
were used to investigate the morphology and microstructure of the samples. The optical absorption and bandgap energy of the samples was investigated by ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) on a UV-vis spectrophotometer with an integrating sphere attachment. The chemical composition and electron binding energies for the elements were measured by X-ray photoelectron spectroscopy (XPS) on a PHI-5702 multi-functional X-ray photoelectron spectrometer, where the binding energy scale of the XPS data was calibrated against the adventitious C 1s peak at the binding energy of 284.8 eV. The photoluminescence (PL) spectrum of the samples was measured by using a fluorescence spectrophotometer (excitation wavelength 315 nm).

Photoelectrochemical measurement

The photoelectrochemical properties of the photocatalysts were measured by electrochemical impedance spectroscopy (EIS) and photocurrent response on a CST 350 electrochemical workstation using a three-electrode cell configuration [55]. A platinum foil was used as the counter electrode, and a standard calomel electrode (SCE) was used as the reference electrode. The working electrode was prepared as follows: 15 mg of the photocatalysts and 0.75 mg of polyvinylidene fluoride (PVDF) were mixed together using 1-methyl-2-pyrrolidone (NMP) as solvent to form slurry. The slurry was uniformly coated onto fluorine-doped tin oxide (FTO) glass substrate with an area of 1 cm × 1 cm and then submitted to drying at 60 °C for 5 h in a thermostat drying oven. Na2SO4 aqueous solution with concentration of 0.1 mol L⁻¹ was used as the electrolyte. The EIS measurement was carried out by the use of the sinusoidal voltage pulse with amplitude of 5 mV and in the frequency range of 10⁻²–10⁵ Hz. The transient photocurrent response was measured at a bias potential of 0.2 V. During the photoelectrochemical measurements, the working electrode was irradiated by a 200 W xenon lamp.

Photocatalytic evaluation

Rhodamine B (RhB) was chosen as the target organic pollutant to evaluate its degradation behavior over the samples under irradiation from a 200 W xenon lamp (solar simulator). RhB was dissolved in distilled water to make 5 mg L⁻¹ RhB aqueous solution. Twenty milligrams of the photocatalyst was loaded in 100 mL of RhB solution. The mixed suspension was firstly stirred by a magnetic stirrer for 20 min in the dark and then submitted to photocatalysis. During the photocatalysis process, the reactor was cooled with a water cooling system to maintain the reaction solution at room temperature. At given time intervals, a small portion of the reaction solution was taken out from the reactor for examining the RhB concentration, which was determined by measuring the absorbance of the solution at λ = 554 nm on a UV-vis spectrophotometer. Before absorbance measurement, the photocatalyst was removed by centrifugalization. The percentage degradation of RhB is defined as (C₀ − Cₜ)/C₀ × 100%, where C₀ is the initial RhB concentration and Cₜ is the remaining RhB concentration after photocatalysis for time t.

Detection of hydroxyl

PL spectroscopy is an important technique that can be used to detect hydroxyl (·OH) radicals formed over the simulated sunlight irradiated photocatalyst. Here, terephthalic acid (TPA) was used as the ·OH scavenger to examine ·OH radicals. NaOH solution with concentration of 1.0 mmol L⁻¹ was prepared by dissolving NaOH in distilled water. A stoichiometric amount of TPA was dissolved in the above NaOH solution to make 0.25 mmol L⁻¹ TPA solution. Twenty milligrams of the photocatalyst was loaded in 100 mL of the TPA solution. The mixture was magnetically stirred for 20 min in the dark and then irradiated by a 200-W xenon lamp. A small portion of the solution was taken out from the reactor after reaction for a certain period of time and submitted to centrifugation to remove the photocatalyst. The PL spectrum of the clear solution was measured on a fluorescence spectrophotometer (excitation wavelength 315 nm).

Results and discussion

XRD analysis

Figure 1 shows the XRD patterns of Bi₄Ti₅O₁₂, Ag₃PO₄, 5% Bi₄Ti₅O₁₂/Ag₃PO₄, 10% Bi₄Ti₅O₁₂/Ag₃PO₄, and 15% Bi₄Ti₅O₁₂/Ag₃PO₄ samples. The standard XRD line patterns for Bi₄Ti₅O₁₂ orthorhombic structure (JCPDS card no. 035-0795) and Ag₃PO₄ cubic structure (JCPDS card no. 006-0505) are also shown in Fig. 1. For Bi₄Ti₅O₁₂ sample, all diffraction peaks are in good agreement with those in the JCPDS card no. 035-0795, indicating that the sample crystallizes in a pure Bi₄Ti₅O₁₂ orthorhombic phase [54]. For Ag₃PO₄ sample, all diffraction peaks can be indexed according to the standard diffraction lines in the JCPDS card no. 006-0505, implying the formation of pure Ag₃PO₄ cubic phase [31]. For the composites, the XRD patterns can be indexed into two sets of diffraction peaks corresponding to Bi₄Ti₅O₁₂ and Ag₃PO₄ phases. The peak intensity from Bi₄Ti₅O₁₂ phase increases with increasing its content, which is clearly seen from the Bi₄Ti₅O₁₂ (171) diffraction peak at 30.1°. No diffraction peaks assignable to other impurity phases are detected, indicating that Bi₄Ti₅O₁₂ and Ag₃PO₄ undergo no structural change in the composites.

SEM analysis

Figure 2a–c shows the SEM images of Ag₃PO₄, Bi₄Ti₅O₁₂, and 10% Bi₄Ti₅O₁₂/Ag₃PO₄ samples, respectively. The SEM image given in Fig. 2a shows that the
Ag$_3$PO$_4$ particles have sphere-like morphology with size ranging from 300 to 600 nm. The SEM image shown in Fig. 2b reveals that the Bi$_4$Ti$_3$O$_{12}$ particles present sphere-like or ellipsoid-like morphology and have a size distribution range of 60–90 nm. From the SEM image in Fig. 2c, one can see that small-sized Bi$_4$Ti$_3$O$_{12}$ particles are assembled onto the surface of large-sized Ag$_3$PO$_4$ particles to form Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ heterostructure, as indicated by arrows.

**TEM analysis**

TEM was used to further investigate the microstructure of Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ composites. Figure 3a shows the TEM image of 10% Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$. The large-sized particles are identified to be Ag$_3$PO$_4$ particles, which have a spherical morphology with size of several hundred nanometers. Much smaller-sized particles with diameter of several tens of nanometers, which are identified to be Bi$_4$Ti$_3$O$_{12}$ nanoparticles, are seen to be assembled onto Ag$_3$PO$_4$ particles, as indicated by arrows. The TEM observation indicates the formation of Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ heterostructure, which agrees with that observed from the SEM image. Figure 3b shows the dark field scanning TEM (DF-STEM) image of 10% Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$. The corresponding elemental mapping images of the region indicated in Fig. 3b are given in Fig. 3c–g. It is seen that the large-sized particles present the elemental distribution of Ag and P and are therefore confirmed to be Ag$_3$PO$_4$ particles. The small-sized particles anchored onto Ag$_3$PO$_4$ particles display the elemental distribution of Bi and Ti, confirming that they are Bi$_4$Ti$_3$O$_{12}$ particles. The elemental mapping images further reveal the integration of Bi$_4$Ti$_3$O$_{12}$ with Ag$_3$PO$_4$ to form Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ heterostructure. Furthermore, the elements Ag and P, as
well as Bi and Ti, have an identical distribution, implying no chemical composition segregation in the Ag₃PO₄ and Bi₄Ti₃O₁₂ phases. The O element distribution is observed through the whole composites. Energy-dispersive X-ray spectroscopy (EDS) was further used to analyze the chemical composition of 10% Bi₄Ti₃O₁₂/Ag₃PO₄. As shown in Fig. 3h, the signals of the constituent elements of the composite are clearly included in the spectrum. The observed C and Cu signals could derive from the microgrid that is used for supporting the sample. It is noted that EDS is suitably used for the quantitative determination of the content of heavy elements (e.g., Bi, Ti, and Ag), but not light elements (e.g., P and O) [56]. The atomic ratio of Bi to Ti is obtained as 4/3 from the EDS spectrum, which agrees well the Bi/Ti atomic ratio of Bi₄Ti₃O₁₂ phase. The atomic ratio of Ti/Ag is very close to 1/9, implying that Bi₄Ti₃O₁₂ phase accounts for about 10% of the total molar content of the composite.

BET surface analysis
Figure 4 shows the N₂ adsorption-desorption isotherm of 10% Bi₄Ti₃O₁₂/Ag₃PO₄. This kind of isotherm is very similar to type II adsorption isotherm according to the IUPAC classification. The desorption curve coincides almost with the adsorption curve with no obvious hysteresis loop, implying the absence of mesopores in the composite. The insert in Fig. 4 shows the Brunauer-Emmett-Teller (BET) surface area plot of the composite, from which the BET surface area is calculated to be 2.08 m² g⁻¹.

XPS analysis
The chemical composition and elemental oxidation state of Ag₃PO₄, Bi₄Ti₃O₁₂, and 10% Bi₄Ti₃O₁₂/Ag₃PO₄ were also investigated by XPS. Figure 5a shows the XPS survey scan spectra of the samples, revealing that the samples clearly include their own constituent elements and no other impurity elements are found. Figure 5b shows the O 1s XPS spectra of the samples. For bare
Bi₄Ti₃O₁₂, the O 1s XPS signal can be fitted into three peaks at 529.6, 531.6, and 533.4 eV. The binding energy at 529.6 eV is attributed to the contribution of the crystal lattice oxygen. The peaks at higher binding energies of 531.6 and 533.4 eV could arise due to surface defects and chemisorbed oxygen species [55]. For bare Ag₃PO₄, the O 1s XPS spectrum is deconvoluted into two peaks at 530.8 and 532.6 eV, which are ascribed to the crystal lattice oxygen and the surface adsorbed oxygen, respectively. For 10% Bi₄Ti₃O₁₂/Ag₃PO₄, the O 1s binding energy of the crystal lattice oxygen in Bi₄Ti₃O₁₂ and Ag₃PO₄ is observed at 529.5 and 530.6 eV, respectively. A slight downshift of the O 1s binding energy peaks is observed in the composite, implying the possible chemical bonding between Bi₄Ti₃O₁₂ and Ag₃PO₄. Figure 5c, d shows the XPS spectra of Ag 3d and P 2p, respectively. The peaks at 368.0 and 374.0 eV belong to the binding energies for Ag 3d₅/₂ and Ag 3d₃/₂, respectively, suggesting the presence of Ag⁺ oxidation state. The presence of Ag⁰ metal state in the samples can be excluded because no
additional peaks are visible on the Ag 3d XPS spectra [37]. The observation of the P 2p binding energy at 133.2 eV is indicative of the presence of P$^{5+}$ oxidation state [37]. The Ag 3d and P 2p XPS signals undergo no change in the composite. Figure 5e, f shows the XPS spectra of Bi 4f and Ti 2p, respectively. For bare Bi$_4$Ti$_3$O$_{12}$, the Bi 4f spectrum presents two sharp peaks at 159.0 and 164.3 eV, which correspond to the binding energies of Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$, respectively [52]. This implies that Bi exists in the +3 oxidation state. On the Ti 2p spectrum, the peaks at 458.0 and 465.8 eV are assigned to the binding energies for Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$, respectively, which indicates that Ti is in the form of Ti$^{4+}$ oxidation state [52]. For the composite, the Bi 4f and Ti 2p peaks exhibit a slight shift toward higher binding energies, which could arise due to the chemical bonding between Bi$_4$Ti$_3$O$_{12}$ and Ag$_3$PO$_4$.

**UV-vis DRS spectra**

Figure 6a shows the UV-vis DRS spectra of Bi$_4$Ti$_3$O$_{12}$, Ag$_3$PO$_4$, and Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ composites, and Fig. 6b gives the corresponding first derivative of the spectra. The absorption edge of the samples can be derived from the peaks on the first derivative spectra. It is seen that Bi$_4$Ti$_3$O$_{12}$ has an absorption edge at 376.9 nm, and Ag$_3$PO$_4$ has an absorption edge at 498.5 nm. The absorption edges arise due to the electron transition from the valence band to the conduction band of the semiconductors, from which the bandgap energies ($E_g$) of Bi$_4$Ti$_3$O$_{12}$ and Ag$_3$PO$_4$ are obtained to be 3.29 and 2.49 eV, respectively. For the composites, the absorption edges of Bi$_4$Ti$_3$O$_{12}$ and Ag$_3$PO$_4$ exhibit a slight shift toward the short wavelength, which could be due to their mutual effect of light absorption on each other. The bandgap energies of Bi$_4$Ti$_3$O$_{12}$ and Ag$_3$PO$_4$ are expected to undergo a negligible change in the composites.

**PL spectra**

PL spectroscopy is used to evaluate the recombination behavior of photogenerated electron-hole pairs in the photocatalysts. The PL intensity is in proportion to the recombination rate of photogenerated electrons and holes. Figure 7 shows the PL spectra of Ag$_3$PO$_4$ and 10% Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ measured at an excitation wavelength of 315 nm. For Ag$_3$PO$_4$ particles, three PL emission peaks are observed at around 430, 490, and 525 nm. In contrast, the intensity of the PL emission peaks from 10% Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ composite is clearly decreased, implying a decrease in the electron-hole recombination. The efficient separation of electron-hole pairs is attributed to the charge transfer between Bi$_4$Ti$_3$O$_{12}$ and Ag$_3$PO$_4$. As a result, photogenerated electrons and holes in Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ composites are increasingly available for the photocatalytic reactions.
Photoelectrochemical properties

EIS and photocurrent response can be also used to investigate the separation and transfer behavior of photogenerated electrons and holes in the photocatalysts. Figure 8a shows the Nyquist plots of the EIS spectra for Ag₃PO₄ and 10% Bi₄Ti₃O₁₂/Ag₃PO₄ electrodes, which present a typical semicircle. The diameter of the semicircle is related to the charge-transfer resistance at the electrode/electrolyte interface. It is obvious that the Nyquist plot of 10% Bi₄Ti₃O₁₂/Ag₃PO₄ shows a much smaller semicircle diameter than that of bare Ag₃PO₄, indicating that the composite has a relatively smaller charge-transfer resistance under simulated sunlight irradiation. The observation of smaller charge-transfer resistance implies an increased separation efficiency of photogenerated electron-hole pairs and fast interface charge transfer occurring in the 10% Bi₄Ti₃O₁₂/Ag₃PO₄ composite. Figure 8b shows the transient photocurrent responses of Ag₃PO₄ and 10% Bi₄Ti₃O₁₂/Ag₃PO₄ recorded for several switch-on and switch-off cycles under intermittent irradiation of simulated sunlight. It is seen that the transient photocurrent responses are highly reproducible when the light is repeatedly switched between on and off. During the irradiation period, the photocurrent density of 10% Bi₄Ti₃O₁₂/Ag₃PO₄ is obtained as ~ 24 μA cm⁻², which is much higher than that of bare Ag₃PO₄ (~ 4 μA cm⁻²), indicating a more efficient separation of photogenerated electron-hole pairs in the composite due to the carrier transfer between Bi₄Ti₃O₁₂ and Ag₃PO₄.

Photocatalytic performances

Figure 9a shows the time-dependent photocatalytic degradation of RhB over Bi₄Ti₃O₁₂, Ag₃PO₄, and Bi₄Ti₃O₁₂/Ag₃PO₄ composites under simulated sunlight irradiation, along with the blank experiment result. Without loading the photocatalyst, RhB exhibits a good stability under simulated sunlight irradiation and its percentage degradation is only about 1.7% after 30 min of irradiation. When Ag₃PO₄ is used as the photocatalyst, RhB undergoes a substantial degradation with increasing the irradiation time, while a relatively weak degradation of the dye is observed for Bi₄Ti₃O₁₂. More importantly, when Ag₃PO₄ is integrated with Bi₄Ti₃O₁₂, the formed Bi₄Ti₃O₁₂/Ag₃PO₄ heterojunction composites exhibit significantly enhanced photocatalytic activity compared to bare Ag₃PO₄ or Bi₄Ti₃O₁₂. The highest photocatalytic activity is observed for 10% Bi₄Ti₃O₁₂/Ag₃PO₄, where the percentage degradation of RhB after 30 min of photocatalysis reaches 99.5%, as shown in Fig. 9c. To further reveal the photocatalytic activity of the samples, the photocatalytic degradation kinetics of RhB is investigated. Figure 9b shows the plots of Ln(Ct/C₀) versus irradiation time (t) for the samples. It is seen that the dye degradation conforms well to the first-order kinetic equation Ln(Ct/C₀) = -kₘₐₓt, where kₘₐₓ is the apparent first-order reaction rate constant (min⁻¹) [57]. The obtained rate constants for the samples are shown in Fig. 9d. The rate constant kₘₐₓ for 10% Bi₄Ti₃O₁₂/Ag₃PO₄ is obtained as 0.17891 min⁻¹, compared to 0.06764 min⁻¹ for Ag₃PO₄. This implies that the photocatalytic activity of 10% Bi₄Ti₃O₁₂/Ag₃PO₄ is about 2.6 times higher than that of bare Ag₃PO₄.

In most of the photocatalytic systems, the dominant active species responsible for the dye degradation include •OH, superoxide (•O₂), and h⁺ [58]. It is known that •OH, •O₂, and h⁺ can be scavenged by ethanol, benzoquinone (BQ), and ammonium oxalate (AO), respectively [56]. Therefore, the role of the active species in the photocatalysis can be verified by investigating the effect of ethanol, BQ, and AO on the photocatalytic degradation of the dye. Five milligrams of ethanol, 0.0011 g of BQ, and 0.0142 g of AO are separately added in 100 mL reaction solution, and then, the photocatalytic experiments are carried out under the same conditions. Figure 10a shows the...
effect of the scavengers on the degradation of RhB over 10% Bi₄Ti₃O₁₂/Ag₃PO₄. The degradation percentages of RhB after 30 min of photocatalysis and the rate constants are shown in Fig. 10b. It is found that the addition of ethanol to the reaction solution has a negligible effect on the degradation of RhB, implying that \( \cdot \text{O}_2 \) is the dominant reactive species causing the dye degradation. However, the addition of BQ or AO leads to an obvious suppression on the dye degradation. Particularly, only 17.9% of RhB is observed to be degraded with the addition of AO. This suggests that h⁺ and \( \cdot \text{O}_2 \) are the dominant and secondary reactive species causing the dye degradation, respectively.

**Information of \( \cdot \text{OH} \) radicals**

We further examine whether there are \( \cdot \text{OH} \) radicals formed over the simulated sunlight-irradiated 10% Bi₄Ti₃O₁₂/Ag₃PO₄ by PL spectroscopy using TPA as the scavenger of \( \cdot \text{OH} \). It is known that TPA will react with \( \cdot \text{OH} \) to produce 2-hydroxyterephthalic acid (TAOH) that can emit photoluminescence having a wavelength of 429 nm [59]. The PL emission intensity is proportional to the amount of \( \cdot \text{OH} \) radicals. Figure 11 shows the PL spectra of the TPA solution after reaction for 30 min over 10% Bi₄Ti₃O₁₂/Ag₃PO₄ and P25. It is well established that \( \cdot \text{OH} \) is easily generated over the irradiated P25 (a mixed-phase TiO₂ photocatalyst) in water solution. As a result, the TPA reaction solution shows a strong PL signal at 429 nm when P25 is used as the photocatalyst. However, when 10% Bi₄Ti₃O₁₂/Ag₃PO₄ is used as the photocatalyst, the TPA reaction solution is very similar to the blank TPA solution, showing no obvious PL signal at 429 nm. This indicates that no \( \cdot \text{OH} \) radicals are produced in the 10% Bi₄Ti₃O₁₂/Ag₃PO₄ photocatalytic system.

**Fig. 9**

**a** Time-dependent photocatalytic degradation of RhB over Bi₄Ti₃O₁₂, Ag₃PO₄, and Bi₄Ti₃O₁₂/Ag₃PO₄ composites. **b** Plots of Ln(C_t/C₀) versus irradiation time t for the samples. **c** Degradation percentages of RhB after 30 min of photocatalysis over the samples. **d** Apparent first-order reaction rate constants k_app for the samples.
Discussion of photocatalytic mechanism

The CB and VB edge potentials of Bi$_4$Ti$_3$O$_{12}$ and Ag$_3$PO$_4$ are determined according the method described in the literature [60], as schematically shown in Fig. 12a. It is seen that the CB potential of Bi$_4$Ti$_3$O$_{12}$ is negative to that of Ag$_3$PO$_4$, and moreover, Bi$_4$Ti$_3$O$_{12}$ is intrinsically an n-type semiconductor and Ag$_3$PO$_4$ behaves as a p-type semiconductor. This indicates that when the two semiconductors are integrated to form p-n heterojunction, electrons will migrate from Bi$_4$Ti$_3$O$_{12}$ to Ag$_3$PO$_4$, leaving behind positive charge centers at the interface of Bi$_4$Ti$_3$O$_{12}$ and negative charge centers at the interface of Ag$_3$PO$_4$. Simultaneously, an internal electric field is created at the interface region of the Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ heterojunction, as shown in Fig. 12b. The direction of the internal electric field is from Bi$_4$Ti$_3$O$_{12}$ to Ag$_3$PO$_4$. Under the action of the internal electric field, photogenerated electrons will migrate from Ag$_3$PO$_4$ to Bi$_4$Ti$_3$O$_{12}$ and conversely the photogenerated holes will migrate from Bi$_4$Ti$_3$O$_{12}$ to Ag$_3$PO$_4$. Due to the carrier transfer process, the recombination of electron-hole pairs can be effectively inhibited. As a result, more photogenerated holes and electrons are able to participate in the photocatalytic reactions, thus leading to an increased photocatalytic performance of the Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ heterojunction composites. It is noted that the photocatalytic performance of the composite photocatalysts is highly associated with...
the number of formed heterostructures. Generally, a proper proportion between two semiconductors is required for the creation of a large number of heterostructures in the composites. In the Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ composites, the optimum content of Bi$_4$Ti$_3$O$_{12}$ is about 10%, and at this Bi$_4$Ti$_3$O$_{12}$ content, the formed composite (i.e., 10%Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$) exhibits the highest photocatalytic activity.

Conclusions

Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ heterojunction composites were prepared by an ion-exchange method. Compared to bare Bi$_4$Ti$_3$O$_{12}$ and Ag$_3$PO$_4$ particles, the as-prepared Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ composites exhibit an enhanced photocatalytic activity toward the degradation of RhB under simulated sunlight irradiation. The highest photocatalytic activity is observed for the composite with Bi$_4$Ti$_3$O$_{12}$ fraction of 10%, which is about 2.6 times higher than that of bare Ag$_3$PO$_4$. The enhanced photocatalytic activity of the composites can be explained by the efficient separation of photogenerated electron-hole pairs due to the migration of the carriers between Bi$_4$Ti$_3$O$_{12}$ and Ag$_3$PO$_4$. As a result, more photogenerated holes and electrons are available for participation in the photocatalytic reactions. The reactive species are determined by investigating the effect of ethanol, BQ and AO on the RhB degradation, and it is concluded that $h^+$ is the dominant reactive species and $\cdot$O$_2$ is the secondary reactive species in the present Bi$_4$Ti$_3$O$_{12}$/Ag$_3$PO$_4$ photocatalytic system.

Abbreviations

BET: Brunauer-Emmett-Teller; CB: Conduction band; EIS: Electrochemical impedance spectroscopy; FTO: Fluorine-doped tin oxide; NMP: 1-Methyl-2-pyrrolidinone; PL: Photoluminescence; TEM: Transmission electron microscopy; TPA: Terephthalic acid; UV-vis DRS: Ultraviolet-visible diffuse reflectance spectroscopy; VB: Valence band; XPS: X-ray photoelectron spectroscopy; XRD: X-ray powder diffraction

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Authors’ contributions

HY conceived the idea of experiments. CZ and ZC carried out the preparation and characterization of the samples. HY, CZ, ZC, HZ, and XW analyzed and discussed the results of the experiments. CZ wrote the manuscript, and HY amended the manuscript. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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