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In Situ Template-Free Synthesis of a Novel 3D p-n Heteroarchitecture Ag₃PO₄/Ta₃N₅ Photocatalyst with High Activity and Stability under Visible Radiation

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A novel 3D p–n heteroarchitecture Ag₃PO₄/Ta₃N₅ composite photocatalyst with double visible-light-response characteristics has been prepared using an in-situ template-free precipitation method. It is found that the fascinating Ag₃PO₄/Ta₃N₅ exhibited high superior photoactivity and photostability compared to bare Ag₃PO₄ and Ta₃N₅ for the degradation of RhB under visible light irradiation. The improved performance of the composite is primarily attributable to sufficient visible-light harvesting, efficient charge separation and transfer of photogenerated electrons and holes resulting from matched energy bandgaps and sufficient p-n hetero-interfaces between Ag₃PO₄ and Ta₃N₅. The quenching effects of different scavengers demonstrate that the reactive h⁺ and O₂⁻ species played a major role in the photodegradation process. It is expected that the 3D p–n heterostructure composite fabricating via a facile precipitation method, may be a promising candidate for organic pollutant degradation. 

Introduction

Visible-light photocatalysis, which can directly harvest energy from incoming solar energy offers a desirable method for solving the issues of energy shortage and environmental remediation.¹² Currently, numerous visible-light-driven photocatalysts, such as doped semiconductors, as well as multiple-metal oxides including Ag, Bi, and In-based semiconductors, have been developed for photocatalytic water-splitting and photocatalytic degradation of organics in the air and wastewater. Among these photocatalysts, silver orthophosphate (Ag₃PO₄; Eg = 2.45 eV), which was reported by Ye and coworkers,¹¹,¹² exhibited extremely high photooxidative capabilities for O₂ evolution from water as well as organic dye decomposition under visible light irradiation. However, Ag₃PO₄ suffers from poor photostability in practical applications because it readily decomposes photochemically when no sacrificial reagent is involved.¹³ The development of photocatalysts with sufficient charge separation capability and high photocatalytic stability in the visible region is still the most challenging task in Ag₃PO₄ based photocatalysis research. The formation of a heterojunction between two semiconductors is an effective strategy for enhancing the separation of photogenerated electron-hole pairs.¹⁴ Recently, some composite photocatalysts based on Ag₃PO₄, such as AgX/Ag₃PO₄ (X = Cl, Br, I), Ag₃PO₄/TiO₂, Ag₃PO₄/Fe₂O₃, Ag₃PO₄/SnO₂ and graphene oxide/Ag₃PO₄ have been fabricated and exhibited enhanced photocatalytic activity and stability compared to the pure Ag₃PO₄ catalyst.¹¹,¹⁵⁻¹⁷ These results indicate that tailoring and fabricating the phase interface/junctions between the light harvesting semiconductors can effectively improve the stability and reduce the photocorrosion of Ag₃PO₄ photocatalysts.

(Oxy)nitride materials with a narrow band gap and a more negative potential for the nitrogen 2p orbital (i.e., TiO₂, Nₓ Ta₃N₅, TaON, LaTiO₃N, and GaN:ZnO) have been extensively developed to induce the photocatalytic reaction under visible light irradiation.¹⁹⁻²⁴ Tantalum nitride (Ta₃N₅) is one of the most promising photocatalysts for solar energy conversion via water splitting because it has a suitable band gap of 2.1 eV and appropriate band edge positions. The maximum solar-to-hydrogen efficiency of the Ta₃N₅ photoelectrode is as high as 15.9% under AM 1.5 G radiation.²⁵ However, due to the self-oxidative decomposition of Ta₃N₅ in which nitrogen anions are oxidized to N₂ by photogenerated holes, the photocatalytic activity of bare Ta₃N₅ is on the decreases during photocatalytic water splitting.²⁶ For example, the reported half-value period of the photocurrent for IrO₂-loaded Ta₃N₅ was estimated to be less than 10 minutes, indicating that the stability remains very poor for photocatalytic water splitting.²⁶ Therefore, prompt separation of the photogenerated electrons and holes is crucial for enhancing the activity and stability of the Ta₃N₅ catalyst. The p-n junction is one design concept for separating the electrons and holes using internal build-in fields induced by band bending.¹⁴ The concept, which originated from the design of high-performance solar cells, has been successfully adopted for fabrication of semiconductor...
photocatalysts. However, because p-type semiconductor oxides are rather rare, only a few p–n heterojunction photocatalysts have been selectively studied so far, such as Co$_3$O$_4$/Ta$_2$N$_5$ and ZrO$_2$/Ta$_2$N$_5$.

Judging from their respective nature and photocatalytic activity of two visible-light-driven photocatalysts as mentioned above i.e. p-type Ag$_3$PO$_4$ and n-type Ta$_2$N$_5$ as well as the possibility of forming p–n heterojunction in the interface of the two species, the combination of Ag$_3$PO$_4$ and n-type Ta$_2$N$_5$ seems to be ideal for the effective separation and transfer of electrons and holes, and consequently improving the photocatalytic efficiency and photostability of the composite photocatalyst. In this paper, we report for the first time the synthesis of 3D heteroarchitected visible-light-driven p–n heterojunction Ag$_3$PO$_4$/Ta$_2$N$_5$ photocatalyst by a facile in-situ template-free precipitation method. As anticipated, the as-obtained 3D heteroarchitected composite photocatalyst exhibited extremely high photocatalytic performance and photostability that is superior to bare Ag$_3$PO$_4$ and Ta$_2$N$_5$ toward degradation of rhodamine B (RhB) under visible-light irradiation (>420 nm). The enhanced performance is discussed in detail based on the inherent nature of heteroarchitected Ag$_3$PO$_4$/Ta$_2$N$_5$, as well as its spectral characterizations and photoelectrochemical measurements. A possible photodegradation mechanism is also proposed.

Results and discussion

In situ growth of Ag$_3$PO$_4$/Ta$_2$N$_5$ composite

Direct precipitation growth is commonly used to fabricate different kinds of composite. In the present work, an in situ precipitation method is adopted for the synthesis of the Ag$_3$PO$_4$/Ta$_2$N$_5$ composite and the synthesis procedure is schematically shown in Fig. 1. Specifically, Ta$_2$N$_5$ nanorod aggregates first obtained via a hydrothermal process was mixed with the precursor for Ag$_3$PO$_4$, silver nitrate. As such, the Ag$^+$ ions could be readily absorbed on the surface of negatively-charged Ta$_2$N$_5$ nanorod aggregates by the electrostatic adsorption to form a compact hetero-interface between the two species. Then, the adsorbed Ag$^+$ reacted with PO$_4^{3-}$ slowly released from bulk HPO$_4^{2-}$ solution to convert into Ag$_3$PO$_4$ particles on the surface of Ta$_2$N$_5$ nanorod aggregates under constant stirring at room temperature. In the process of subsequent reaction Ag$_3$PO$_4$ particles deposited on the surface of the Ta$_2$N$_5$ nanorod aggregates grew up gradually, with size enlarging from nanometer-scale to submicron-sized hierarchical scale. This in situ precipitation method for the synthesis of an Ag$_3$PO$_4$/Ta$_2$N$_5$ hybrid composite photocatalyst can also be summarized as follows:

\[ \text{Ag}^+ (aq) + \text{Ta}_2\text{N}_5 \rightarrow \text{Ag}^+/\text{Ta}_2\text{N}_5 \]  
\[ \text{Ag}^+/\text{Ta}_2\text{N}_5 + \text{PO}_4^{3-} (aq) \rightarrow \text{Ag}_3\text{PO}_4/\text{Ta}_2\text{N}_5 \]  

Characterization of Ag$_3$PO$_4$/Ta$_2$N$_5$ photocatalyst

The phase purity and crystal structure of the as-synthesized Ag$_3$PO$_4$/Ta$_2$N$_5$ composite were confirmed by XRD characterization. As shown in Fig. 2, all of the diffraction peaks for Ag$_3$PO$_4$ and Ta$_2$N$_5$ can be readily indexed to body-centered cubic Ag$_3$PO$_4$ (ICPDS No.06-0505) and orthorhombic Ta$_2$N$_5$ (ICPDS No.79-1533). The results for the Ag$_3$PO$_4$/Ta$_2$N$_5$ composites indicated the coexistence of both the Ag$_3$PO$_4$ and Ta$_2$N$_5$ phases, and no other crystal phases were observed in the XRD patterns, suggesting the high purity of the Ag$_3$PO$_4$/Ta$_2$N$_5$ composite.

![Schematic diagram of the growth process of Ag$_3$PO$_4$/Ta$_2$N$_5$.](image1)

![XRD patterns of the Ag$_3$PO$_4$, Ta$_2$N$_5$, and Ag$_3$PO$_4$/Ta$_2$N$_5$ photocatalysts.](image2)

![SEM images of the a) Ta$_2$N$_5$, b) Ag$_3$PO$_4$, and c) Ag$_3$PO$_4$/Ta$_2$N$_5$ photocatalysts, TEM image of d) Ag$_3$PO$_4$/Ta$_2$N$_5$, and HRTEM images of e) Ta$_2$N$_5$ and f) Ag$_3$PO$_4$ in the Ag$_3$PO$_4$/Ta$_2$N$_5$ photocatalysts.](image3)

The morphology and microstructure of Ag$_3$PO$_4$/Ta$_2$N$_5$ were characterized by SEM and TEM. As shown in Figure 3a-c, the micro-sized secondary Ta$_2$N$_5$ aggregates are composed of numerous primary nanorods with diameters of 40–60 nm and lengths of 200–300 nm (Fig. 3a). The Ag$_3$PO$_4$ particles exhibit an irregular spherical-like structure with an integral size ranging from 300 nm to
in other reported Ag₃PO₄ based composite photocatalysts. After Ag₃PO₄ particles grown on the surface of the Ta₃N₅ nanorods, one can observe that the size of Ag₃PO₄ decreases remarkably in the hybrid Ag₃PO₄/Ta₃N₅ composite (Fig. 3c). The average size of Ag₃PO₄ particles is in the range of 70–300 nm, which is much smaller than that of the pure Ag₃PO₄ sample. The reason is that the primary Ta₃N₅ nanorods carry negative charge (zeta potential = −39.8 mV, aqueous media) that allows offering sufficient nucleate sites for Ag₃PO₄ precipitation, and thus effectively prevent the formation of micron-sized Ag₃PO₄ bulks. Furthermore, it is worth noting that the 70–300 nm-sized secondary Ag₃PO₄ particle is spherical in shape and made of packed nanocrystallites with 10–20 nm in diameter, as shown in SEM image of Ag₃PO₄/Ta₃N₅ hybrid composite (Fig. 3c). Such 3D hierarchical structures of the composite facilitate forming a rough surface and thus provide sufficient hetero-interfaces for photocatalytic reaction. The magnified image shown in Figure 3d shows the Ta₃N₅ nanorod aggregates to point outward coupling with the dispersed Ag₃PO₄ nanocrystals. The corresponding HRTEM images of the Ag₃PO₄/Ta₃N₅ composites show the distinct crystallographic planes of Ag₃PO₄ (Fig. 3e) and Ta₃N₅ (Fig. 3f), in which a lattice spacing of 0.511 nm corresponds to the (020) plane of the orthorhombic Ta₃N₅ phase and the lattice spacings of 0.428 and 0.301 nm correspond to the (110) and (200) planes of the cubic Ag₃PO₄ phase. EDS mapping images further confirmed the successful preparation of the Ag₃PO₄/Ta₃N₅ composite (Fig. S1).

1.0 μm, and some of the granules adhered to the surface of submicron–sized Ag₃PO₄ (Fig. 3b). Indeed, a number of large-sized Ag₃PO₄ with several to tens of nanometers have also been observed in other reported Ag₃PO₄ based composite photocatalysts. After Ag₃PO₄ particles grown on the surface of the Ta₃N₅ nanorods, one can observe that the size of Ag₃PO₄ decreases remarkably in the hybrid Ag₃PO₄/Ta₃N₅ composite (Fig. 3c). The average size of Ag₃PO₄ particles is in the range of 70–300 nm, which is much smaller than that of the pure Ag₃PO₄ sample. The reason is that the primary Ta₃N₅ nanorods carry negative charge (zeta potential = −39.8 mV, aqueous media) that allows offering sufficient nucleate sites for Ag₃PO₄ precipitation, and thus effectively prevent the formation of micron-sized Ag₃PO₄ bulks. Furthermore, it is worth noting that the 70–300 nm-sized secondary Ag₃PO₄ particle is spherical in shape and made of packed nanocrystallites with 10–20 nm in diameter, as shown in SEM image of Ag₃PO₄/Ta₃N₅ hybrid composite (Fig. 3c). Such 3D hierarchical structures of the composite facilitate forming a rough surface and thus provide sufficient hetero-interfaces for photocatalytic reaction. The magnified image shown in Figure 3d shows the Ta₃N₅ nanorod aggregates to point outward coupling with the dispersed Ag₃PO₄ nanocrystals. The corresponding HRTEM images of the Ag₃PO₄/Ta₃N₅ composites show the distinct crystallographic planes of Ag₃PO₄ (Fig. 3e) and Ta₃N₅ (Fig. 3f), in which a lattice spacing of 0.511 nm corresponds to the (020) plane of the orthorhombic Ta₃N₅ phase and the lattice spacings of 0.428 and 0.301 nm correspond to the (110) and (200) planes of the cubic Ag₃PO₄ phase. EDS mapping images further confirmed the successful preparation of the Ag₃PO₄/Ta₃N₅ composite (Fig. S1).

X-ray photoelectron spectroscopy (XPS) was also carried out to further investigate the composition and chemical status of the Ag₃PO₄/Ta₃N₅ heterostructure photocatalyst, and the results are shown in the Fig. 4. Only Ag, P, O, Ta and N elements were detected in the XPS survey spectrum (Fig. 4a) and no peaks corresponding to other elements were observed. The binding energies for the Ta 4f5/2, Ta 4f7/2 and N 1s peaks at 27.1, 25.3 and 396.8 eV are typical values for Ta₅⁺ and N in Ta₃N₅. The binding energy of 403.9 eV assigned to Ta 4p3/2 indicates that some portion of the Ta-N bonds form. The binding energies for the Ag 3d5/2, Ag 3d3/2, P 2p3/2 and P 2p1/2 peaks located at 367.7, 373.7, 132.3 and 133.5 eV are typical values for Ag⁺ and PO₄³⁻ in Ag₃PO₄. The O 1s peak centered at 530.4 eV was associated with the O²⁻ in Ag₃PO₄. The other O 1s peak at 532.2 eV was associated with the presence of an -OH group or a water molecule on the surface of the Ag₃PO₄/Ta₃N₅ composite.  

Photocatalytic performance and photostability under visible light irradiation

The optical absorption property of Ag₃PO₄/Ta₃N₅ was investigated with the UV-Vis spectra, as shown in Fig. 5. Pure Ag₃PO₄ exhibits strong absorbance in wavelengths shorter than 500 nm, corresponding to its band gap energy of 2.41 eV. For Ta₃N₅, the absorption edge was found to be at approximately 600 nm. Ag₃PO₄/Ta₃N₅ composite exhibits two absorption edges at 500 and 640 nm, implying a combination of the optical absorption characteristics of Ta₃N₅ and Ag₃PO₄. According to the Kubelka-Munk function, the relationship between the absorption coefficient and the bandgap energy of a semiconductor can be described by the following equation: \( \alpha h\nu = A (h\nu - E_g)^{1/2} \), where \( \alpha \), \( h \), \( n \), and \( E_g \) are the absorption coefficient, Planck’s constant, light frequency, proportionality constant and band-gap energy, respectively. The plot of \( \alpha h\nu \) as a function of \( E_g \) is shown in Fig. S2. The band gaps for Ag₃PO₄ and Ta₃N₅ are estimated to be 2.41 and 2.11 eV, respectively, which are similar to the values reported previously (2.36 eV for Ag₃PO₄ and 2.1 eV for Ta₃N₅). The band gap of the Ag₃PO₄/Ta₃N₅ heterostructure photocatalyst was estimated to be 2.08 eV. The relatively narrow bandgap energy observed for Ag₃PO₄/Ta₃N₅ may be due to the strong interaction in the hybrid structure, which results in more efficient use of the solar spectrum.
The photocatalytic performance of the as-prepared Ag$_3$PO$_4$/Ta$_3$N$_5$ was evaluated based on the degradation of RhB solution under visible light irradiation without the addition of any sacrificial reagents. For comparison, Ag$_3$PO$_4$, and Ta$_3$N$_5$ were also studied under the same conditions. Prior to irradiation with light, the suspension solution consisting of RhB and the photocatalyst was magnetically stirred in the dark for 30 min to establish an adsorption-desorption equilibrium (see Fig. S3). Fig. 6a shows the photocatalytic degradation of RhB as a function of irradiation time over different photocatalysts. In the absence of a photocatalyst (blank), direct photolysis of RhB under visible light irradiation could be neglected. The photocatalytic performance of different photocatalysts were in the following order: Ag$_3$PO$_4$/Ta$_3$N$_5$ > Ag$_3$PO$_4$ > Ta$_3$N$_5$. For pure Ta$_3$N$_5$, the photocatalytic activity is the lowest and the degradation of RhB was only 17% for 10 min. For pure Ag$_3$PO$_4$, the degradation of RhB was 96% for 10 min. It is important to note that only 6 min of visible-light irradiation is required for complete degradation of RhB over Ag$_3$PO$_4$/Ta$_3$N$_5$. The notably enhanced photocatalytic performances of Ag$_3$PO$_4$/Ta$_3$N$_5$ composite are mainly attributed to more photocatalytic active sites owing to the rough surface and sufficient hetero-interfaces of composite and rapid separation and transfer of charge carriers within the compact hetero-interface between Ag$_3$PO$_4$ and Ta$_3$N$_5$. The apparent rate constants (k) calculated from the degradation curves of $-\ln(C/C_0)$ as a function of irradiation time are 0.02, 0.26, and 0.63 min$^{-1}$ for Ta$_3$N$_5$, Ag$_3$PO$_4$ and Ag$_3$PO$_4$/Ta$_3$N$_5$, respectively (Fig. 6b). The photocatalytic rate of Ag$_3$PO$_4$/Ta$_3$N$_5$ was approximately 2.5 times that of Ag$_3$PO$_4$ and 32 times that of Ta$_3$N$_5$. The characteristic absorption band of RhB at approximately 554 nm decreases rapidly under visible light irradiation in the presence of the Ag$_3$PO$_4$/Ta$_3$N$_5$ photocatalyst and no blue-shift in the absorption band occurred, indicating that the entire conjugated chromophore structure of RhB was easily cleaved. During the photodegradation the absorption band at approximately 200-300 nm also decreases gradually, indicating that the small molecular compounds/intermediates (i.e. benzene ring based species) that were formed during the reaction were also degraded (Fig. S4). Furthermore, the photodegradation curves of Ag$_3$PO$_4$/Ta$_3$N$_5$ composite photocatalyst with different atom ratio (1:1 and 4:1) are also provided in supporting information (Fig. S5). It is found that 3:1 mole ratio of Ag$_3$PO$_4$ to Ta$_3$N$_5$ results in the best photodegradation performance among a series of mole ratios of 1:1, 3:1, and 4:1.

In addition to the photocatalytic activity, the stability of the photocatalysts is another important issue for practical application. To investigate the stability of bare Ag$_3$PO$_4$, Ta$_3$N$_5$ and Ag$_3$PO$_4$/Ta$_3$N$_5$, three runs of cycling photodegradation experiments under identical conditions were performed (Fig. 7). The photocatalytic efficiency of pure Ag$_3$PO$_4$ decreases as the color changes from an initial yellow color to a dark yellow color after three cycles. This result indicated that bare Ag$_3$PO$_4$ photocatalyst was unstable owing to the formation of metallic Ag$^0$ species resulting from the reduction of Ag$^+$ from Ag$_3$PO$_4$ by photoinduced electrons during the photocatalytic process. This was also evidenced by XRD pattern of the Ag$_3$PO$_4$ sample after three cycles, which clearly displayed a weak XRD diffraction peak at around 38° indexed to the (111) lattice plane of metallic Ag (see Fig. 8). In contrast, the photocatalytic activity of Ag$_3$PO$_4$/Ta$_3$N$_5$ maintains a high level of activity during the cycling degradation of RhB. In addition, no metallic Ag was detected after three successive experimental runs in the Ag$_3$PO$_4$/Ta$_3$N$_5$ system (Fig. 8), which demonstrates the good photostability of the Ag$_3$PO$_4$/Ta$_3$N$_5$ composite. The above results manifest that the introduction of Ta$_3$N$_5$ nanorod aggregates as the support for the Ag$_3$PO$_4$ could efficiently prevent the formation of Ag nanoparticles on the surface of Ag$_3$PO$_4$ by the construction of compact hetero-interface between Ag$_3$PO$_4$ and Ta$_3$N$_5$. The detailed reasons for the enhancement of the Ag$_3$PO$_4$/Ta$_3$N$_5$ photocatalyst associated with activity and stability will be discussed in the following section.

Fig. 6 a) RhB (1x10$^{-5}$ M) photodegradation as a function of illumination time for the Ta$_3$N$_5$, Ag$_3$PO$_4$, and Ag$_3$PO$_4$/Ta$_3$N$_5$ photocatalysts and no catalyst. b) Plot of $-\ln(C/C_0)$ as a function of time. (C$_0$ is the initial concentration of RhB prior to irradiation, and C is the concentration at the specified irradiation time.)

Fig. 7 Recycling tests of the Ta$_3$N$_5$, Ag$_3$PO$_4$, and Ag$_3$PO$_4$/Ta$_3$N$_5$ photocatalysts for the degradation of RhB (1x10$^{-5}$ M).

Fig. 8 XRD patterns of Ag$_3$PO$_4$ and Ag$_3$PO$_4$/Ta$_3$N$_5$ photocatalysts after 3 cycles.
Mechanism for the improved photocatalytic activity and stability of Ag$_3$PO$_4$/Ta$_3$N$_5$

The above experimental results and discussions demonstrate that the photocatalytic activity and stability of Ag$_3$PO$_4$ can be improved via coupling Ag$_3$PO$_4$ with Ta$_3$N$_5$ nanorod aggregates, which is primarily due to the effective charge separation and transfer of photoinduced electrons and holes by the internal build-in field in the p-n junction region. One direct piece of evidence is that the PL intensity of the Ag$_3$PO$_4$/Ta$_3$N$_5$ photocatalyst is much lower than that of the Ag$_3$PO$_4$ sample (see Fig. 9), indicating that the recombination of the photoexcited electron-hole on the Ag$_3$PO$_4$ surface is suppressed due to the formation of a heterojunction between Ag$_3$PO$_4$ and Ta$_3$N$_5$.

EIS is a powerful characterization technique for studying the interfacial charge-transfer properties of photocatalyst. In this study, EIS spectra measurements were performed. The semicircle at high frequency is characteristic of the charge transfer process and the diameter of the semicircle represents the charge transfer resistance. In Fig. 10, the arc for Ag$_3$PO$_4$/Ta$_3$N$_5$ is much smaller than that for Ag$_3$PO$_4$ and Ta$_3$N$_5$ under illumination, suggesting that Ag$_3$PO$_4$/Ta$_3$N$_5$ has a smaller electronic transmission resistance, and a higher efficient charge separation/transfer. On one hand, the compact hetero-interface formed with submicron-sized Ag$_3$PO$_4$ and Ta$_3$N$_5$ nanorod aggregates could serve as a bridge and provide barrier-free access to transport photo-induced carriers (electrons and holes) between Ag$_3$PO$_4$ and Ta$_3$N$_5$ during the photocatalytic process, hence greatly improving the separation efficiency of the electrons and holes. On the other hand, the internal build-in fields existing in the hetero-interface could also be beneficial to separate and transfer the electrons and holes within the hybrid composite. Therefore, the efficiency of the photocatalytic degradation of RhB dyes over the Ag$_3$PO$_4$/Ta$_3$N$_5$ sample is much better.

To elucidate the photocatalytic reaction mechanism, we attempted to examine the main reactive species including h$^+$, O$_2$•$^-$ and •OH that are involved in the photocatalytic process. In the experiments, disodium ethylenediaminetetraacetate (EDTA), benzoquinone (BQ), and isopropanol (IPA) that acted as the scavengers for h$^+$, O$_2$•$^-$ and •OH were separately introduced into the photocatalytic reaction processes. Fig. 11 shows a comparison of the photocatalytic activity of the Ag$_3$PO$_4$/Ta$_3$N$_5$ sample for the degradation of RhB in the presence of different scavengers. The addition of EDTA (h$^+$ scavenger) in the RhB solution results in fast deactivation of Ag$_3$PO$_4$/Ta$_3$N$_5$ for the degradation of RhB. When BQ (O$_2$•$^-$ scavenger) was added, the efficiency of the photocatalytic degradation decreased substantially. However, the addition of IPA (hydroxyl radical scavenger) has little effect on the photocatalytic activity. These results indicate that in the photocatalytic reaction process of Ag$_3$PO$_4$/Ta$_3$N$_5$, h$^+$ and O$_2$•$^-$ are the main reactive oxidizing species, and •OH may only play a less important role. The valence band (VB) edge potential of Ag$_3$PO$_4$ (2.81 eV) is close to E$^\theta$ (•OH/H$_2$O) (2.68 eV) and its conduction band (CB) edge potential (0.45 eV) is less negative than E$^\theta$ (O$_2$/O$_2$•$^-$) (0.13 eV). Therefore, for pure Ag$_3$PO$_4$, it is difficult for holes to directly oxidize H$_2$O molecules into •OH radicals, and electrons cannot directly reduce O$_2$ molecules into O$_2$•$^-$ radicals. However, the CB edge potential (~0.5 eV) of Ta$_3$N$_5$ is more negative than E$^\theta$ (O$_2$/O$_2$•$^-$) (0.13 eV), and
the photogenerated electrons from Ta$_3$N$_5$ can reduce O$_2$ to O$_2^{2-}$ through a one-electron reduction reaction. Therefore, for Ag$_3$PO$_4$/Ta$_3$N$_5$ heterojunction photocatalyst, holes in the VB. Due to the transfer from the electrons in the CB of Ta$_3$N$_5$ to the CB of Ag$_3$PO$_4$, the existence of a built-in electrical potential at the p-n junction, the fabricated p-n heterojunction Ag$_3$PO$_4$/Ta$_3$N$_5$ system act as two photosensitizers responsive to visible light. Under visible irradiation, the absorption of photons by Ag$_3$PO$_4$ and Ta$_3$N$_5$ leads to the exciton of electrons from their separated VB to CB, leaving holes in the VB. Due to the existence of a built-in electrical potential at the p-n junction, the transfer of the electrons in the CB of Ta$_3$N$_5$ to the CB of Ag$_3$PO$_4$ is suppressed. However, the electron transfer path from the CB of Ag$_3$PO$_4$ to the VB of Ta$_3$N$_5$ is feasible. Therefore, the photoinduced electrons and holes are efficiently separated between Ag$_3$PO$_4$ and Ta$_3$N$_5$. In addition, the photogenerated electrons move easily towards the surface of Ta$_3$N$_5$, and react with adsorbed O$_2$ to form reactive oxygen species such as O$_2^{2-}$. The photoinduced holes may shift to the surface of Ag$_3$PO$_4$ to oxidize RhB. Therefore, this fabricated p-n heterojunction Ag$_3$PO$_4$/Ta$_3$N$_5$ photocatalyst exhibits high photocatalytic activity and stability under visible light irradiation.

![Fig. 12 Schematic illustration of the band alignments and the corresponding proposed charge separation and transfer of p-n heterostructure Ag$_3$PO$_4$/Ta$_3$N$_5$ composite under visible light irradiation.](image)

**Conclusions**

In summary, a novel 3D p-n heteroarchitecture Ag$_3$PO$_4$/Ta$_3$N$_5$ composite has been successfully synthesized by a facile and reproducible in situ template-free precipitation process. The heteroarchitecture Ag$_3$PO$_4$/Ta$_3$N$_5$ composite exhibits excellent optical absorption property attributed to double visible-light-response characteristics and matched energy bandgaps of the two components. The unique 3D heteroarchitecture provides sufficient hetero-interfaces to form internal build-in field in the p-n heterojunction region between Ag$_3$PO$_4$ and Ta$_3$N$_5$, which greatly improve the charge separation efficiency and transfer of photogenerated electrons and holes. Owing to these beneficial features, Ag$_3$PO$_4$/Ta$_3$N$_5$ composites exhibited excellent photocatalytic activity and stability for the degradation of RhB, superior to those of pure Ta$_3$N$_5$ and Ag$_3$PO$_4$ under visible light irradiation (≥420 nm). Reactive oxidative species detection studies indicated that the photodegradation of RhB over Ag$_3$PO$_4$/Ta$_3$N$_5$ under visible light is primarily via holes and O$_2^{2-}$ radicals. Our work provides a highly efficient p-n heterojunction Ag$_3$PO$_4$/Ta$_3$N$_5$ photocatalyst via a fabrication approach that may be beneficial for the development of other heterostructure photocatalysts.

**Experimental Section**

**Materials**

All of the chemicals used in this study were of analytical grade and used without further purification. Ethanol, hydrogen peroxide (H$_2$O$_2$) and hydrofluoric (HF) acid were supplied by Sinopharm Chemical Reagent Beijing Co. (Beijing, China). Tantalum powders (99.9%), silver nitrate (AgNO$_3$), and sodium dihydrogen phosphate hydrate (Na$_2$HPO$_4$.12H$_2$O) were supplied by Aladdin. Ammonia gas was supplied by HaiPu Gas (Beijing, China) Co. Ltd. Rhodamine B (RhB) was purchased from Fisher Scientific (Hong Kong) Co., Ltd. Deionized (DI) water was used in all of the experiments.

**Preparation of heterostructure Ag$_3$PO$_4$/Ta$_3$N$_5$ composite**

Ta$_2$O$_5$ was prepared via a facile hydrothermal process. In a typical procedure, 0.5 g of tantalum powder (99.9%, black-color) was added to 50 mL of a 0.5 mol L$^{-1}$ aqueous hydrofluoric acid solution with 12 mL of a 30 wt% hydrogen peroxide solution under stirring for 10 min. Then, the mixture was loaded into a Teflon-lined autoclave for thermal treatment at 240 °C for 12 h. After cooling, Ta$_2$O$_5$ was obtained by filtration followed by rinsing with ethanol and drying at 60 °C for 12 h. Next, Ta$_3$N$_5$ was obtained via thermal nitridation of the homemade Ta$_2$O$_5$ powder at 850 °C for 6 h under an ammonia gas flow (40 mL min$^{-1}$). Then, the nitridation reaction was allowed to cool to room temperature in the presence of the ammonia flow.

The Ag$_3$PO$_4$/Ta$_3$N$_5$ composites were obtained by immersing homemade Ta$_3$N$_5$ nanorods into an AgNO$_3$ solution followed by phosphorylation in an aqueous Na$_2$HPO$_4$ medium. Typically, an appropriate amount of Ta$_3$N$_5$ powder was suspended in an aqueous AgNO$_3$ solution followed by stirring at room temperature for 1 h. In addition, 10 mL of a 0.15 M aqueous Na$_2$HPO$_4$ solution was dropped into the previously mentioned suspended solution and stirred for 3 h. The obtained product (i.e., Ag$_3$PO$_4$/Ta$_3$N$_5$) was collected by washing and drying. For comparison, a pure Ag$_3$PO$_4$ sample was also prepared using the same procedure without the addition of Ta$_3$N$_5$.

**Characterizations**

The phase structure of the samples was characterized by X-ray diffraction (XRD) on a Rigaku D/max 2500 VB+PC diffractometer using Cu K radiation (λ = 0.15406 nm) at 40 kV and 40 mA. The morphologies of the samples were examined by scanning electron microscopy (SEM) (JEOL JSM-6701F) and transmission electron microscopy (TEM) (JEOL JEM-3010). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB 250 X-ray photoelectron spectrometer using Al Kα as an X-ray source. The optical properties of Ag$_3$PO$_4$/Ta$_3$N$_5$ were studied using the adsorption spectra recorded on a UV-Vis spectrophotometer.
(Lambda 950 UV/VIS). The photoluminescence (PL) spectra were obtained on a Hitachi F7000 at an excitation wavelength of 315 nm.

**Photocatalytic activity measurement**

The photocatalytic activities of the sample photocatalysts were evaluated based on the degradation of RhB under visible light irradiation. In a typical process, 30 mg of the photocatalyst were added to 80 mL of RhB (1×10⁻⁵ M). Prior to irradiation, the suspension was stirred in the dark for 30 min to establish adsorption-desorption equilibrium. Then, the suspension was exposed to a 300 W Xe lamp with an ultraviolet cutoff filter. The working electrodes were prepared using the dipping method on indium-tin oxide (ITO) conductive glass. Briefly, 0.3 g of the photocatalyst and 10 mL of isopropyl alcohol were mixed for 1 h and dipped on the ITO glass to form a uniform film. Then, the photocatalyst and 10 mL of isopropyl alcohol were mixed for 1 h and then centrifuged to remove the photocatalyst particles. The concentration of RhB was determined by measuring the maximum absorption peak at 554 nm with a UV-Vis spectrophotometer.

**Photoelectrochemical characterization of Ag₃PO₄/Ta₃N₅**

Electrochemical impedance spectroscopy (EIS) was performed using a standard three electrode configuration with Ag/AgCl as the reference, and counter electrode, respectively. The supporting electrolyte was a 0.5 M Na₂SO₄ solution. The visible light source was a 300 W Xe lamp with a 420 nm cut-off filter. The photocatalysts were obtained from a 300 W Xe lamp with a 420 nm cut-off filter. The working electrodes were prepared using the dipping method on ITO glass. Then, the photodegradation systems were exposed to a 300 W Xe lamp with an ultraviolet cutoff filter. The reactive oxidative species in the photodegradation were detected using in situ trapping experiments.

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**Notes and references**