Tetrahedral UMOFNs/Ag₃PO₄ Core–Shell Photocatalysts for Enhanced Photocatalytic Activity under Visible Light

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Supporting Information

ABSTRACT: A new visible-light-responsive tetrahedral ultrathin metal–organic framework nanosheet (UMOFNs)/Ag₃PO₄ composite photocatalyst with a core–shell structure was readily synthesized by sonication in an organic solvent. Characterization methods for the photocatalyst included X-ray diffraction (XRD), scanning electron microscopy, transmission electron microscopy, and UV–vis diffuse reflectance spectroscopy. The XRD patterns of the composite photocatalyst before and after visible-light irradiation demonstrated that trace amounts of Ag ions in the composite photocatalyst easily transformed into Ag nanoparticles, which play a role in promoting charge separation at the interface of a heterojunction. The UMOFNs/Ag₃PO₄ composite photocatalyst showed higher photocatalytic activity for the photo-degradation of 2-chlorophenol (2-CP) under visible-light irradiation (>420 nm) than Ag₃PO₄. The complete degradation of 2-CP was achieved in 7 min using the tetrahedral UMOFNs/Ag₃PO₄ core–shell photocatalyst, and the apparent reaction rate was approximately 26 times higher than that of pure Ag₃PO₄. Further, a scavenger experiment showed h⁺ and O₂•− were the major reactive species involved in the photocatalytic reaction system. This enhanced photocatalytic activity results from the efficient separation of photoinduced electron–hole pairs and the increase of interface area between Ag₃PO₄, UMOFNs, and the Ag nanoparticles.

1. INTRODUCTION

Photocatalytic reaction systems are one of the most promising purification technologies used to address environmental problems. That is because they can degrade various organic pollutants using solar energy in a variety of environments.¹,² Conventional photocatalysts, including TiO₂, ZnO, and SrTiO₃ are photocatalytically reactive only under UV light irradiation. However, UV light is less than 4% of solar energy and it is therefore impossible to bring out sufficient photocatalytic performance under solar energy, limiting their practical application in many environments. For this reason, there has been significant interest in efficient visible-light-responsive photocatalysts for utilizing the full spectrum of solar energy.

In the field of photocatalysts, metal–organic frameworks (MOFs), which are composed of metal clusters and organic ligands, have received considerable attention in recent years as promising porous photocatalysts.¹⁻⁵ They provide a variety of excellent properties, including large surface area, adjustable functions, and high porosity. They also have been widely utilized in catalysis, separation, gas storage, chemical sensors, and biomedicine because of the various outstanding properties of porous materials.⁶⁻¹⁸ In recent years, worldwide attention has increasingly been drawn to applying MOFs to photocatalysis. Various MOFs have been introduced as semiconductor materials and used as photocatalysts under UV light, including MOF-5,¹⁹ MIL-125,²⁰ UIO-66,²¹ MIL-53,²² MOF-253,²³ and MIL-100.²⁴ However, these MOFs have the drawbacks of absorbing only short-wavelength light in the UV range, as well as low effective separation of photoinduced charge carriers because of a wide-band gap and a fast recombination rate of electron–hole pairs. Furthermore, most of these MOFs are unstable in water because water molecules change the metal–organic coordination bond to a metal–water coordination bond. It is therefore recommended to introduce other highly conductive, visible-light-responsive and mechanically stable materials as photocatalysts to solve the above drawbacks of MOFs.²⁵

To construct composite materials with heterojunction systems, studies have combined MOFs with various semiconductor materials, including TiO₂,²⁶ g-C₃N₄,²⁷ and GrO.²⁸ Heterojunction semiconductor-based MOFs showed superior photocatalytic performance and stability compared with single components because of the efficient separation of photoinduced charge carriers at the hetero-interface between the MOFs and other semiconductor materials. Specifically, Li et al. reported that TiO₂ encapsulated in salicylaldehyde-NH₂-MIL-101(Cr) has superior photocatalytic performance for MB degradation under visible-light irradiation.²⁶ Yang et al. demonstrated that MIL-68-(In)-NH₂ combined with GrO...
showed superior electron transport properties, leading to enhanced photocatalytic activity for the visible-light-driven photocatalytic degradation of amoxicillin. Chen et al. prepared CdS/g-C3N4/MIL-125(Ti) via a facial solvothermal method, which has excellent photocatalytic performance owing to the formation of an interface between CdS, g-C3N4, and MIL-125(Ti). However, it is still necessary to develop new photocatalysts because the above MOF-based composite photocatalysts have insufficient photocatalytic performance for practical use.

Ultrathin MOF nanosheets (UMOFNs), which are composed of terephthalic acid (H2BDC) as an organic ligand and Ni2+ and Co2+ as central metals, have attracted significant attention in the field of photocatalysts as two-dimensional structural materials. UMOFNs with a two-dimensional structure have many superior properties compared with three-dimensional structural materials. For example, the charge transfer in ultrathin nanosheets is so fast that efficient charge separation is facilitated and there are many exposed active sites with unsaturated metals. In addition, combining UMOFNs with other semiconductors provides a large interface area at the heterojunction between the UMOFNs and the other semiconductor materials, improving the photocatalytic activity of the semiconductor materials. These advantages make two-dimensional UMOFNs promising materials for practical application in the field of photocatalysts.

In recent years, silver-based photocatalysts, such as AgVO4, Ag2CO3, Ag2O, AgBr, and Ag3PO4, have been widely reported as promising environmental purification technologies. Ag3PO4 in particular shows superior photocatalytic performance for the degradation of organic contaminants under visible-light irradiation as a result of the narrow band gap and high oxidizability of the photoinduced hole. Furthermore, the photocatalytic performance of Ag3PO4 can be enhanced by controlling the shape, morphology, and crystal plane during preparation. However, the Ag ions in Ag3PO4 are easily changed to Ag metal by photocorrosion of Ag3PO4 under light irradiation. An excessive amount of these Ag metal particles interferes with charge transfer, light adsorption, and contact with organic contaminants on Ag3PO4. As a result of these factors, photocorrosion gradually degrades the structure and photocatalytic activity of Ag3PO4 in the process of the photocatalytic reaction, hindering the practical application of Ag3PO4 in environmental purification technologies. Therefore, to effectively separate photoinduced electrons on Ag3PO4 and thereby prevent its photocorrosion, researchers all over the world have developed hybrid composite photocatalysts based on Ag3PO4, including MoSe2/Ag3PO4, g-C3N4/Ag3PO4, Ag3PO4/TiO2, Ag3PO4/Fe2O3, Ag3PO4/SnO2, and GO/Ag3PO4. These catalysts show superior photocatalytic performance and stability compared with pure Ag3PO4. Similarly, the incorporation of MOFs into Ag3PO4 is also a reasonable approach for improving photocatalytic activity and stability. For example, Ag3PO4/UMOFNs, Ag3PO4/BiPO4/Cu terephthalic acid, Ag3PO4/UiO-66, Ag3PO4/HKUST-1, Ag3PO4/MIL-101/FeO3, Ag3PO4/NH2-MIL-125, and Ag3PO4/MIL-53(Fe) have been reported. These studies provided limited information with regard to hybrid composite photocatalysts combining MOFs and Ag3PO4.

To further improve photocatalytic performance by the modification of surface properties, photocatalysts with exposed highly reactive crystal faces have received considerable attention. For the Ag3PO4 photocatalysts, the surface energies of {111}, {110}, and {100} planes were calculated by Martin et al., who found that {111} planes have the highest surface energy. Furthermore, this result was consistent with the photocatalytic results. On the basis of the above information, the photocatalytic activity of Ag3PO4 can be remarkably enhanced by the synergy of controlling the exposed crystal faces and introducing UMOFNs. Although studies on UMOFNs/Ag3PO4 composite photocatalysts have already been reported, they had insufficient photocatalytic performance for practical use.

To address these issues, in this paper, we report a new visible-light-responsive tetrahedral UMOFNs/Ag3PO4 composite photocatalyst with a {111} plane core–shell structure for improved photocatalytic performance. UMOFNs/Ag3PO4, in which UMOFNs and Ag3PO4 were the shell and core, respectively, was readily synthesized by sonication in an organic solvent. Further, to the best of our knowledge, there are few reports on the synthesis of the tetrahedral UMOFNs/Ag3PO4 composite photocatalyst with core–shell structure and its photocatalytic activity. The composite is expected to have significantly improved photocatalytic performance over that of other photocatalysts. The photocatalytic activity of the tetrahedral UMOFNs/Ag3PO4 core–shell photocatalyst was evaluated by the photodegradation of 2-chlorophenol (2-CP) under visible-light irradiation (>420 nm). In addition, we also present the photocatalytic mechanism of 2-CP degradation by UMOFNs/Ag3PO4 under visible light. The findings in this study will provide feasible routes to fabricate tetrahedral UMOFNs/Ag3PO4 composites with highly efficient photocatalytic activity for environmental applications.

2. RESULTS AND DISCUSSION

2.1. Characterization. X-ray diffraction (XRD) was employed to confirm the crystal structure of the photocatalytic materials. Figure 1 shows the XRD patterns of UMOFNs,

![Figure 1](https://example.com/image.png)

**Figure 1.** XRD patterns of Ag3PO4, UMOFNs, and UMOFNs/Ag3PO4.

Ag3PO4 and UMOFNs/Ag3PO4 (5 wt %). The XRD patterns of Ag3PO4 show that the crystalline phase is body-centered cubic (JCPDS No. 06-0505). Furthermore, it shows narrow and sharp peaks, confirming that the microcrystals of Ag3PO4 contain no impurities and have a high degree of crystallization. The XRD pattern of the UMOFNs was consistent with that of a previous work, indicating that the UMOFNs were successfully fabricated. In the UMOFNs/Ag3PO4 composite
photocatalyst, the characteristic peak attributed to Ag$_3$PO$_4$ remained after combination with UMOFNs while the UMOFNs peaks were not seen owing to the weak diffraction intensity and the low amount of UMOFNs in the composite photocatalysts. Furthermore, there are no additional peaks in the composite photocatalyst, which indicates the crystal structure of Ag$_3$PO$_4$ was not altered during fabrication of the composite photocatalysts. The XRD patterns of the composite photocatalysts with various mass ratios of UMOFNs (1, 5, and 10%) are shown in Figure S1. No differences were found among the diffraction patterns of the photocatalysts with various contents of UMOFNs. These results can also be attributed to the weak diffraction intensity and low amounts of UMOFNs.

To confirm the morphology of the photocatalytic materials, UMOFNs, Ag$_3$PO$_4$, and UMOFNs/Ag$_3$PO$_4$ composite photocatalysts were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). These results are shown in Figure 2. Figure 2a,b shows that the Ag$_3$PO$_4$ particles have a tetrahedral morphology and are about 0.5−2.0 μm in size, indicating Ag$_3$PO$_4$ with {111} facets was successfully prepared by the kinetic control method. The {111} planes of Ag$_3$PO$_4$ have higher energy than other planes, which leads to enhanced photocatalytic activity.48 It can be clearly seen in Figure 2c,d that the UMOFNs possess an ultrathin two-dimensional nanosheet structure with a slightly rolled edge. The morphology of the UMOFNs/Ag$_3$PO$_4$ composite photocatalyst can be seen in Figure 2e,f. The two-dimensional UMOFNs primarily wrap the surface of the tetrahedral Ag$_3$PO$_4$ particles, suggesting the formation of a core−shell structure. The core−shell structure of UMOFNs/Ag$_3$PO$_4$ can promote the efficient separation of photoinduced charge carriers, owing to a large contact area at the interface between the UMOFNs shell and Ag$_3$PO$_4$ core.41

To investigate the porosity and specific surface area of Ag$_3$PO$_4$, UMOFNs, and the UMOFNs/Ag$_3$PO$_4$ composites, we measured the nitrogen adsorption−desorption isotherms. Figures 3 and S2 show the nitrogen sorption isotherms and the pore size distribution of UMOFNs, Ag$_3$PO$_4$, and UMOFNs/Ag$_3$PO$_4$. It can be clearly seen in Figure 3 that UMOFNs/Ag$_3$PO$_4$ exhibits a type IV isotherm according to the IUPAC classification, indicating UMOFNs/Ag$_3$PO$_4$ has mesopores with a microporous structure. In addition, the Brunauer−Emmett−Teller surface area of the UMOFNs/Ag$_3$PO$_4$ composite photocatalyst is 1.60 m$^2$ g$^{-1}$ while that of Ag$_3$PO$_4$ is 0.78 m$^2$ g$^{-1}$.

The Fourier transform infrared (FTIR) spectra of UMOFNs, Ag$_3$PO$_4$, and UMOFNs/Ag$_3$PO$_4$ with various mass ratios of UMOFNs (1, 5, and 10%) can be seen in Figure 4. For the pristine UMOFNs, the two characteristic peaks located at 1647 and 1370 cm$^{-1}$ are attributed to the asymmetric stretching vibration and symmetric stretching vibration, respectively, of the carboxyl group in the terephthalic acid.41 The two peaks from 1000 to 1250 cm$^{-1}$ in the UMOFNs resulted from the C−N stretching vibration of DMF, which could not be removed during preparation of the UMOFNs. The peak around 600−800 cm$^{-1}$ is due to the vibration of Co−O and Ni−O bonds in the UMOFNs.41 In comparison with the IR spectra of Ag$_3$PO$_4$, the two strong peaks located at 539 and 923 cm$^{-1}$ were derived from the P−O stretching vibration in PO$_4^{3-}$.49 In comparison with the IR spectra of Ag$_3$PO$_4$, UMOFNs/Ag$_3$PO$_4$ has three prominent peaks at 748, 1370, and 1647 cm$^{-1}$, which are derived from the UMOFNs. In addition, with a gradual increase of UMOFNs content, the intensities of the UMOFNs peaks are strengthened in the IR spectrum of UMOFNs/Ag$_3$PO$_4$. These results imply that there is a weak interaction between the UMOFNs shell and Ag$_3$PO$_4$. 

![Figure 2. SEM and TEM images of (A, B) Ag$_3$PO$_4$, (C, D) UMOFNs, and (E, F) UMOFNs/Ag$_3$PO$_4$.](image)

![Figure 3. Nitrogen adsorption−desorption isotherm of UMOFNs/Ag$_3$PO$_4$ (5 wt %).](image)
core\textsuperscript{11} and also suggests the successful formation of a heterojunction in the core–shell composite photocatalyst.

The UV–visible diffuse reflectance spectra (UV–vis DRS) of the materials were obtained to investigate the photocatalytic mechanism and optical characteristics and can be seen in Figure 5a. Ag\textsubscript{3}PO\textsubscript{4} has an adsorption edge at 510 nm, indicating that it is a visible-light-responsive photocatalyst that can efficiently absorb light energy. It can also be clearly seen that UMOFNs/Ag\textsubscript{3}PO\textsubscript{4} has much higher light absorption compared with Ag\textsubscript{3}PO\textsubscript{4}. Moreover, the band gaps (\(E_g\)) of Ag\textsubscript{3}PO\textsubscript{4} and UMOFNs were calculated on the basis of the Kubelka–Munk formula described below

\[
\alpha \nu = A(\nu - E_g^n)^{n/2}
\]

where \(\alpha\), \(h\), \(\nu\), and \(A\) are the absorption coefficient, Planck constant, light frequency, and constant, respectively. The value of \(n\) is varied according to the transition type; that is, the \(n\) value is 1 for direct transition and 4 for an indirect one, respectively. In this formula, the value of \(n\) was 1 because Ag\textsubscript{3}PO\textsubscript{4} and UMOFNs are direct transition semiconduc-

tors\textsuperscript{38,50} As shown in Figure 5b, the band gap energies (\(E_g\)) of Ag\textsubscript{3}PO\textsubscript{4} and UMOFNs can be estimated on the basis of the Tauc plot of \((\alpha \nu)^2\) vs \(\nu\) and were calculated to be 2.46 and 3.01 eV, respectively. In addition, the valance band edges (\(E_{VB}\)) of Ag\textsubscript{3}PO\textsubscript{4} and UMOFNs were measured by valence bond X-ray photoelectron spectroscopy (VBXPS) (Figure S3). It can be clearly seen in Figure S3 that the \(E_{VB}\) values for Ag\textsubscript{3}PO\textsubscript{4} and UMOFNs were 2.65 and 1.59 V (vs normal hydrogen electrode (NHE)), respectively. From the above results, their conduction band edges (\(E_{CB}\)) were calculated to be 0.19 and −1.41 V (vs NHE), respectively, according to the following equation

\[
E_{CB} = E_{VB} - E_g
\]

The photoluminescence (PL) emission spectra of the photocatalysts using excitation light of 360 nm were analyzed to confirm the recombination rate of the electron–hole pairs, as shown in Figure 6. UMOFNs/Ag\textsubscript{3}PO\textsubscript{4} shows a lower PL intensity than Ag\textsubscript{3}PO\textsubscript{4}, which indicates that the charge separation was promoted effectively; that is, the recombination

\[
\text{Figure 4. (a) FTIR spectra of Ag}_3\text{PO}_4, \text{UMOFNs, and UMOFNs/Ag}_3\text{PO}_4. \text{(b) FTIR spectra of UMOFNs/Ag}_3\text{PO}_4 \text{with various mass ratios of UMOFNs (1, 5, and 10%).}
\]

\[
\text{Figure 5. (a) UV–vis diffuse reflectance spectra of Ag}_3\text{PO}_4, \text{UMOFNs, and the 1, 5, and 10 wt % UMOFNs/Ag}_3\text{PO}_4 \text{hybrid photocatalysts. (b) Tauc plots of Ag}_3\text{PO}_4, \text{UMOFNs, and UMOFNs/Ag}_3\text{PO}_4.}
\]
of the photoinduced electron–hole pairs was suppressed after the introduction of UMOFNs. Furthermore, these results confirm that the heterojunction interface was successfully constructed between the UMOFNs and Ag3PO4 because their suitable band positions could easily migrate photoinduced charge carriers at the hetero-interface.

The chemical composition of UMOFNs/Ag3PO4 was evaluated by X-ray photoelectron spectroscopy (XPS) measurements. Figure 7a gives the XPS survey spectrum of UMOFNs/Ag3PO4, which indicates UMOFNs/Ag3PO4 is composed of C, O, P, Ni, Co, and Ag. In addition, no peaks for other elements were observed, confirming UMOFNs/Ag3PO4 was of high purity. In Figure 7b, the C 1s spectrum of the composite photocatalyst has two peaks located at 284.5 and 288.1 eV. The strong peak at 284.5 eV corresponds to C=–C for aromatic hydrocarbons, while the small peak at 288.1 eV is associated with the C–O in carbonate species. Figure 7c shows the O 1s peak of the composite photocatalyst at 531.2 eV is associated with the Ni–O bond, Co–O bond, or hydroxyl oxygen. Figure 7d displays the P 2p spectrum of the composite photocatalyst, which is associated with the phosphorus from PO4−3. In Figure 7e, the Co 2p spectrum gives two main peaks at 781.2 and 785.2 eV. The former is associated with Co 2p3/2, while the latter corresponds to the shakeup satellite peak, indicative of the presence of Co2+.

It can be seen in Figure 7f that the composite photocatalyst showed two Ni 2p peaks located at 856.3 and 861.8 eV, which were attributed to the characteristic peak of Ni2+ (Ni 2p3/2) and its shakeup satellite peak, respectively. As shown in Figure 7g, the two peaks located at 367.9 and 373.9 eV were assigned to Ag 3d5/2 and Ag 3d3/2, indicating the presence of Ag+ in the composite photocatalyst.

2.2. Photocatalytic Activity of UMOFNs/Ag3PO4 Core–Shell Photocatalysts. The photocatalytic performance of the prepared photocatalysts was examined by measuring the degradation efficiency of 2-CP under visible light (Figures 8 and S4) and the apparent reaction rates (kapp) were obtained using pseudo-first-order rate equations (Figure S5). Figure S4 shows the photocatalytic degradation of 2-CP over UMOFNs/Ag3PO4 composite photocatalysts with different amounts of UMOFNs (1, 5, 10, 20, and 30%). Among the composite photocatalysts, UMOFNs/Ag3PO4 (5 wt %) showed the best photocatalytic performance. Hence, 5 wt % of UMOFNs content was selected as the optimal amount. As shown in Figure 8, 2-CP hardly deteriorated under visible-light irradiation without photocatalysts, which confirms any self-degradation of 2-CP could be neglected during the experiment. The tetrahedral Ag3PO4 with {111} facet showed higher photocatalytic performance than Ag3PO4 irregular spheres owing to the exposure of the {111} facet having high surface energy. Among the photocatalytic materials, tetrahedral UMOFNs/Ag3PO4 composite photocatalysts showed the best photocatalytic performance and complete degradation of 2-CP was achieved in only 7 min. The excellent photocatalytic performance resulted from the efficient separation of charge carriers and the large contact area at the hetero-interface between UMOFNs, Ag3PO4, and the Ag nanoparticles. In contrast, M-UMOFNs/Ag3PO4 prepared by mechanically mixing UMOFNs and Ag3PO4 exhibited lower photocatalytic performance compared with UMOFNs/Ag3PO4 core–shell photocatalysts prepared by sonication in an organic solvent. This further confirms that the formation of a core–shell structure occurred via an UMOFNs/Ag3PO4 chemical mixture rather than a physical mixture, leading to the efficient separation of photoinduced electron–hole pairs at the hetero-interface between the UMOFNs shell and Ag3PO4 core. UMOFNs were also unable to degrade 2-CP under visible-light irradiation. The kapp of 2-CP for various photocatalysts was calculated from the pseudo-first-order rate equations, according to the following equation

\[
\ln(C_0/C_t) = k_{app}t
\]

where \(C_0\) and \(C_t\) are the concentration of 2-CP before and after irradiation for \(t\) min, respectively. The \(k_{app}\) values of the Ag3PO4 spheres, Ag3PO4 tetrahedrons, UMOFNs/Ag3PO4 spheres, and UMOFNs/Ag3PO4 tetrahedrons were calculated as 0.026, 0.262, 0.047, and 0.782 min−1, respectively. The \(k_{app}\) for the UMOFNs/Ag3PO4 tetrahedrons was approximately 26 times higher than that of Ag3PO4 spheres.

The removal of total organic carbon (TOC) in the reaction system was analyzed to evaluate the photocatalytic mineralization abilities of Ag3PO4 and UMOFNs/Ag3PO4 (Figure S6). After visible-light irradiation for 120 min, the TOC removal percent reached 22.1 and 69.8% in the presence of Ag3PO4 and UMOFNs/Ag3PO4, respectively. This result indicates that the photocatalytic mineralization performance of UMOFNs/Ag3PO4 was higher than that of Ag3PO4, which is good agreement with the photocatalytic degradation results as described above.

It is known that the long stability of photocatalyst plays an important role in its practical application. Therefore, we conducted the cycle experiments using Ag3PO4 and UMOFNs/Ag3PO4 as shown in Figure 9. After three cycles, the photocatalytic performance of UMOFNs/Ag3PO4 remained at a high level, while that of Ag3PO4 significantly deteriorated. This result reflects the efficient charge separation at the hetero-interface; that is, the photoinduced electrons and holes effectively migrate to the surface of the composite, preventing the photocorrosion in the photocatalyst.

2.3. Photocatalytic Mechanism of UMOFNs/Ag3PO4 Core–Shell Photocatalysts. To further confirm the photocatalytic mechanism of 2-CP degradation by UMOFNs/Ag3PO4 under visible-light irradiation, the main reactive species was examined by using radical scavenging effects in the same way as the photocatalytic experiments (Figure 10). Ammonium oxalate (AO), t-butyl alcohol (TBA), and p-
benzoquinone (BQ) were used in the photocatalytic degradation system to quench h⁺, *OH, and O₂⁻, respectively. As seen in Figure 10, the degradation rate was hardly affected after the addition of TBA to the reaction solution. In contrast, the addition of BQ and AO suppressed the photocatalytic degradation of 2-CP. These results suggest that h⁺ and O₂⁻ were the major reactive species involved in the photocatalytic degradation of 2-CP by UMOFNs/Ag₃PO₄ under visible-light irradiation.

XRD patterns, PL spectra, and DRS of the photocatalysts before and after visible-light irradiation were examined to further support the mechanism of photocatalytic reaction for 2-CP degradation (Figure S7). In Figure S7a, peaks assigned to Ag⁰ at 38.2, 42.5, and 61.4° were observed in the used photocatalysts, indicating Ag⁺ was reduced to Ag⁰ during the photocatalytic reaction. Trace amounts of Ag⁰ in UMOFNs/Ag₃PO₄ composite photocatalyst play the role of electron trapping centers, which suppresses recombination of the photogenerated electron and hole in the photocatalytic process.

Figure 7. XPS (a) survey and (b) C 1s, (c) O 1s, (d) P 2p, (e) Co 2p, (f) Ni 2p, and (g) Ag 3d narrow spectra of UMOFNs/Ag₃PO₄.
reaction.2,52 On the other hand, an excessive amount of Ag metal particles can be found in pure Ag₃PO₄ after visible-light irradiation, which interferes with charge transfer, light adsorption, and contact with organic contaminants on Ag₃PO₄.50,53 These results also suggest that the formation of UMOFNs/Ag₃PO₄ composite leads to the effective transfer of photoinduced electrons on Ag₃PO₄ to UMOFNs and prevents excessive Ag reduction. As seen in Figure S7b, the recycled UMOFNs/Ag₃PO₄ photocatalyst shows much higher light adsorption in the visible region (400–800 nm) owing to the surface plasmonic resonance (SPR) effect of Ag nanoparticles.54 The PL emission intensity of the recycled UMOFNs/Ag₃PO₄ photocatalyst was lower than that of the fresh one (Figure S7c), indicating that charge separation was effectively promoted during the photocatalytic process because the trace amount of Ag⁰ nanoparticles acts as a charge separation center.54 The results obtained from these experiments explain that trace amounts of Ag⁰ were deposited in UMOFN/Ag₃PO₄ composite during the photocatalytic reaction, which can play roles of a photosensitizer and charge separation center.

From the above results, a possible mechanism of the photodegradation of 2-CP by UMOFNs/Ag₃PO₄ under visible light irradiation is shown in Figure 11. In the early stage of the photocatalytic process, Ag ions in UMOFNs/Ag₃PO₄ are reduced to Ag⁰ nanoparticles from photocorrosion of Ag₃PO₄ under visible-light irradiation. The trace amounts of Ag⁰ nanoparticles in the composite photocatalyst can act as a charge separation center, leading to the effective separation of photoinduced charge carriers at the interface between Ag₃PO₄ and UMOFNs.2 In the presence of visible light, Ag₃PO₄ can be activated when absorbing energy greater than the band gap of Ag₃PO₄, resulting in photoinduced holes and electrons in the valence band (VB) and the conduction band (CB), respectively. In addition, Ag⁰ nanoparticles also can be activated under visible-light irradiation through the SPR effect, resulting in the formation of electron–hole pairs.54 The photoelectrons in the Ag₃PO₄ are easily transferred to Ag⁰ nanoparticles and then recombine with the SPR-induced holes on Ag⁰ nanoparticles.50,56 As a result, the photocorrosion is prevented by the translation of electrons from the CB of Ag₃PO₄ to Ag⁰ nanoparticles, leading to the improved stability of the composite photocatalyst. On the other hand, the SPR-effect, resulting in the formation of electron–hole pairs.54 Replacing these electron–hole pairs with a photosensitizer could enhance the photocatalytic activity.

Figure 8. Photocatalytic degradation of 2-CP with various photocatalysts.

Figure 9. Cycling runs of 2-CP degradation with Ag₃PO₄ and UMOFNs/Ag₃PO₄.

Figure 10. Photocatalytic activities of UMOFNs/Ag₃PO₄ (5 wt %) photocatalyst on the photodegradation of 2-chlorophenol under visible-light irradiation in the presence of different scavengers.

Figure 11. Photocatalytic mechanism scheme of UMOFNs/Ag₃PO₄ under visible-light irradiation.
induced electrons on the Ag\textsuperscript{0} nanoparticles migrate to the CB of UMOFNs to reduce from O\textsubscript{2} to O\textsubscript{2}\textsuperscript{−}. As a result, the potential of CB of UMOFNs is high enough to produce O\textsubscript{2}\textsuperscript{−}. These reactive species exhibit a high oxidation power to degrade 2-CP. In contrast, the holes left on the VB of Ag\textsubscript{3}PO\textsubscript{4} directly oxidize 2-CP because of the inductive effect of the PO\textsubscript{4}\textsuperscript{3−} group and the high positive potential of the VB.\textsuperscript{7} The effective charge separation could be achieved in this reaction system under visible-light irradiation by the photocatalytic mechanism described above.

3. CONCLUSIONS

A highly efficient visible-light-responsive UMOFNs/Ag\textsubscript{3}PO\textsubscript{4} core−shell photocatalyst was successfully fabricated by sonication in an organic solvent. During the photocatalytic reaction, trace amounts of Ag nanoparticles were formed at the interface between the UMOFNs and Ag\textsubscript{3}PO\textsubscript{4}. These nanoparticles act as a charge separation center, leading to the efficient separation of the photoinduced charge carriers. The photocatalytic performance of UMOFNs/Ag\textsubscript{3}PO\textsubscript{4} was much higher than that of pure Ag\textsubscript{3}PO\textsubscript{4} under visible-light irradiation because of the highly reactive facets of the Ag\textsubscript{3}PO\textsubscript{4} tetrahedrons and the core−shell structure with a large interface area between UMOFNs, Ag\textsubscript{3}PO\textsubscript{4}, and Ag\textsubscript{0}. These results in this study show that the UMOFNs/Ag\textsubscript{3}PO\textsubscript{4} core−shell photocatalyst has great potential for practical application in environmental purification technology.

4. EXPERIMENTAL SECTION

4.1. Preparation of Photocatalyst.

All chemical reagents used in this study were analytical grade and used without further purification. Ag\textsubscript{3}PO\textsubscript{4} tetrahedrons were prepared by a kinetic control method.\textsuperscript{48} First, AgNO\textsubscript{3} (12 mmol) was dissolved in ethanol (80 mL) using ultrasound. After AgNO\textsubscript{3} completely dissolved, H\textsubscript{3}PO\textsubscript{4} (20 mL) was also mixed with ethanol (80 mL) and then the H\textsubscript{3}PO\textsubscript{4} solution was added to the AgNO\textsubscript{3} solution and sonicated for 1 h in the darkness. The resulting light-yellow product was collected by centrifugation, washed with ethanol four times, and desiccated to obtain the Ag\textsubscript{3}PO\textsubscript{4} tetrahedrons. To evaluate the effect of morphology on photocatalytic performance, Ag\textsubscript{3}PO\textsubscript{4} spheres were also prepared by a facile precipitation method.\textsuperscript{57} First, AgNO\textsubscript{3} (0.8 mmol) was dissolved in water (10 mL) using ultrasound. Then, Na\textsubscript{2}HPO\textsubscript{4} (1.0 mmol) was also dissolved in water (20 mL), and then the Na\textsubscript{2}HPO\textsubscript{4} solution and AgNO\textsubscript{3} solution were combined and magnetically stirred for 3 h in the darkness. The resulting yellow product was collected, washed four times with ethanol, and desiccated to obtain the Ag\textsubscript{3}PO\textsubscript{4} spheres.

UMOFNs were prepared according to a previous report.\textsuperscript{30} 1,3,5-Triformyl-2,4,6-trimethylbenzene (0.75 mmol) was added to a mixed solution of N,N-dimethylformamide (32 mL), ethanol (2 mL), and distilled water (2 mL) and thoroughly dissolved under ultrasonication. Next, CoCl\textsubscript{2}·6H\textsubscript{2}O (0.375 mmol) and NiCl\textsubscript{2}·6H\textsubscript{2}O (0.375 mmol) were added to the above solution. Then, triethylamine (0.8 mL) was quickly added dropwise to the solution and sonicated for 8 h under airtight condition. Finally, the obtained product was collected, washed with ethanol four times, and desiccated using a vacuum dryer.

The UMOFNs/Ag\textsubscript{3}PO\textsubscript{4} core−shell photocatalysts were fabricated by sonication in an organic solvent. The prepared Ag\textsubscript{3}PO\textsubscript{4} tetrahedrons were mixed with a solution of the desired amount of UMOFNs in tetrahydrofuran (100 mL). The mixture was then perfectly dispersed using ultrasound for 30 min. After dispersing, the reaction mixture was sonicated in the darkness for 6 h. The obtained product was collected by centrifugation, washed with ethanol four times, and desiccated to get the UMOFNs/Ag\textsubscript{3}PO\textsubscript{4} core−shell photocatalysts. UMOFNs/Ag\textsubscript{3}PO\textsubscript{4} composite photocatalysts with different amounts of UMOFNs were also fabricated following the same method.

4.2. Characterization of Photocatalyst.

A powder X-ray diffractometer (RIGAKU Ultima IV, sample horizontal type) equipped with a Cu Kα radiation source was used to measure the XRD patterns of the materials. The morphologies and particle sizes of the samples were analyzed by a Hitachi S-4000 SEM and a JEOL JEM-1011 TEM. Nitrogen adsorption−desorption measurements were carried out using a BEL-SORP-miniII (BEL, Japan) apparatus. A Spectrum 100 FTIR spectrometer (Perkin Elmer) equipped with an attenuated total reflection assembly was used to record the FTIR spectra of the photocatalysts. XPS analysis was performed on a PHI Quantera SXM photoelectron spectrometer with an Al Kα radiation source. The DRS of the photocatalysts were recorded using a Shimadzu UV-2450 spectrophotometer equipped with an integral sphere assembly. PL spectra of the photocatalysts were acquired by a Shimadzu RF-5300PC system with an excitation wavelength of 360 nm. The changes for TOC of the 2-CP solution were analyzed using a TOC-VE analyzer (Shimadzu, Japan).

4.3. Photocatalytic Degradation Activity.

To evaluate the photocatalytic performance of the photocatalysts, photodegradation of 2-CP was performed under visible-light irradiation (λ > 420 nm). The photocatalyst (30 mg) was added to 35 mL of aqueous 2-CP solution (30 mg/L) in a 50 mL Pyrex glass cell. Before irradiation, the 2-CP solution containing the photocatalyst was magnetically stirred for 30 min in the dark to reach an adsorption−desorption equilibrium between the photocatalyst and 2-CP. Then, the reaction solution was irradiated by a 300 W Xe lamp (MAX-303, Asahi Spectra) combined with a UV cut filter (L-42, HOYA). During the experiment, 2 mL aliquots were sampled from the reaction solution at specified intervals and centrifuged to remove the photocatalyst particles. The obtained solution was used to determine the concentration of residual 2-CP by high-performance liquid chromatography with a TSKgel ODS-100V column (internal diameter of 150 × 4.6 mm\textsuperscript{2}, TOSOH) and a GL-7450 UV detector (GL Science). An acetonitrile aqueous solution (water/acetonitrile = 50:50 v/v) was used for the mobile phase. The flow velocity was 1.0 mL/min, and the detector wavelength was 273 nm. For radical trapping experiments, various quenchers of reactive species were added to the reaction solution in a manner similar to the above photocatalytic experiment. The amounts of scavengers used were determined according to a previous work.\textsuperscript{59}

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02042.

XRD patterns of UMOFNs/Ag\textsubscript{3}PO\textsubscript{4} with different amounts of UMOFNs; nitrogen adsorption−desorption isotherms of UMOFNs, Ag\textsubscript{3}PO\textsubscript{4}, and UMOFNs/
Ag₃PO₄ with different amounts of UMOFs; VBXPS spectra of UMOFs, Ag₃PO₄; photocatalytic photo-degradation of 2-CP by UMOFs/Ag₃PO₄ composite photocatalysts with different amounts of UMOFs; TOC removal rate of 2-CP in the presence of Ag₃PO₄ and UMOFs/Ag₃PO₄; pseudo-first-order kinetic curves of various photocatalysts for 2-CP degradation; XRD patterns, DRS, PL spectra of UMOFs/Ag₃PO₄ (5 wt %) before and after visible-light irradiation (PDF)

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**Notes**

The authors declare no competing financial interest.

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