Synthesis of an Ag₃PO₄/Nb₂O₅ Photocatalyst for the Degradation of Dye

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Abstract: In this work, the photocatalytic performance of Ag₃PO₄, Nb₂O₅ and Ag₃PO₄/Nb₂O₅ hybrid photocatalysts to degrade methyl orange dye, MO, in an aqueous solution under visible light irradiation was evaluated. The Ag₃PO₄ and Ag₃PO₄/Nb₂O₅ photocatalysts, with various Ag to Nb molar ratios, were prepared using a facile precipitation method. The photocatalysts were characterized by X-ray diffraction, UV–Visible, X-ray Photoelectron, and Photoluminescence spectroscopies. Upon the addition of Ag₃PO₄, the band gap energy of Nb₂O₅ decreased from 3.0 eV to 2.7 eV, indicating the possible use of the Ag₃PO₄/Nb₂O₅ hybrid photocatalysts under visible light irradiation. All of the prepared Ag₃PO₄/Nb₂O₅ catalysts exhibited higher photocatalytic performance than Ag₃PO₄ in degrading methyl orange dye under 23-watt visible light irradiation. The Ag₃PO₄/Nb₂O₅ catalyst, with a mole ratio of 2:1, exhibited the fastest MO degradation rate of 7.3 × 10⁻² min⁻¹, which is twice faster than that of Ag₃PO₄. The catalyst also shows better stability, as it is reusable for up to six experimental cycles while maintaining its photocatalytic activity above 60%.

Keywords: Ag₃PO₄/Nb₂O₅; methyl orange; photocatalyst; photocatalytic activity; visible light

1. Introduction

Dyes, widely used in the textile, paint, ink, and paper industries, are the most significant chemical contaminants that cause water pollution [1]. Up to 200,000 tons of dyes are lost to effluents in textile industries every year during dyeing and finishing operations. The release of colored water in the effluents causes hazards and environmental problems. Since its discovery by Fujishima and Honda in 1972, heterogeneous photocatalysis has been widely explored as a water decontamination method [1]. Through heterogeneous photocatalysis, the complete mineralization of parents and their intermediate compounds is possible at ambient operating temperatures and pressures, and at low operational costs [2]. Nowadays, visible-light-driven photocatalysis has gained research interest, with Ag₃PO₄ being reported as a promising photocatalyst for the photodegradation of the aqueous dye solution. Its ability to utilize visible light irradiation is due to its narrow band gap energy. Unfortunately, self-photo corrosion is a significant problem, which means that the stability of Ag₃PO₄ remains an issue [3]. One of the initiatives to enhance the photocatalytic activity and the stability of the Ag₃PO₄ photocatalyst is by coupling it with other semiconductors, such as TiO₂ [4–6], ZnO [7], and CeO₂ [8]. This coupling method decreased the recombination probability of the electron-hole pairs, and enhanced the photocatalytic efficiency.
Niobium (V) oxide, Nb$_2$O$_5$, which has a band gap energy (3.4 eV), which is similar to TiO$_2$, is one of the promising photocatalysts, as it exhibits excellent photocatalytic performance in the photodegradation of dyes [9]. Although Souza et al. (2016) reported similar catalytic activity between Nb$_2$O$_5$ and TiO$_2$-P25 in the degradation of textile wastewater [10], Prado and his co-workers (2008) showed that Nb$_2$O$_5$ is a more stable photocatalyst as it successfully maintained its 85% catalytic activity in indigo carmine degradation after ten reaction cycles [11].

This work aimed to produce a stable visible-light-driven photocatalyst by coupling Ag$_3$PO$_4$ with Nb$_2$O$_5$. There are very few works on Ag$_3$PO$_4$/Nb$_2$O$_5$ photocatalysts available in the literature [3]. To the best of our knowledge, using a fluorescence lamp (23 W) as a source of light irradiation to degrade a dye over Ag$_3$PO$_4$/Nb$_2$O$_5$ photocatalysts has not been reported. Previously, the degradation of rhodamine B over Ag$_3$PO$_4$/Nb$_2$O$_5$ under simulated sunlight irradiation (Xe, 600 W) was reported [3]. In this work, Ag$_3$PO$_4$/Nb$_2$O$_5$ photocatalysts were synthesized via the deposition–precipitation method, and their photocatalytic activity was evaluated by the photodegradation of methyl orange (MO) under fluorescent light (23 W) irradiation. The experiments were performed under various parameters in order to determine the best-suited conditions for the degradation of MO. The effect of scavengers and a reusability test were conducted in order to determine the active species responsible for the degradation, and to evaluate the stability of the catalysts, respectively.

2. Results

2.1. Characteristics of the Photocatalysts

Figure 1 shows the XRD patterns of the Ag$_3$PO$_4$, Nb$_2$O$_5$, and Ag$_3$PO$_4$/Nb$_2$O$_5$ catalysts. All of the diffraction peaks of pure Ag$_3$PO$_4$ and Nb$_2$O$_5$ were in good agreement with those of the cubic phase of Ag$_3$PO$_4$ (JCPDS No. 010840510) and the orthorhombic phase of Nb$_2$O$_5$ (JCPDS No. 000271003), respectively. The XRD pattern of the Ag$_3$PO$_4$/Nb$_2$O$_5$ catalysts clearly shows peaks of Ag$_3$PO$_4$ and Nb$_2$O$_5$, confirming the presence of these materials in their pristine form in the Ag$_3$PO$_4$/Nb$_2$O$_5$ composite. The peak intensity of Ag$_3$PO$_4$ also increased corresponding to the increase in the content of Ag$_3$PO$_4$ in the catalyst.

Figure 1. XRD patterns of the pure Nb$_2$O$_5$, pure Ag$_3$PO$_4$, and the prepared Ag$_3$PO$_4$/Nb$_2$O$_5$ photocatalysts.
The optical response of the catalysts in the visible light region was determined using the UV–Vis DRS spectrum. The data collected was transformed using the Kubelka-Munk function, and the band gap energy was extrapolated from the intercept of the x-axis of the Tauc plot (Figure 2). The band gap energy of Nb2O5 (3.3 eV) and Ag3PO4 (2.3 eV) is similar to the values reported in the literature [3,12]. Upon the addition of Ag3PO4, the band gap energy of Nb2O5 slightly decreased to 3.2 eV.

The optical properties and band structure of the samples were further evaluated using steady-state photoluminescence analysis. The results are presented in Figure 3. For the Nb2O5, two broad peaks ranged from (i) the UV region: 350 nm to 400 nm, and (ii) the visible region: 400 nm to 550 nm. From Figure 3b, the first deconvoluted peak (blue) can be ascribed to the near band edge emission of the bulk Nb2O5 samples, whereas the second peak (green) can be referred to as the defect-assisted band alignment transition [13]. The Ag3PO4 sample also showed a broad emission peak from 400 nm to 600 nm, which can be deconvoluted into four peaks via Gaussian function analysis. The peaks were located at the wavelength 425 nm (violet), 480 nm (blue), 525 (green), and 575 nm (green). This result is consistent with the literature, stating that the carrier recombination arose from the shallow defect between the [PO4] and highly distorted tetrahedral [AgO4] clusters [14]. Upon the incorporation of Ag3PO4 into the Nb2O5 at a 1:1 molar ratio, it was found that the PL emission at the visible region from 400 nm to 600 nm (shallow defect) was quenched. This phenomenon signifies that the carrier recombination becomes more dominant in the heterojunction structure than the direct band edge at UV region of Nb2O5 (blue region in Figure 3b). In order to further evaluate the peak quenching, a normalised peak with respect to the direct band edge of Nb2O5 (382 nm) was conducted for all of the Ag3PO4/Nb2O5 samples. The result is presented in Figure 3d. It can be observed that the further increases of the Ag content in Nb2O5 have proved to suppress the PL intensity further in the shallow defect states, as compared to the Ag3PO4 sample. None of the defect states were observed in the Nb2O5 semiconductor material. This observation may be attributed to the agglomeration of the Ag3PO4 cluster, which contributed to the bulk trapping states. It is also worth mentioning that the increased Ag concentration can alter the charged polarization between the distorted Ag cluster, and could eventually promote intrinsic and extrinsic defect trapping states in the electronic structure of the Nb2O5 semiconductor materials. The plausible charge transfer mechanism is illustrated in Figure 3e. For the Nb2O5 sample, a charge transfer only occurred between the valance band and the conduction band.
band of the semiconductor material. For the Ag$_3$PO$_4$/Nb$_2$O$_5$ sample, a charge carrier was photoexcited from the valance band to the conduction band of Nb$_2$O$_5$ under the simulated sunlight. The charge carrier was later transferred to the conduction band of Ag$_3$PO$_4$ before it further underwent the reduction process with the analyte during the photodegradation process. Therefore, it is believed that the Ag$_3$PO$_4$/Nb$_2$O$_5$ semiconductor materials served as better photocatalysts than Nb$_2$O$_5$ owing to its two charge transfer pathways, which lower the direct carrier recombination in the Nb$_2$O$_5$ semiconductor.

Figure 3. (a) Photoluminescence spectra of Nb$_2$O$_5$, Ag$_3$PO$_4$, and Ag:Nb nanocomposite with different molar ratios, and the deconvoluted sample for (b) Nb$_2$O$_5$ and (c) Ag$_3$PO$_4$. (d) the normalized peaks for all of the samples with respect to 382 nm of the direct band edge emission of Nb$_2$O$_5$. (e) the plausible charge transfer mechanism in Nb$_2$O$_5$ and Ag$_3$PO$_4$/Nb$_2$O$_5$ semiconductor materials.

The XPS spectrum of the 2:1 Ag:Nb photocatalyst (Figure 4)—which shows the presence of Ag, P, O, and Nb—verified the coexistence of Ag$_3$PO$_4$ and Nb$_2$O$_5$ in the composite. The peaks at 284.8 eV and 286.3 eV for C 1s belong to contaminant carbon C–C or C–O (Figure 4b). The peaks with the binding energy of 370.4 eV and 376.4 eV in the high-resolution XPS spectrum of Ag 3d (Figure 4c) are assigned to Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$, indicating the existence of Ag$^+$ in the composite [15]. The peak of P 2p, observed at 132.6 eV (Figure 4d), is due to the $P^{5+}$ of the phosphate. The deconvolution of the O 1s spectrum (Figure 4e) resulted in two peaks at 531.0 eV and 532.8 eV. The former corresponds to a crystal lattice oxygen of Ag$_3$PO$_4$ [16,17] and Nb$_2$O$_5$ [18,19]; the latter could be derived from the hydroxyl group on the surface of the catalyst. The high resolution of Nb 3d (Figure 4f) peaked for
Nb 3d$_{5/2}$ at 207.3 eV, and Nb 3d$_{3/2}$ at 210.0 eV corresponds to Nb$^{5+}$, in good agreement with the binding energy of Nb$_2$O$_5$ [20].

The morphology of Ag$_3$PO$_4$, Nb$_2$O$_5$, and Ag$_3$PO$_4$ /Nb$_2$O$_5$ was illustrated in Figure 5. All of the samples exhibit similar morphology, being irregular spherical shapes. The image of Ag$_3$PO$_4$/Nb$_2$O$_5$ showed the severe agglomeration of the particles. EDX was employed in order to detect the elemental composition in the Ag$_3$PO$_4$/Nb$_2$O$_5$ composite photocatalyst, and the data are listed in Table 1. The as prepared catalyst different atomic percentage of Ag, Nb, P, and O. Based on the atomic percentage of Nb$_2$O$_5$ and Ag$_3$PO$_4$, the compositions of the catalysts were closely correlated with the mole ratio used in the preparation of the samples.

Table 1. The elemental composition of the Ag$_3$PO$_4$/Nb$_2$O$_5$ catalyst, as detected by EDX.

| Sample         | Elemental Composition (Atom %) | Ag:Nb |
|----------------|-------------------------------|-------|
|                | 3Ag  | 2Nb  | P   | O   |       |
| Ag:Nb (1:1)    | 13.37 | 7.83 | 4.14 | 74.66 | 4.4:4.0 |
| Ag:Nb (2:1)    | 21.93 | 6.97 | 6.43 | 64.67 | 7.3:3.5 |
| Ag:Nb (3:1)    | 30.18 | 6.73 | 8.86 | 54.23 | 10.1:3.3 |

The BET surface area and particle size determination of the Ag$_3$PO$_4$, Nb$_2$O$_5$, and Ag$_3$PO$_4$/Nb$_2$O$_5$ composite photocatalysts were analyzed by N$_2$ adsorption/desorption and Zetasizer; the data are summarized in Table 2. Based on the results, as the Ag$_3$PO$_4$ loading increased in the composites, a larger aggregate particle size was clearly observed compared to pristine Ag$_3$PO$_4$ and Nb$_2$O$_5$. 

Figure 4. (a) XPS survey spectrum and high resolution spectra of (b) C 1s, (c) Ag 3d, (d) P 2p, (e) O 1s, and (f) Nb 3d of 2:1 Ag:Nb.
Figure 4. (a) XPS survey spectrum and high resolution spectra of (b) C 1s, (c) Ag 3d, (d) P 2p, (e) O 1s, and (f) Nb 3d of 2:1 Ag:Nb.

Figure 5. The morphology of the (a) Ag$_3$PO$_4$, (b) Nb$_2$O$_5$, and (c) Ag$_3$PO$_4$/Nb$_2$O$_5$ (Ag:Nb = 2:1).

Table 2. Particle size and BET surface area of the prepared catalysts.

| Sample          | Particle Size (µm) | BET Surface Area (m$^2$g$^{-1}$) |
|-----------------|-------------------|-----------------------------------|
| Ag$_3$PO$_4$    | 0.89 ± 0.11       | 1.63                              |
| Nb$_2$O$_5$     | 0.68 ± 0.06       | 6.92                              |
| Ag:Nb (1:1)     | 1.02 ± 0.11       | 1.70                              |
| Ag:Nb (2:1)     | 1.17 ± 0.09       | 0.89                              |
| Ag:Nb (3:1)     | 1.31 ± 0.12       | 1.07                              |

The incorporation of Ag$_3$PO$_4$ into Nb$_2$O$_5$ resulted in the reduction of the surface area, which is attributed to the method of preparation. When contacted with the Nb$_2$O$_5$, the Ag$^+$ ions would be adsorbed onto the Nb$_2$O$_5$ surface, possibly near the mouth of the pore or in the pore of Nb$_2$O$_5$. When the phosphate solution was added into the solution mixture, Ag$^+$ would react to precipitate Ag$_3$PO$_4$ on the Nb$_2$O$_5$. The formation of Ag$_3$PO$_4$ in the pore or on the mouth of the pore of Nb$_2$O$_5$ would block the pore, hence reducing the accessibility of the N$_2$ gas to the adsorption sites. Consequently, the prepared catalysts exhibited a lower surface area compared to pristine Nb$_2$O$_5$ and Ag$_3$PO$_4$.

2.2. Photocatalytic Activity

The photocatalytic activity of the prepared photocatalysts was evaluated by the photodegradation of methyl orange, and the results are as shown in Figure 6. The degradation of MO by Nb$_2$O$_5$ was insignificant because it is inactive under visible light irradiation due to its wide band gap energy. The Ag$_3$PO$_4$ and Ag$_3$PO$_4$/Nb$_2$O$_5$ photocatalysts, however, exhibited a similar percentage of MO degradation, ranging from 91 to 96%. The experiment data was then fitted to the pseudo-first-order kinetic in order to determine the rate constant for the reaction. The MO degradation rate was faster when using Ag$_3$PO$_4$/Nb$_2$O$_5$ catalysts. The reaction rate initially increased with increasing Ag$_3$PO$_4$ loading up to a ratio of 2:1 before it decreased at a higher loading (3:1), which could be due to the agglomeration of...
Ag\textsubscript{3}PO\textsubscript{4} particles on the surface of the Nb\textsubscript{2}O\textsubscript{5}. Because of its highest MO degradation rate (rate constant = 0.073 min\textsuperscript{-1}), the Ag:Nb = 2:1 was the suitable photocatalyst for this study.

Figure 6. Plot of (a) the percentage degradation and (b) ln C\textsubscript{0}/C against the irradiation time for the pure Ag\textsubscript{3}PO\textsubscript{4}, pure Nb\textsubscript{2}O\textsubscript{5}, and Ag:Nb = 1:1, Ag:Nb = 2:1 and Ag:Nb = 3:1 photocatalysts.

Several factors influence photocatalytic efficiency, including the mass of the photocatalyst and the concentration of the pollutant. Figure 7 shows the photodegradation activity using a various amount of Ag:Nb = 2:1 photocatalyst and the initial concentration of MO. The MO degradation rate increases with increasing catalyst mass, up to 0.5 g, before it decreases at a higher catalyst mass [21]. The use of an excessive amount of catalyst loading reduces the degradation activity by increasing the light scattering effect and the opacity of the solution. It also leads to the aggregation of the catalyst and reduces the interfacial area between the reaction solution and the photocatalyst. The fastest rate of degradation was observed when degrading 5 ppm of MO. The MO degradation rate, however, decreased with the increasing MO initial concentration. This decrement may occur due to the light screening effect, which reduces the photon’s path length and the number of photons that arrive on the surface of the catalyst. Thus, it reduces the generation of electron-hole pairs, and consequently the photocatalytic activity of the photocatalyst [22].

\begin{align*}
\text{y} &= 0.0356x \\
R^2 &= 0.9667 \\
\text{y} &= 0.0038x \\
R^2 &= 0.8817 \\
\text{y} &= 0.0611x \\
R^2 &= 0.9715 \\
\text{y} &= 0.0729x \\
R^2 &= 0.9859 \\
\text{y} &= 0.0515x \\
R^2 &= 0.9577 \\
\text{y} &= 0.0356x \\
R^2 &= 0.9667 \\
\text{y} &= 0.0611x \\
R^2 &= 0.9715 \\
\text{y} &= 0.0729x \\
R^2 &= 0.9859 \\
\text{y} &= 0.0515x \\
R^2 &= 0.9577 \\
\end{align*}
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In order to determine the species responsible for the photodegradation, 10 mL of a scavenger solution—such as ethylene diamine tetraacetic acid (EDTA), tert-butanol, or benzoquinone (BQ)—was added to the MO solution. These solutions scavenge the h⁺,
OH, and O$_2^-$ radicals, respectively. In the absence of the scavengers, the photocatalytic degradation of MO was 96% (Figure 8). Upon the addition of the EDTA and BQ solutions, the photodegradation decreased significantly to 1% and 32%, respectively. However, there was no significant effect on the photodegradation efficiency observed with the addition of tert-butanol. These results demonstrate that the h$^+$ and O$_2^-$ species are responsible for the photodegradation of MO.

![Figure 8](image-url-for-fig8)

**Figure 8.** Comparison of the photocatalytic activities of the Ag:Nb = 2:1 photocatalyst with different scavengers during the photocatalytic reaction under 60 min visible light irradiation.

### 2.3. Reusability of the Ag$_3$PO$_4$/Nb$_2$O$_5$ Photocatalyst

The catalyst’s lifetime is an essential parameter of the photocatalytic degradation process, so it is crucial to evaluate the catalyst’s reusability for practical applications. As shown in Figure 9, the decrease in the photocatalytic efficiency of the Ag:Nb = 2:1 photocatalyst was gradual, but remained above 60% up to the fifth cycle of the photodegradation experiment. This gradual loss might be due to the self-photo corrosion of Ag$_3$PO$_4$. The enhanced photocatalytic activity and stability of the Ag:Nb = 2:1 photocatalyst may be due to the insoluble Nb$_2$O$_5$ layer, which can effectively protect the dissolution of Ag$_3$PO$_4$ to Ag$^+$ ions, thus improving the structural stability of the photocatalyst.

![Figure 9](image-url-for-fig9)

**Figure 9.** Reusability of the Ag:Nb = 2:1 photocatalyst in MO degradation.
3. Materials and Methods

3.1. The Synthesis of the $\text{Ag}_3\text{PO}_4/\text{Nb}_2\text{O}_5$ Photocatalyst

$\text{Ag}_3\text{PO}_4/\text{Nb}_2\text{O}_5$ photocatalysts with different $\text{Ag}_3\text{PO}_4$ to $\text{Nb}_2\text{O}_5$ mole ratios were prepared via a facile deposition–precipitation method. In a typical experiment, a fixed amount of $\text{Nb}_2\text{O}_5$ (Merck, Darmstadt, Germany) was dispersed in 150 mL deionized water and sonicated for 30 min. Various amounts of $\text{AgNO}_3$ salt (Merck, Germany) were added into the solution mixture and magnetically stirred for 30 min. In total, 150 mL of disodium hydrogen phosphate and $\text{Na}_2\text{HPO}_4$ (Fisher Scientific, Shah Alam, Malaysia) solution were added dropwise into the solution mixture with continuous stirring. The mole ratio of $\text{AgNO}_3$ to $\text{Na}_2\text{HPO}_4$ was kept constant at 3:1 in order to produce the $\text{Ag}_3\text{PO}_4$ catalyst. The yellow precipitate formed was collected by filtration, washed several times with distilled water and ethanol, and dried in an oven at 80°C overnight. The final product was ground and characterized before being used in the photodegradation studies. A similar procedure, without the addition of $\text{Nb}_2\text{O}_5$, was employed to produce a pure $\text{Ag}_3\text{PO}_4$ photocatalyst.

3.2. Characterization of the Catalyst

The crystalline phase of the catalysts was analyzed using an XRD 6000 (Shimadzu, Kyoto, Japan) with Cu-Kα radiation, operated at $\lambda = 1.54$ nm, 30 kV, and 40 mA. The morphology and elemental composition of the catalysts were determined using a FESEM Nova Nanosem 230 (Fei, Eindhoven, The Netherlands) integrated with an energy dispersive X-ray detector. A fluorescence spectrophotometer (Perkin Elmer LS55, Waltham, MA, USA) with a wavelength excitation of 290 nm was used to record the photoluminescence spectra of the samples. The UV–vis diffuse reflectance spectra were recorded by a Shimadzu UV 3101 spectrophotometer at a wavelength between 220 and 800 nm. The chemical state of the elements was analysed using Auger Electron Spectroscopy with an X-Ray Photoelectron Spectrometer (Axis Ultra DLD, Kratos, Manchester, UK). The BET surface area was obtained by the application of BET modelling, conducting in TriStar II Plus (Micromeritics, Norcross, GA, USA). The particle size measurement was determined by Zetasizer, (Malvern Instruments, Worcestershire, UK).

3.3. Photoactivity of the $\text{Ag}_3\text{PO}_4/\text{Nb}_2\text{O}_5$ Photocatalyst

The photodegradation of methyl orange dye (MO) was performed in a glass photoreactor, as shown in Figure 10. A fixed amount of photocatalyst was added into 0.5 L of 10 ppm MO solution and stirred in the dark for 30 min. Air was bubbled into the solution throughout the experiment in order to ensure a constant supply of oxygen. During irradiation with a compact fluorescent lamp (23 W, Phillips, 1600 Lumens), an aliquot of the sample was withdrawn from the bulk solution at predetermined time intervals and filtered to remove catalyst particles. The samples were analyzed using UV–vis Perkin-Elmer Lambda 30 spectrophotometer at $\lambda_{\text{max}}$ of 464.4 nm in order to determine the MO dye’s residual concentration. The percentage of degradation and the amount of MO degraded are calculated using Equations (1) and (2), respectively:

$$\% \text{Degradation} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

$$\text{Amount of degraded (mg/g)} = \frac{C_0 - C_t \left( \frac{\text{mass}}{\text{g}} \right)}{\text{mass of catalyst (g)}} \times V \,(L) \quad (2)$$

where $C_0$ is the initial MO concentration, $C_t$ is the MO concentration at a time ‘$t$’, and $V$ is the volume of the MO solution used in the reaction.
Figure 10. Schematic representation of the photocatalytic reactor for the photodegradation of methyl orange.

3.4. Reusability Test

The reusability of the catalyst was evaluated by performing several cycles of MO photodegradation in the best-suited conditions. Once the first experiment ended, the treated MO solution was removed by decantation after the catalyst had settled at the bottom of the photoreactor. A fresh MO solution was then added to the reactor in order to start the next cycle.

4. Conclusions

The Ag$_3$PO$_4$/Nb$_2$O$_5$ photocatalysts, synthesized via the deposition–precipitation method, exhibited irregular and spherical shapes with a surface area of 0.89–1.70 m$^2$/g. The catalysts also showed a faster MO degradation rate than Ag$_3$PO$_4$. Ag$_3$PO$_4$/Nb$_2$O$_5$, and a molar ratio of 2:1 showed the highest photocatalytic degradation of 10 ppm MO (96%) with a catalyst loading of 0.5 g. The incorporation of Nb$_2$O$_5$ in Ag$_3$PO$_4$ enhanced the catalysts’ photocatalytic performance and stability, and thus can be used effectively under visible light irradiation for up to five cycles. h$^+$ and •O$_2^-$ are the main active species for the degradation.

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