Fabrication and characterization of high efficiency and stable Ag/AgFeO$_2$/Ag$_3$PO$_4$ ternary heterostructures nanocatalyst

Zhe Song$^1$ · Gangsheng Huang$^1$ · Haotian Wei$^1$ · Bowen Chen$^1$ · Zhuhui Liao$^1$ · Ruiyang Liu$^1$ · Zhaohui Dai$^1$ · Yiqiang He$^2$

Received: 29 December 2021 / Accepted: 27 April 2022 / Published online: 3 June 2022
© The Author(s), under exclusive licence to Springer-Verlag GmbH, DE part of Springer Nature 2022

Abstract
An Ag/AgFeO$_2$/Ag$_3$PO$_4$ ternary was synthesized by hydrothermal method with polyvinylpyrrolidone (PVP). The composite materials were characterized by XRD, SEM, TEM, DRS and XPS. XRD, SEM and TEM results are used to characterize the structure and morphology of Ag/AgFeO$_2$/Ag$_3$PO$_4$ samples, DRS results are mainly used to characterize the light absorption capacity of Ag/AgFeO$_2$/Ag$_3$PO$_4$ samples. Photocatalytic results showed that the photocatalytic performance of Ag/AgFeO$_2$/Ag$_3$PO$_4$ photocatalyst was significantly improved, which was 10.6 times than that of pure AgFeO$_2$. The optimal photocatalyst can degrade MO (Methyl Orange) up to 98% in 1 h. Simultaneously, the cyclic experiments showed that it had good stability, from 80% for Ag/AgFeO$_2$/Ag$_3$PO$_4$ to 58% for pure Ag$_3$PO$_4$ after five cycles. To obtain further insight into the high photooxidative activity of AgFeO$_2$, ab initio density functional theory (DFT) calculations have also been carried out. The mechanism study shows that the synergistic effect of heterojunction and strong SPR of silver nanorods make the catalyst have higher photocatalytic performance and better stability.

Keywords AgFeO$_2$ · Ag/AgFeO$_2$/Ag$_3$PO$_4$ · Photocatalyst · SPR

1 Introduction
Semiconductor photocatalysis has received extensive attention and rapid development, which provides an ideal method for energy utilization and environmental pollution control. In view of the efficient utilization of solar energy, a large number of active photocatalysts for visible light have been studied in recent years [1, 2]. For example, Ag$_2$S-Au, AgBr@rGO, Ag$_3$PO$_4$@PANI [3–5] and other photocatalysts show good photocatalytic effects. [6] Silver orthophosphate (Ag$_3$PO$_4$) is an excellent basis for visible light-driven photocatalyst. Previous studies have shown that Ag$_3$PO$_4$ has an indirect bandgap of 2.45 eV [7, 8], which can absorb visible light and generate photoexcited holes. Ag$_3$PO$_4$ has good oxidation activity due to high positive potential in the valence band (VB), and the electron mobility is significantly higher than that of holes. [9]
However, there are still some problems that limit its development. One is photo corrosion of photoexcited electrons under light irradiation, and the other is greater solubility in water [10]. The above factors seriously reduced the stability of Ag$_3$PO$_4$. So far, coupling of Ag$_3$PO$_4$ with semiconductors such as Fe$_2$O$_3$ [11], AgI [12], ZnO [13], NiFe$_2$O$_4$ [14], CeO$_2$ [15], BiOI [16], graphene [17], TiO$_2$ [18], AgX (X = Cl, Br, I) [19] and g-C$_3$N$_4$ [20] can alleviate these adverse effects and accelerate photoinduced charge separation [21]. To sum up, the Ag/AgFeO$_2$/Ag$_3$PO$_4$ composite nano-heterojunction photocatalyst was constructed by adjusting the experimental conditions, which enabled it to have excellent photocatalytic REDOX ability, non-toxicity and low cost.

As a new type of photocatalyst, compound oxide AgFeO$_2$ has a relatively narrow bandgap of 1.31 eV [22, 23], which can expand the range of visible light absorption and has good photocatalytic performance in theory. However, the narrow bandgap leads to a high electron-hole recombination rate, which limits the development of AgFeO$_2$ as a photocatalyst. To improve the photocatalytic performance of AgFeO$_2$, it is attempted to couple AgFeO$_2$ with other semiconductors, such as AgFeO$_2$/g-C$_3$N$_4$ [24], AgCl/Ag/AgFeO$_2$ [25] and Ag/AgFeO$_2$ [26], all of which show good photocatalytic performance. An Ag/AgFeO$_2$/Ag$_3$PO$_4$ composite semiconductor nanomaterial was prepared by hydrothermal synthesis. In Ag/AgFeO$_2$/Ag$_3$PO$_4$ ternary heterostructure photocatalyst, elemental silver protects Ag$_3$PO$_4$ from photocorrosion in photocatalytic reaction, thus improving the stability of Ag$_3$PO$_4$ photocatalyst. In addition, the heterostructure of Ag$_3$PO$_4$/Ag/AgFeO$_2$ can promote the transport of photogenerated carriers and effectively separate electron-hole. The mechanism of photocorrosion inhibition and photocatalytic activity enhancement was discussed.

2 Experimental

2.1 Materials

All reagents utilized in the work are of analytical purity. Reagents polyvinylpyrrolidone (PVP, Mw = 58000), silver nitrate (AgNO$_3$), Iron (III) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O), ammonium hydroxide (NH$_3$·H$_2$O), were purchased from different manufacturers, corresponding to Shanghai Macklin Biochemical Co. Ltd, Tianjin Yingda Rare Chemical Reagents Factory, Xilong Scientific Co. Ltd, Tianjin Kemiou Chemical Reagent Co. Ltd, respectively. Besides, ethanol (C$_2$H$_5$OH), sodium hydroxide (NaOH), and sodium Dihydrogen Phosphate (NaH$_2$PO$_4$) were all bought from Beijing Chemistry Company, China. All the materials were used directly without further treatment.

2.2 Catalyst preparation

2.2.1 Synthesis of Ag/AgFeO$_2$ composite

In a typical synthesis process, Ag/AgFeO$_2$ was prepared by the flowing steps. First, 8 g PVP (Mw = 58000) was solved in 50 ml distilled water. Then, 0.85 g AgNO$_3$ and 2.02 g Fe(NO$_3$)$_3$·9H$_2$O were first added to the solution followed by fierce stirring for 30 min. Sodium hydroxide (NaOH) solution (1.5 g, 10 ml) was added drop by drop to the above solution to form an alkaline system, and the resulting mixture was then stirred for another 20 min. The mixed solution was transferred to an autoclave for hydrothermal reaction at 100 °C for 12 h. The precipitates were collected by centrifuging at a speed of 5000 rpm and washed with anhydrous ethanol and distilled water repeatedly 3 times. Finally, it was dried in an oven at 60 °C for 12 h. The acquired Ag/AgFeO$_2$ samples were sealed and stored before use.

2.2.2 Preparation of different molar ratio of Ag/AgFeO$_2$/Ag$_3$PO$_4$ sample

The Ag$_3$PO$_4$ nanoparticles were loaded onto the crystallized Ag/AgFeO$_2$ samples by a deposition-precipitation method. Preparation of Ag/AgFeO$_2$/Ag$_3$PO$_4$ (mole ratio is 2:1 of Ag$_3$PO$_4$ to Ag/AgFeO$_2$) sample: AgNO$_3$ (1.02 g, 6 mmol) was dissolved in 25 ml ultrapure water. Then ammonia aqueous solution (1.0 M) was dropwise added to the above solution to form a transparent solution. Afterward, 1 mmol of as-prepared Ag/AgFeO$_2$ (0.196 g) was added and stirred drastically for 30 min. 0.312 g of NaH$_2$PO$_4$ dissolved in 10 ml deionized water and on the electromagnetic stirrer forms NaH$_2$PO$_4$ solution, after that the solution was added dropwise in the preceding suspension within 20 min of stirring. The product was collected from the solution by centrifugation and washed with anhydrous ethanol and distilled water repeated for 3 times. Finally, it was dried in an oven at 60 °C for 12 h. Different Ag/AgFeO$_2$/Ag$_3$PO$_4$ samples were synthesized through the same method as the preparation of Ag/AgFeO$_2$/Ag$_3$PO$_4$ (mole ratio is 2:1) sample, just adjusted the mole ratio of AgNO$_3$ and NaH$_2$PO$_4$. Corresponding names are AFP-0.5 (mole ratio is 0.5:1), AFP-1 (mole ratio is 1:1), AFP-2 (mole ratio is 2:1), AFP-3 (mole ratio is 3:1) and AFP-4 (mole ratio is 4:1), respectively, AFP means Ag/AgFeO$_2$/Ag$_3$PO$_4$ ternary compounds. The synthesis process of pure Ag$_3$PO$_4$ was similar without adding Ag/AgFeO$_2$.

2.3 Material characterization techniques

The crystalline structure of AFP composites was explored by X-ray diffraction (XRD) using an instrument (BRUKER-D8)
with Cu Kα radiation (Cu Kα radiation, accelerating voltage = 30 kV, applied current = 40 mA, scan range 10–80°). The morphological features of the composites were imaged by scanning electron microscopy (SEM; SU8000, Hitachi, Japan) and transmission electron microscopy (TEM; JEOLJE-2010). UV–vis diffuse reflectance spectra were recorded on a UV–vis spectrometer (Puxi, UV1901). X-ray photoelectron spectroscopy (XPS) was carried out on a K-Alpha X-ray photoelectron spectrometer (Thermo Scientific).

2.4 Photocatalytic experiments

The photocatalytic activity of AFP was investigated using an aqueous solution of MO (10 mg/L) at 298 K via a thermostatic bath. Experimental process was as follows: 100 ml of MO aqueous solution and 0.05 g of as-prepared AFP samples were placed in a glass vessel to form a suspension under stirring. After that suspensions were magnetically stirred in dark for 20 min to establish adsorption/desorption equilibrium between the photocatalyst and dye aqueous solution. Then, a 300 W xenon lamp was used as a light source to provide simulated solar light irradiation. During the illumination, 3 ml of suspension was drawn from the reaction vessel at regular time intervals and centrifuged at 5000 rpm for 10 min to get the supernatant. The degradation of organic dyes was analyzed by measuring the absorbance of samples at 466 nm (MO) with UV–Vis absorption spectra.

3 Results and discussion

3.1 Electronic property calculation of AgFeO₂

The spatial structure of AgFeO₂ is edge-connected O-Ag⁷⁺-O octahedra and edge-shared Fe³⁺O₆ octahedra (Fig. 1a). So far, AgFeO₂ crystals have two varieties of shapes and morphologies such as 3R structure and 2H structure. Based on the GGA and GGA+U calculations by Ong and co-workers, it was demonstrated they have the same bandgap for 3R and 2H, which was calculated to be 1.15 eV and 1.7 eV, respectively [22, 23]. Furthermore, Shuxin Ouyang et al. described the crystal structure and found that (AgMO₂ (M) Al, Ga, In) has a narrower bandgap at 3R than at 2H, which favors the photoproduction hole migration and thus a stronger oxidation capacity. Therefore, we mainly study the structures of 3R-type AgFeO₂.

As the key photocatalyst, the electronic structures of 3R-type oxide AgFeO₂ were examined by using the ab initio density functional theory (DFT) calculations. The corresponding results are as follows: band structures are shown in Fig. 1(b), and it had a direct bandgap of about 1.31 eV, which agreed well with the previously calculated result [22, 23]. It’s easy noting that valence bands and conduction bands are so close that could cause harm to the transport of photexcited electrons and holes. This in turn may result in a high electron-hole recombination rate, thus account for the low photocatalytic activity [7]. Furthermore, the density of state (DOS) and the project density of state (PDOS) of AgFeO₂ are depicted in Fig. 1c–f, and there are some points that should be explained. One is the existence of strong hybridization at energy from −7 to −2 eV, and another is the top of the VB next to Fermi level are dominating contributed from O 2p orbital. Therefore, an improved photocatalyst will be based on AgFeO₂, supplemented with Ag, Ag₃PO₄ to form a ternary heterojunction, solving the problem of the high recombination rate of AgFeO₂, and achieve the best catalytic effect.

3.1.1 XRD analyses

X-ray diffraction (XRD) was explored to determine the composition and crystallographic structure of obtained samples, and the results are shown in Fig. 2. And they could be illustrated in two main steps. First, Fig. 2a shows the XRD patterns of Ag/AgFeO₂ photocatalysts with different masses of PVP. There are two characteristic peaks that are marked and belong to the Ag and AgFeO₂ structures, respectively. Moreover, it could be observed the characteristic diffraction peaks of Ag structures gradually strong up to 8 g when the masses of PVP increase, indicating the decoration of more Ag nanorods onto AgFeO₂ surfaces. And second, in the case of AFP samples, there are three groups of standard diffraction peaks that can be clearly assigned to corresponding samples, as presented in Fig. 2b, respectively. Characteristic peaks at 33.30, 35.40, and 38.10 correspond to (210)(Ag₃PO₄, JCPDS file No. 70-0702), (012)(AgFeO₂, JCPDS file No. 75-2147) and (111)(Ag, JCPDS file No. 99-0094) planes, respectively. [27–29] Besides, for the pattern of the AFP-2 sample, no other peaks of any impurities are observed, indicating that Ag₃PO₄ have been deposited on Ag/AgFeO₂ composite with success.

3.1.2 Morphology analysis

Further characterization of the morphologies and microstructures of obtained samples was studied by scanning electron microscopy (SEM) and high-resolution TEM (HR-TEM). As shown in Fig. 3, the uniform dispersion and structures of Ag/AgFeO₂ were observed in the larger scale image of Fig. 3a, and Ag nanorods were formed over the entire surface of the AgFeO₂ cakes. The high-magnification image Fig. 3b showed clearly that Ag nanorods were uniform in size with the estimated average diameter ranging from 68 to 125 nm, which may favor the electron transfer in ternary heterostructures system. And Fig. 3c shows the SEM image.
Fig. 1  a Crystal structure, b band structure and c DOS of AgFeO$_2$, together with PDOS of d Ag atom, e Fe atom and f O atom
of the pure $\text{Ag}_3\text{PO}_4$, they were found to consist of agglomerated grains composed of irregular particles (2–5 μm). As for $\text{Ag}/\text{AgFeO}_2/\text{Ag}_3\text{PO}_4$ ternary heterostructures (Fig. 3d), by adjusting the molar ratio of $\text{Ag}_3\text{PO}_4$, $\text{Ag}_3\text{PO}_4$ particles grown to the surface of $\text{Ag}/\text{AgFeO}_2$ composites were obtained, which indicates an intimate contact between $\text{Ag}_3\text{PO}_4$ and $\text{Ag}/\text{AgFeO}_2$. Because $\text{Ag}_3\text{PO}_4$ and $\text{AgFeO}_2$ are too similar to be distinguished, the AFP-2 composite was further investigated by HRTEM to ascertain the decoration of $\text{Ag}_3\text{PO}_4$ on the surface of $\text{Ag}/\text{AgFeO}_2$. As shown in its TEM image (Fig. 4), these $\text{Ag}_3\text{PO}_4$ particles were in intimate contact with the $\text{AgFeO}_2$, and the lattice fringes of $\text{AgFeO}_2$ could be clearly identified, which have a spacing of 0.306 nm (012 planes, JCPDS file No. 75-2147).

### 3.1.3 XPS analysis

The elemental composition and chemical states of AFP-2 composite were investigated by the XPS technique, to reveal more detailed information about the $\text{Ag}/\text{AgFeO}_2/\text{Ag}_3\text{PO}_4$
ternary heterostructures, and the results are shown in Fig. 5. First, the full XPS spectrum (Fig. 5a) shows that the AFP-2 sample consists of major elements Fe, Ag, P and O. Then in Fig. 5b, the P 2p peak is located at 133.4 eV. The bands at 710.3 and 723.9 eV in Fig. 5c were assigned to Fe 2p3/2 and Fe 2p1/2 peaks. And for O 1s XPS spectrum (Fig. 5d), the peak at 529.3 eV could be attributed to the lattice oxygen in Ag3PO4 and AgFeO2. Finally, and most importantly, it should be noticed the analysis results of the XPS spectrum of Ag 3d. In Fig. 5e, the stronger peaks at 368.8 and 374.8 eV could be confirmed as Ag0 on the surface of AgFeO2, in consistent with the SEM and HRTEM result. And the rest peaks at 367.6 and 373.5 eV corresponding to Ag 3d5/2 and Ag 3d3/2 are Ag+ (Fig. 5f). [30, 31]

3.2 UV–vis DRS

UV–vis diffuse reflectance spectra (DRS) were used to explore the optical absorption abilities of obtained samples, and the results were displayed in Fig. 6. From Fig. 6a, as compared to pure Ag3PO4, the Ag/AgFeO2 and AFP-2 photocatalysts both showed better performance in the visible light region of 400 to 800 nm, and the enhanced visible light absorption capability of AFP-2 suggests that it might have higher photocatalytic activity for degradation. [32, 33]

On the other hand, the bandgap energy (Eg) of these two samples was calculated based on the DRS results to evaluate the optical absorption performance. As can be seen in Fig. 6b, the bandgap energy of Ag/AgFeO2 and pure Ag3PO4 is about 1.14 and 2.61 eV, respectively. The calculation of semiconductor bandgap width is mainly based on the formula proposed by Tauc, Davis, Mott et al., commonly known as Tauc Plot. The calculation formula is as follows: (ahv)n = A(hv-Eg). [34–36] Comparing with the theoretical calculation result above (1.35 eV), the Eg of Ag/AgFeO2 is slightly lower which could be assigned to the SPR effect of Ag nanorods formed on the AgFeO2 surface. When Ag/AgFeO2 and Ag3PO4 are doped, Ag3PO4 increases the density of oxygen vacancy on the Ag/AgFeO2 surface could act as an electron trap that could hinder the electron-hole recombination and in turn increase the photo-catalytic degradation, the lower bandgap values also indicated it may have the better photocatalytic capability. [37, 38] Thus, the photocatalytic performance potentiality of the obtained samples was further demonstrated by the results above.

3.2.1 Photocatalytic activity of the photocatalyst

The photocatalytic behaviors of obtained catalysts for the MO degradation under visible light are shown in Fig. 7. As can be seen in Fig. 7a, compared with the photocatalytic activities of Ag/AgFeO2 samples (degradation efficiency of MO was only approximately 25%), approach to 98% of MO was degraded with 60 min irradiation in the presence of AFP-2 photocatalyst, which proved its superior photocatalytic activity. Moreover, the proper molar ratio of Ag3PO4 to Ag/AgFeO2 can greatly improve the photocatalytic activity, indicating the heterojunction was formed well, which was also demonstrated above. Meanwhile, Fig. 7b illuminated the MO structure (a model pollutant with a major absorption band at 466 nm) was successfully destructed by the AFP-2 photocatalyst. On the other hand (As shown in Fig. 7c), the kinetics of these photocatalytic reactions can be described using a pseudo-first-order kinetic model ln(C0/C) = kt (where C0 is the premier MO solution and C is the MO concentration at time t, the slope k is the first-order kinetic rate constant) for MO solutions. In comparison, the apparent rate constants for pure Ag/AgFeO2 and AFP-2 photocatalyst are 0.0053 min–1 and 0.0521 min–1, respectively (see Fig. 7d), it is 10.6 times higher than that by pure Ag/AgFeO2 (Table 1).

3.2.2 Photocatalytic stabilities of photocatalyst

Besides the improvement of photocatalytic activities, the enhancement stability for Ag3PO4 is also one of the key points of the article, via the fabrication of Ag/AgFeO2/Ag3PO4 ternary heterostructures system. As is known, the stability of a photocatalyst is very important for a photocatalyst to be useful. To study the stability and reusability of Ag/AgFeO2/Ag3PO4 ternary heterostructures system, used AFP-2 composite powder was collected and reused in five successive MO degradation experiments, this result was showed in Fig. 8. Although some photocatalytic activity losses are observed for the AFP-2 photocatalyst after five times reutilization (but still retained over 80% of its original activity), the rate of MO degradation over pure Ag3PO4 decreased more significantly in the similar conditions (decreasing from 98 to 58%). These results demonstrate Ag/AgFeO2/Ag3PO4 ternary heterostructures system is very stable.
3.3 Reaction mechanism

3.3.1 Effects of reactive species

Radical-trapping experiments with different scavengers were employed to clarify the main active species worked during the photocatalytic degradation of MO and thus determine the reaction mechanism. Figure 9 clearly shows that HO, O$_2^-$ and h$^+$ were detected using isopropanol (IPA), benzoquinone (BQ), and ammonium oxalate (AO) as trapping agents, respectively, which all were 1 mmol/L. As depicted in Fig. 8, h$^+$ was not the active species in the reaction, since the addition of AO did not significantly inhibit the photocatalytic reaction. In contrast, the addition of IPA and BQ showed a significant effect on the photocatalytic degradation (decreased obviously from 90 to 20%), which suggested the HO- and O$_2^-$ radicals can play a significant role in the photodegradation under visible light irradiation.

On the basis of the above analysis, a possible mechanism for the degradation of MO of Ag/AgFeO$_2$/Ag$_3$PO$_4$ composite under visible irradiation is illustrated in Fig. 10.
As is known, both Ag$_3$PO$_4$ and AgFeO$_2$ can be excited to generate electrons and holes when irradiated by visible light [26, 43]. On the one hand, all holes generated in the VB of Ag$_3$PO$_4$ could easily transfer to AgFeO$_2$ for the valence band of AgFeO$_2$ has a higher value than that of Ag$_3$PO$_4$, then the holes in the VB of AgFeO$_2$ could oxidize H$_2$O to form HO•.

Fig. 6 UV–vis diffuse reflectance spectra (a) and the bandgap energy (Eg) of Ag$_3$PO$_4$ and Ag/AgFeO$_2$ composites (b).

Fig. 7 a MO degradation dynamics curves over different catalysts under visible light irradiation, b time-dependent UV–vis absorption spectra of MO solution over AFP-2 and kinetic curves of MO degradation over c the as-obtained samples in this work and (d)
radicals, which are then involved in the photodegradation reaction of MO [44]. They determine the efficiency of the whole photocatalytic reaction. On the other hand, as shown in Fig. 9, the direct coupling of Ag nanowires and AgFeO₂ causes the Fermi level to equilibrate which could attain an energy level close to the conduction band of AgFeO₂ [45, 46], and the conduction band of Ag₃PO₄ is very close but lower than that of AgFeO₂, so the delicately matched band structures of Ag₃PO₄, AgFeO₂ and Ag, are very favorable for the excited electrons to transfer from the conduction bands of Ag₃PO₄ and AgFeO₂ to the newly rebuilt surface energy band of Ag. Further, the excited electrons (Ag) could be trapped by molecular oxygen in solution to form ·O₂⁻ and other oxidative species [47]. Simultaneously, the effective migration of interfacial electrons could prevent the photocorrosion of Ag₃PO₄ (the photo-corrosion of Ag₃PO₄ in the absence of electron acceptors), which guarantees stability of the whole photocatalytic system. Hence, the photocatalytic activity of AgFeO₂ and the photocatalytic stability of Ag₃PO₄ were greatly improved by the SPR effect of Ag in two ways, more amounts of electrons and holes generation as well as superior charge carrier separation rate [48–50].

4 Conclusions

In this work, novel Ag/AgFeO₂/Ag₃PO₄ ternary heterostructures were successfully prepared by simple hydrothermal and solution co-precipitation method for the first time. As a novel ternary heterostructured Ag/AgFeO₂/Ag₃PO₄ photocatalyst, it showed excellent photocatalytic activity and stability for organic pollutants degradation, the degradation of MO over AFP-2 composite photocatalyst reached 98% within 1 h and remained 80% after five cycling runs. On the basis of the above analysis, the enhanced photocatalytic activity and stability could be attributed to a synergistic effect, which includes the effective separation of charge carriers under the SPR effect, the energy band structure match of the selected components (Ag, AgFeO₂ and Ag₃PO₄) and high structural stability of AgFeO₂. More attractively, this kind of Ag/AgFeO₂/Ag₃PO₄ ternary heterostructures photocatalysts could provide new insight for the design and fabrication of narrow bandgap photocatalysts like AgFeO₂.
Funding This work was financially supported by the Program of the “12th Five” Science and Technology Research of Education Department of Jilin Province ([2014]268).

Data availability Derived data supporting the findings of this study are available from the corresponding author on request.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Open access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third-party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

1. K. Fujishima, Honda, electrochemical photolysis of water at a semiconductor electrode. Nature 238, 37–38 (1972). https://doi.org/10.1038/238037a0
2. G.F. Liao, J.S. Fang, Q. Li, S. Li, Z.S. Xu, B.Z. Fang, Ag-Based nanocomposites: synthesis and applications in catalysis. Nanoscale 11, 7062–7096 (2019). https://doi.org/10.1039/c9nr01408j
3. Z.Z. Lou, S. Kim, M. Fujitsuka, X.G. Yang, B.J. Li, T. Majima, Anisotropic Ag₅S-Au triangular nanorods with desired configuration for plasmonic photocatalytic hydrogen generation in visible/near-infrared region. Adv. Funct. Mater. (2018). https://doi.org/10.1002/adfm.201706969
4. F.Y. Chen, W.J. An, L. Liu, Y.H. Liang, W.Q. Cui, Highly efficient removal of bisphenol A by a three-dimensional graphene hydrogel-AgBr@rGO exhibiting adsorption/photocatalysis synergy. Appl. Catal. B 217, 65–80 (2017). https://doi.org/10.1016/j.apcatb.2017.05.078
5. L. Liu, L. Ding, Y.G. Liu, W.J. An, S.L. Lin, Y.H. Liang, W.Q. Cui, A stable Ag₃PO₄@PANI core@shell hybrid: enrichment photocatalytic degradation with π-π conjugation. Appl. Catal. B 201, 92–104 (2017). https://doi.org/10.1016/j.apcatb.2016.08.005
6. O. Akhavan, Lasting antibacterial activities of Ag–TiO₂/Ag/a-TiO₂ nanocomposite thin film photocatalysts under solar light irradiation. J. Colloid Interface Sci. 336, 117–124 (2009). https://doi.org/10.1016/j.jcis.2009.03.018
7. Z.G. Yi, J.H. Ye, N. Kikugawa, T. Kako, S.X. Ouyang, H. Stuart-Williams, H. Yang, J.Y. Cao, W.J. Luo, Z.S. Li, Y. Liu, R.L. Withers, An orthophosphate semiconductor with photoxidation properties under visible-light irradiation. Nat Mater. 9, 559–564 (2010). https://doi.org/10.1038/nmat2780
8. J.W. Xu, Z.D. Gao, K. Han, Y.M. Liu, Y.Y. Song, Synthesis of magnetically separable Ag₃PO₄/TiO₂/Fe₃O₄ heterostructure with enhanced photocatalytic performance under visible light for photoinactivation of bacteria. ACS Appl Mater Interfaces. 6, 15122–15131 (2014). https://doi.org/10.1021/am5032277
9. S.X. Ouyang, N.K. Kikugawa, D. Chen, Z.G. Zou, J.H. Ye. A systematical study on photocatalytic properties of AgMO₃ (M = Al, Ga, In): effects of chemical compositions, crystal structures, and electronic structures. J. Phys. Chem. C 113, 1560–1566 (2009). https://doi.org/10.1021/jp806513t
10. C. Cui, Y.P. Wang, D.Y. Liang, W. Cui, H.H. Hu, B.Q. Lu, S. Xu, X.Y. Li, C. Wang, Y. Yang, Photo-assisted synthesis of Ag₃PO₄/reduced graphene oxide/Ag heterostructure photocatalyst with enhanced photocatalytic activity and stability under visible light. Appl. Catal. B 158–159, 150–160 (2014). https://doi.org/10.1016/j.apcatb.2014.04.007
11. Y.H. Yan, H.Y. Guan, S. Liu, R.Y. Jiang, Ag₃PO₄/Fe₃O₄ composite photocatalysts with an n–n heterojunction semiconductor structure under visible-light irradiation. Ceram. Int. 40, 9095–9100 (2014). https://doi.org/10.1016/j.ceramint.2014.01.123
12. J. Yan, C. Wang, H. Xu, Y.G. Xu, X.J. She, J.J. Chen, Y.H. Song, H. Li, Q. Zhang. AgI/Ag₃PO₄ heterojunction composites...
Fabrication and characterization of high efficiency and stable Ag/AgFeO$_2$/Ag$_3$PO$_4$ ternary…

13. C. Jin, G.L. Liu, L.H. Zu, Y. Qin, J.H. Yang, Preparation of Ag@Ag$_3$PO$_4$/ZnO ternary heterostructures for photocatalytic studies. J Colloid Interface Sci. 453, 36–41 (2015). https://doi.org/10.1016/j.jcis.2015.03.066

14. G.Y. Zhao, L.J. Liu, J.R. Li, Q. Liu, Efficient removal of dye MB: through the combined action of adsorption and photodegradation from NiFe$_2$O$_4$/Ag$_3$PO$_4$. J. Alloy. Compd. 664, 169–174 (2016). https://doi.org/10.1016/j.jallcom.2016.01.004

15. Z.M. Yang, G.F. Huang, W.Q. Huang, J.M. Wei, X.G. Yan, Y.Y. Liu, C. Jiao, Z. Wan, A. Pan, Novel Ag$_3$PO$_4$/CeO$_2$ composite with high efficiency and stability for photocatalytic applications. J. Mater. Chem. 2, 1750–1756 (2014). https://doi.org/10.1039/c3ta14286h

16. Y.Q. Wang, X.F. Cheng, X.T. Meng, H.W. Feng, S.G. Yang, C. Sun, Preparation and characterization of Ag$_3$PO$_4$/BiOI heterostructurephotocatalyst with highly visible-light-induced photocatalytic properties. J. Alloy. Compd. 632, 445–449 (2015). https://doi.org/10.1016/j.jallcom.2014.11.231

17. X.F. Yang, H.Y. Cui, Y. Li, J.L. Qin, R.X. Zhang, H. Tang, Fabrication of Ag$_3$PO$_4$/graphene composites with highly efficient and stable visible light photolytic performance. ACS Catal. 3, 363–369 (2013). https://doi.org/10.1021/cs3008126

18. W.F. Yao, B. Zhang, C.P. Huang, C. Ma, X.L. Song, Q.J. Xu, Synthesis and characterization of high efficiency and stable Ag$_3$PO$_4$/TiO$_2$ visible light photocatalyst for the degradation of methylene blue and rhodamine B solutions. J. Mater. Chem. (2012). https://doi.org/10.1039/c2jm14410g

19. Y.P. Bi, S.X. Ouyang, J.Y. Cao, J.H. Ye, Facile synthesis of rhombic dodecahedral Ag$_x$Ag$_3$PO$_4$ (X = Cl, Br, I) heterocrystals with enhanced photocatalytic properties and stabilities. Phys Chem Chem Phys. 13, 10071–10075 (2011). https://doi.org/10.1039/c3cp02488h

20. S. Kumar, T. Surendar, A. Baruah, V. Shanker, Synthesis of a novel and stable c-C$_x$N$_y$-Ag$_3$PO$_4$ hybrid nanocomposite photocatalyst and study of the photocatalytic activity under visible light irradiation. J. Mater. Chem. A. (2013). https://doi.org/10.1039/c3ta00186e

21. M.R. Gholipour, C.T. Dinh, F. Béland, T.O. Do, Nanocomposite heterojunctions as sunlight-driven photocatalysts for hydrogen production from water splitting. Nanoscale 7, 8187–8208 (2015). https://doi.org/10.1039/c4nr07224c

22. K.P. Ong, K. Bai, P. Blaha, P. Wu, Electronic structure and optical properties of AFeO$_2$ (A: Ag, Cu) within GGA calculations. J. Alloy. Compd. 634–640 (2007). https://doi.org/10.1016/j.jallcom.2006.01.449

23. H.M. Mukhair, A.H. Abdullah, Z.K. Zainal, H.N. Lim, PES-APES/AgNPs-APES composite membranes with controlled silver ion release for antibacterial and water treatment applications. Mater. Sci. Eng C 62, 732–745 (2016). https://doi.org/10.1016/j.msec.2016.02.025

24. O. Akhavan, E. Ghaderi, Self-accumulated Ag nanoparticles on mesoporous TiO$_2$ thin film with high bactericidal activities. Surf. Coat. Technol. 204, 3676–3683 (2010). https://doi.org/10.1016/j.surfcoat.2010.04.048

25. D.D. Tang, G.K. Zhang, Ultrasonic-assistant fabrication of cocoon-like Ag/AgFeO$_2$ nanocatalyst with excellent plasmon enhanced visible-light photocatalytic activity. Ultrason. Sonochem. 37, 208–215 (2017). https://doi.org/10.1016/j.ulsoch.2017.01.010

26. U. Sulaeman, F. Febiyanto, S. Yin, T. Sato, The highly active saddle-like Ag$_3$PO$_4$ photocatalyst under visible light irradiation. Catal. Commun. 85, 22–25 (2016). https://doi.org/10.1016/j.catcom.2016.07.001

27. J. Tauc, R. Grigorovici, A. Vancu, Optical properties and electronic structure of a morphous germanium. Basic solid state physics. Phys. Status Solidi 15, 627–637 (1966). https://doi.org/10.1002/pssb.19660150224

28. M.R. Tubbs, Optical properties of solids. Nature 241, 75 (1973). https://doi.org/10.1038/241075a0

29. E.A. Davis, N.F. Mott, Conduction in non-crystalline systems V. Conductivity, optical absorption and photocconductivity in amorphous semiconductors. Philos. Mag. 22, 179 (1970). https://doi.org/10.1080/14786437008221061

30. F.S. Omar, H. Nay Ming, S.M. Hafiz, L.H. Ngee, Microwave synthesis of zinc oxide/ reduced graphene oxide hybrid for adsorption-photocatalysis application. Int J Photoenergy (2014). https://doi.org/10.1155/2014/176835

31. J. Puneeth, K. Nagaraju, A. Rathna, Investigation of photocatalytic degradation of crystal violet and its correlation with bandgap in ZnO and ZnO/GO nanohybrid. Inorg. Chem. Commun. (2021). https://doi.org/10.1016/j.inoche.2021.108460

32. H.M. Mukhair, A.H. Abdullah, Z.K. Zainal, H.N. Lim, PES-APES/Ag$_3$PO$_4$/c-C$_x$N$_y$ mixed matrix film photocatalyst for degradation of methyl orange dye. Polymers 13, 1746 (2021). https://www.mdpi.com/2073-4360/13/11/1746.

33. Y. Feng, J. Shen, Q. Cai, H. Yang, Q. Shen, The preparation and properties of a c-C$_x$N$_y$/AgBr nanocomposite photocatalyst based on protonation pretreatment. New J. Chem. 39, 1132–1138 (2015). https://doi.org/10.1039/c4nj01433b

34. Y. He, L. Zhang, X. Wang, Y. Wu, H. Lin, L. Zhao, W. Weng, H. Wan, M. Fan, Enhanced photodegradation activity of methyl orange over Z-scheme type MoO$_3$/c-C$_x$N$_y$ composite under visible light Irradiation. RSC Adv. 4, 13610–13619 (2014). https://doi.org/10.1039/c4ra00693c

35. H. Xu, J. Yan, Y. Xu, Y. Song, H. Li, J. Xia, C. Huang, H. Wan, Novel visible-lightdriven AgX/graphite-like c-C$_x$N$_y$ (X = Br, I) hybrid materials with synergistic photocatalytic activity. Appl.
43. H.Y. Hu, Z.B. Jiao, T. Wang, J.H. Ye, G.X. Lu, Y.P. Bi, Enhanced photocatalytic activity of Ag/Ag₃PO₄ coaxial hetero-nanowires. J. Mater. Chem. A. (2013). https://doi.org/10.1039/c3ta12061a

44. L. Liu, Y.H. Qi, J.R. Lu, S.L. Lin, W.J. An, Y.H. Liang, W.Q. Cui, A stable Ag₃PO₄@g-C₃N₄ hybrid core@shell composite with enhanced visible light photocatalytic degradation. Appl. Catal. B 183, 133–141 (2016). https://doi.org/10.1016/j.apcatb.2015.10.035

45. W.S. Wang, H. Du, R.X. Wang, T. Wen, A.W. Xu, Heterostructured Ag₃PO₄/AgBr/Ag plasmonic photocatalyst with enhanced photocatalytic activity and stability under visible light. Nanoscale 5, 3315–3321 (2013). https://doi.org/10.1039/c3nr00191a

46. T.J. Yan, J. Tian, W.F. Guan, Z. Qiao, W.J. Li, J.M. You, B.B. Huang, Ultra-low loading of Ag₃PO₄ on hierarchical In2S3 microspheres to improve the photocatalytic performance: the cocatalytic effect of Ag and Ag₃PO₄. Appl. Catal. B 202, 84–94 (2017). https://doi.org/10.1016/j.apcatb.2016.09.017

47. Y.P. Bi, H.Y. Hu, S.X. Ouyang, Z.B. Jiao, G.X. Lu, J.H. Ye, Selective growth of metallic Ag nanocrystals on Ag₃PO₄ submicro-cubes for photocatalytic applications. Chemistry 18, 14272–14275 (2012). https://doi.org/10.1002/chem.201201435

48. D.B. Ingram, P. Christopher, J.L. Bauer, S. Linic, Predictive model for the design of plasmonic metal/semiconductor composite photocatalysts. ACS Catal. 1, 1441–1447 (2011). https://doi.org/10.1021/cs200320h

49. Y. Lu, H.T. Yu, S. Chen, X. Quan, H.M. Zhao, Integrating plasmonic nanoparticles with TiO₂ photonic crystal for enhancement of visible-light-driven photocatalysis. Environ. Sci. Technol. 46, 1724–1730 (2012). https://doi.org/10.1021/es202669y

50. T. Torimoto, H. Horibe, T. Kameyama, K.I. Okazaki, S. Ikeda, M. Matsumura, A. Ishikawa, H. Ishihara, Plasmon-enhanced photocatalytic activity of cadmium sulfide nanoparticle immobilized on silica-coated gold particles. J. Phys. Chem. Lett. 2, 2057–2062 (2011). https://doi.org/10.1021/jz2009049

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.