High-efficiency visible-light-driven Ag$_3$PO$_4$ photocatalysts modified by conjugated polyvinyl alcohol derivatives

Xuewang Zhu$^1$, Yaxin Shi$^1$, Qingzhi Luo$^{2,4}$, Jing An$^1$, Rong Yin$^1$, Xueyan Li$^1$ and Desong Wang$^{1,2,3,4}$

$^1$ School of Sciences, Hebei University of Science and Technology, Shijiazhuang 050018, People’s Republic of China
$^2$ Metastable Materials Science and Technology State Key Laboratory, Yanshan University, Qinhuangdao, 066004, People’s Republic of China
$^3$ School of Materials Science and Engineering, Hebei University of Technology, Tianjin, 300401, People’s Republic of China
$^4$ Authors to whom any correspondence should be addressed.

E-mail: lqz2004-1@163.com, dswang06@126.com and wangdesong@hebust.edu.cn

**Keywords:** photodegradation, photoreduction, CDPVA, Ag$_3$PO$_4$, composite

Supplementary material for this article is available online

**Abstract**

Due to its high-efficiency Ag$_3$PO$_4$ serves as a photocatalyst driven by visible light, which in this study was prepared through surface modification using a small amount of conjugated polyvinyl alcohol derivatives (CDPVA) via a simple chemisorption and heat treatment approach. The as-prepared CDPVA/Ag$_3$PO$_4$ composite photocatalysts were characterized via a variety of analyses. The photocatalytic performance of the as-prepared composite photocatalysts was estimated through the photodegradation of methyl orange solution and the photoreduction of aqueous Cr(VI) solution with visible light. Results showed that the introduction of a trivial part of CDPVA on the surface of Ag$_3$PO$_4$ particles did not change their crystallinity and sizes but significantly reduced the aggregation of particles, strengthened the visible-light absorbance, and produced a more efficient separation of the photogenerated electron–hole pairs in the investigated composite photocatalysts. The visible-light photocatalysis of the composites exhibited a higher stability and activity than pure Ag$_3$PO$_4$. The visible-light photocatalysis of the composites exhibited an initial rise and a later reduction with increase in CDPVA content in the composites and heat treatment temperature and time. The synthetic photocatalysts exhibited the strongest visible-light photocatalysis when the CDPVA to Ag$_3$PO$_4$ mass ratio, heat treatment temperature, and treatment time were 1: 8000, 180 °C, and 1 h respectively. The mechanism for visible-light photocatalysis of the CDPVA/Ag$_3$PO$_4$ composites was also investigated. The solubility of Ag$_3$PO$_4$ in water environment was significantly decreased by the surface modification of CDPVA.

1. Introduction

During the past decades, more and more focus has been paid to the design and synthesis of highly visible-light-driven photocatalysts because of their practical potential during production process of hydrogen from photocatalytic water splitting, decrease of CO$_2$ into reusable chemical fuel, and alleviation of pollution under solar irradiation [1–6]. Highly efficient photocatalytic activity was achieved with Silver orthophosphate (Ag$_3$PO$_4$) in O$_2$ production from photoxidated water and photodegraded organic pollutants under visible-light irradiation. It could accomplish an impressive quantum efficiency as high as 90% with wavelengths above 420 nm, which implies a quite low rate of recombinated electron–hole pairs [5–10]. Therefore, Ag$_3$PO$_4$-based photocatalysts belongs to a rather promising solution for the environmental contamination and energy crisis [11]. However, several drawbacks generally restrict the large-scale application of Ag$_3$PO$_4$ photocatalyst. Firstly, photocatalytic activity for Ag$_3$PO$_4$ under the visible-light is featured with a low stability during photocatalysis because of massive transformation of Ag$^+$ into Ag° by photogenerated electrons. Second, Ag$_3$PO$_4$ easily dissolves in water media owing to its large solubility, producing a decrease in visible-light driven photocatalytic activity [12].
A series of methods were proposed to address the limitations of using Ag₃PO₄; such methods include noble metal deposition (Ag, Au, and Pt) [13–15], composites with other semiconductors (TiO₂, ZnO, AgX (X = Cl, Br, I), CdS, and g–C₃N₄) [16–25], modification by carbon materials (carbon quantum dots, carbon nanotubers, and graphene and its derivatives) [24–30]. Given the excellent electron-capturing ability of Ag, Au, and Pt nanoparticles, the photogenerated electrons in Ag₃PO₄ can be easily transferred to these nanoparticles, thereby producing a more efficient separation of photogenerated electron–hole pairs and decreasing the amount of the photogenerated electrons on the Ag₃PO₄ surface; the use of these particles can thus enhance photocatalytic activity driven by visible light and decrease the reduction probability of Ag⁺ to form Ag°. Ag₃PO₄ photocatalysts modified by the other semiconductors or carbon materials display enhanced photocatalytic activity driven by visible light because of the well band gap match between Ag₃PO₄ and other semiconductors or the excellent electron transfer ability of carbon materials. However, these noble metal nanoparticles, other semiconductors, or carbon materials cannot uniformly and continuously cover the Ag₃PO₄ surface to decrease the transfer of Ag⁺ to Ag and the solubility of Ag₃PO₄ in water; as such, improvement in the chemical composition stability and photocatalytic stability in the water environment is hindered. Therefore, developing a novel strategy for preparing Ag₃PO₄-based photocatalysts with high stability and activity and stable chemical composition in water media is a valuable research direction.

Polyvinyl alcohol (PVA) with flexible macromolecular chains is a widely used water-soluble polymer. Conjugated derivatives from PVA (CDPVA) can be easily formed with heated PVA to a temperature range of 180°C–270°C (scheme 1); these conjugated derivatives exhibit physical and chemical properties similar to those of typical organic semiconductors, such as polyaniline and polythiophene [31, 32]. The conjugated PVA derivatives can be used for enhancing visible-light photocatalytic performance to modify inorganic semiconductors. Therefore, surface modification of Ag₃PO₄ particles by a little CDPVA could evidently enhance photocatalytic performance driven by visible light, including stability and activity.

In this work, Ag₃PO₄ particles were dispersed in PVA solution to adsorb PVA macromolecules to the adsorption–desorption equilibrium. After rapid filtration and drying, the PVA molecules uniformly and continuously covered on the Ag₃PO₄ surface. The obtained PVA/Ag₃PO₄ composites were treated at 180 °C to prepare CDPVA/Ag₃PO₄ composite photocatalysts. The photocatalysts were evaluated with XRD, Raman, XPS, SEM, UV–vis DRS, PL, and EIS analyses. Visible-light photocatalytic performance was studied by evaluating the photodegradation of MO (methyl orange) solution and the photoreduction of aqueous Cr(VI) solution irradiated by visible light. The solubility of pure Ag₃PO₄ and CDPVA/Ag₃PO₄ composites in water was then tested, and the possible photocatalytic mechanism governing the composite was studies through several experiments of reactive species trapping.

2. Experimental

2.1. Materials and instruments

Materials and Instruments are shown in S1.

2.2. Preparation of CDPVA/Ag₃PO₄ composite photocatalysts and photocatalytic activity measurement

Scheme 2 presents the idealized preparation process. The detailed description of the process is shown in S2.

The visible-light photocatalytic activity of pure Ag₃PO₄ and CDPVA/Ag₃PO₄ composites was evaluated by the photodegradation of MO solutions and the photoreduction of aqueous Cr(VI) solution under visible light irradiation. The typical processes are shown in S3.

3. Results and discussion

3.1. Composition and microstructure

3.1.1. SEM

The morphology of the investigated photocatalysts was analyzed through SEM, as illustrated in figure 1. Pure Ag₃PO₄ particles display regular sphere with rough surface and have size within 200–400 nm. CDPVA/Ag₃PO₄...
(1: 8000) particles possess similar shape and size to those of pure Ag₃PO₄ but with smooth surface and decreased agglomeration because of the presence of the CDPVA layer on the Ag₃PO₄ surface.

3.1.2. XRD and Raman spectra

The XRD patterns of CDPVA/Ag₃PO₄(1: 8000) and pure Ag₃PO₄ particles are shown in Figure 2(a). Diffraction spectrum for pure Ag₃PO₄ exhibit clearer peaks at 20.93, 29.76, 33.37, and 36.66°, which correspond to the planes (110), (200), (210), and (211) for cubic Ag₃PO₄ phase (ICPDS Card No. 01–089–7399), respectively. CDPVA/Ag₃PO₄ (1: 8000) presents the same XRD spectrum as that of pure Ag₃PO₄, revealing that CDPVA coated on Ag₃PO₄ particles surface produces little alteration of Ag₃PO₄ crystal structure. The absence of characteristic peaks of CDPVA is attributable to its low crystallinity and poor content in the composites.

Figure 2(b) displays spectra for CDPVA/Ag₃PO₄ synthetic photocatalysts and pure Ag₃PO₄. Pure Ag₃PO₄ exhibits dual bands, namely, a stronger narrow one at 912 cm⁻¹ and a weak broader one at 1012 cm⁻¹, which are associated with the antisymmetric and symmetric stretching vibrations of (PO₄)³⁻, respectively [33, 34]. The Raman characteristic peaks of the CDPVA/Ag₃PO₄ composite photocatalysts at 910 and 1012 cm⁻¹ weaken compared with those of pure Ag₃PO₄ owing to the existence of the CDPVA layer on the Ag₃PO₄ surface; the peaks further weaken with increasing CDPVA content on the composite surface.
Meanwhile, two new characteristic peaks at ca. 1350 and 1589 cm\(^{-1}\) are visible in Raman spectrum of the CDPVA/Ag\(_3\)PO\(_4\) composites, which can be related to the C=C stretching vibration of the conjugated polymers CDPVA\([35]\). The results reveal the existence of Ag\(_3\)PO\(_4\) and CDPVA in the CDPVA/Ag\(_3\)PO\(_4\) composites.

3.1.3. XPS
The valence state and chemical composition of various species could be determined by means of XPS measurement\([36, 37]\). Peak strength is affected by the sample preparation, the resolution of the instrument and the method of background subtraction. The XPS survey spectra (figures 3(a) and (b)) show that the Ag\(_3\)PO\(_4\) surface contains Ag (2.4\%), P (3.4\%), O (18.6\%), and C (75.7\%) and the surface of CDPVA/Ag\(_3\)PO\(_4\) (1: 8000, 180 °C, 1 h) predominantly contains Ag (2.0\%), P (2.1\%), O (17.2\%), and C (78.7\%), indicating that the contents of Ag, P, and O decrease with increasing C content. Hence, CDPVA adheres to the surface of Ag\(_3\)PO\(_4\) particles, consistent with the Raman result.

The spectrum decomposition was performed using the XPS PEAK 4.1 program with Gaussian functions after subtraction of a Shirley background. Measurements for Ag 3d, O 1s, P 2p, and C 1s core levels were performed to clarify the chemical state of Ag, P, O, and C. Figure 3(c) reveals dual peaks of 367.8 and 373.6 eV because of Ag 3d\(_{3/2}\) and Ag 3d\(_{5/2}\), implying that Ag\(^{+}\) exists in CDPVA/Ag\(_3\)PO\(_4\) composite photocatalysts\([38]\).

Figure 3. XPS survey spectra of Ag\(_3\)PO\(_4\)(a) and CDPVA/Ag\(_3\)PO\(_4\)(1: 8000) (b). Spectra of XPS analysis for Ag 3d (c), O 1 s (d), P 2p (e), and C 1s (f).
The O 1 s XPS spectrum in figure 3(d) displays two characteristic peaks. The peak spectrum corresponding to 531.7 eV could be associated with the bridge of the Ag—O—P and P—O—P groups, and the peak of 533.1 eV could be assigned to P=O and C—O [39, 40]. The XPS peak of P 2p is located at 133.7 eV (figure 3(e)), which is possibly due to P$^{5+}$ in PO$_4^{3-}$ [41, 42]. Figure 3(f) shows the deconvoluted XPS peaks of C 1 s. The peaks are observed at 284.6 and 288.4 eV in the XPS spectra of Ag$_3$PO$_4$ and CDPVA/Ag$_3$PO$_4$ (1: 8000); these peaks are typically assigned to adventitious elemental carbon and C—O/C=O [43, 44], respectively. Additionally, the peak at 286.3 eV can only be observed in XPS spectrum of CDPVA/Ag$_3$PO$_4$ (1: 8000), which is associated with the C=C bonds in CDPVA [45]. The result further confirms the co-existence of the conjugated CDPVA in the investigated composites.

### 3.2. Optical and electrical properties

Figure 4 presents the DRS spectra of pure Ag$_3$PO$_4$ and CDPVA/Ag$_3$PO$_4$ composite photocatalysts. The conjugated polyvinyl alcohol derivatives coated on Ag$_3$PO$_4$ particles surface can efficiently improve their absorption performance of visible light. The enhanced absorption of visible light is superior compared with the Ag$_3$PO$_4$ photocatalytic activity.

CDPVA content, both temperature and time of heat treatment produce a significant influence on absorption of visible light. With increase in CDPVA content, their visible-light absorption intensity continuously increases (figure 4(a)), and their color continuously darkens. With increasing temperature and time of heat treatment, the visible-light absorption intensity of the CDPVA/Ag$_3$PO$_4$ composite photocatalysts is enhanced firstly and then weakens; their absorption intensity reaches the highest value with heat treatment temperature of 180 °C and time of 1 h. Without sufficient temperature or adequate time, the thermal elimination reaction of PVA macromolecules is insufficient, resulting in lack of perfect conjugate structure. When the temperature is too high or the time is too long, side reactions, such as chain breaking, chain transfer, and peroxidation will occur, leading to decreased conjugated degree of CDPVA [31, 32].

PL spectrum offers a method to evaluate the efficiency of separation for the photogenerated electron–hole pairs in semiconductors [46]. Figure 5(a) exhibits the PL spectra for pure Ag$_3$PO$_4$ and CDPVA/Ag$_3$PO$_4$ (1: 8000). Pure Ag$_3$PO$_4$ presents higher PL emission than CDPVA/Ag$_3$PO$_4$ (1: 8000), implying less combined pairs of the photogenerated electron–hole. The reduced recombination probability in CDPVA/Ag$_3$PO$_4$ composite photocatalysts results from strong mobility of electron of spatially extended π-bonding conjugated system, thereby promoting the visible-light photocatalytic activity.

![Figure 4](image_url)
indicating that the MO content decreases with prolonged reaction. In the case of CDPVA particles. The result agrees well with the PL spectrum analysis.

3.3. Photocatalytic activity
Figure 6 shows MO photodegradation catalyzed by pure Ag₃PO₄ and CDPVA/Ag₃PO₄ composite photocatalysts prepared under different conditions with irradiated light. The deterioration percentage of MO with CDPVA/Ag₃PO₄ composite photocatalysts is larger compared to that of pure Ag₃PO₄, indicating the trivial amount of CDPVA can enhance the visible-light photocatalytic activity of Ag₃PO₄ photocatalysts. Hence, the optimal preparation conditions are 1:8000 mass ratios of PVA and Ag₃PO₄, treatment temperature of 180 °C, and treatment time of 1 h.

Figure 6(d) exhibits the correlation between photodegradation time and ln(C₀/c) with pure Ag₃PO₄ and CDPVA/Ag₃PO₄ composite photocatalysts with different mass ratios. The plot shows obviously first-order kinetic reaction, as well as its kinetics is determined by:

\[ \ln(C₀/c) = kt \]

where \( k \) denotes the rate constant for degradation; \( c \) corresponds to pollution concentration at instant \( t \), and \( C₀ \) represents absorption equilibrium concentration of MO [49]. CDPVA/Ag₃PO₄ (1:8000) has a rate constant approximately 6.2 larger than pure Ag₃PO₄, in case of the same experiment conditions.

The UV–vis absorption spectra of MO solution degraded by pure Ag₃PO₄ and CDPVA/Ag₃PO₄ (1:8000) with visible-light were recorded, as presented in figures 7(a) and (b). With prolonged irradiation time, the maximum absorption of the solution with pure Ag₃PO₄ decreases slightly, and that of the solution with CDPVA/Ag₃PO₄ (1:8000) rapidly decreases and even disappears when irradiated for more than 90 min. The efficiency of MO degraded by CDPVA/Ag₃PO₄ composite photocatalysts is superior compared to that of pure Ag₃PO₄ under the same experimental conditions.

Figure S1 is available online at stacks.iop.org/MRX/6/125558/mmedia presents the High Performance Liquid Chromatography (HPLC) patterns of MO solution degraded by pure Ag₃PO₄(a) and CDPVA/Ag₃PO₄ (1:8000)(b). The characteristic peak of MO with a retention time of about 4.0 min decreases gradually, indicating that the MO content decreases with prolonged reaction. In the case of CDPVA/Ag₃PO₄ composite photocatalysts, the intensity of the peak rapidly decreases, and then disappears, but no other peaks appear. Hence, both decolorization and mineralization of MO are also efficiently.

Figure 8 offers the photocatalytic decrease of Cr(VI) (a) and its first-order kinetic curves (b). The Cr(VI) concentration with CDPVA/Ag₃PO₄ (1:8000) decreases faster than that of CDPVA and Ag₃PO₄, and the rate constant (k) of CDPVA/Ag₃PO₄ (1:8000) is twice that of pure Ag₃PO₄ under the same experimental conditions.

3.4. Stability of the photocatalyst
It is of great importance that a photocatalyst possesses a high stability, particularly for its use and estimation. The recycling photocatalytic deterioration of MO over pure Ag₃PO₄ and CDPVA/Ag₃PO₄ (1:8000) was performed to evaluate photocatalytic stability. As illustrated by figure 9, the photocatalytic activity of CDPVA/Ag₃PO₄ (1:8000) slightly decreases with increasing number of recycling runs, and that of pure Ag₃PO₄ becomes...
evidently deteriorated. The efficiency of photocatalytic deterioration of MO over CDPVA/Ag₃PO₄ (1: 8000) reaches 70% within 75 min after six recycling runs, indicating its photocatalytic stability.

The XRD patterns of the two photocatalysts were acquired after the recycling photocatalytic experiments, as illustrated by figure 10. The XRD pattern of the recycled CDPVA/Ag₃PO₄ (1: 8000) is similar to that of the original one. However, some new peaks attributed to Ag are found in the XRD pattern of pure Ag₃PO₄, and the Ag content is ca. 1.3%, indicating that pure Ag₃PO₄ particles have slight photocorrosion during photocatalysis. We can infer from the two partial enlargements that CDPVA/Ag₃PO₄ composite photocatalysts are more stable than pure Ag₃PO₄.

The conductivity of an electrolyte solution offers an estimation of its concentration, thus representing the dissolution condition of the photocatalysts to a certain extent. Generally, electrolyte solution with high concentrations presents high conductivity. Mettler Toledo FE3 conductivity meter was used for measurement of...
the conductivities of the suspensions, and the measured data are presented in figure S2. The conductivities of the suspensions containing CDPVA/Ag₃PO₄ composite photocatalysts are much smaller compared to those of suspensions containing pure Ag₃PO₄, implying a lower solubility of the CDPVA/Ag₃PO₄ composite photocatalysts compared to that of pure Ag₃PO₄ because of the protective effect of CDPVA on the surface. This property makes great sense for large-scale application of Ag₃PO₄ photocatalysts in practice.

3.5. Photocatalytic mechanism of CDPVA/Ag₃PO₄ photocatalyst

Carrier trapping experiments were conducted to elucidate the governing mechanism of reaction. The influences of DMSO (dimethylsulfoxide, a typical e⁻ scavenger) [50], EDTA (ethylene diamine tetraacetic acid, a hole scavenger) [51], TBA (tert butyl alcohol, a hydroxyl radicals ·OH scavenger) [52, 53] and p-BQ (p-benzoquinone, a typical ·O₂⁻ scavenge) [54] on MO photodegradation with CDPVA/Ag₃PO₄(1: 8000) were studied, and figure 11 provides the results. DMSO produces a small increase of the photodegradation rate for MO, implying a negligible effect of e⁻ on MO degradation. Meanwhile, the addition of TBA slightly suppresses the photodegradation of MO, suggesting that ·OH is not the active species. EDTA obviously inhibits MO photodegradation, revealing that h⁺ is the primary active species for MO degradation. In the presence of p-BQ, the photodegradation of MO was inhibited compared with no scavenger at the same conditions, indicating the main roles of ·O₂⁻ for MO degradation.

Calculation for The HOMO-LUMO gap of CDPVA is given by the equation [55]:

$$\alpha\nu = A(\nu - E_g)^n/2,$$

where A stands for a constant parameter and n = 1 for a direct transition and n = 4 for an indirect. The magnitudes of E_g and n can be identified with the subsequent steps [43]: firstly, ln(\alpha\nu) is plotted against ln(\nu - E_g) by using an means of an approximation of E_g. And then n is determined based on the slope of the straightest line near the band edge. With such approach, n = 1 for CDPVA, and the band gap is ca. 1.87 eV, as determined through an extrapolation the linear line, as shown in figure 12 (a). The HOMO potential of CDPVA
determined from the XPS valence band spectra (figure 12(b)) is ca. 1.01 V [56, 57]. For CDPVA, the potential of HOMO is 1.01 V versus NHE and LUMO is −0.86 V.

The following method provides an evaluation for the enhanced photocatalytic activity. When the as-prepared CDPVA/Ag3PO4 receives visible light, both CDPVA and Ag3PO4 are excited, and the photogenerated electrons and holes are in their conduction and valence band, respectively. ·O2− is the important active species for MO degradation. The mounting electrons in the CB of Ag3PO4 would not decrease O2 into ·O2− since the CB potential of Ag3PO4 (0.45 V versus NHE) is more positive compared to the standard redox potential \( E^\theta (\text{O}_2/\text{·O}_2^-) \) (0.13 V versus NHE). But the CB potential of CDPVA (−0.86 V versus NHE) is more negative than \( E^\theta (\text{O}_2/\text{·O}_2^-) \), the electrons left on the CB of CDPVA reduce O2 to ·O2− through one-electron reducing reaction. In this case, ·O2− is mostly from the mounting electrons in the CB of CDPVA. The schematic for the separation pairs of the photoexcited electron–hole is elucidated by scheme 3. At the beginning of catalysis, the HOMO
electrons of CDPVA transfer to the CB of Ag₃PO₄ according to the traditional dual-charge transfer mode, then the mounting electrons in the CB of Ag₃PO₄ would decrease Ag⁺ to Ag. The trace Ag might acts as a charge transmission bridge. Due to the CB potential of Ag₃PO₄ is more negative than the Fermi level of metallic Ag, the photogenerated electrons in the CB of Ag₃PO₄ shift to metallic Ag. Simultaneously, the holes in the VB of CDPVA move to metallic Ag and combine with the electrons [54, 58]. The silver content is stable and does not increase because of combining of h⁺ and e⁻. This type of charge transmission leads to accumulation of abundant electrons in the LUMO of CDPVA in reduction reaction and the participation of holes in the VB of Ag₃PO₄ in oxidation reaction. The major reactions during MO photodegradation can be presented as follows.

\[
\begin{align*}
CDPVA/Ag_3PO_4 + hv & \rightarrow CDPVA^*/Ag_3PO_4^* \\
CDPVA^*/Ag_3PO_4^* & \rightarrow CDPVA(e^- e^- / h^+ h^+) / Ag_3PO_4(e^- e^- / h^+ h^+) \\
CDPVA(e^- e^- / h^+ h^+) / Ag_3PO_4 & \rightarrow CDPVA(e^- e^- / h^+ h^+) / Ag_3PO_4(e^- e^- / h^+ h^+) \\
e^- + O_2 & \rightarrow O_2^- \\
O_2^- + MO & \rightarrow CO_2 + H_2O \\
h^+ + MO & \rightarrow CO_2 + H_2O
\end{align*}
\]

4. Conclusion

Visible-light-driven CDPVA/Ag₃PO₄ synthetic photocatalysts were produced through impregnation and applied to photocatalytic deterioration of MO solution and photocatalytic decrease of aqueous Cr (VI). The promoted photocatalytic activity and stability could might result from the unique optical and electrical properties of CDPVA, leading to reduced aggregation of particles, strengthened absorption of visible light, and
decreased rate of recombined pairs for photogenerated electron–hole. The underlying photocatalytic mechanism could be Z scheme, as confirmed by the carrier trapping experiments and analysis of the Ag content in the photocatalyst after recycling experiments. The results could shed some light on the design of Z-scheme heterostructures with engineered band structure and provide significant understanding in solar visible-light-driven catalysis.

**Acknowledgments**

The work was supported by the National Natural Science Foundation of China (No. 21271061), the Natural Science Foundation of Hebei Province (No. B2014208103, No. E2015208030) and the Key Basic Research Program of Hebei Province (No. 15961401D).

**ORCID iDs**

Desong Wang https://orcid.org/0000-0003-1315-7886

**References**

[1] Chen X B, Chen S H, Guo L J and Mao S S 2010 Semiconductor-based photocatalytic hydrogen generation Chem. Rev. 110 6503–70
[2] Fan W Q, Zhang Q H and Wang Y 2013 Semiconductor-based nanocomposites for photocatalytic H2 production and CO2 conversion. Phys. Chem. Chem. Phys. 15 2632–49
[3] Habirzeitung S N, Schmidt-Mende L and Stolarczyk J K 2013 Photocatalytic reduction of CO2 on TiO2 and other semiconductors Angew. Chem. Int. Ed. 52 7372–408
[4] Qu X L, Alvarez P J and Li Q L 2013 Applications of nanotechnology in water and wastewater treatment Water Res. 47 3931–46
[5] Liu Y, Tian L H, Tan X Y, Li X and Chen X B 2017 Synthesis, properties, and applications of black titanium dioxide nanomaterials. Sci. Bull. 62 431–41
[6] Li X, Yu J G, Jaroniec M and Chen X B 2019 Cocatalysts for selective photoreduction of CO2 into Solar Fuels Chem. Rev. 119 3962–4179
[7] YI G et al 2010 An orthophosphate semiconductor with photooxidation properties under visible-light irradiation Nat. Mater. 9 559–64
[8] Kim T W and Choi K S 2014 Nanoporous BiVO4 photoanodes with dual-layer oxygen evolution catalysts for solar water splitting Science 343 990–1
[9] Kim Y G and Jo W K 2019 Efficient decontamination of textile industry wastewater using a photochemically stable n–n-type CdSe/Ag3PO4 heterostructured nanohybrid containing metallic Ag as a mediator J. Hazard. Mater. 361 64–72
[10] Liu L, Hu P R, Li Y, An W J, Lu J R and Cui W Q 2019 PHT-coated Ag3PO4 core–shell structure for enhanced photocatalysis under visible light irradiation Appl. Surf. Sci. 466 928–36
[11] Huang G F, Ma Z L, Huang W Q, Tian Y, Jiao C, Yang Z M, Wan Z and Pan A L 2013 Ag3PO4 semiconductor photocatalyst: possibilities and challenges J. Nanomater. 2013 371356
[12] Wang B, Wang L, Hao Z B and Luo Y 2015 Study on improving visible light photocatalytic activity of Ag3PO4 through morphology control. Catal. Commun. 58 117–21
[13] Liu Y P, Fang L, Lu H D, Li T W, Hu C Z and Yu H G 2012 One-pot pyridine-assisted synthesis of visible-light-driven photocatalyst Ag/Ag3PO4 Appl. Catal. B-Environ. 115 116–425–52
[14] Teng W, Li X Y, Zhao Q D, Zhao J J and Zhang D K 2012 In situ capture of active species and oxidation mechanism of RhB and MB dyes over sunlight-driven Ag/Ag3PO4 plasmonic nanocatalyst. Appl. Catal. B-Environ. 125 538–45
[15] Yan T J, Zhang H W, Liu Y P, Guan W F, Long J L, Li W J and You J M 2014 Fabrication of robust M/Ag3PO4 (M = Pt, Pd, Au) Schottky-type heterostructures for improved visible-light photocatalysis. RSC Adv. 4 37220–30
[16] Niraula M, Adhikari S, Lee D Y, Kim E K, Yoon S J, Dubneng S K, Lee W, Shresha N K and Han S H 2014 Titania nanotube–silver phosphate hybrid heterostructure for improved visible light induced photocatalysis Chem. Phys. Lett. 593 193–7
[17] Liu W, Wang M L, Xu C X, Chen S F and Fu X L 2013 Ag3PO4/Ag3PO4@Ag3PO4: an efficient visible-light-sensitized composite with its application in photocatalytic degradation of Rhodamine B. Mater. Res. Bull. 48 106–13
[18] Katsumata H, Hayashi T, Taniguchi M, Suzuki T and Kaneco S 2014 Highly efficient visible-light-driven AgBr/Ag3PO4 hybrid photocatalysts with enhanced photocatalytic activity. Mater. Sci. Semicond. Process. 25 68–75
[19] Zhao Y J, Cao J, Lin H L, Wang Y J and Chen S F 2015 Facile assembling of Ag3/Ag3PO4 via dissolution–precipitation mechanism and its excellent photocatalytic activity for contaminant removal. Mater. Res. Bull. 62 168–76
[20] Jo Y K, Kim Y J, Lee J M, Nahm S, Choi J W and Hwang S J 2014 Surface–anchored CdSe/Ag3PO4 nanocomposite with efficient visible light photocatalytic activity. Mater. Lett. 114 152–5
[21] Kumar S, Surendar S, Baruah A and Shanker V 2013 Synthesis of a novel and stable g-C3N4/Ag3PO4 hybrid photocatalyst and study of the photocatalytic activity under visible light irradiation J. Mater. Chem. A. 1 5333–40
[22] Katsumata K, Sakai T, Suzuki T and Kaneco S 2014 Highly efficient photocatalytic activity of g-C3N4/Ag3PO4 hybrid photocatalysts through Z-scheme photocatalytic mechanism under visible light. Ind. Eng. Chem. Res. 53 8018–25
[23] Xiu Z L, Bo H, Wu Y Z and Hao X P 2014 Graphite-like C3N4 modified Ag3PO4 nanoparticles with highly enhanced photocatalytic activities under visible light irradiation. Appl. Surf. Sci. 289 394–9
[24] Zhang H C, Huang H, Ming H, Li H T, Zhang J L, Liu Y and Kang Z H 2012 Carbon quantum dots/Ag3PO4 complex photocatalysts with enhanced photocatalytic activity and stability under visible light J. Mater. Chem. 22 10501–6
[25] Yang X F, Cui H Y, Li Y, Qin J L, Zhang R X and Tang H 2013 Fabrication of Ag3PO4-graphene composites with highly efficient and stable visible light photocatalytic performance ACS Catal. 3 363–9
[26] Xiang Q J, Lang D, Shen T T and Liu F 2015 Graphene-modified nanosized Ag3PO4 photocatalysts for enhanced visible-light photocatalytic activity and stability Appl. Catal. B-Environ. 162 196–203
Zhong W W, Lou Y F, Jin S F, Wang W J and Guo L W 2016 A new Bi-based visible-light sensitive photocatalyst BiLa1.4Ca0.6O4.2: crystal structure, optical property and photocatalytic activity. J. Mater. Chem. 23 2869–75

Boronin A I, Koscheev S V and Zhidomirov G M 1998 XPS and UPS study of oxygen states on silver. Surf. Sci. 423 87–95

Biesinger M C, Lau L W M, Gerson A R and Smart R S C 2010 Resolving surface chemical states in XPS analysis of metal/metal-oxide interfaces. Surf. Interface Anal. 42 563–70

Yang H G, Xu S B, Jiang L and Dan Y 2012 Thermal decomposition behavior of poly(vinyl Alcohol) with different Hydroxyl content. J. Polym. Sci., Part A-1: Polym. Chem. 50 3846–49

Chen Z H, Wang W L, Zhang Z G and Fang, X M 2013 High-efficiency visible-light-driven Ag3PO4/AgI photocatalysts: Z-scheme photocatalytic mechanism for their enhanced photocatalytic activity. J. Phys. Chem. C 117 19346–52