

Ag₂O/Ag₃PO₄ heterostructures: highly efficient and stable visible-light-induced photocatalyst for degradation of methyl orange and phenol

Ping-Quan Wang, Yang Bai, Ping-Ya Luo, Jian-Yi Liu

State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, People's Republic of China

E-mail: baiyanghyq@foxmail.com

Published in Micro & Nano Letters; Received on 14th April 2013; Revised on 24th May 2013; Accepted on 31st May 2013

Ag₂O/Ag₃PO₄ heterostructures photocatalysis was prepared for the first time. Photocatalytic tests displayed that the Ag₂O/Ag₃PO₄ heterostructures possessed a much higher degradation rate of methyl orange and phenol than pure Ag₃PO₄ under visible light. The enhanced photocatalytic activity could be attributed to effective separation of photogenerated carriers driven by photoinduced potential difference generated at the Ag₂O/Ag₃PO₄ heterojunction interface. Repetitive tests showed that the Ag₂O/Ag₃PO₄ heterostructures maintained high stability over several cycles, and it had better regeneration capability under mild conditions. The good stability could be attributed to the protection of insoluble Ag₂O nanoparticles on the surfaces of Ag₃PO₄ crystals in aqueous solution.

1. Introduction: Photocatalysis under solar light has attracted worldwide attention because of its potential applications in water splitting and degradation of organic contaminants [1–3]. Since visible light takes up ca. 43% of the solar energy whereas ultraviolet (UV) light only ca. 4%, visible-light active photocatalysts have been the major focus [4–9]. Recently, a breakthrough was made by Ye *et al.* [10–12], who reported the use of silver orthophosphate (Ag₃PO₄) as a new visible-light photocatalyst for oxidation of water and the photodecomposition of organic compounds. Those results show that the Ag₃PO₄ semiconductor has an extremely high photooxidation capability for O₂ evolution from water, and highly efficient organic dye degradation activity under visible light, significantly higher than that of commercial TiO_{2-x}N_x. However, some limitation of this novel photocatalyst may prevent its wide use in the environmental and energy fields. First, Ag₃PO₄ is slightly soluble in aqueous solution, which greatly reduces its structural stability during the photocatalytic process [10]. Secondly, the photocatalytic process is usually accompanied by transformation of Ag⁺ into Ag, resulting in photocorrosion of Ag₃PO₄ in the absence of electron acceptors [12]. Thirdly, the rapid recombination of photoinduced electrons and holes greatly lowers the quantum efficiency [13, 14]. Considering Ag₃PO₄ as a possible visible light responding photocatalyst, its photocatalytic efficiencies must be further improved in order to be suitable for practical application.

Here, we demonstrate a successful general procedure to resolve the above problems by the epitaxial growth of Ag₂O nanoparticles on the surfaces of Ag₃PO₄ crystals at room temperature. The insoluble Ag₂O nanoparticles could effectively protect the Ag₃PO₄ core-crystals from dissolution in aqueous solutions and enhance their stabilities during the photocatalytic process. Moreover, the conduction band and valence band potentials of Ag₂O semiconductors are more negative than those of Ag₃PO₄ [15], which could promote the transfer and separation of photoexcited electron-hole pairs through their heterojunctions. The photocatalytic performance of the Ag₂O/Ag₃PO₄ heterostructures was evaluated by photocatalytic decolourisation of methyl orange (MO) and phenol solution under visible-light irradiation ($\lambda > 420$ nm). The results revealed that Ag₂O/Ag₃PO₄ heterostructures photocatalysts exhibited much higher photocatalytic activity and stabilities than pure Ag₃PO₄ crystals. A possible mechanism of Ag₂O as an efficient cocatalyst was proposed to account for the enhanced photocatalytic performance of Ag₃PO₄ nanoparticles. To the best of our knowledge, this is the first report about Ag₂O working as an active cocatalyst to

increase the photocatalytic activity of the semiconductor. This work may provide new insights for the design and preparation of new high-efficiency visible-light photocatalysts.

2. Experimental

2.1. Synthesis of Ag₃PO₄ and Ag₂O/Ag₃PO₄ heterostructures: Pure Ag₃PO₄ samples were prepared by the ion-exchange method. Briefly, 0.2 g CH₃COOAg was dissolved in 200 ml of deionised water. Na₂HPO₄ aqueous solution was added drop by drop to the solution with magnetic stirring until the initial white colour changed to yellow. The mixture was then washed with water to dissolve any unreacted raw material and dried under atmospheric conditions. Ag₂O/Ag₃PO₄ heterostructures were prepared by the precipitation method. A typical process of Ag₂O/Ag₃PO₄ is as follows: 0.5 g of Ag₃PO₄ was dispersed in 100 ml of distilled water and 0.58 g of AgNO₃ was added to the suspension. The mixture was stirred magnetically for 30 min. About 100 ml of 0.2 M NaOH was dropped to the above mixture of AgNO₃ and Ag₃PO₄. The amount of NaOH was more than sufficient to precipitate Ag₂O from the added AgNO₃, with a final pH of 14. Finally, the Ag₃PO₄ coated by Ag₂O nanoparticles was washed thoroughly with deionised water, followed by a filtration and drying process. Pure Ag₂O nanoparticles were synthesised from AgNO₃ and NaOH aqueous solutions by the precipitation method, which was used as the blank sample.

2.2. Characterisation: X-ray diffraction (XRD) patterns of the samples were recorded at room temperature by a Bruker D8 Advance X-ray diffractometer using Cu K α radiation and a 2θ scan rate of 6 min⁻¹. Diffraction patterns were taken over the 2θ range 20–70°. Scanning electron microscopy (SEM) images were obtained by a JEOL JSM-6700F field emission SEM operating at an accelerating voltage and applied current of 15 kV and 10 mA, respectively. Transmission electron microscope (TEM) analyses were performed by a JEOL JEM-2100F field emission electron microscope. UV–vis diffuse reflectance spectra (DRS) were obtained using a Shimadzu UV-3600 spectrometer by using BaSO₄ as a reference.

2.3. Photocatalytic reactivity test: Photocatalytic activities were evaluated by degradation of phenol under visible-light irradiation. For MO degradation, the catalysts (50 mg) were put into a MO dye solution (50 ppm, 100 ml). For phenol degradation, the catalysts (50 mg) were put into phenol aqueous solution (20 ppm,

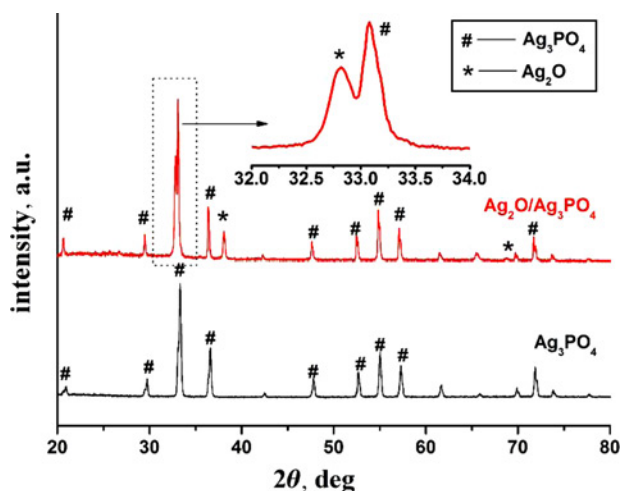


Figure 1 XRD patterns of Ag_3PO_4 and $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$

100 ml). Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 min to obtain desorption–adsorption equilibrium. The suspensions were kept under constant air-equilibrated conditions during irradiation. A magnetic stirrer was employed for continuous mixing. The light source used was a 300 W Xe arc lamp equipped with a cold mirror to provide visible light. At given intervals of illumination, 4 ml suspensions were sampled and centrifuged by a TGL-16G centrifuge (Shanghai Anting Scientific Instrument Factory, China) at 10 000 rpm for 15 min to remove the particles. The upper clear liquid was analysed by recording the maximum absorption band (553 nm for MO, 269 nm for phenol) and the UV–vis spectra of dyes, using a Shimadzu UV-3600 spectrophotometer.

3. Results and discussion: The powder XRD patterns of Ag_3PO_4 and $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ are recorded. Fig. 1 shows the XRD patterns of the as-prepared samples. For Ag_3PO_4 , all the reflections could be readily indexed to the characteristic peak of Ag_3PO_4 [JCPDS No. 06–0505]. No impurities could be detected from the pattern of the Ag_3PO_4 , which indicates that well-crystallised Ag_3PO_4 can be prepared by the ion-exchange method.

As compared with pure Ag_3PO_4 crystals, small diffraction peaks of Ag_2O crystals have been detected, confirming that Ag_2O nanoshells have been formed on their surfaces.

Ag_3PO_4 and $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ were examined by SEM and their images were presented in Fig. 2. Rhombic dodecahedral-like Ag_3PO_4 nanoparticles with a relatively smooth surface and an average diameter of ca. 700–800 nm could be clearly seen.

However, it should be noted that the intrinsic limitations, including slight solubility and photocorrosion, are independent of the morphology and crystal structure of the as-prepared Ag_3PO_4 product. Therefore the surfaces of Ag_3PO_4 crystals have been covered by Ag_2O layers of lower solubility and higher resistance to corrosion. Fig. 2b shows typical SEM images of the heterostructures that were fabricated by the precipitation method at room temperature. It seems that large amounts of Ag_2O particles were distributed on the surface of the Ag_3PO_4 . Interestingly, novel core–shell heterocrystals have been obtained by this simple precipitation process.

Fig. 3 shows the TEM image of the obtained $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ heterostructures photocatalysts. It is also clear that the $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ heterostructures exhibit a core–shell morphology, with Ag_3PO_4 particles (the light-coloured region) in the core and Ag_2O (the dark-coloured region) coats on the surface. This image further confirms that the entire surface of the Ag_3PO_4 is covered by Ag_2O , which was very consistent with the XRD and SEM results. A representative high resolution TEM (HRTEM) image is shown in Fig. 3b. The two types of lattice fringes are clearly visible with a spacing of about 0.236 and 0.268 nm, which correspond to the lattice spacing of the (220) planes of the Ag_2O and the (210) lattice spacing of Ag_3PO_4 . The TEM image of $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ reveals that the Ag_2O nanoparticle is deposited on the surface of the Ag_3PO_4 , coinciding with the above characterisation results.

To investigate the optical properties, the as-prepared samples were analysed by UV–vis absorption spectra in the wavelength range of 200–750 nm, and the absorption spectra of Ag_3PO_4 and $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ samples are shown in Fig. 4. Ag_3PO_4 exhibits a steep absorption edge located at 535 nm. Ag_2O nanoparticles display strong capability of light absorption in both the UV and the visible-light range of 200–650 nm in addition to the intrinsic absorption band derived from the band gap transition. The UV–vis spectra of the $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ heterostructure also exhibit a wide visible-light absorption band around 550–650 nm and an absorption band in the UV region. The absorption in the $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ heterostructure photocatalyst is attributed to the presence of Ag_2O nanoparticles as visible-light sensitisation, which has a strong and wide absorption band in the visible-light region. Notably, the $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ heterostructures have a suitable band gap for photocatalytic decomposition of organic contaminants under visible-light irradiation.

To demonstrate the photoactivity of the $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ heterostructure photocatalyst for degradation of organic pollutants, we carried out experiments of the photocatalytic degradation of MO as a test reaction. MO was selected as a model pollutant, because it is a common contaminant in industrial wastewater and has good resistance to light degradation compared with other dyes (Rhodamine B, Methylene blue etc.). What is more, MO cannot be photodegraded in the absence of any photocatalyst under UV light irradiation. Fig. 5a exhibits the photocatalytic activities of different catalysts in degradation of MO under visible-light irradiation.

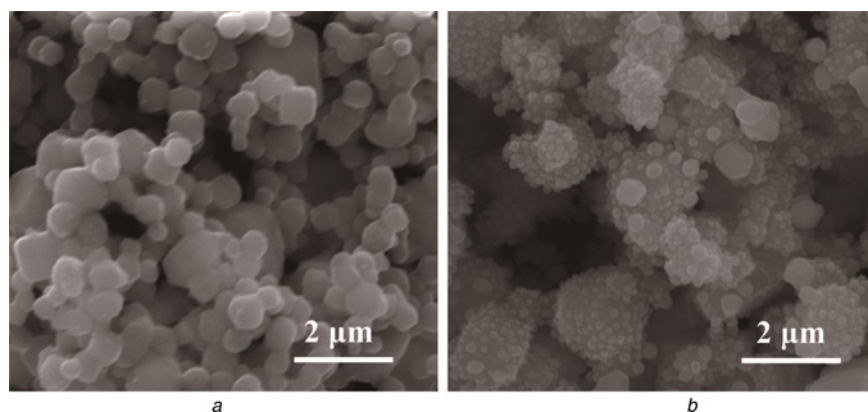


Figure 2 SEM images of Ag_3PO_4 (Fig. 2a) and $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ (Fig. 2b)

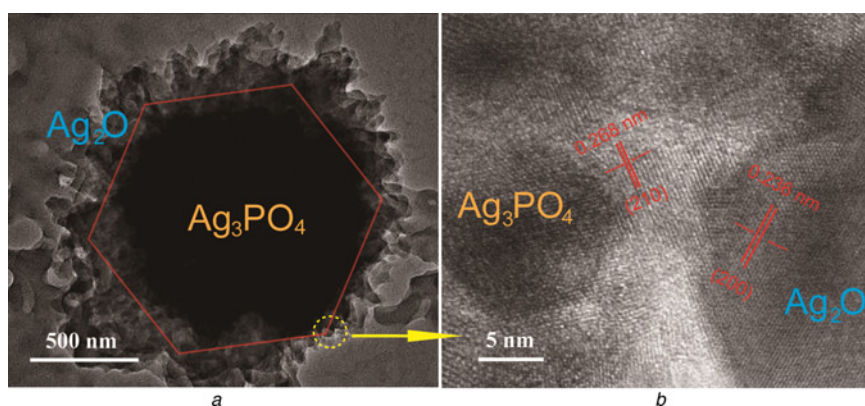


Figure 3 TEM image of $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ (Fig. 3a) and HRTEM image of $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ (Fig. 3b)

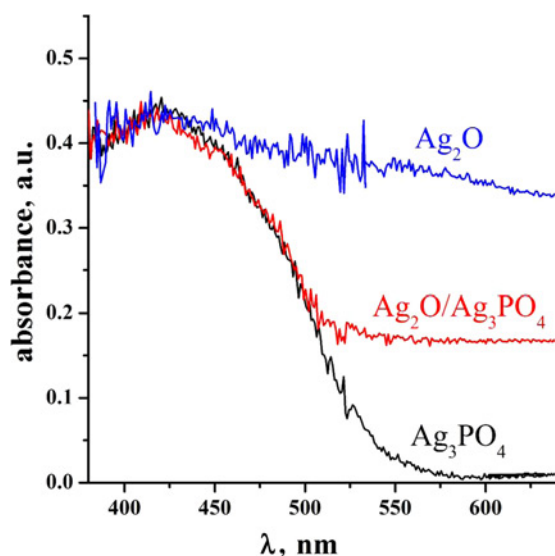


Figure 4 UV-vis DRS of Ag_3PO_4 and $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$

The blank test in Fig. 5a showed that MO cannot be degraded under visible-light irradiation without photocatalysts, which indicated that the phenol has high structural stability. It could be seen that P25 had less photocatalytic activity under visible-light irradiation. TMO degradation over pure Ag_3PO_4 is 88.7% after 30 min of

visible-light irradiation, respectively. In contrast, the $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ heterostructures exhibited the highest photocatalytic activity. The corresponding degradation rates of MO reached about 100% within 30 min, which demonstrated that $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ exhibits an enhanced visible light driven photocatalytic performance.

To investigate further the photocatalytic properties of the as-prepared photocatalyst, we also chose the phenol to evaluate photocatalytic activity as it was more difficult to be degraded than the dyes in aqueous media. As shown in Fig. 5b, after visible-light irradiation for 40 min, the degradation efficiencies of phenol were about 7.4, 82.2 and 96.2% for P25, Ag_3PO_4 and $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$, respectively. Similarly, $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ showed much higher photocatalytic activities than those of pure Ag_2O and Ag_3PO_4 , whereas the $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ heterostructures displayed the best photocatalytic activities among all samples.

The enhanced photocatalytic performance of the $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ heterostructures was because of the following factors: first, the insoluble Ag_2O layer on the surface of Ag_3PO_4 can effectively protect Ag_3PO_4 from dissolution in aqueous solution; thus, the structural stability of $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ can be greatly enhanced during the photocatalytic process. Secondly, according to DRS analysis, $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ exhibited enhanced visible-light absorption in the region of 550–650 nm. Thus, it was believed that better optical absorption of $\text{Ag}_2\text{O}/\text{Ag}_3\text{PO}_4$ in the visible-light range was an essential condition to conduct photocatalytic reaction under visible-light irradiation. Lastly, but not the least, the formed junction between Ag_2O and Ag_3PO_4 in the heterostructured photocatalysts could further prevent recombination between photoelectrons and holes. In this work, the as-adopted fabrication route was successful to

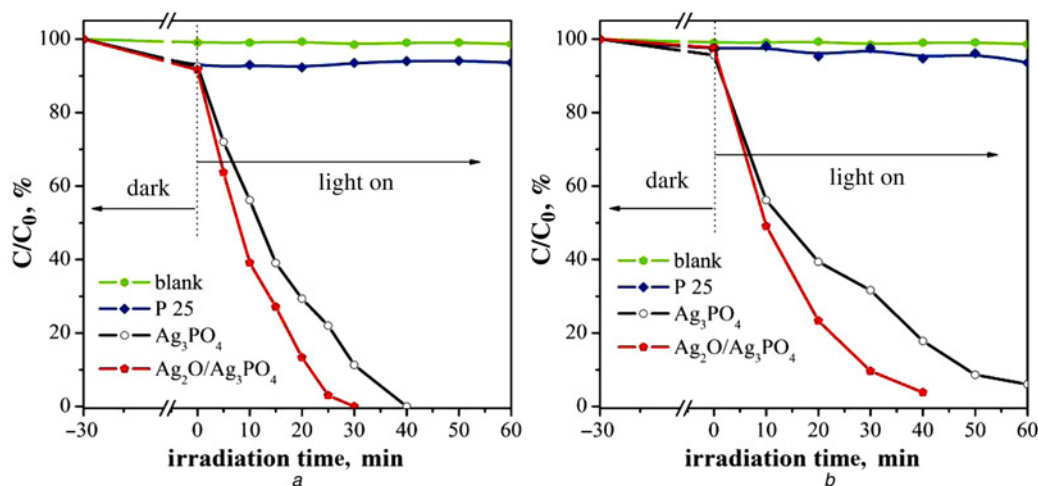


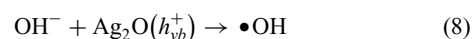
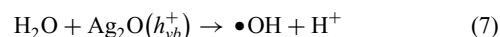
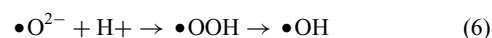
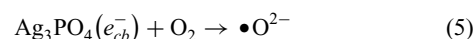
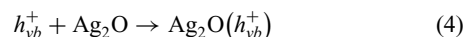
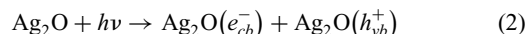
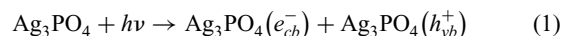
Figure 5 Degradation curve of MO over different catalysts under visible light (Fig. 5a) and of phenol over different catalysts under visible light (Fig. 5b)

realise a close contact of Ag₂O with Ag₃PO₄ nanoparticles in the Ag₂O/Ag₃PO₄ heterostructure, as evidenced by the SEM and TEM observations above. Such close contact was more effective in the suppression of the electron–hole recombination. The migration of photogenerated carriers was promoted because less barrier exists between the Ag₂O/Ag₃PO₄ heterostructures.

It was known that photocorrosion or photodissolution of the catalyst might occur on the photocatalyst surface in photocatalytic reaction. Consequently, the stability of photocatalysts is another important issue for their practical applications. To test the stability of Ag₂O/Ag₃PO₄, the photocatalytic properties of Ag₂O/Ag₃PO₄ were investigated by recycling in the repeated MO and phenol degradation experiments. As shown in Fig. 6a, each experiment was carried out under identical conditions, and the photocatalytic activity of Ag₂O/Ag₃PO₄ photocatalysts remained almost unchanged in the recycling reactions. Therefore the as-prepared Ag₂O/Ag₃PO₄ can work as effective photocatalysts for organic compounds degradation with good stability in the absence of electron acceptors.

On the basis of the above results, a proposed mechanism is discussed to explain the enhancement of the photocatalytic properties of Ag₂O/Ag₃PO₄ heterostructures (Fig. 6b). Both Ag₂O and Ag₃PO₄ can be simultaneously excited to form electron–hole pairs under visible light [15–17]. From the energy band structure diagram of the Ag₂O/Ag₃PO₄ heterostructures, it could be found that photogenerated electron transfer occurred from the conduction band (CB) of Ag₂O to the CB of Ag₃PO₄, conversely the photogenerated holes transfer could take place from the VB of Ag₃PO₄ to the VB of Ag₂O, suggesting that the photogenerated electrons and holes were efficiently separated. Moreover, the formed junction between Ag₂O and Ag₃PO₄ in the heterostructured photocatalysts could further prevent recombination between photoelectrons and holes. Furthermore, electronic acceptors like adsorbed O₂ can easily trap the electrons (transferred to the surface of Ag₃PO₄) to produce a superoxide anion radical $\bullet\text{O}_2^-$, which effectively protects Ag₃PO₄ semiconductors to avoid their photoreduction

($\text{Ag}^+ + e^- \rightarrow \text{Ag}$). Then, the formed $\bullet\text{O}_2^-$ may either attack organic molecules or provide hydroxyl radical species ($\bullet\text{OH}$) by reacting with hydron and photogenerated electrons. On the other hand, photoinduced holes transfer can take place from the valence band of Ag₃PO₄ to the valence band of Ag₂O. Then, some of the photoinduced holes on the surface of Ag₃PO₄ can be trapped by OH[−] to further produce $\bullet\text{OH}$ species, which is an extremely strong oxidant for partial or complete mineralisation of organic chemicals. All photocatalytic reactions are summarised in (1)–(8)



4. Conclusions: In summary, by using a hydrothermal technique and in situ precipitation method, Ag₂O/Ag₃PO₄ heterostructures with novel architectures have been successfully fabricated. Compared with pure Ag₃PO₄ particles, Ag₂O/Ag₃PO₄ heterostructures photocatalysts display enhanced photocatalytic activity and good structural stability for MO and phenol degradation under irradiation of visible light. The insolubility of Ag₂O can effectively protect Ag₃PO₄ from dissolution. The Ag₂O/Ag₃PO₄ heterostructures improve separation of photogenerated electron–hole pairs, thus enhancing photocatalytic activity and avoiding photoreduction of Ag₃PO₄. It is expected that Ag₂O/Ag₃PO₄ heterostructures with high photocatalytic activities will greatly promote their practical application to eliminate organic pollutants from wastewater.

5. Acknowledgment: This work was supported by the seventh instalment of the Graduate Innovation Fund of the Southwest Petroleum University (grant no. GIFSB0704).

6 References

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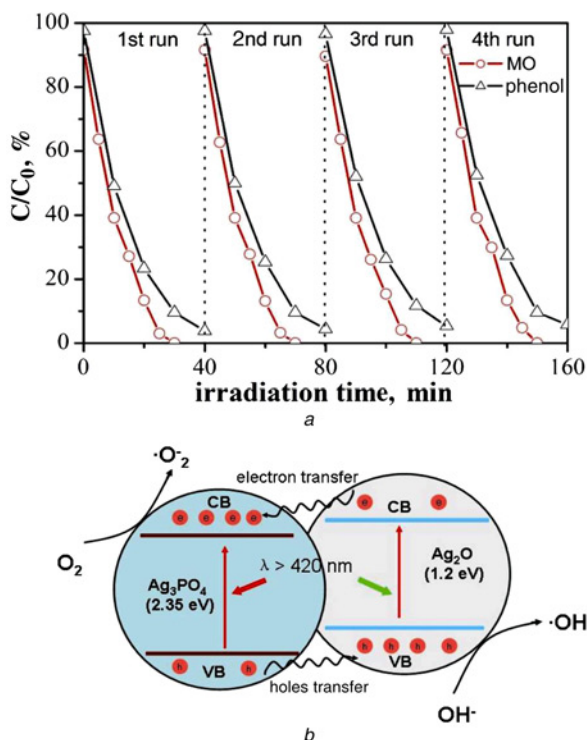


Figure 6 Photocatalytic activity for MO and phenol degradation recycling the photocatalyst four times (Fig. 6a) and postulate mechanism of visible-light-induced photodegradation of phenol with Ag₂O/Ag₃PO₄ (Fig. 6b)

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