**RESEARCH**

**Novel magnetically separable of Fe₃O₄/Ag₃PO₄@WO₃ nanocomposites for enhanced photocatalytic and antibacterial activity against *Staphylococcus aureus* (S. aureus)**

Hind Baballa Gasmalla¹², Xiaoquan Lu³, Mahgoub Ibrahim Shinger⁴, Lubin Ni¹, Aadil Nabi Chishti¹ and Guowang Diao¹*

**Abstract**

**Background:** Iron oxide nanocomposites have received a great attention for their application in various fields like physics, medicine, biology, and material science etc., due to their unique properties, such as magnetism, electrical properties, small size, biocompatibility and low toxicity.

**Methods:** Fe₃O₄/Ag₃PO₄@WO₃ nanocomposites with different weight percent of Ag₃PO₄ were successfully prepared through fabricated Ag₃PO₄/Fe₃O₄ with WO₃ via in situ fabrication method, electrospinning involved precursor solution preparation and spinning to enhance photocatalyst performance under simulated sunlight for the degradation of methylene blue (MB) and antibacterial activity against *Staphylococcus aureus* (S. aureus).

**Results:** The photocatalytic degradation of methylene blue (MB) under simulated light irradiation indicated that the nanocomposite with 0.25 mg of Ag₃PO₄ has the best activity. An additional advantage of these photocatalysts is magnetic recoverability, using external magnetic field and photocatalytic stability of the nanocomposites was evaluated for three cycles. In addition, using different scavengers, holes (h⁺) and superoxide radical (O₂·−) radicals and hydroxide radical (·OH) were identified the main oxidative species in the degradation reaction of methylene blue.

**Conclusions:** The results reveal that Fe₃O₄/Ag₃PO₄@WO₃-0.25 nanocomposites have photocatalytic and antibacterial activity against *S. aureus*. The photocatalyst and mechanism based on the enhancement of electron transfer processes between Ag₃PO₄ and WO₃ nanoparticles.

**Keywords:** Fe₃O₄/Ag₃PO₄@WO₃, Photocatalyst, Simulated light irradiation, Antibacterial activity

**Introduction**

In recent years, research attention has been focused on processes that lead to an improved oxidative degradation of organic pollutants. Therefore, semiconductor photocatalysis technology has aroused scientists' interest in environmental remediation. Although several semiconductors have proven to be ideal candidates for the treatment of water pollution, the efficient separation and recycling of this fine powdered photocatalyst is still a scientific problem when applied in practice, including separation process, selectivity, and dispersion [1, 2]. A photocatalyst with magnetic properties allow the use of the technique of magnetic separation, which is one of the most effective and simple methods for removing suspended solids from wastewater without need for further separation processes. The magnetic photocatalyst allows its use as a suspended material and providing the advantage to have a high surface area for reaction [3]. Several complexes such as Fe₂O₃, WO₃, BiVO₄, Bi₂WO₆ and Ag₃PO₄ [4–8] have been tested as visible
light photocatalyst. Fe3O4 has been broadly applied as a significant ferromagnetic material for extensive application areas, including catalysis, recording materials, pigment, magnetocaloric refrigeration, and drug delivery carrier, because of its promising properties such as low cost, good hydrophilicity, and biocompatible properties [4]. Although Fe3O4 is not a suitable semiconductor for the photocatalyst process, it wasn’t expensive and possess high band gap energies as they willingly go through photocathodic corrosion [9, 10]. But the magnetic Ag3PO4/TiO2/Fe3O4 heterostructured nanocomposite was enhanced photocatalytic activity, cycling stability, and long-term durability in the photodegradation of acid orange 7 (AO7) under visible light. Moreover, the anti-bacterial activity toward Escherichia coli (E. coli) cells under visible-light irradiation [11].

Ag3PO4 has a relatively narrow band gap (2.36–2.43 eV) and is thus active under visible-light irradiation (λ < 530 nm). Therefore, as a highly efficient photocatalyst, Ag3PO4 could behave as a potential antimicrobial material and could have promise in various antimicrobial applications [12, 13]. Magnetically separable composite photocatalysts Fe3O4–Ag3PO4 [14], Ag3PO4/ NiFe2O4 [15] and Fe3O4@LDH@Ag/Ag3PO4 [16] with high photocatalytic activity. Recently, magnetic and silver phosphate core–shell photocatalysts composed of a magnetic core and photocatalytic shell have attracted great interest Fe3O4@Ag3PO4/AgCl under simulated solar light [17] and Fe3O4@SiO2@Ag3PO4 with excellent visible-light-responding photocatalytic activity [18].

WO3 has a narrow band gap (2.6–2.7 eV), is very hopeful visible light active photocatalyst. It has been used in the photocatalytic degradation of organic contaminants and in the photocatalytic development of O2 [19–21]. Micro and nanoscaled core–shell materials have attracted great interest because their essential properties can be conveniently adjusted by controlling the morphology and chemical composition of both core and shell [22–24]. Moreover, the interactions between the various ingredients of the core and shell can significantly improve the overall performance of the core–shell system and even produce beneficial synergistic effects [25, 26]. For example, metal–semiconductor as core–shell photocatalysts have been synthesized and shown to display superior photocatalytic efficiency, because a metallic core can accelerate charge separation and the large-surfaced nanostructures enhance light absorption [27]. However, the photocatalytic activity of WO3 is not reasonable because of its relatively low conduction band level. There are some reports on the synthesis of chestnut, such as Fe3O4/WO3 hierarchical core–shell structures that integrate conductive Fe3O4 microspheres and visible light active WO3 nanoplates as a magnetically recyclable visible light active photocatalyst [27]. In another study the fabrication of a magnetically recyclable Fe3O4/WO3 core–shell visible-light photocatalyst has been developed [28]. Nanosilver-decorated WO3 nanofibers incorporating paramagnetic CoFe2O4 nanoparticles were fabricated for the first time as model solar light-active photocatalyst with potent antibacterial property and recoverability. Formation of semiconductor composites is an effective way to enhance the photo-induced charges separation efficiency and the photocatalytic performance, which has been extensively studied for the last decades [20].

Magnetic photocatalysts are recognized as low cost, efficient, and robust techniques desirable to remove dyes from contaminated water before their discharge and to produce clean water on a large scale. In principle, the rapid separation of photogenerated electrons and holes can be achieved by forming heterojunctions within the semiconductors. Further, multiscale structuring can beneficially increase the light scattering and absorption in such heterojunctions, thus increasing the light absorption range [29]. Hence, such a strategy can be successfully used for the fabrication of high-efficiency semiconductor composites.

In the present work, through in situ ion exchange method, we fabricated Ag3PO4/Fe3O4 with WO3 for the first time as model simulated light-active photocatalyst for the degradation of methylene blue (MB). The antibacterial activity of Ag3PO4/Fe3O4@WO3 composite toward Staphylococcus aureus (S. aureus) was studied. The as synthesized Ag3PO4/Fe3O4@WO3 composite exhibited high antibacterial performance than the other prepared composites. The effect of the presence of the reactive species on the photocatalytic activity was studied, and the possible photocatalytic mechanism of Fe3O4/Ag3PO4@WO3 and photodegradation pathway of MB was suggested.

**Experimental section**

**Materials**

All materials have analytical purity and used as received without further purification. All of the solutions were prepared using deionized water (18.2 MΩ), FeSO4·7H2O, FeCl3·6H2O, NH4OH and Disodium ethylenediamine tetraacetate (Na2-EDTA) solution were obtained from Yantai both chemical Co., Ltd, AgNO3 (99.8%), MDF and p-benzoquinone (BQ) were obtained from Tianjin Chemical reagent technology Co., Ltd. Disodium hydrogen phosphate dodecahydrate (Na2HPO4·12H2O) and H2WO4 (AR, 99.95%) was bought from Aladdin reagent Co., Ltd, Ethanol (AR, 99.7%), was purchased from Tianjin Baishi Chemical Co., Ltd. PVP, MB and tert-butanol obtained from Tianjin city Tianxin chemicals development center, Nutrient Broth powder was obtained from
Hanzhou Microbiology Co., Ltd and agar powder was obtained from Beijing life science and technology. Co., Ltd.

Preparation of Fe₃O₄ nanoparticles

The functionalized Fe₃O₄ was prepared by the modified co-precipitation method. Typically, 2.7 g FeSO₄·7H₂O and 5.4 g FeCl₃·6H₂O were dissolved in 50 ml deionized water separately, and mixed together in water bath maintained at 80 °C. Then 2 ml of oleic acid (OA) was added into the FeSO₄/FeCl₃ mixture, and sonicated for 20 min under 60 °C, then 15 ml of ammonium hydroxide was added drop by drop with stirring (600 revolutions/min) under nitrogen atmosphere. After 0.5 h, 2 ml of OA was added again drop-by-drop to the mixture with stirring and reacted for 1 h at 80 °C under nitrogen gas. After that, the precipitate was isolated from the solvent by a permanent magnet. Then washed with water and ethanol in sequence, followed by drying at 50 °C under vacuum for 24 h. Non-functionalized Fe₃O₄ was prepared following the same method without the addition of OA, and labeled as Fe₃O₄-non.

Preparation of Fe₃O₄/Ag₃PO₄

For the preparation of Fe₃O₄/Ag₃PO₄, room temperature in situ anion-exchange method was used. Typically, 0.5 g of the as prepared Fe₃O₄ was dispersed into 50 ml distilled water and sonicated for 1 h to give black aqueous suspension and then 10 ml of three different amount of AgNO₃ (0.25 g, 0.5 g and 0.75 g) was added into the suspension solution and stirred for 0.5 h. Subsequently, 10 ml of aqueous solution with different content of Na₃HPO₄ (0.13 g, 0.26 g, 0.39 g) was added drop-by-drop with continues stirring for more 0.5 h. Finally, the precipitates were separated by a permanent magnet and washed with distilled water several time and dried under vacuum for 24 h. The obtained composites were labeled as Fe₃O₄/Ag₃PO₄@WO₃-0.25, Fe₃O₄/Ag₃PO₄@WO₃-0.5 and Fe₃O₄/Ag₃PO₄@WO₃-0.75. Functionalized Fe₃O₄/Ag₃PO₄-non was prepared using Fe₃O₄-non and (0.25 g/10 ml) AgNO₃ and (0.13 g/10 ml) Na₃HPO₄.

Preparation of tungsten oxide WO₃

Fabrication of WO₃ square like nanoplates by electrospinning. The polymer solution could be prepared by dissolving a selected polymer in a suitable solvent. The following protocol is given as a specific example; A PVP solution was prepared by adding 0.7 g of polyvinylpyrrolidione into 7 ml of ethanol under magnetic stirring. In a separate beaker, 0.2 g of tungstic acid was added to 2 ml of DMF. Then, the two solutions were mixed followed by magnetic stirring at room temperature for 15 min. Then the precipitates were separated by a permanent magnet and washed with distilled water several time and dried under vacuum for 24 h.

Preparation of Fe₃O₄/Ag₃PO₄@WO₃

The fabrication of magnetic with silver phosphate involved WO₃ precursor solution preparation and electrospinning was chosen as a facile and an effective approach to fabricate plates with diameters at nanometer length scale. The precursor solutions were derived from mixtures Fe₃O₄/Ag₃PO₄ nanoparticles with different concentration and tungsten oxide precursor. A typical method is as follows. A PVP solution was prepared by adding 0.7 g of polyvinylpyrrolidione into 7 ml of ethanol under magnetic stirring. In a separate beaker, 0.2 g of tungstic acid was added to 2 ml of DMF. Then, the two solutions were mixed followed by magnetic stirring at room temperature for 15 min. To the mixture above, determined about 0.1 mg of different amounts of Fe₃O₄/Ag₃PO₄ nanoparticles were added. The final mixture was then stirred by a magnetic stirrer at room temperature for 15 min, followed by sonication for 10 min. Then the precipitates were separated by a permanent magnet and washed with distilled water several time and dried under vacuum for 24 h. The obtained composites were labeled as Fe₃O₄/Ag₃PO₄@WO₃-0.25, Fe₃O₄/Ag₃PO₄@WO₃-0.5 and Fe₃O₄/Ag₃PO₄@WO₃-0.75. Non-functionalized Fe₃O₄/Ag₃PO₄@WO₃ was synthesized by the same method using Fe₃O₄/Ag₃PO₄-non instead of Fe₃O₄/Ag₃PO₄, and labeled as Fe₃O₄/Ag₃PO₄@WO₃-non.

Characterization

The morphology and the composition were characterized; Transmission Electron Microscopy (TEM, FEI TECNAI-G2 operating at 300 kV) and Field-emission Scanning Electron Microscope (FESEM, JEOL, JSM-7001F) were used to determine the morphology and size of the magnetite particles, The structures of composites were characterized by X-ray diffractometer (XRD) using a Brucker 8 Advanced, Germany with a Cu Kα (λ = 1.5406˚ A) source in the 2θ range of 10˚ to 80˚ at room temperature. A vibration sample magnetometer VSM (Model EV9System) was employed for magnetic properties of the samples at room temperature, The Fourier Transform Infrared (FTIR) spectra of the samples were recorded on a Bruker Vertex 70 FT-IR spectrophotometer using the KBr method, The UV-visible diffuse reflectance spectroscopy (DRS) spectra of photocatalyst powder was obtained for the dry-pressed disk samples using scan Shimazu, Japan UV-2450 spectrometer equipped with the integrated sphere accessory for diffuse
reflectance spectra, using BaSO₄ as the reflectance sample, UV–vis absorption spectra of the as-prepared samples were obtained using a Hitachi U-4500 spectrophotometer (Hitachi High-Technology Corporation). The electron transfer properties of the synthesized composites were studied using electrochemical impedance spectrometer (EIS) VMP2 multi-potentiostat with ZsimpWin program (Princeton Applied Research, USA) and its frequencies swept from 10 kHz to 100 mHz.

**Evaluation of the antibacterial activity**

**Preparation of photocatalyst film**

In general, suspensions of the as-prepared Fe₃O₄/Ag₃PO₄@WO₃ composites (0.001 mg/1 ml) were dripped onto filter paper (Φ 6 mm), and then placed onto the bottom of a Petri dish (nutrient agar plate) for antibacterial experiments. For comparison, the same film was prepared using Fe₃O₄, Ag₃PO₄ or WO₃.

**Antibacterial tests**

The antibacterial activity was evaluated using *S. aureus* and *E. coli* as representative microorganisms. Before the antimicrobial experiments, all glass wares were sterilized by autoclaving at 120 °C for 30 min. To measure antibacterial activity, 100 μl of the bacterial suspension was serially diluted with sterile water to make sure the final colony count is not more than 10⁻⁷ colony-forming units per milliliter (CFU ml⁻¹). Then 100 μl aliquots were spread onto nutrient agar plates that were prepared already and incubated at 37 °C for 24 h. The experiment was further repeated. For each antibacterial experiment, the prepared photocatalyst film was placed onto the bottom of a Petri dish (onto an agar plate) for antibacterial experiments. For comparison, the same film was prepared using Fe₃O₄, Ag₃PO₄ or WO₃.

**Photocatalytic activity**

The photocatalytic evaluation study was carried out at room temperature. Typically, MB solution (50 ml, 5 mg 1⁻¹) and 15 mg of the catalyst were placed in a sealed glass. The suspension was ultrasonicated in the dark for 10 min before irradiation to reach an adsorption/desorption equilibrium between MB and the surface of the catalyst under room temperature. Then the mixture was illuminated with 350 Xe lamp as a light source system equipped with a UV cutoff filter (λ > 420 nm). The distance between the light source and the reaction containers was fixed at 10 cm. After simulated light irradiation, 3 ml of the mixture was taken out at a regular time interval of 1 min. Then centrifuged to remove the photocatalyst and the concentration of MB was measured with UV–Vis spectrophotometer at 664 nm.

**Analysis of hydroxyl radical (·OH)**

Terephthalic acid photoluminescence probe technique was used in the detection of ·OH. Terephthalic acid readily reacted with OH to produce highly fluorescent product, 2-hydroxy-terephthalic acid. The method relied on the PL signal at 426 nm of 2-hydroxyterephthalic acid. The PL intensity of 2-hydroxyterephthalic acid was proportional to the amount of OH formed. Experimental procedures were reported in early reports [30, 31], a basic terephthalic acid solution was added to the reactor and the concentration of terephthalic acid was set at 5 × 10⁻⁴ M in 2 × 10⁻³ M NaOH solution. The solution was irradiated for intervals time 10 min using ultraviolet light 365 for 50 min under magnetic stirring. The PL spectra of generated 2-hydroxyterephthalic acid were measured on a Hitachi F-4500 fluorescence spectrophotometer. The reaction solution was used to measure the increase of the PL intensity at 426 nm excited by 365 nm ultraviolet light.

**Result and discussion**

**Characterization**

**Transmission electron microscopy**

This synthesis procedure of Fe₃O₄/Ag₃PO₄@WO₃ nanocomposites is presented Schematic diagram in Fig. 1. A Fe₃O₄ nanoparticle was first synthesized by co-precipitation method and fabrication of magnetic with silver phosphate involved WO₃ precursor solution preparation and electrospinning method.

Figure 2a–c presents typical TEM images of the bare Fe₃O₄, Ag₃PO₄ and WO₃, Fe₃O₄/Ag₃PO₄@WO₃ composites, respectively. As seen in Fig. 2c, the as prepared Fe₃O₄/Ag₃PO₄ well cabled with the WO₃ nanoplates, indicating the Fe₃O₄/Ag₃PO₄@WO₃ composite has been successfully fabricated spherical shape with wide size distribution, and the aggregation of the particles is dense and the size range of bare Fe₃O₄ nanoparticles is 29 nm Fig. 2d–f shows the SEM images of the Ag₃PO₄, Fe₃O₄/Ag₃PO₄, and Fe₃O₄/Ag₃PO₄@WO₃ composites, respectively. As been seen in (Fig. 2e), the Fe₃O₄ nanoparticles obviously decorated the Ag₃PO₄. While the SEM image of the Fe₃O₄/Ag₃PO₄@WO₃ shows the presence of Fe₃O₄, Ag₃PO₄ and WO₃. Which further confirm the fabrication of Fe₃O₄/Ag₃PO₄@WO₃.

**X-Ray energy-dispersive spectroscopy analysis**

The purity of the samples was investigated using EDS analysis and the results are shown in Fig. 3a. As can be seen the peaks in the spectra of Fe₃O₄/Ag₃PO₄@WO₃-0.25 composite are described to O, W, P, Fe, and Ag elements. Moreover, the EDS elemental mapping further elucidated the composition of the Fe₃O₄/Ag₃PO₄@
WO₃-0.25 nanocomposite. As can be seen in Fig. 3b–g, the elemental mapping images of O, W, P, Fe and Ag have similar shape and location, indicating the definite existence of Fe₃O₄, Ag₃PO₄, and WO₃.

**X-ray diffraction**

The XRD analysis was used to investigate the different crystalline structures of the synthesized composites (Fig. 4). The Fe₃O₄ shows six characteristic peaks at 2θ = 30.1, 35.3, 43.6, 53.6, 57.3 and 62.8, indexed to (220), (311), (400), (422), (511) and (440) facets, respectively, which can be well indexed to the standard data (JCPDS File, no: 19-0629) [32]. The XRD pattern of Ag₃PO₄ shows diffraction peaks at 2θ = 20.848, 29.648, 33.248, 36.518, 42.428, 47.718, 52.608, 54.928, 57.188, 61.548, 65.728, 69.788, 71.768, and 73.728 corresponded to the planes (110), (200), (210), (211), (220), (222), (320), (321), (400), (330), (420), (421) and (332) of Ag₃PO₄.
respectively, which can be indexed to the standard XRD data of the cubic-phase $\text{Ag}_3\text{PO}_4$ crystal (JCPDS File, no: 06-0505, 74-1876) [33, 34]. The square-like $\text{WO}_3$ nano-plates indicate that the as-synthesized $\text{WO}_3$ crystal structure with obvious diffraction peaks at 2θ value of 16.5° (020), 19.2° (011), 23.8° (120), 25.8° (111), 35.5° (131), and 78.6° (313) which are similar to the pattern of the reference $\text{WO}_3$ crystals (JCPDS File no: 84-886) [35]. The XRD pattern of $\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4/\text{WO}_3$ composite displayed all the characteristic peaks of $\text{Fe}_3\text{O}_4$, $\text{Ag}_3\text{PO}_4$ and $\text{WO}_3$, and no other peaks were detected. This further confirms the fabrication of the synthesized composite.

The particle size play important role on the photocatalytic performance of the semiconductors, the less particle sizes the higher catalytic activity. To calculate the particle size of the synthesized composites, Scherrer’s Eq. 1 [36] was used.

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where $\beta$ is full width at half-maximum, $D$ is crystallite size, $\lambda$ is X-ray wavelength, $\theta$ is Bragg’s diffraction angle.

The average sizes of the $\text{WO}_3$ were estimated to be 450, 411 and 383 corresponding to the patterns of $\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4$ and $\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4/\text{WO}_3$, respectively.
From the calculations, the crystalline size of Fe$_3$O$_4$/Ag$_3$PO$_4$ markedly decreased after the synthesis of Fe$_3$O$_4$/Ag$_3$PO$_4$@WO$_3$ composite. Which it’s beneficial enhance the photocatalytic activity.

**Magnetic properties**

The magnetic properties have been quantified by using a superconducting quantum interference device a vibrating sample magnetometer (VSM Model EV9System) at room temperature. Figure 5, displayed the hysteresis loops at 300 K of the as prepared Fe$_3$O$_4$ microspheres and Fe$_3$O$_4$/Ag$_3$PO$_4$@WO$_3$-0.25 composites catalysts. The saturation magnetization (Ms), remanence (Mr), coercivity (Hc) and loop Squares ratio (Mr/Ms) of samples is shown in (Tables 1 and 2) and the magnetization curve with a hysteresis loop displays ferromagnetic behavior with a coercivity of about 2.20 and 1.87Oe of Fe$_3$O$_4$ and Fe$_3$O$_4$/Ag$_3$PO$_4$@WO$_3$ respectively. The saturation magnetization of the Fe$_3$O$_4$/Ag$_3$PO$_4$@WO$_3$-0.25 composites is about 36.225 and 20.525 emu$^{-1}$ respectively. Such a decrease of their saturated magnetization could be attributed to the decrease in effective mass of the Fe$_3$O$_4$ in these cases. Fortunately, the magnetism of these hybrid nanostructures was still strong enough to be separated easily from solution with the help of an external magnetic field.

**Fourier transforms infrared spectroscopy**

The typical vibration peaks of the Fe$_3$O$_4$, Ag$_3$PO$_4$, WO$_3$, and Fe$_3$O$_4$/Ag$_3$PO$_4$@WO$_3$ composite are shown in the FT-IR spectrum in (Fig. 6). In the spectra of the functionalized Fe$_3$O$_4$, the presence of OA layer can be confirmed. The bands at 2840 cm$^{-1}$ and 2917 cm$^{-1}$ can be ascribed to the stretching modes of –CH$_2$ and –CH$_3$ of the OA, respectively. The vibrations at 1699 cm$^{-1}$ and 1454 cm$^{-1}$ can be assigned to the stretching modes of –C=O and –C–C– of the OA, respectively. The characteristic band of the pure Fe$_3$O$_4$ usually appears at 570 cm$^{-1}$, in the case of the present sample, this peak was shifted to 579 cm$^{-1}$, due to the functionalization process. In the spectra of Ag$_3$PO$_4$, the intense absorption peak at 1016 cm$^{-1}$ is ascribed to the stretching vibration of the phosphate (PO$_4^{3-}$) group, and the absorption peaks at 574 and 538 cm$^{-1}$ is ascribed to the bending vibration of the phosphate (PO$_4^{3-}$) group. The absorption peaks at 3450 and 1660 cm$^{-1}$ are corresponding to the $\tilde{\text{OH}}$ stretching and bending vibrations of physically absorbed H$_2$O molecules, respectively. The precursor of WO$_3$ has strong

| Parameter | Upward part | Downward part | Average | Hysteresis parameter |
|-----------|-------------|---------------|---------|----------------------|
| Mr (emu/l) | 0.2394      | 0.207125      | 0.223275| Remanent magnetization: M H = 0 |
| S          | 0.007       | 0.006         | 0.006   | Squares: Mr/Ms |
| $S^*$      | 0.134       | 0.157         | 0.146   | 1 – (Mr/Hc)/(1/slop at Hc) |
| Ms (emu/g) | 36.225      | 36.2          | 36.225  | Saturation magnetization: maximum M measure |
| Hc Oe      | 2.36        | – 2.04        | 2.20    | Coercive field: field at which M/H changes sign |
bands in the 500–900 cm\(^{-1}\) region are assigned to the \(\nu(O–W–O)\) stretching mode [37]. A band at 950 cm\(^{-1}\) was observed in the spectra of the terminal of vibrations \(W=O\) groups that were changed from the \(W–O\) bond on the surface of \(WO_3\) or in the grain boundaries in \(WO_3\) [38, 39]. Bands at 3380 and 1618 cm\(^{-1}\) can be indexed to the \(\sigma(O–H)\) bending vibrations of coordinated water [37]. In the spectra of \(Fe_3O_4/Ag_3PO_4@WO_3\) composite, all the characteristic peaks of \(Fe_3O_4\), \(Ag_3PO_4\) and \(WO_3\) are present with a red shift for the peak of \(Fe_3O_4\) (from 579 to 675 cm\(^{-1}\)) and blue shift for the peaks of \(Ag_3PO_4\) (from 1028 to 1013 cm\(^{-1}\)). The FT-IR analysis further confirms the fabrication of the \(Fe_3O_4/Ag_3PO_4@WO_3\) composite.

**UV–vis diffuse reflectance spectroscopy and band structure**

The study of the light absorption behaviors clearly shows the efficient photocatalytic properties of the semiconductor [40, 41]. The light absorption behaviors of the synthesized photocatalysts were studied by DRS analysis, and the results are shown in (Fig. 7a). The results show that the light absorptivity of the products shown a trend to increase in the range of 200–520 nm and reached a peak at 510 nm, which belonged to the visible region. The band gap of the synthesized composites was determined by a plot of \((\alpha hv)^2\) versus energy \((hv)\), (Fig. 7b). The band gaps were estimated to be 2.42 eV, 2.22 eV and 2.13 eV for \(WO_3\), \(Fe_3O_4/Ag_3PO_4@WO_3\) and \(Fe_3O_4/Ag_3PO_4@WO_3\)-non, respectively. The as synthesized \(Fe_3O_4/Ag_3PO_4@WO_3\) composite exhibited the narrower band gap, which is beneficial to its enhanced photocatalytic activity.

### Table 2 Magnetic properties of the \(Fe_3O_4Ag_3PO_4@WO_3\)

| Parameter       | Upward part | Downward part | Average | Hysteresis parameter |
|-----------------|-------------|---------------|---------|----------------------|
| \(Mr\) (emu/l)  | 0.0096      | 0.0084        | 0.0090  | Remanent magnetization: \(M H = 0\) |
| \(S\)           | 0.005       | 0.004         | 0.003   | Squares: \(Mr/Ms\)   |
| \(S^*\)         | 0.118       | 0.136         | 0.127   | 1 – (\(Mr/Hc\))/\(1/slop at Hc\) |
| \(Ms\) (emu/g)  | 20.520      | 20.53         | 20.525  | Saturation magnetization: maximum M measure |
| \(Hc\) Oe       | 2.00        | – 1.75        | 1.87    | Coercive field: field at which M/H changes sign |

**Fig. 6** FTIR Spectrums of the \(WO_3\), \(Fe_3O_4\), \(Fe_3O_4/Ag_3PO_4@WO_3\) and \(Ag_3PO_4\) Composite

**Fig. 7**

**a** UV–visible absorption spectra \(WO_3\), \(Fe_3O_4/Ag_3PO_4@WO_3\)-0.25 mg, \(Fe_3O_4/Ag_3PO_4@WO_3\)-0.50 and \(Fe_3O_4/Ag_3PO_4@WO_3\)-0.75 mg and \(Fe_3O_4/Ag_3PO_4@WO_3\)-non

**b** plots of \((\alpha hv)^2\) versus energy \((hv)\) for the band gap energy of \(WO_3\), \(Fe3O4/Ag3PO4@WO3\) and \(Fe3O4/Ag3PO4@WO3\)-non
**Evaluation of antibacterial activity**

Concerning the prospective application of Fe₃O₄/Ag₃PO₄/WO₃, the antibacterial properties of the as-synthesized catalyst were investigated in the present work. *S. aureus* even was chosen as representative microorganism. Following the findings above, it was presumed that successful deposition of Ag₃PO₄ imparted antibacterial functions on the nanocomposites [42–44]. To further assess this function, we employed the test method of antimicrobial in term of the inhibitory zone. In a control sample, bacterial colony growth was induced on an Agar dish as illustrated in (Fig. 8a–f), following interfacial contact between the test samples and the Agar plate, which should lead to inhibition of the bacterial growth. The radius of the inhibition zones was measured. As seen in Fig. 8a and c, no bacterial growth inhibition observed in the presence of both Fe₃O₄ and WO₃. The inhibition zone radius for the synthesized composites are ∼13, 19 and 17 mm for Ag₃PO₄, Fe₃O₄/Ag₃PO₄ and Fe₃O₄/Ag₃PO₄/WO₃, respectively. Showed that all Ag₃PO₄-based composite has significant bactericidal activity against *S. aureus*. The comparative between Fe₃O₄/Ag₃PO₄/WO₃ and Fe₃O₄/Ag₃PO₄/WO₃-non composite shows inhibition zone of 12 mm and 17 mm, respectively.

**Study of photocatalytic activity**

For the evaluation of the photocatalytic activity of the synthesized composites, MB was used as a representative sample. Figure 9a shows the photocatalytic activities of the Fe₃O₄/Ag₃PO₄/WO₃ photocatalysts with different ratios of Ag₃PO₄ under simulated light irradiation and the MB solution shows light absorption edge at λ_max of 664 nm. In order to investigate the optimum amount of Ag₃PO₄ on the synthesized composite, Fe₃O₄/Ag₃PO₄/WO₃ with different Ag₃PO₄ was synthesized, and their photocatalytic activity against MB degradation was studied, and the results are shown in (Fig. 9b). As seen Fe₃O₄/Ag₃PO₄/WO₃-0.25 composite, exhibited the highest photocatalytic activity compared with Fe₃O₄/Ag₃PO₄/WO₃-0.50 and Fe₃O₄/Ag₃PO₄/WO₃-0.75. This is due to the best charge separation and transforming of Fe₃O₄/Ag₃PO₄/WO₃-0.25.

To get deeply into the study of the photocatalytic efficiency of Fe₃O₄/Ag₃PO₄/WO₃-0.25, its catalytic performance was compared with the Fe₃O₄/Ag₃PO₄/WO₃-non...
The results are shown in Fig. 9c. As clearly been seen Fe₃O₄/Ag₃PO₄@WO₃-0.25 displayed higher photocatalytic activity. 90% of MB degraded within 6 min, while the non-functionalized composite required 8 min to degrade 50% of the dye. The results of the MB degradation revealed that, the Fe₃O₄/Ag₃PO₄@WO₃ composite was exhibited the highest photocatalytic performance. This is because; the functionalization process significantly induced the electron transfer properties of the Fe₃O₄. Therefore, enhanced the electron–hole separation and transfer in the Fe₃O₄/Ag₃PO₄@WO₃ composite.

**Electrochemical impedance spectroscopy (EIS)**

The electrochemical impedance spectroscopy of the WO₃, Ag₃PO₄@WO₃, Fe₃O₄/Ag₃PO₄@WO₃-non and Fe₃O₄/Ag₃PO₄@WO₃ composite was carried out to further investigated the charge transfer and recombination processes in the Fe₃O₄/Ag₃PO₄@WO₃ composites under simulated light irradiation, and the result shown in (Fig. 10), a smaller arc radius can be observed on the EIS Nyquist plot of Fe₃O₄/Ag₃PO₄@WO₃-non and Fe₃O₄/Ag₃PO₄@WO₃ composite compared with WO₃ and Ag₃PO₄@WO₃ indicating that a more effective separation of the photogenerated electron/hole pairs and a faster interfacial charge transfer occurred on the surface of the Fe₃O₄/Ag₃PO₄@WO₃ composite.

**Kinetic study**

In order to investigate the kinetic behavior of the synthesized photocatalysts on the degradation of MB under simulated sunlight irradiation, ln (C/Co) for MB is plotted versus irradiation time according to the following first-order kinetic model 2:

\[
\ln \left( \frac{C}{Co} \right) = -kt
\]

where k is the degradation rate constant, Co and C the initial concentration and the concentration at different irradiation time t of the organic dye respectively. From the result presented in (Fig. 11), the disappearance of MB over the Fe₃O₄/Ag₃PO₄@WO₃ synthesized photocatalysts under simulated light irradiation is shown to fit a pseudo first order kinetics pattern, with degradation
rate constants of 0.0018, 0.098 and 0.4906 min$^{-1}$ and $R^2$: 0.704, 0.918 and 0.959 for WO$_3$, Fe$_3$O$_4$/Ag$_3$PO$_4$@WO$_3$-non and Fe$_3$O$_4$/Ag$_3$PO$_4$@WO$_3$ respectively. It is concluded that the degradation of MB over the as-synthesized Fe$_3$O$_4$/Ag$_3$PO$_4$@WO$_3$ under light irradiation is five times faster than that of Fe$_3$O$_4$/Ag$_3$PO$_4$@WO$_3$-non, indicating the enhanced charge separation in the Fe$_3$O$_4$/Ag$_3$PO$_4$@WO$_3$ composite compared with Fe$_3$O$_4$/Ag$_3$PO$_4$@WO$_3$-non.

Stability study
The stability of a photocatalyst is important for its practical application. The stability and recyclability of Fe$_3$O$_4$/Ag$_3$PO$_4$@WO$_3$ are evaluated by additional experiments to degrade MB under simulated light irradiation cycled for three times. Figure 12a, shows the repeated visible light photocatalytic activity of Fe$_3$O$_4$/Ag$_3$PO$_4$@WO$_3$, it can be observed that composite have good stability for the degradation of MB under simulated light irradiation during three cycles.

Active species responsible for MB degradation
The recombination of photogenerated electron–hole pairs is an important limiting factor for the performance of photocatalysts [45, 46]. To study the photocatalytic mechanism of the Fe$_3$O$_4$/Ag$_3$PO$_4$@WO$_3$-0.25 composite in detail, the effects of different scavengers on the decomposition of dye molecules were investigated. In order to determined the predominant reactive oxygen species in the photocatalytic process. In this study, p-benzoquinone (BZQ), disodium ethylenediamine tetraacetate (Na$_2$-EDTA) and tert-butanol (t.B) were used as scavengers for O$_2^-$, $h^+$, and OH, respectively [47]. As seen in (Fig. 12b), the addition of B.Q and t.B has slight effect on the inhibition of the dye degradation. Introducing EDTA to the reaction system the photocatalytic activity significantly reduced. Which indicate that the photocatalytic reaction mainly depends on the $h^+$. While O$_2^-$ and OH have negligible effect. Herein, the highly enhanced photodegradation and antimicrobial activities achieved on Fe$_3$O$_4$/Ag$_3$PO$_4$@WO$_3$ can be assigned to its composite structure.

The formation of OH on the surface photo-illuminated of composite Fe$_3$O$_4$/Ag$_3$PO$_4$@WO$_3$ (0.25, 0.50 and 0.75) was further confirmed by the PL technique using terephthalic acid as a probe molecule. Figure 13a shows that an obvious difference in PL intensity at about $\sim$425-430 nm was observed using different catalysts. It was clear that the formation rate of OH on the Fe$_3$O$_4$/Ag$_3$PO$_4$@WO$_3$-0.25 was higher than that of other composite. This implied that the former has higher photocatalytic activity than the latter. Moreover, the inset of (Fig. 13a) the pure Ag$_3$PO$_4$ exhibited higher PL intensity than pure WO$_3$ and pure Fe$_3$O$_4$, suggesting that doping of Ag$_3$PO$_4$ with WO$_3$ and Fe$_3$O$_4$ was a good route to accelerate the interfacial charge transfer and inhibit the recombination of electron–hole pairs, which resulted in the increase in OH formation. Moreover, the Fig. 13b depicts the change of PL spectra with irradiation time for the case of Fe$_3$O$_4$/Ag$_3$PO$_4$@WO$_3$-0.25. A gradual increase in PL intensity was observed with increasing irradiation time, which suggested that the fluorescence was caused by chemical reactions of terephthalic acid with OH formed during photo-illuminated reactions. Thus, these results confirmed the evidence of OH formation and indeed participated in degradation process.

Probable mechanism
As illustrated in Fig. 14 the semiconductors of WO$_3$ (with an optical band gap of 2.44 eV) and Ag$_3$PO$_4$ (with an optical band gap of 2.35 eV), especially, the redox potentials (CB and VB) of WO$_3$ are more positive than
those of Ag₃PO₄. The electrons from the CB of Ag₃PO₄ can migrate to that of WO₃ and the photogenerated holes could migrate from the VB of WO₃ to that of Ag₃PO₄. The holes could directly oxidize the organic dyes adsorbed on Ag₃PO₄ surface [48–50] and the electrons could be consumed through a multi-electron reaction with oxygen (O₂ + 2H⁺ + 2e⁻ → H₂O₂, E⁰ = +0.682 V vs. NHE) [51]. The produced H₂O₂ reacts with an additional electron to produce ·OH (H₂O₂ + e⁻ → ·OH + OH⁻) [52], which could accelerate the antimicrobial activity.

Fig. 13. a PL spectra of the aqueous basic solution of terephthalic acid and Fe₃O₄/Ag₃PO₄@WO₃ (0.25, 0.50 and 0.75) with an excitation at 365 nm under different composites for 50 min. Inset of a is the PL spectra of pure sample Ag₃PO₄, WO₃ and Fe₃O₄ and b PL spectra of changing with irradiation time for the case of the Fe₃O₄/Ag₃PO₄@WO₃-0.25.

Fig. 14. Scheme diagrams for the enhanced activity of Fe₃O₄/Ag₃PO₄@WO₃-0.25 photocatalysts.

\[
\text{WO}_3 + \text{hv} \rightarrow \text{WO}_3^* \quad (3)
\]

\[
\text{Ag}_3\text{PO}_4(e) + \text{O}_2 \rightarrow \text{Ag}_3\text{PO}_4 + \text{O}_2^- \quad (5)
\]

\[
\text{O}_2^- + \text{H}^+ \rightarrow \cdot \text{OOH} \quad (6)
\]

\[
\cdot \text{OOH} + \text{Ag}_3\text{PO}_4(e) + \text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{Ag}_3\text{PO}_4 \quad (7)
\]

\[
\text{H}_2\text{O}_2 + \text{Ag}_3\text{PO}_4(e) \rightarrow \cdot \text{OH} + \text{OH}^- + \text{Ag}_3\text{PO}_4 \quad (8)
\]

Organic pollutant with OH, O₂⁻ or H₂O₂ → degraded or mineralized products and bacterial activity.

At the same time, the enhanced photocatalytic activity could be expected the composites Fe₃O₄/Ag₃PO₄/WO₃-0.25 catalyst due to the effective separation of photogenerated electron–hole pairs. According to the plot of (Ahν)² vs. hν, the band gaps (E₉) of Ag₃PO₄ and WO₃ are estimated to be 2.35 and 2.44 eV, respectively. The band structure of Fe₃O₄/Ag₃PO₄/WO₃ composites can be estimated according to the empirical equations as shown below:

\[
\text{VB} = \text{X} - \text{E}_e + 0.5 \text{E}_g \quad (10)
\]

\[
\text{CB} = \text{VB} - \text{E}_g \quad (11)
\]

where EVB and ECB are the valence and conduction band edge potentials, respectively; χ is the electronegativity of the semiconductor; Ee is the energy of free electrons on the hydrogen scale (about 4.5 eV vs. NHE). The χ values for bare Fe₃O₄, Ag₃PO₄ and WO₃ are 5.78, 5.96 and 6.49 eV and, respectively [53–55]. Thus, the EVB of Fe₃O₄, Ag₃PO₄ and WO₃ have been calculated to be 2.18,
2.63 and 3.31 eV vs. NHE, and the corresponding ECB are 0.38, 0.28 and 0.77 eV vs. NHE, respectively.

**Conclusions**

In this work, novel Fe₃O₄/Ag₃PO₄@WO₃ photocatalysts were successfully synthesized via in situ ion-exchange method, and employed in the simulated light degradation of organic contaminants (Methylene Blue). The as synthesized composite exhibited enhanced photocatalytic activity compared with Fe₃O₄/Ag₃PO₄@WO₃-non and the bare WO₃. In addition, the effect of the Ag₃PO₄ amount on the photocatalytic activity of the Fe₃O₄/Ag₃PO₄@WO₃ was investigated. The Fe₃O₄/Ag₃PO₄@WO₃-0.25 exhibited the higher photocatalytic activity. The antibacterial behaviors of the synthesized composite were studied. All the Ag₃PO₄, Fe₃O₄/Ag₃PO₄ and Fe₃O₄/Ag₃PO₄@WO₃ based composites exhibited enhancement in bactericidal efficiency. The oleic acid functionalized composite Fe₃O₄/Ag₃PO₄@WO₃ also exhibited the high inhibition zone. The reactive species trapping study revealed that, the hole played the main role on the photocatalytic activity enhancement.

**Authors’ contributions**

HBG: carried all most experiment and write the paper, MIS: participate of the analysis of photocatalyst data, ANC: participated in experiment of active core–shell nanostructured magnetic photocatalyst Fe₃O₄@SiO₂@Ag complexing agent. Appl Catal A. 2013;408(1):364–8.

**Author details**

1 Key Laboratory of Environmental Materials & Environmental Engineering of Jiangsu Province, College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China. 2 Forest Products and Industries Department, Faculty of Forestry, University of Khartoum, Khartoum, Sudan. 3 Key Laboratory of Bioelectrochemistry & Environmental Analysis of Gansu Province, College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou 730070, China. 4 Chemistry Department, Faculty of Science, International University of Africa, Khartoum, Sudan.

**Acknowledgements**

We want to thank Natural Science Foundation of China, Jiangsu Key Laboratory of Environmental Material and Environmental Engineering in College of Chemistry and Chemical Engineering-Yangzhou University and Key Laboratory of Bioelectrochemistry & Environmental Analysis of Gansu Province in College of Chemistry & Chemical Engineering-Northwest Normal University.

**Competing interests**

The authors declare that they have no competing interests.

**Availability of data and materials**

Not applicable.

**Consent for publication**

The manuscript is not under consideration for publication elsewhere.

**Ethics approval and consent to participate**

Not applicable.

**Funding**

This work was supported by the National Science Foundation of China (Grant Nos. 21773203 and 21401162), Jiangsu Key Laboratory of Environmental Material and Environmental Engineering (K11032, K13062), the Program for Chang Jiang Scholars and Innovative Research Team, Ministry of Education, China (Grant No. IRT1283); the Program for Innovative Research Group of Gansu Province, China (Grant No. 1210RJA001), Key Laboratory of Bioelectrochemistry & Environmental Analysis of Gansu Province, College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou 730070, China.

**Publisher’s Note**

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

**Received:** 6 September 2018  **Accepted:** 4 April 2019

**Published online:** 29 April 2019

**References**

1. Sclafani A, Palmisano L, Schiavello M. Influence of the preparation methods of TiO₂ sub 2 on the photocatalytic degradation of phenol in aqueous dispersion. J Phys Chem USA. 1990;94(2):829–32.

2. Sato J, Kobayashi H, Ikarashi K, Saito N, Nishiyama H, Inoue Y. Photocatalytic activity for water decomposition of RuO₂-dispersed Zn₂GeO₄ with c₁₀ configuration. J Phys Chem B. 2004;108(14):4569–75.

3. Bagheri S, Juliapari NW. Magnetite hybrid photocatalysis: advance environmental remediation. Rev Inorg Chem. 2016;36(3):135–51.

4. Cheng XL, Jiang JS, Jin CY, Lin CC, Zeng Y, Zhang Q-H. Cauliflower-like α-Fe₂O₃ 0.25 microstructures: toluene–water interface-assisted synthesis, characterization, and applications in wastewater treatment and visible-light photocatalysis. Chem Eng J. 2014;236:139–48.

5. Martinez DS, Martínez-De La Cruz A, Cuéllar EL. Photocatalytic properties of WO₃ nanoparticules obtained by precipitation in presence of urea as complexing agent. Appl Catal A. 2011;398(1):179–86.

6. Sun J, Chen G, Wu J, Dong H, Xiong G. Bismuth vanadate hollow spheres: bubble template synthesis and enhanced photocatalytic properties for photodegradation. Appl Catal B. 2013;132:304–14.

7. Zhang F-J, Xie F-Z, Liu J, Zhao W, Zhang K. Rapid sonochemical synthesis of irregular nanolaminar-like Bi₂WO₆ 0.2 WO₃ 0.2 as efficient visible-light-active photocatalysts. Ultrason Sonochem. 2013;20(1):209–15.

8. Bi Y, Ouyang S, Ummezawa N, Cao J, Ye J. Facet effect of single-crystalline Ag₃PO₄ sub-microcrystals on photocatalytic properties. J Am Chem Soc. 2011;133(17):6490–2.

9. Kang YS, Rokud S, Rabolt JF, Stroeva P. Synthesis and characterization of nanometer-size Fe₃O₄ and y-Fe₃O₄ particles. Chem Mater. 1996;8(9):2209–11.

10. Wang Y, Li S, Xing X, Huang F, Shen Y, Xie A, Wang X, Zhang J. Self-assembled 3D flowerlike hierarchical Fe₃O₄@Bi₂O₃ core–shell architectures and their enhanced photocatalytic activity under visible light. Chem A Eur J. 2011;17(17):4822–8.

11. Xu J-W, Gao Z-D, Han K, Liu Y, Song Y-Y. Synthesis of magnetically separable Ag₃PO₄/TIO₂/Fe₃O₄ heterostructure with enhanced photocatalytic performance under visible light for photoinactivation of bacteria. ACS Appl Mater Interfaces. 2014;6(17):15122–31.

12. Wu A, Tian C, Chang W, Hong Y, Zhang Q, Qu Y, Fu H. Morphology-controlled synthesis of Ag 3 PO 4 nano/microcrystals and their antibacterial properties. Mater Res Bull. 2013;48(9):3643–8.

13. Liu J-K, Luo C-X, Wang J-D, Yang X-H, Zhong X-H. Controlled synthesis of silver phosphate crystals with high photocatalytic activity and bacteriostatic activity. CrystEngComm. 2012;14(24):8714–21.

14. Li G, Mao L. Magnetically separable Fe 3 O 4–Ag 3 PO 4 sub-micrometre composite: facile synthesis, high visible light-driven photocatalytic efficiency, and good recyclability. RSC Adv. 2012;2(12):5108–11.

15. Patil SS, Tamboli MS, Deonikar VG, Umarji GG, Ambekar JD, Kulkarni MV, Kolekar SS, Kale BB, Patil DR. Magnetically separable Ag 3 PO 4/NiFe 2 O 4 composites with enhanced photocatalytic activity. Dalton Trans. 2015;44(47):20426–34.

16. Sun J, Fan H, Nan B, Ai S. Fe₃O₄@LDH@Ag/Ag₃PO₄ submicrosphere as a magnetically separable visible-light photocatalyst. Sep PurifTechnol. 2014;130:84–90.

17. Yao YR, Huang WZ, Zhou H, Cui X, Zheng YF, Song XC. Synthesis of core–shell nanostructured magnetic photocatalyst Fe 3 O 4@SiO 2@Ag core–shell nanostructured magnetic photocatalyst Fe 3 O 4@SiO 2@Ag.
3 PO 4 with excellent visible-light-responding photocatalytic activity. J Nanoparticle Res. 2014;16(11):2742.

18. Guo X, Chen N, Feng C, Yang Y, Zhang B, Wang G, Zhang Z. Performance of magnetically recoverable core-shell Fe3O4/Ag3PO4/AgCl for photocatalytic removal of methylene blue under simulated solar light. Catal Commun. 2013;38:26–30.

19. Misey K, Kusama H, Sugihara H, Sayama K. C-s-modified WO3 photocatalyst showing efficient solar energy conversion for O2 production and Fe(II) ion reduction under visible light. J Phys Chem Lett. 2010;18:1196–200.

20. Liu Z, Zhao Z-G, Miyachi M. Efficient visible light active CaFe2O4/WO3 based composite photocatalysts: effect of interfacial modification. J Phys Chem C. 2009;113(39):13172–7.

21. Seifollahi Bazargani M, Hojamberdiev M, Morita K, Zhu G, Cherkashinin G, Fasel C, Herrmann T, Breitkreiz H, Curto A, Riedel R. Visible light photocatalysis with c-WO3–x/WO3 x H2O nanostructures in situ formed in mesoporous polyacrylsilane-silicone polymer. J Am Chem Soc. 2013;135(1):4467–75.

22. Zhang G, Wang W, Li X. Enhanced thermoelectric properties of core/shell heterostructure nanowire composites. Adv Mater. 2008;20(19):3654–6.

23. Sun X, Li Y. Colloidal carbon spheres and their core/shell structures with noble-metal nanoparticles. Angew Chem Int Ed. 2004;43(5):597–601.

24. Subramanian V, Wolf EE, Karmat PV. Catalysis with TiO2/gold nanocomposites. Effect of metal particle size on the Fermi level equilibration. J Am Chem Soc. 2004;126(15):4943–50.

25. Formo E, Lee E, Campbell D, Xia Y. Functionalization of electrosyn TiO2 nanofibers with Pt nanoparticles and nanowires for catalytic applications. Nano Lett. 2008;8(2):668–72.

26. Awaazu K, Fujimaki M, Rockstuhl C, Tominaga J, Munakami H, Ohki Y, Yoshida N, Watanabe T. A plasmonic photocatalyst consisting of silver nanoparticles embedded in titanium dioxide. J Am Chem Soc. 2008;130(5):1676–80.

27. Wu W, Jiang C, Roy VA. Recent progress in magnetic iron oxide–semiconductor composite nanomaterials as promising photocatalysts. Nanoscale. 2015;7(1):38–58.

28. Xi G, Yue B, Cao J, Ye J. Fe3O4/WO3 hierarchical core–shell structure: high-performance and recyclable visible-light photocatalyst. Chem Eur J. 2011;17(18):5145–54.

29. Zhou M, Lou XWD, Xie Y. Two-dimensional nanosheets for photocatalytic applications. Nano Lett. 2008;8(2):668–72.

30. Seifollahi Bazargani M, Hojamberdiev M, Morita K, Zhu G, Cherkashinin G, Fasel C, Herrmann T, Breitkreiz H, Curto A, Riedel R. Visible light photocatalysis with c-WO3–x/WO3 x H2O nanostructures in situ formed in mesoporous polyacrylsilane-silicone polymer. J Am Chem Soc. 2013;135(1):4467–75.

31. Tang J, Liu Y, Li H, Tan Z, Li D. A novel Ag 3 AsO 4 visible-light-responsive photocatalyst: facile synthesis and exceptional photocatalytic performance. Chem Commun. 2013;49(48):5498–500.

32. Katsumata H, Taniguchi M, Kanoce S, Suzuki T. Photocatalytic degradation of bisphenol A by Ag 3 PO 4 under visible light. Catal Commun. 2013;34:30–4.

33. Kumar S, Surendar T, Baruah A, Shanker V. Synthesis of a novel and stable gC 3 N 4–Ag 3 PO 4 hybrid nanocomposite photocatalyst and study of the photocatalytic activity under visible light irradiation. J Mater Chem A. 2013;1(17):5333–40.

34. Rawal SB, Do Sung S, Lee WJ. Novel Ag 3 PO 4/TiO 2 composite for efficient decomposition of gaseous 2-propanol under visible-light irradiation. Catal Commun. 2012;17:131–5.

35. Kim J, Lee CW, Choi W. Platinized WO3 as an environmental photocatalyst that generates OH radicals under visible light. Environ Sci Technol. 2010;44(17):6849–54.

36. Katsumata H, Sakai T, Suzuki T, Kanoce S. Highly efficient photocatalytic activity of g-C3N4/Ag3PO4 hybrid photocatalysts through Z-scheme photocatalytic mechanism under visible light. Ind Eng Chem Res. 2014;53(19):8018–25.

37. Chen S, Hu Y, Meng S, Fu X. Study on the separation mechanisms of photogenerated electrons and holes for composite photocatalysts gC 3 N 4–WO 3. Appl Catal B. 2014;150:564–73.

38. Xu Y, Schoenen MA. The absolute energy positions of conduction and valence bands of selected semiconducting minerals. Am Miner. 2000;85(3–4):543–56.

39. Díaz-Reyes J, Dorantes-García V, Pérez-Benítez A, Balderas-López J. Obtaining of films of tungsten trioxide (WO3) by resistive heating of a tungsten filament. Superficies y vacío. 2008;21(2):12–7.

40. Alamri SN. Study of thermocracked WO3 thin film under direct solar radiation. Smart Mater Struct. 2009;18(2):025010.

41. Yu Z, Ye J, Kikugawa N, Kako T, Ouyang S, Stuart-Williams H, Yang H, Cao J, Luo W, Li Z. An orthophosphate semiconductor with photooxidation properties under visible-light irradiation. Nat Mater. 2010;9(7):559–64.

42. Zhao G, Stevens SE. Multiple parameters for the comprehensive evaluation of the susceptibility of Escherichia coli to the silver ion. Biometals. 1998;11(1):27–32.

43. Yamanaka M, Hara K, Kudo J. Bactericidal actions of a silver ion solution on Escherichia coli, studied by energy-filtering transmission electron microscopy and proteomic analysis. Appl Environ Microbiol. 2005;71(11):7589–93.

44. Jung WK, Koo HC, Kim KW, Shin S, Kim SH, Park YH. Antibacterial activity and mechanism of action of the silver ion in Staphylococcus aureus and Escherichia coli. Appl Environ Microbiol. 2008;74(7):2171–8.

45. Wu K, Zhu H, Liu Z, Rodríguez-Córdoba W, Lian T. Ultrafast charge separation and long-lived charged separated state in photocatalytic CdS–Pt nanorod heterostructures. J Am Chem Soc. 2012;134(25):10337–40.

46. Yu J, Mu T, Liu S. Enhanced photocatalytic activity of mesoporous TiO2 2 aggregates by embedding carbon nanotubes as electron-transfer channel. J Phys Chem C. 2011;115(50):24911–501.

47. Wang J-D, Liu J-K, Luo C-X, Yang X-H. Light-dependent controlled synthesis and photocatalytic properties of stable Ag 3 nanocrystals. Mater Res Bull. 2010;45(5):910–4.

48. Mohite S, Rajpure K. Synthesis and characterization of Sb doped ZnO thin films for photodetector application. Opt Mater. 2014;36(4):833–8.

49. Nogueira HI, Cavaleiro AM, Rocha J, Trindade T, de Jesus JDP. Synthesis and characterization of tungsten trioxide powders prepared from tungstenic acids. Mater Res Bull. 2004;39(4):683–93.

50. Daniel M, Desbat B, Lassegues J, Gerard B, Figlarz M. Infrared and Raman study of WO3 tungsten trioxides and WO3, xH2O tungsten trioxide hydrates. J Solid State Chem. 1987;67(2):235–47.