Preparation of Ag₃PO₄/CoWO₄ S-scheme heterojunction and study on sonocatalytic degradation of tetracycline

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ABSTRACT

In this study, 0.6Ag₃PO₄/CoWO₄ composites were synthesized by hydrothermal method. The prepared materials were systematically characterized by techniques of scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS), N₂ adsorption/desorption, and UV-vis diffuse reflectance spectrum (DRS). Furthermore, the sonocatalytic degradation performance of 0.6Ag₃PO₄/CoWO₄ composite towards tetracycline (TC) was investigated under ultrasonic radiation. The results showed that, combined with potassium persulfate (K₅S₂O₈), the 0.6Ag₃PO₄/CoWO₄ composites achieved a high sonocatalytic degradation efficiency of 97.89 % within 10 min, which was much better than bare Ag₃PO₄ or CoWO₄. By measuring the electrochemical properties, it was proposed that the degradation mechanism of 0.6Ag₃PO₄/CoWO₄ is the formation of S-scheme heterojunction, which increases the separation efficiency of electron-hole pairs (e⁻·h⁺) and generates more electrons and holes, thereby enhancing the degradation activity. The scavenger experiments confirmed that hole (h⁺) was the primary active substance in degrading TC, and free radicals (·OH) and superoxide anion radical (·O₂⁻) were auxiliary active substances. The results indicated that 0.6Ag₃PO₄/CoWO₄ nanocomposites could be used as an efficient and reliable sonocatalyst for wastewater treatment.

1. Introduction

As one of the significant discoveries of the last century, antibiotics have considerably changed the treatment of a series of infectious diseases. It has been widely used in bacterial infections [1] of humans and animals as well as in agricultural and aquacultural areas [2]. However, only a tiny part of antibiotics can be metabolized or absorbed in humans or animals during the process of application. Most antibiotics (about 40–90 %) are discharged into the water environment or soil in the form of original drugs or primary metabolites [3]. With the deposition of antibiotics in different areas of the environment (including surface water, groundwater, drinking water, municipal sewage, soil, plants and sludge) [4], which leads to the spread of antibiotic-resistant bacteria (ARBs) and antibiotic-resistant genes (ARGs), with severe impacts on agriculture, aquaculture, humans and livestock [5]. TC is the second most produced and used antibiotic due to its broad-spectrum antibacterial activity and low production cost [6–7]. It is not easily to be destroyed [8–9] and enriched over time in various aquatic environments for its benzene skeleton structure and high hydrophilicity. Since TC is biologically toxic and carcinogenic [10–11], it is potentially harmful to human health [12], aquatic ecosystems, and microbial populations [13] if it is accumulated in large quantities in the environment for a long time.

Traditional sewage treatment plants and biological treatment technologies are not sufficient to remove antibiotics from wastewater [14], so an advanced technology with simple operation, high efficiency, good effect, low price, and eco-friendliness is sought to alleviate the problem of environmental pollution. Advanced oxidation processes (AOPs) degrade pollutants by generating free radicals with strong oxidizing ability [15], which have the advantages of simple operation [16], fast degradation rate, good degradation effect [17], low toxicity of degradation products [18], and non-selectivity in the oxidation of contaminants [19]. As a kind of AOPs, sonocatalytic is a chemical effect of ultrasonic waves caused by acoustic cavitation [15], which refers to the propagation of ultrasonic waves in a liquid that could change local ultrasonic pressures over time and space and lead to the formation of bubbles. The radii of the bubbles expand, contract and/or collapse as these pressures change [20]. The collapse of transient bubble leads to the appearance of
sonoluminescence (SL) and “hot spots”, which can generate high temperature and high pressure, exceeding 5000 K and 1000 atm, respectively [21–22]. Under such extreme conditions, water thermally decomposes to form free radicals, such as •OH, •H, •O2, which are highly reactive and non-selective, attack organic molecules to produce CO2, H2O, and inorganic ions, or less toxic intermediates [23–24]. Since ultrasonic degradation combines sonic decomposition and photocatalysis, it is easier to increase the degradation of organic matter than AOPs alone [25], and has the advantages of strong penetrating ability, simple operation, and no secondary pollution [26–27]. However, the degradation of pollutants by a simple sonocatalytic process usually requires long reaction times, limited degradation efficiency, and high energy consumption [25,28]. So, some scientists have combined ultrasonic with other AOPs technologies to further improve the performance of catalysts for the removal of pollutants. Aydin Hassan et al. found that the combination of ultrasonic and electrochemical processes have synergistic effects that lead to enhanced mineralization of organic pollutants [29], such as the combination of Electro-Peroxone (EP) and ultrasound effectively enhanced acid orange 7 degradation [30]. At the same time, studies have shown that solid catalysts in ultrasonic systems could provide more nucleation sites for bubble cavitation and more charge carriers for the formation of free radicals, thereby enhancing the ultrasonic degradation effect [31–32]. For example, some nanoparticles act as sonocatalysts, which can reduce the energy and time required for the degradation of organic pollutants [33]. According to recent studies, many semiconductor materials, such as TiO2 [34], CdS [35], ZnO [31], N-TiO2/Ti3C2 [36], CoFe2O4-rGO [37], Fe3O4/SnO2/NGP [38] etc., have been used as sonocatalysts.

The nano-semiconductor material cobalt tungstate (CoWO4) has excellent catalytic and electrochemical properties [39–40]. At the same time, it has the advantages of a simple preparation method [41], high chemical stability [42], and environmental friendliness [43]. It is used in the fields of photo voltaic electrochemical cell luminates materials [44], supercapacitors [41], conventional oxidation catalysts, and environmental purification photocatalysts [45–46]. Although CoWO4 has a good application in catalysis, it has a low utilization rate of sunlight, slow degradation efficiency, and low separation efficiency of e−h+, which may limit its catalytic degradation ability. These disadvantages can be ameliorated by modifying it [47]. For example, the CoWO4/g-C3N4 heterostructure prepared by Prabavathi et al. has better photocatalytic activity [48]; Cui et al. [49] constructed a Z-scheme-based CoWO4/CdS, which greatly enhanced the activity for hydrogen production and dye degradation. Recently, silver-based photocatalysts, such as Ag3PO4, Ag5WO4 [50], Ag2CO3 [51], AgX (X = Cl, Br, I) and Ag2MoO4 [52] have received extensive attention in the field of photocatalytic degradation of organic pollutants. Among them, Ag3PO4 has a strong oxidizing ability under visible light excitation and nearly 90% quantum utilization efficiency [53–54], which is considered as a promising visible-light-driven photocatalyst. However, the stability of the Ag3PO4 photocatalytic system has always been a significant problem. First, the slight solubility of Ag3PO4 in aqueous solution will reduce its stability under working conditions [55]; second, during the degradation of Ag3PO4, Ag+ in the lattice is reduced to metallic Ag by photogenerated electrons [56], which leads to the structural destruction of Ag3PO4, which affects the absorption of visible light by Ag3PO4 and reduces its photocatalytic activity [55]. This problem can be addressed by techniques such as structure and morphology control, metal doping, coupling carbonaceous materials [57] and coupling with other semiconductors [58]. Therefore, this study, for the first time, considered the application of Ag3PO4 to the sonocatalytic degradation of pharmaceutical wastewater. Compositing it with CoWO4 to form a heterojunction and accelerate electron migration, thereby reducing the recombination rate of photogenerated e−h+ [59] and the probability of electron reduction of Ag+ [54], making the composites exhibit more excellent sonocatalytic activity and stability.

In this paper, Ag3PO4 was used for the first time in the application of sonocatalysis, and the Ag3PO4/CoWO4 composites sonocatalyst was produced by combining with CoWO4 by hydrothermal method. The prepared composites sonocatalyst was characterized, and the physical and chemical properties of the modified catalysts were analyzed. The sonocatalytic performance of Ag3PO4/CoWO4 was studied by degrading TC, and the influence of different factors on the degradation performance during the degradation process was investigated. In addition, added K2S2O8 to improve the catalytic activity further. At the same time, the reuse experiment was carried out to investigate the stability and reusability of 0.6Ag3PO4/CoWO4. Furthermore, the sonocatalytic mechanism of 0.6Ag3PO4/CoWO4 was discussed by radical trapping experiments and the Mott-Schottky equation. At present, there’s no report about Ag3PO4/CoWO4 composites, and this is the first time that Ag3PO4/CoWO4 composites have been synthesized and used in the field of sonocatalytic degradation of organic pollutants.

2. Experiment

2.1. Materials

Cobalt nitrate hexahydrate (Co(NO3)2·6H2O) was analytical reagent (AR) and purchased from Tianjin Damao Chemical Reagent Factory. Sodium tungstate dihydrate (Na2WO4·2H2O, AR) was purchased from Tianjin No.4 Chemical Reagent Factory. Sodium phosphate (Na3PO4·12H2O, AR) was purchased from Tianjin Yongda Chemical Reagent Co., Ltd. Silver nitrate (AgNO3, 98 %) was purchased from Tianjin Fengchuan Chemical Reagent Technology Co., Ltd. Mannitol (AR, AR) was purchased from Tianjin Bodi Chemical Co., Ltd. K2S2O8 (AR) was purchased from Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd. Ammonium oxalate monohydrate (AO, AR) and TC (96 %) was purchased from Maya Reagent Co., Ltd. Deionized water was used in the experiments.

2.2. Preparation of Ag3PO4 and Ag3PO4/CoWO4

CoWO4 was prepared by a simple hydrothermal method [60]. The preparation method of Ag3PO4/CoWO4 composites material was as follows: 0.6156 g of CoWO4 was ultrasonically dissolved in 20 ml of deionized water, and 0.6115 g of AgNO3 was weighed and dissolved in 20 ml of deionized water. Then 0.45614 g of 20 ml Na2PO4·12H2O deionized aqueous solution was added dropwise to the mixed solution, and the magnetic stirring was continued for 1 h. The obtained precipitate was vacuum filtered, washed several times with deionized water, dried at 60 °C for 15 h and then ground. Ag3PO4/CoWO4 composites material was obtained finally. Ag3PO4/CoWO4 composites with different molar ratios (0.3, 0.6, 0.9, 1.2) were obtained by adjusting the addition amounts of AgNO3 and Na3PO4·12H2O. Pure Ag3PO4 was prepared by using a similar process without the addition of CoWO4.

2.3. Characterization of Ag3PO4/CoWO4

The morphology of the samples was observed by TESCAL MIRA4 SEM. The elemental composition and content of the samples were determined by Thermo Scientific K-alpha XPS at 12 kV monochromatic Al Kα radiation. The crystal structures of the samples was determined by using a MiniFlex 600 XRD under Cu Ka radiation with a 2θ scan range of 10°/min and a scan range from 10° to 80°. The UV absorption spectrum and UV DRS were measured by using a Shimadzu UV-3600 UV–vis–NIR spectrophotometer with BaSO4 as a reference and a wavelength range of 200–800 nm. The Brunauer-Emmet-Teller (BET) and pore distribution of the samples were determined by using a Mack TriStar II 3020 N2 adsorption/desorption analyzer at 60 °C.

2.4. Sonocatalytic degradation experiment of TC

In the ultrasonic degradation experiment, the initial conditions were
set follows: 20 mg Ag₃PO₄/CoWO₄ powder was added to 20 ml of TC solution, the TC concentration was 45 mg/L, the ultrasonic power was 500 W, and the ultrasonic time was 2 h. Interrelated factors were adjusted in a single factor test. Added Ag₃PO₄/CoWO₄ powder to the TC solution before sonication, then stirred magnetically for 30 min in the darkness to ensure that the adsorption/desorption equilibrium was reached. Afterwards, according to the above conditions, samples were irradiated by using an ultrasonic bath (KQ5200, 40 kHz, 500 W, Kunshan Ultrasonic Instrument Co., ltd., China) at 313 K, during which light was avoided. After ultrasonication, the solution was filtered with a 0.22 μm microporous membrane, and the absorbance at 354.5 nm of the obtained solution was measured with a UV–vis spectrophotometer. The degradation rate was calculated according to the Eq. (1).

\[
\text{Degradation rate (\%)} = \left[\frac{A_0 - A_t}{A_0}\right] \times 100\% 
\]

where \(A_0\) is the initial absorbance of TC, and \(A_t\) is the absorbance of TC when the ultrasonic time is \(t\).

To examine the cycling stability of 0.6Ag₃PO₄/CoWO₄, the samples used in the sonocatalysis reaction were recovered and used repeatedly for four cycles. To detect the active species in the sonocatalysis process, \(\cdot\)Man [61], AO [62], and N₂ [63] were used as ‘OH, \(\cdot\)O₂ scavengers for active substance studies.

3. Results and discussion

3.1. Characterization of nanocomposites

The crystal structure and phase purity of the as-prepared composites were determined by using XRD patterns. Fig. 1 showed the standard patterns of CoWO₄, Ag₃PO₄ and the XRD patterns of Ag₃PO₄/CoWO₄ with different molar ratios, respectively. According to Fig. 1, the peak of 20 values was 20.8°, 29.7°, 33.3°, 36.6°, 42.5°, 47.8°, 52.7°, 55.1°, 57.3°, 61.7°, 65.9°, 70.0°, 71.9°, 73.9°, 77.7°, corresponded to the (110), (200), (210), (211), (220), (310), (320), (321), (400), (420), (421), (332) and (422) plane of Ag₃PO₄ (JCPDS No. 06-0505) [56]. The diffraction peaks of 20 characteristic peaks at 23.8°, 24.6°, 30.6°, 36.3°, 38.5°, 41.4°, 52.0°, 54.0°, 61.8°, 65.1°, 68.6° were similar to (011), (110), (−111), (002), (200), (−121), (130), (−222), (−113), (−132) and (041) plane of Ag₃PO₄ (JCPDS-72-0479) [64]. For the spectrum of Ag₃PO₄/CoWO₄ composites in Fig. 1, all the diffraction peaks could be marked as characteristic peaks of Ag₃PO₄ or CoWO₄. The intensity of the (200), (210), (211), (310),

\[\text{(222), (320), (321), (400), (421)}\]

peak increased significantly with the increasing of Ag₃PO₄ composites ratio, indicating that the successful assembly of these two materials did not cause obvious change or destruction of the crystal structure. And it could be seen that the shape of the diffraction peaks was very sharp and the intensity is high, indicating that the synthesized Ag₃PO₄/CoWO₄ had a high crystallinity.

The surface morphology of the prepared bare CoWO₄, Ag₃PO₄, and 0.6Ag₃PO₄/CoWO₄ were investigated by SEM. As shown in Fig. 2a that CoWO₄ is a spherical nanoparticle with large particle size, about 100–200 nm, and the agglomeration phenomenon is obvious. Fig. 2b is the SEM image of Ag₃PO₄, and its nanoparticles are also spherical, with a particle size slightly smaller than that of CoWO₄ about 50–80 nm, with slight agglomeration. Fig. 2c is the SEM of the composite material. It could be seen that Ag₃PO₄ particles are uniformly wrapped on the surface of CoWO₄, forming a spherical shape. Compared with the pure material, the dispersion degree is slightly improved and the agglomeration phenomenon is reduced. The elemental purity of 0.6Ag₃PO₄/CoWO₄ was determined by the EDX system. As the EDX peaks shown in Fig. 2d 0.6Ag₃PO₄/CoWO₄ is composed of Ag, P, Co, W, and O elements. In addition, no-negligible peaks appear, indicated that the obtained 0.6Ag₃PO₄/CoWO₄ is of high purity, and the relative element/weight ratio was shown in the table (inset Fig. 2d). Fig. 2e showed the specified SEM images of 0.6Ag₃PO₄/CoWO₄ nanocomposites and corresponding elemental mapping. It was further explained that the Ag, P, Co, W, and O elements in the composite are evenly distributed, indicated that Ag₃PO₄ and CoWO₄ are thoroughly combined.

In order to shed more light on inner structure of the sample, TEM analysis was taken for 0.6Ag₃PO₄/CoWO₄. As shown in Fig. 3a that Ag₃PO₄ particles were uniformly fixed on the surface of CoWO₄ particles, and the particle size of CoWO₄ was reduced to 20–50 nm, while that of Ag₃PO₄ was reduced to 2–5 nm. The HRTEM in Fig. 3b showed clear lattice fringe of the composites, with band spacing of 0.269 nm and 0.36 nm corresponded to plane (210) of Ag₃PO₄ [56] and plane (011) of CoWO₄ [43], respectively.

The chemical state and composition of 0.6Ag₃PO₄/CoWO₄ were further affirmed by high-resolution XPS. Fig. 3a showed the XPS scanning spectra of CoWO₄, Ag₃PO₄, and 0.6Ag₃PO₄/CoWO₄ composites. It could be seen that the composites sonocatalysis contained Ag, P, Co, W, and O elements. The high-resolution XPS spectra of Ag 3d, P 2p, Co 2p, and W 4f were shown in Fig. 4 a-c. At the binding energies of 787.78 eV and 737.48 eV in Fig. 4 b, which were attributed to Ag 3d₃/₂ and Ag 3d₅/₂ photon electrons, respectively, indicated that Ag exists in the form of Ag⁺. It could be seen from Fig. 4c that the p⁵⁻ ion in PO₄³⁻ had a single peak [56] at 132.38 eV, and combined with Fig. 4a, we could infer the formation of Ag₃PO₄. Two prominent peaks of Co 2p were observed at 781.18 eV and 797.88 eV in Fig. 4d, which were attributed to Co 2p₃/₂ and Co 2p₁/₂ photons, respectively, indicated that Co exists in the form of Co²⁺. At the binding energies of 787.78 eV and 803.65 eV, two satellite peaks on the catalyst surface, corresponded to the adsorption of hydroxide and cobalt salt [65]. At 35.78 eV and 37.98 eV in Fig. 4e, two prominent peaks of W 4f were observed, ascribed to W 4f₇/₂ and W 4f₅/₂ photons, respectively, indicated that W in WO₄²⁻ exists as + 6 ion [66]; and combined with Fig. 4a, we could infer the formation of CoWO₄. Compared with the pure material, the binding energy of the composite had shifted, in which the binding energy of Ag and P elements were reduced, while the binding energy of Co and W elements were enhanced, indicated that there was a strong interaction between CoWO₄ and Ag₃PO₄, which might be related to the formation of S-scheme heterojunctions. In conclusion, the XPS results indicated that 0.6Ag₃PO₄/CoWO₄ was successfully synthesized.

It is well known that specific surface area and pore size are crucial for catalytic activity [67]. Therefore, N₂ adsorption/desorption isotherms were used to study the specific surface area and pore size distribution of the samples. The results were shown in Table 1. The corresponding N₂ adsorption/desorption isotherms and the pore distribution were shown in Fig. 5. It was indicated that the prepared sonocatalyst has scheme IV
isotherm. From the BET surface area analysis, it could be seen that the BET of Ag$_3$PO$_4$ and CoWO$_4$ were comparatively smaller, 35.78 and 18.20 m$^2$/g, respectively, while the BET increases to 40.48 m$^2$/g when the 0.6Ag$_3$PO$_4$/CoWO$_4$ composites is formed. Used the Barrett-Joyner-Harenda (BJH) diagram to give the pore size of the composites, the average pore size of 0.6Ag$_3$PO$_4$/CoWO$_4$ was 0.10 cm$^3$/g, which is larger than that of Ag$_3$PO$_4$ (0.06 cm$^3$/g) and CoWO$_4$ (0.08 cm$^3$/g). It could be found that the addition of Ag$_3$PO$_4$ could increase the specific surface area and pore size. Due to the large specific surface area and abundant pore structure, the adsorption performance of the catalyst can be enhanced and more active catalytic sites can be provided [60]. Therefore, the large specific surface area and pore size of 0.6Ag$_3$PO$_4$/CoWO$_4$ are beneficial for improving its sonocatalytic activity [35].

The light absorption capacity of the catalyst has a significant influence on its catalytic activity [64]. Therefore, to study the absorption of the sample in the UV–visible region, its UV–visible absorption spectrum was scanned, as shown in Fig. 6a. It could be seen that, Ag$_3$PO$_4$, CoWO$_4$, and 0.6Ag$_3$PO$_4$/CoWO$_4$ all have excellent UV–vis responses. Among them, the absorption limit of Ag$_3$PO$_4$ was 580 nm, and the peak shape was wider, indicated that Ag$_3$PO$_4$ has strong visible light absorption. There are two prominent absorption peaks in the absorption curve of CoWO$_4$, which were located in the ultraviolet area of 225–375 nm and
the visible area of 550–600 nm, and an inconspicuous peak was formed at about 525 nm. The peak shape in the ultraviolet area was broader, and the peak shape distribution in the visible area was narrower. It shows that CoWO₄ has a high absorption and utilization efficiency for ultraviolet light, but relatively low utilization for visible light. Compared with pure CoWO₄, the absorbance of 0.6Ag₃PO₄/CoWO₄ composites decreased after adding Ag₃PO₄, but the absorbance appeared red-shifted in the visible region, indicated that 0.6Ag₃PO₄/CoWO₄ has better photoresponse [56]. The band gap energy (Eg) of each sample was calculated with the following Eq. (2):

\[ a\nu = A(h\nu - E_g)^{2/n} \]  

(2)

where \( a \) represents the absorption coefficient, \( h\nu \) represents the photon energy, \( E_g \) represents the band gap, and \( A \) represents the proportionality constant [68]. The value of \( n \) depends on the transition scheme of the semiconductor (\( n = 1 \) when the transition is allowed directly, \( n = 4 \) when the transition is allowed indirectly [69]). Using the light absorption data and Tauc equation, the band gap values of pristine Ag₃PO₄, CoWO₄ and 0.6Ag₃PO₄/CoWO₄ were 2.55 eV, 2.64 eV and 2.60 eV respectively (Fig. 6 b).

3.2. Influence of operating parameters on sonocatalytic performance

3.2.1. Influence of different Ag₃PO₄ compound ratios

By changing the addition amount of AgNO₃ and Na₃PO₄⋅12H₂O in the preparation process, the composites with compound ratios of 0.3, 0.6, 0.9, and 1.2 were synthesized, and TC was degraded under the same ultrasonic conditions. As shown in Fig. 7, with the increasing compound amount of Ag₃PO₄, the degradation of TC by the composites showed a trend of increasing firstly (from 0.3 to 0.6) and then decreasing (from 0.6 to 1.2). It showed that the molar ratio of Ag₃PO₄ in Ag₃PO₄/CoWO₄ has a great contribution to the catalytic activity of the composites, because the photogenerated holes in the Ag₃PO₄ conduction band represent a robust oxidizing ability, when there was an excess of Ag₃PO₄ in the composites, not only the light absorption intensity of the composites being reduced, but also the photo corrosion of Ag₃PO₄ being enhanced, thereby reducing the sonocatalysis activity of the composites [54]. When the compound molar ratio of Ag₃PO₄ to CoWO₄ was 0.6, the sonocatalytic degradation rate was the highest, so the subsequent degradation experiments used a composites material with a molar ratio of 0.6.

3.2.2. Influence of the amount of catalyst added

By changing the addition amount of 0.6Ag₃PO₄/CoWO₄ catalyst, the effect of the additional amount on the degradation rate was studied. The results were presented in Fig. 8 (a). It could be seen that when the addition amount was changed from 0.5 to 2 g/L, the degradation rate increased (from 0.5 to 1 g/L) firstly and then remained almost unchanged. The degradation rate was the highest (71 %) when the dosage was 1 g/L. The reason for the improved degradation efficiency is that an appropriate amount of catalyst can provide sufficient surface area and active sites for sonocatalysis [70], while when the dose continues to increase, the solid particles will have a masking effect on the penetration ability of the ultrasonic wave, thereby reducing the surface reaction sites of ‘OH radical generation. Moreover, the ultrasound might be disseminated by the additional catalyst in the solution, which could inhibit heat and energy conduction near the surface of the catalyst [71].

3.2.3. Effect of initial TC concentration

The effect of different TC concentrations (15, 25, 35, 45, and 55 mg/L) on the degradation effect was investigated, and the results are shown in Fig. 8(b). It could be seen that the degradation rate decreased continuously when the concentration increased (from 15 mg/L to 25 mg/L), and the degradation efficiency was the highest when the concentration was 25 mg/L. The reason is that at low concentration, the catalyst can be fully contacted with the solution, and a large number of reactive oxygen species in the solution can react with TC molecules, resulting in a higher degradation rate [72]. However, when the initial solution concentration of TC increases and the catalyst was quantitative, the generated active sites and the surface area of bubbles used for the reaction cannot meet the progress of the catalytic reaction, resulting in a decrease in the degradation rate of TC [73]. By calculating the degradation quality, it was found that although the degradation rate decreased when the initial concentration of TC increased, the degradation quality showed an increasing state, indicated that the 0.6Ag₃PO₄/CoWO₄ composites still had an excellent sonocatalytic degradation effect for high concentrations of TC.

3.2.4. Influence of ultrasonic power

The effect of ultrasonic power on the degradation rate was shown in Fig. 8(c). When the ultrasonic power was small, the degradation rate was lower. This is because with the increase of ultrasonic power, not only the energy of cavitation is enhanced, but also the threshold of cavitation is lowered. Therefore, more cavitation microbubbles will be generated during the ultrasonic process, and accordingly more active free radicals will be generated, which significantly improves the catalytic activity [74].

3.2.5. Effect of different ultrasound time

Fig. 9a showed the degradation of TC at different time without catalyst and with Ag₃PO₄, CoWO₄, and 0.6Ag₃PO₄/CoWO₄ catalysts, respectively. It could be seen that when the degradation time was 120 min, the self-degradation of TC was only 34.52 % without the addition of catalyst. Among the three catalysts, the degradation effect of 0.6Ag₃PO₄/CoWO₄ was the best, reaching 73.45 %, which was 1.6 times...
that of CoWO$_4$ (45.11 %) and 1.5 times that of Ag$_3$PO$_4$ (48.41 %), respectively.

The kinetic behavior of TC degradation under different catalysts was investigated by using pseudo-first-order equations, and the results were shown in Fig. 9b. The sonocatalytic rate constant could be estimated by Eq. (3).

$$\ln\left(\frac{C_t}{C_0}\right) = kt \quad (3)$$

where $C_0$ is the initial drug concentration, $C_t$ is the drug concentration at time $t$, $t$ is the irradiation time, and $k$ is the rate constant. The first-order

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**Table 1**

| Sample             | BET Surface Area (m$^2$/g) | Pore Volume (cm$^3$/g) | Pore Size (nm) |
|--------------------|-----------------------------|------------------------|---------------|
| CoWO$_4$           | 35.78                       | 0.08                   | 9.22          |
| Ag$_3$PO$_4$       | 18.20                       | 0.06                   | 12.27         |
| 0.6CoWO$_4$/Ag$_3$PO$_4$ | 40.48                      | 0.10                   | 9.43          |
rate constants \( k \) of Ag\(_3\)PO\(_4\), CoWO\(_4\), and 0.6Ag\(_3\)PO\(_4\)/CoWO\(_4\) were 0.00404 min\(^{-1}\), 0.00409 min\(^{-1}\) and 0.01454 min\(^{-1}\), respectively. It could be seen that \( k \) value of 0.6Ag\(_3\)PO\(_4\)/CoWO\(_4\) was the largest, which was 3.55 times that of Ag\(_3\)PO\(_4\) and CoWO\(_4\). The synergy factor (SF) was obtained by Eq. (4) [75–76], it was found that SF > 1 (SF = 1.79), indicated that Ag\(_3\)PO\(_4\) compound CoWO\(_4\) has a positive synergistic effect on the degradation of TC.

\[
SF = \frac{k_{(0.6\text{Ag}_3\text{PO}_4/\text{CoWO}_4)}}{k_{\text{Ag}_3\text{PO}_4} + k_{\text{CoWO}_4}} \tag{4}
\]

To sum up, when the addition amount of sonocatalyst was 1 g/L, the initial concentration of TC was 15 mg/L, the ultrasonic power was 500 W, and the ultrasonic time was 90 min, the degradation rate of TC by the 0.6Ag\(_3\)PO\(_4\)/CoWO\(_4\) composites was 75.3 %.

### 3.2.6 Effect of adding K\(_2\)S\(_2\)O\(_8\)

According to literature reports, SO\(_4^*\) can be generated by ultrasonic activation after adding persulfate during the degradation process [77]. Compared with •OH, SO\(_4^*\) has greater redox capacity and longer half-life, which may help to enhance the degradation effect [78,79]. Therefore, K\(_2\)S\(_2\)O\(_8\) in different concentrations was added during the degradation process, and their influence on the degradation effect was studied. The results were presented in Fig. 10. It could be observed that adding K\(_2\)S\(_2\)O\(_8\) can significantly improve the degradation rate and shorten the degradation time. When 10 mg of K\(_2\)S\(_2\)O\(_8\) was added, the degradation rate of TC could reach 97.89 % in 10 min. It showed that K\(_2\)S\(_2\)O\(_8\) was an ideal additive in sonocatalytic degradation reaction, which had a synergistic effect with the 0.6Ag\(_3\)PO\(_4\)/CoWO\(_4\) composites in the degradation process.

### 3.3. Mechanism of sonocatalysis

In order to study the main active substances in the degradation of TC by 0.6Ag\(_3\)PO\(_4\)/CoWO\(_4\) composites, •Man (•OH scavengers), AO (h\(^+\) scavengers), N\(_2\) (•O\(_2\) scavengers) were added as scavengers to the TC degradation process. The results were presented in Fig. 11. It could be
observed that the degradation rate of TC decreased when α-Man and N₂ were added, but did not fluctuate significantly. In contrast, the degradation rate decreased significantly when AO was added. It showed that h⁺ was the primary active substance, and •OH and •O₂⁻ were auxiliary active substances.

The semiconductor band gap positions have an essential impact on their catalytic performance, as they determine the interfacial charge transfer behavior. Therefore, the band structures and semiconductor type of Ag₃PO₄ and CoWO₄ were analyzed by using the Mott-Schottky dot plots, as shown in Fig. 12. Flat band potentials (Eᶠ) can be estimated from intercepts of the X-axis and are close to Fermi Levels (Eᶠ) [80]. The Eᶠ of Ag₃PO₄ and CoWO₄ were 1.45 V and −0.55 V versus saturated calomel electrode (SCE), respectively [81]. According to the Nernst equation, the potentials are 1.69 V and 0.31 V (vs NHE), respectively. For n-type semiconductors, the position of CB is 0.1–0.3 V above the Eᶠ, and for p-type semiconductors, the position of VB is 0.1–0.3 V above the Eᶠ [82]. It could be known from Fig. 6b that the E₉ of Ag₃PO₄ and CoWO₄ were 2.55 eV and 2.64 eV, respectively. Since the
energy difference of 1 eV in solid-state physics is the same as the difference in energy of 1 V in the field of electrochemistry. According to the empirical formula \( E_{\text{VB}} = E_{\text{CB}} + E_g \) [83], the calculated VB values of \( \text{Ag}_3\text{PO}_4 \) and CoWO\(_4\) were 1.89 V and 2.13 V, respectively, and the CB values were −0.66 V and −0.51 V.

Based on the above discussion about the band structure, the left side of Fig. 13 showed the band arrangement diagram of the composite \( \text{Ag}_3\text{PO}_4/\text{CoWO}_4 \) before contact. As observed, the valence band (VB) and conduction band (CB) of \( \text{Ag}_3\text{PO}_4 \) and CoWO\(_4\) generated \( h^+ \) and \( e^- \), respectively, because of the appropriate band structure. As shown on the right of Fig. 13, when \( \text{Ag}_3\text{PO}_4 \) formed heterojunctions with CoWO\(_4\), \( e^- \) on CoWO\(_4\) CB spontaneously transferred to VB on \( \text{Ag}_3\text{PO}_4 \). Depletion layer was generated on the CoWO\(_4\) side and accumulation layer was formed on the \( \text{Ag}_3\text{PO}_4 \) side, forming the internal electric field from CoWO\(_4\) to \( \text{Ag}_3\text{PO}_4 \). Since \( e^- \) was acquired by \( \text{Ag}_3\text{PO}_4 \), the binding energy of Ag and P in \( \text{Ag}_3\text{PO}_4 \) decreased. Conversely, the binding energy of Co and W in CoWO\(_4\) increased due to the loss of \( e^- \) in CoWO\(_4\), which was consistent with the XPS results [84]. Then the \( e^- \) in the CB of CoWO\(_4\) were recombined with the \( h^+ \) in the VB of \( \text{Ag}_3\text{PO}_4 \) through conventional charge separation [85]. Therefore, the \( e^- \) of \( \text{Ag}_3\text{PO}_4 \) on relatively negative CB and the \( h^+ \) of CoWO\(_4\) on relatively positive VB are maintained, facilitating to produce more radicals ‘\( \text{O}_2 \)’ and ‘\( \text{OH} \)’ [86]. Then the \( e^- \) on the CB (\( \text{Ag}_3\text{PO}_4 \)) reacted with the adsorbed \( \text{O}_2 \) to generate ‘\( \text{O}_2^- \)’, because the CB of \( \text{Ag}_3\text{PO}_4 \) more negative than the potential of \( \text{O}_2^-/\text{O}_2 \) \((E^{\text{O}_2^-/\text{O}_2} = -0.33 \text{ V})\). Meanwhile, a part of the \( h^+ \) on VB (CoWO\(_4\)) could directly catalyze TC, and the other part \( h^+ \) could oxidize \( \text{OH}^- \) to ‘\( \text{OH} \)’ (because its oxidation potential is higher than \( \text{OH}^-/\text{OH} \) (1.99 V)). According to the above mechanism, \( \text{Ag}_3\text{PO}_4 \) and CoWO\(_4\) produced interfacial contact, which effectively prevented \( e^- - h^+ \) pairs from recombining, improves its separation efficiency, and generated more \( e^- \) and \( h^+ \), thereby enhancing the degradation activity. Possible reactions were listed in Eq. (5)-(8). These results indicated that the heterojunction formed by \( \text{Ag}_3\text{PO}_4 \) and CoWO\(_4\) could effectively improve the ultrasonic catalytic performance.

\[
0.6\text{Ag}_3\text{PO}_4/\text{CoWO}_4 + \text{Ultrasound} \rightarrow e^- (\text{CB}) + h^+ (\text{VB}) \tag{5}
\]

\[
e^- + \text{O}_2 \rightarrow \text{O}_2^- \tag{6}
\]

\[
h^+ + \text{H}_2\text{O/}\text{OH}^- \rightarrow \text{OH} \tag{7}
\]

\[
h^+ + \text{OH}^- + \text{TC} \rightarrow \text{Degradation products} \tag{8}
\]

After the addition of \( \text{K}_2\text{S}_2\text{O}_8 \) Eq. (9), \( \text{S}_2\text{O}_8^{2-} \) could react with the \( e^- \) reaction on \( \text{Ag}_3\text{PO}_4 \) VB to produce \( \text{SO}_4^{2-} \) [87]. \( \text{SO}_4^{2-} \) is a strong oxidant and can effectively degrade many organic pollutants Eq. (10) [79]. In addition, \( \text{SO}_4^{2-} \) can also be converted to ‘\( \text{OH} \)’ by reacting with \( \text{H}_2\text{O} \) in solution, which can degrade TC and further improve the catalytic activity [88] Eq. (8). In this paper, the reaction time was reduced, and the degradation effect was improved by adding \( \text{K}_2\text{S}_2\text{O}_8 \).

\[
\text{S}_2\text{O}_8^{2-} + 2 e^- \rightarrow 2\text{SO}_4^{2-} \tag{9}
\]

\[
2\text{SO}_4^{2-} + \text{H}_2\text{O/}\text{OH}^- \rightarrow \text{H}^+ + \text{SO}_4^{2-} + \text{OH} \tag{10}
\]
3.4. Stability and cycling

The stability and reproducibility of sonocatalytic materials is critical for their applications [56]. Therefore, the 0.6Ag₃PO₄/CoWO₄ composites were recycled 4 times. All nanocomposites were collected after each sonication, washed and dried at 60 °C for 2 h. The results were shown in Fig. 14(a). It could be observed that the degradation rate was only reduced by 3% after 4 cycles. This result indicated that the 0.6Ag₃PO₄/CoWO₄ composites had excellent reproducibility. As shown in Fig. 14(b), the XPS patterns of the recycled composites and the newly prepared composites were the same. The decrease in TC degradation rate might be related to the decline of Ag ions. Therefore, after cycling experiments, we used ICP to measure the leaching of individual ions in the solution. The results showed that the leaching rate of Ag ions was slightly higher, about 2.65%, and the leaching rates of Co and W were lower, 0.0008% and 1.77%, respectively. It showed that Ag ions were still consumed in the experimental process, but had little effect on the degradation rate. Both XPS and ICP results proved good stability of 0.6Ag₃PO₄/CoWO₄ composites.

3.5. Comparison of catalytic activity with published catalysts

Due to the harmful effects of antibiotic wastewater pollution on the environment and human beings, many research have been devoted to developing materials that can degrade TC wastewater in recent years. Table 2 reports a comprehensive comparison of this study, together with other sonocatalysts for TC degradation activity published recently. It could be observed in the table that it usually takes a long time for each material to degrade TC. For example, Qiao et al. [9] used the ternary SrTiO₃/Ag₂S/CoWO₄ composites as a sonocatalyst to degrade TC solution in 300 min. In contrast, the 0.6Ag₃PO₄/CoWO₄ composites in this study can achieve a degradation rate of 75.3% in only 120 min. In addition, Reza Darvishi Cheshmeh et al. [89] found that adding some free radical enhancers (hydrogen peroxide, periodate, persulfate, and percarbonate, etc.) during the reaction can increase the degradation effect. For example, Hoseini et al. [90] added H₂O₂ in TiO₂ ultrasonic degradation of TC, and the degradation rate could reach 100% within 75 min. Compared with that, this work achieved a degradation rate of 97.89% within 10 min by adding K₂S₂O₈, which considerably shortened the reaction time and improved the degradation effect. It indicated that combining K₂S₂O₈ with 0.6Ag₃PO₄/CoWO₄ is a promising TC degradation scheme. These results provide valuable references for the practical application of 0.6Ag₃PO₄/CoWO₄.

4. Conclusion

The 0.6Ag₃PO₄/CoWO₄ composite sonocatalyst was prepared for the first time by a simple hydrothermal method and characterized by SEM, TEM, XRD, XPS, BET and UV–vis DRS. 0.6Ag₃PO₄/CoWO₄ had an average particle size of 20 ~ 50 nm, a narrow band gap of 2.60 eV and a large specific surface area. Compared with Ag₃PO₄ and CoWO₄, the 0.6Ag₃PO₄/CoWO₄ composites had a better sonocatalytic degradation effect on TC solution, and the degradation rate could get 75.3% within 90 min. After adding 10 mg of K₂S₂O₈, the degradation effect could reach 97.89% in 10 min. The mechanism was that Ag₃PO₄ and CoWO₄ form an S-scheme heterojunction, which accelerated the separation efficiency of e⁻-h⁺, and the generated h⁺, •OH, and •O₂ effectively mineralized TC. In addition, the 0.6Ag₃PO₄/CoWO₄ composites still had...
good recyclability and high stability after 4 cycles. This study provides a feasible idea for the modification of CoWO₄, and provides a direction for preparing a new high-efficiency sonocatalyst and the solution to wastewater treatment problems.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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