A research on shape-controllable synthesis of Ag_3PO_4/AgBr and its degradation of ciprofloxacin

Jingran Chen, Xingyu Yang, Chenyu Zhu, Xin Xie, Cuiping Lin, Yalei Zhao and Qishe Yan

ABSTRACT

Antibiotic ciprofloxacin is one of the commonly used broad spectrum fluoroquinolone human and veterinary drugs. Because of the overuse of human beings, the presence of ciprofloxacin has been detected in a variety of environmental matrices. To solve this problem, a facile, environmentally-friendly Ag_3PO_4/AgBr composite photocatalyst was synthesized by a simple precipitation method at room temperature in the presence of cetyltrimethyl ammonium bromide (CTAB). CTAB was served as surfactant and the source of bromide ions. The as-prepared Ag_3PO_4/AgBr microspheres were characterized by means of powder X-ray diffraction (XRD), scanning electron microscope (SEM) and UV-visible diffuse reflectance spectroscopy (UV-vis DRS). The results revealed that the Ag_3PO_4/AgBr sample (synthesized with CTAB, 0.8 g) exhibited the highest photocatalytic activity to the photodegradation rate of 96.36%. Moreover, mechanism detection experiment indicated that h^+ was the major active species in the degradation process. So the enhanced photocatalytic activity of Ag_3PO_4/AgBr composites is attributed to its excellent separation of photogenerated electron-hole pairs through Ag_3PO_4/AgBr heterojunction. Also, Ag_3PO_4/AgBr heterojunction has a lower band gap compared to pure Ag_3PO_4 and pure AgBr, so higher efficiency of light harvesting is equipped.

Key words | Ag_3PO_4/AgBr, ciprofloxacin, heterojunction, nanoparticle, photocatalyst, visible light

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INTRODUCTION

In recent years, the antibiotic issue has greatly increased public awareness and concern because antibiotics which are extensively and increasingly used contribute to the antibiotics pollution (Taiwo 2011). Various pharmaceuticals have been detected in many environmental samples worldwide on account of a large portion of antibiotics being discharged with excretion into the water without any treatment. (Scanziani *et al.* 2007). For example, in Nairobi River Basin, Kenya, Victoria Harbour, the Pearl River, South China and in tropical river antibiotics were detected more or less (Xu *et al.* 2007; Devarajan *et al.* 2015; Ngumba *et al.* 2016). Their occurrence has also been reported in wastewater, treatment plant effluents, surface water, seawater, groundwater, soils and sediments (Xekoukoulotakis *et al.* 2011). With large amounts of antibiotics released to the river, there is a great chance that the water we use may contain antibiotics (Wang *et al.* 2016a, 2016b). What makes matter worse is that we may eat food that contains antibiotics, too. People eating that sort of food may contribute to urticaria or allergic reactions such as anaphylactic shock (Krowchuk 2001). Besides that, when medicine is overly used, people's resistance to antibiotics will be imperceptibly enhanced. Once the virus attacks human beings again, the use of these antibiotics can be less effective. In addition, antibiotics can directly influence the environment by disturbing ecosystem equilibrium, which may even bring about knock-on effects (Jain *et al.* 2016). It is almost impossible to list all the severe consequences because everything in nature is interrelated. Antibiotic ciprofloxacin is one of them, which is a commonly used broad spectrum fluoroquinolone human and veterinary drug. Because antibiotics are not easy to be degraded compared to organic dyes for their resistance decomposition to the robust molecular structures (Li & Shi 2016), we need to find a new way.

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For solving many environmental and energy issues, semiconductor-based photocatalysis is taken as a promising avenue. Many semiconductor photocatalysts help to degrade antibiotics in water. Several examples are listed as follows: V_2O_5 nanoflakes were synthesised on polyethylene terephthalate (PET) fiber to degrade Rhodamine B (RhB) dye (Chan *et al.* 2014). Antibiotic oxolinic acid and toxic chloramphenicolsodium can be degraded by TiO_2 in suspension (Giraldo *et al.* 2010; Lofrano *et al.* 2016). Sulfamethoxazole can also be coped with by ultraviolet (UV)-A/TiO_2 photocatalytic degradation (Su *et al.* 2016). The most widely studied semiconductor photocatalyst TiO_2 has high stability, low cost, non-toxicity and high redox ability. But there are some drawbacks that cannot be neglected: the high electron-hole recombination rate and absorption of ultraviolet light only, which consists of about 5% of the solar spectrum due to its relatively wide band gap (Wang *et al.* 2016a, 2016b).

Lately, nonmetallic p-block elements, P or C elements were incorporated into a simple oxide of narrow band gap. It was found that Ag_3PO_4 nanoparticles had great ability in degrading organic dye under visible light because of its terrific photocatalytic properties and efficient separation ability of photocatalytic electrons and holes (Yi *et al.* 2010; Bi *et al.* 2012; Zhang *et al.* 2015). Many antibiotics have the similar structure to organic dye, for they are all organic compounds, and some may contain benzene rings. As for the ciprofloxacin we studied, it also contained a benzene ring. So we chose photocatalyst of silver series. Ag_3PO_4 nanoparticles can absorb light with wavelength less than 530 nm, which greatly improves its efficiency in using visible light. It was found by other learners that the novel photocatalyst can achieve a quantum efficiency of up to 90% at wavelengths greater than 420 nm, which is significantly higher than the previous reported values (Yi *et al.* 2010; Bi *et al.* 2011). But if we synthesize Ag_3PO_4 by reacting $AgNO_3$ and Na_2HPO_4 directly, only Ag_3PO_4 with irregular spherical structures can be obtained (Huang *et al.* 2013). Furthermore, pure Ag_3PO_4 has many drawbacks such as its large band gap and instability. If we incorporate AgBr, photocatalytic properties of the composite can be obviously lifted. The main idea in this paper is using a different ratio of CTAB/water to construct a proper shape of Ag_3PO_4/AgBr in a facile way. Then the most suitable nanoparticles can be selected to solve the problem as ciprofloxacin pollution, which is promising in the disposal of wastewater.

Cetyltrimethyl ammonium bromide (CTAB) is a kind of surfactant, which plays a key role in nanoparticle synthesis by adsorbing to the surface of the forming nanoparticle and lowering its surface energy (Mehta *et al.* 2009; Wang *et al.* 2013). It can also help to prevent aggregation by charge rejection: when it is well-distributed in the solution, it can help to disperse positive ions (in this paper, the cation is Ag^+). When they are fully dispersed in the solution, the smaller nanoparticles with larger specific surface area formed more easily. Simultaneously, Br^- and Ag^+ can form precipitation to prepare for the generation of Ag_3PO_4/AgBr compounds afterwards. So we chose CTAB as surfactant and the source of bromide ions to control its morphology and to form Ag_3PO_4/AgBr heterojunctions.

EXPERIMENTAL

Chemicals and reagents

All the chemicals were analytical grade (AR) and used as received without further purification or other treatments. Silver nitrate ($AgNO_3$) and disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4.12H_2O$) were purchased from Tianjin Kermel Chem. Reagent Co., Ltd. CTAB was obtained from Shanghai Sinopharm Chemical Reagent Co., Ltd. Absolute ethyl alcohol (CH_3CH_2OH) was purchased from Tianjin Fuchen Chem. Reagent Co., Ltd. Deionized water (Ultrapure water for laboratory use, Millipore, USA) was used to prepare the solutions in the experiments. The brand of ciprofloxacin is greater than or equal to 98%.

Preparation of Ag_3PO_4/AgBr based photocatalysts

Ag_3PO_4/AgBr microparticles were prepared by heterogeneous precipitation. Different amounts of CTAB were used to control the shape of sample. They were fabricated by two different adding sequences. The first group: 0 g, 0.2000 g, 0.4000 g, 0.6000 g, 0.8000 g, 1.6000 g, 2.0000 g, and 2.6000 g of CTAB was dispersed in deionized water (300 mL), respectively, with strong stirring and heating for 10 min. After cooling down the solution, we added $AgNO_3$ (3 mmol, 0.5096 g) into CTAB solution with strong stirring. Then Na_2HPO_4 solution (1 mmol, in 20 mL deionized water) was added dropwise to the above solution over a period of 30 min. The precipitation process would last for 4 h. Then, the product was washed by deionized water and ethanol three times by centrifuge. Finally, the oven was set at 120 °C overnight to dry out the product. The as-synthesized Ag_3PO_4/AgBr composite photocatalysts were marked as 1-A_1A_2-0, 1-A_1A_2-0.2, 1-A_1A_2-0.4, 1-A_1A_2-0.6, 1-A_1A_2-0.8, 1-A_1A_2-1.6, 1-A_1A_2-2.0 and 1-A_1A_2-2.6,

respectively, and the 1-A_1A_2-n for short (A_1 means Ag_3PO_4, A_2 means AgBr, 1 means the first group, n means the mass of CTAB). The second group: 0 g, 0.2000 g, 0.4000 g, 0.6000 g, 0.8000 g, 1.6000 g, 2.0000 g, and 2.6000 g CTAB was dispersed in deionized water (300 mL) with strong stirring and heating for 10 min. After cooling down the solution, we added Na_2HPO_4 (1 mmol, 0.3581 g) to the above solution. After $AgNO_3$ (3 mmol in 20 mL deionized water) was added dropwise to the above solution for about 30 min, the yellow precipitates produced from that chemical reaction were collected by centrifugation, then washed with deionized water and ethanol for three times. Finally, the samples were dried out at 120 °C in a vacuum oven overnight. The as-synthesized Ag_3PO_4/AgBr composite photocatalysts were marked as 2-A_1A_2-0, 2-A_1A_2-0.2, 2-A_1A_2-0.4, 2-A_1A_2-0.6, 2-A_1A_2-0.8, 2-A_1A_2-1.6, 2-A_1A_2-2.0 and 2-A_1A_2-2.6, respectively, and the 2-A_1A_2-n for short (A_1 means Ag_3PO_4, A_2 means AgBr, 2 means the second group, n means the mass of CTAB). In other studies, polyvinylpyrrolidone (PVP) was used as surfactant to determine the geometric shape and size of Ag_3PO_4 crystals in a similar way (Yang *et al.* 2014).

COD_{cr}

In this paper, we chose microwave digestion to determine chemical oxygen demand (COD) in ciprofloxacin hydrochloride solution, and carried out this method in conditional experiment as follows: using a direct blow transfer pipette to 5 mL learning solution, 5 mL potassium dichromate solution and 5 mL H_2SO_4-Ag_2SO_4 to the digestion tank. In order to eliminate the chlorine ion interference, the mercury sulfate was added as the screening agent to mask it (Cai *et al.* 2016). The degradation time was 10 min, 30 min, 60 min and 120 min. At the specific time, 5 mL of the tested solution was taken out and put into the digestion tank to digest about 6 min. Then, the amounts of residual potassium dichromate in the reaction liquid was determined by the titration with ammonium ferrous sulfate standard solution (Chen *et al.* 2001) which was in accordance with ferrous ammonium sulfate in water samples to calculate the amounts of material and to restore the volume of oxygen consumption (Wei *et al.* 2007).

Characterization of as-synthesized samples

X-ray diffraction (XRD) analysis was performed on an X-ray diffractometer (X'Pert PRO MRD, PANalytical, The Netherlands). UV-visible diffuse reflection spectra (UV-vis DRS) of the samples were obtained using a UV-vis spectrophotometer (Caly 5000, Agilent, USA). The morphology of the samples was investigated by scanning electron microscopy (SEM, Quonxe-2000, Philips, The Netherlands). The photoabsorption was evaluated by UV-vis spectroscopy (UV-2450, Shimadzu, Japan).

Photocatalytic activity test

The photocatalytic properties of Ag_3PO_4/AgBr composite were evaluated by its degradation of ciprofloxacin in aqueous solution under visible light irradiation. In a typical photocatalytic experiment, 0.05 g photocatalyst was dispersed into 50 mL ciprofloxacin solution (20 mg/L) for 30 min in darkness to reach the adsorption and desorption equilibrium. The concentration of ciprofloxacin solution was evaluated by UV-vis spectroscopy (UV-2450, Shimadzu, Japan). After that, the suspension was exposed to a 350 W xenon lamp under magnetic stirring. At given time intervals, about 5 mL suspensions was collected to analyze its concentration.

The degradation rate was calculated by $1 - C/C_0$, while the C was instantaneous concentration and C_0 was solution concentration after adsorption process. The data of degradation experiment were the average value of parallel experiments three times.

RESULTS AND DISCUSSION

Characterization

Surface morphology

The morphology and size of the Ag_3PO_4/AgBr samples were surveyed by scanning electron microscopy (SEM). Figure 1 shows that the as-prepared Ag_3PO_4/AgBr is subglobose and the size decreases gradually with the increase of CTAB. The size of 1-A_1A_2-0.4 is in the range of 10–100 μm (Figure 1(a)), whereas the size of 1-A_1A_2-1.6 is nano-size particles (Figure 1(c)). The smaller particle leads to the larger specific surface area and the larger specific surface area improves the photocatalytic efficiency (Xu *et al.* 2017). Therefore, the particle size changes are attributed to CTAB's dispersion effect, influencing the photocatalytic activities at the same time.

Structure and composition

The powder XRD pattern can authoritatively provide crystal structure and phase information of the as-prepared products. To figure out the purity of the samples, XRD detection was carried out. For pure Ag_3PO_4 and AgBr, it is

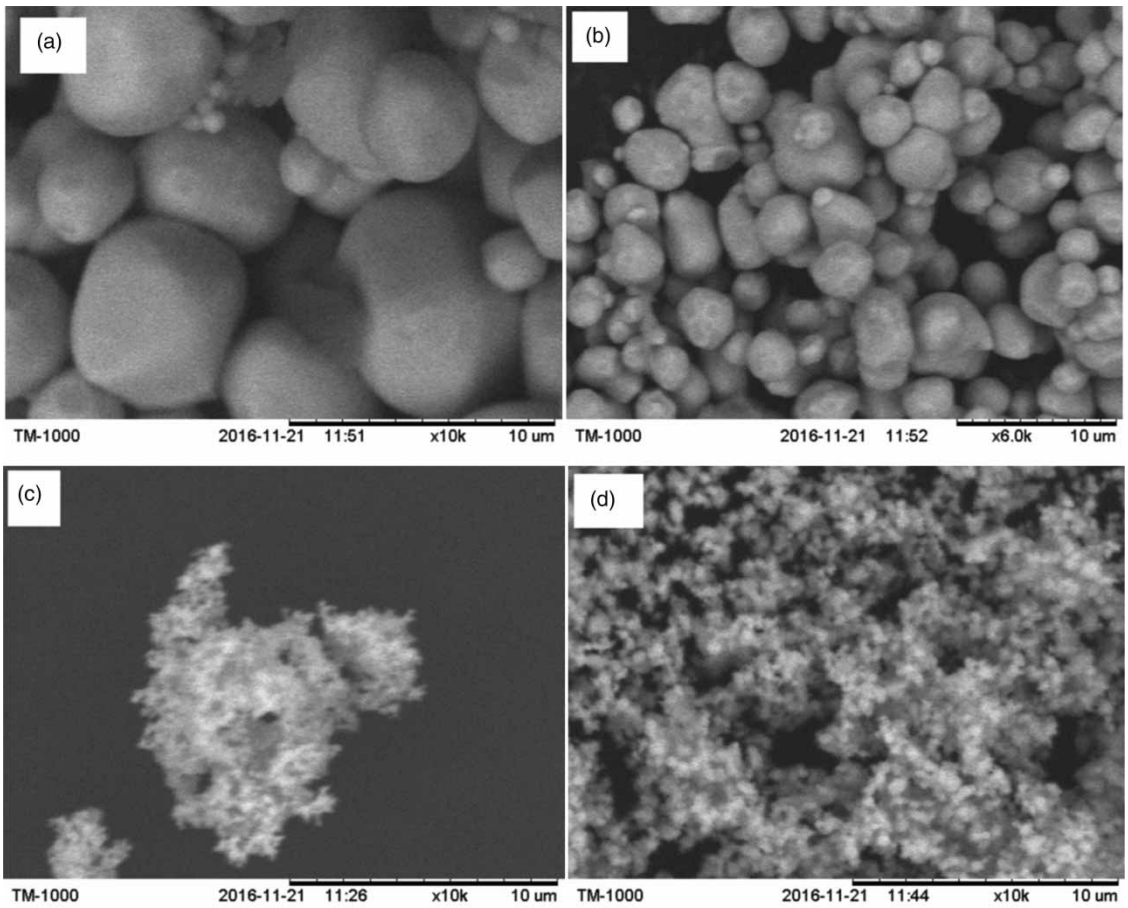

Figure 1 | SEM images of Ag_3PO_4/AgBr products prepared with different amounts of CTAB: (a) 1-A_1A_2-0.4, (b) 1-A_1A_2-0.8, (c) 1-A_1A_2-1.6, (d) 1-A_1A_2-2.0.

using (▲) and (■) to show all the diffraction peaks, respectively. Figure 2 shows the diffraction peaks of pure Ag_3PO_4, pure AgBr,1-A_1A_2-0.8 and 1-A_1A_2-1.6. The XRD patterns of Ag_3PO_4/AgBr samples (Figure 2) show that all the diffraction peaks of the samples can be indexed to the body-centered cubic structure of Ag_3PO_4 (JCPDS card No. 06-0505) and AgBr (JCPDS card No. 06-0438). No diffraction peaks of metallic Ag or other impurities has been observed, indicating a high purity of Ag_3PO_4/AgBr samples. In addition, the peak intensity of 1-A_1A_2-0.8 and 1-A_1A_2-1.6 are stronger than those of pure Ag_3PO_4 and AgBr, indicating the composite was well crystallized.

The results of the photocatalytic tests indicated that 1-A_1A_2-0.8 possessed the highest photocatalytic ability, the adding of CTAB created a certain amounts of Ag_3PO_4/AgBr heterojunction, which might be the reason for their increasing photocatalytic efficiency.

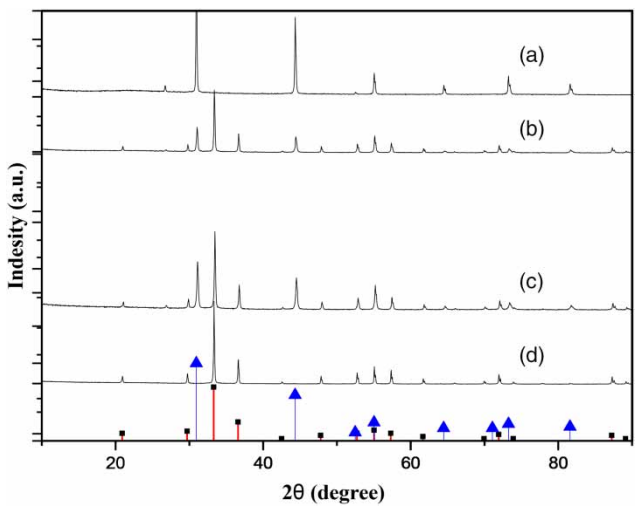

Figure 2 | The XRD pattern: (a) pure silver phosphate, (b) 1-A_1A_2-0.8, (c) 1-A_1A_2-1.6, (d) pure silver bromide.

Photoabsorption property

The band gap structure of a semiconductor is regarded as an important part to determine its photocatalytic property. UV-vis absorption spectra can help us to calculate the band gap. Figure 3 shows the UV-vis absorption spectra of the different synthesized samples. It is clear from the figure that Ag_3PO_4/AgBr exhibits stronger absorbance than pure Ag_3PO_4 and AgBr. The high photoabsorption ability is within the range of visible light. Although Ag_3PO_4/AgBr composite exhibited lower absorption within the range from 350 nm to 500 nm compared to pure Ag_3PO_4 and pure AgBr, their absorption became much higher from 500 nm to 700 nm. That is, the absorption spectrum of Ag_3PO_4/AgBr shifts to red dramatically compared with the pure Ag_3PO_4 and pure AgBr, which meant Ag_3PO_4/AgBr compound could absorb and use visible light with lower energy, making it more effective in the usage of visible light.

The band gap of these samples can be evaluated by using the equation: $E = 1240/\lambda$ (where λ is the maximum absorption wavelength of photon). We can estimate the band gap energy of each sample from Figure 3: the calculated band gap of AgBr is 2.52 eV, the calculated band gap of Ag_3PO_4/AgBr heterojunction is 2.19 eV and for pure Ag_3PO_4, it is 2.33 eV. So it is evident that Ag_3PO_4/AgBr has a significantly lower band gap, making it easier to absorb visible light.

Visible-light photocatalytic activity

To demonstrate the potential application of these samples, photocatalytic activity of which were evaluated by the degradation of ciprofloxacin solution at room temperature.

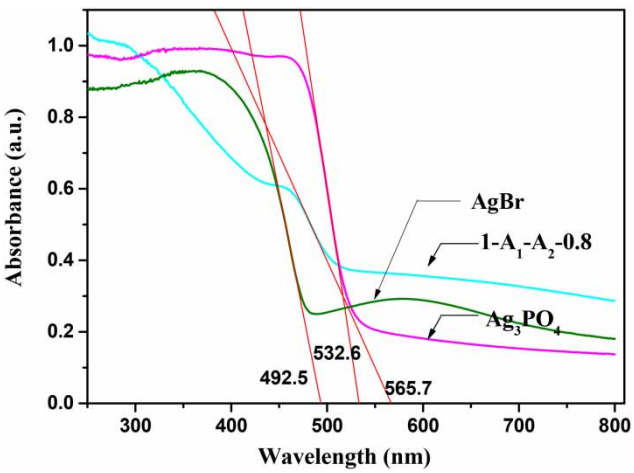

Figure 3 | The UV-vis diffuse reflection spectrums of 1-A_1A_2-0.8, pure Ag_3PO_4 and pure AgBr.

Figure 4 shows the variation in ciprofloxacin concentration (C/C_0) with irradiation time over different catalysts prepared with different amounts of CTAB, where C_0 is the initial concentration and C is the concentration at t time. The concentration of ciprofloxacin decreased negligibly without photocatalyst both in dark and under visible light irradiation. The degradation efficiency of ciprofloxacin obviously increased with the addition of photocatalyst on the whole. Moreover, it had different efficiency with the increase of CTAB, which is because adequate CTAB is beneficial to the combination of silver ions and phosphate ions as cationic surfactant, whereas excessive CTAB blocks the combination of silver ions and phosphate ions. It is obvious that 1-A_1A_2-0.8 exhibits the highest photocatalytic degradation efficiency.

Figure 5 shows the absorption spectroscopic changes of ciprofloxacin in the presence of samples (1-A_1A_2-0.6, 1-A_1A_2-1.0) in the dark and with visible light irradiation. It can be clearly seen that the absorption intensities decreases gradually, the absorption peak intensity significantly decreases with the irradiation time, indicating the excellent photocatalytic activity of as-prepared samples for the ciprofloxacin degradation under visible light.

Figure 6 shows the effect of adding CTAB in different ways. It is absolutely clear from the figure that the first group presents a much better photocatalytic effect. It can be roughly illustrated that CTAB is a kind of cationic surfactant which can disperse silver ions efficiently. Moreover, silver ions have a positive electric charge, which is exactly the same with CTA^+. The same electric charge will not let

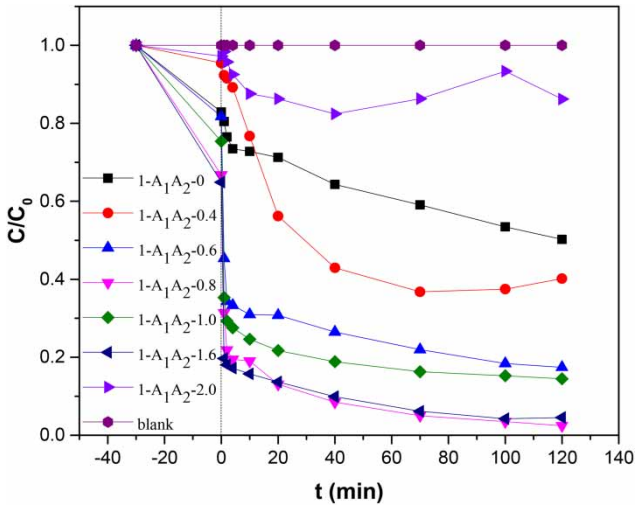

Figure 4 | Photocatalytic activities of composites prepared with different amounts of CTAB for degradation of ciprofloxacin solution under visible light irradiation ($\lambda > 420$ nm) at room temperature.

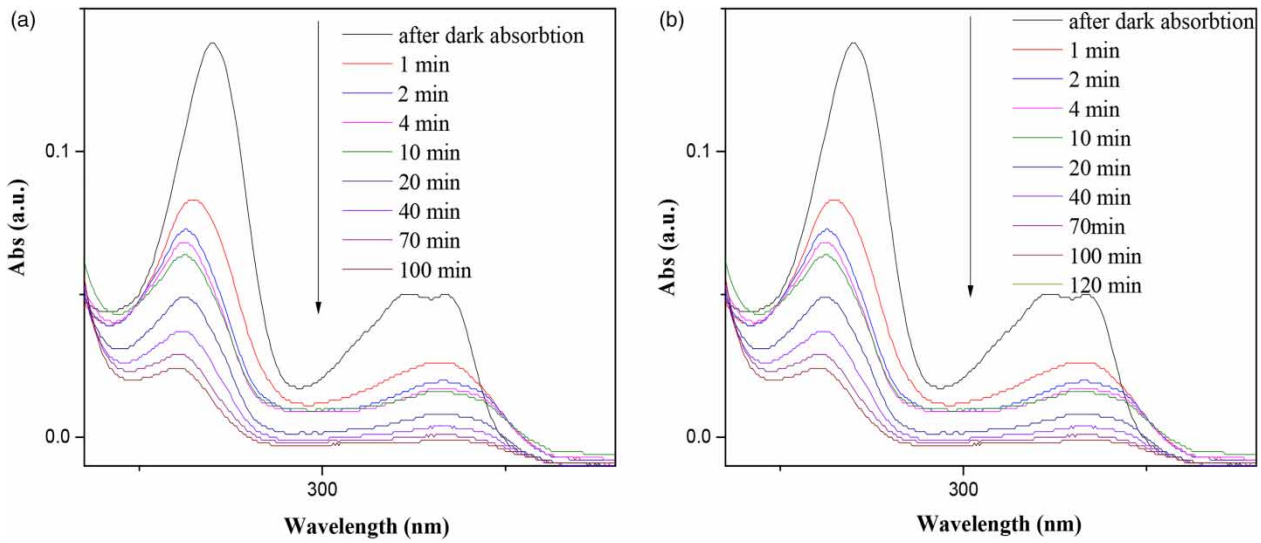

Figure 5 | The absorption variation of ciprofloxacin solution over Ag_3PO_4/AgBr products at different irradiation time: (a) 1-A_1A_2-1.0, (b) 1-A_1A_2-0.6.

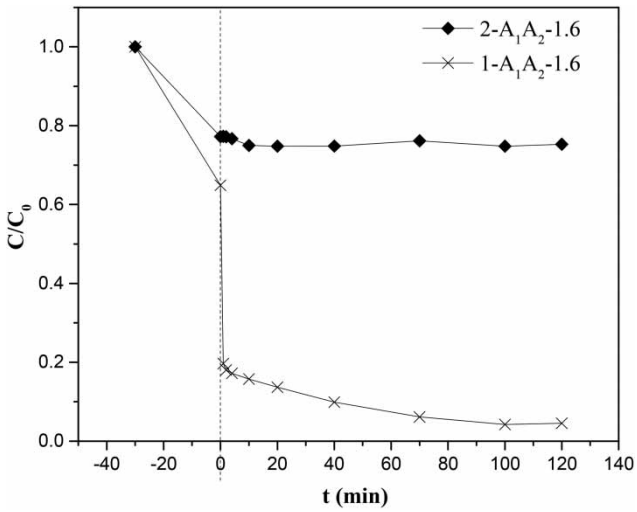

Figure 6 | The photocatalytic results of 1-A_1A_2-1.6 and 2-A_1A_2-1.6.

the ions aggregate together and at the same time help to disperse silver ions. On the contrary, if phosphate radical is mingled with CTAB first, the large group CTA^+ will gather with it, so the dispersion effect will not be fully, making it difficult to go on reacting with silver ions later.

Photocatalytic degradation mechanism

Oxidation radical species

It is universally known that photodegradation of organic contaminant by semiconductor is usually completed through photocatalytic oxidation process. To fully understand the specific photocatalytic mechanism of Ag_3PO_4/AgBr, the effects of different active scavengers including hydroxyl radicals (•OH), active holes (h^+) and superoxide radicals ($•O_2^-$) on the degradation of ciprofloxacin was investigated, respectively. Various scavengers (6 mmol/L ammonium oxalate for holes (h^+), 0.5 mmol/L silver nitrate for electrons, 10 mmol/L isopropanol for •OH) were added, respectively, into the degradation solution. It is obvious from Figure 7 that all of the scavengers above have negative effects on the photocatalytic process to some extent. But the influence of ammonium oxalate

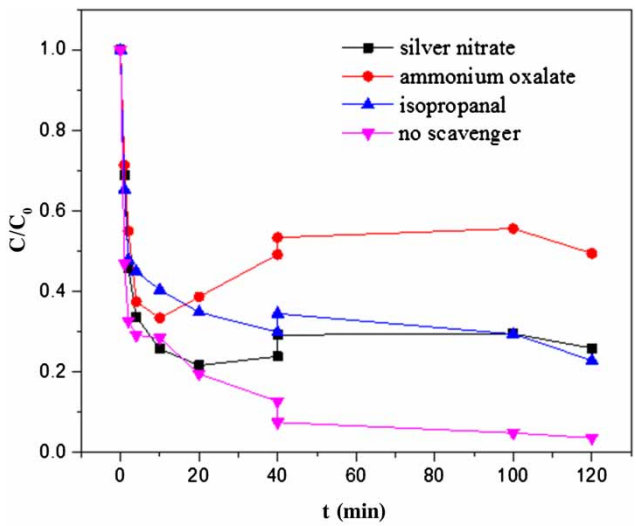

Figure 7 | Effect of various scavengers on degradation of ciprofloxacin by Ag_3PO_4/AgBr, with ciprofloxacin concentration of 20 mg/L.

plays the most important role, which indicates that h^+ is the main reactive species in the photodegradation of ciprofloxacin (Jing *et al.* 2012).

COD_{cr}

Chemical oxygen demand (COD) is one of the important indexes in the industrial wastewater and environmental water quality monitoring. The size of the data represents a gauge of water pollution when it is polluted by organic matter, nitrite, ferrite and so on. The photocatalytic activity of composite catalyst prepared at different concentration of CTAB was investigated through the determination of COD value in ciprofloxacin hydrochloride solution.

The method has the features of short digestion time, high accuracy and simple operation. After being properly tested, it was calculated that the COD_{Cr} was decreasing largely with increasing the time of catalytic photodegradation in ciprofloxacin solution in its entirety (Guo *et al.* 2014). Among them, 1-A_1A_2-0.8 reached the minimum value. As a result, the data of the experimental group were lower than those of the blank group. So all of the composite photocatalysts have favorable photocatalytic activity. Above all, 1-A_1A_2-0.8 has the best photocatalytic property.

This study provides a new way to fabricate Ag_3PO_4/AgBr heterojunction composite, with no need to introduce extra bromine ions to form AgBr precipitation. The novel fabrication method is much more convenient and efficient compared to the traditional methods: using NaBr or KBr as bromine source (Cao *et al.* 2012; Amornpitoksuk & Suwanboon 2016). Through this fabrication process, we got an excellent photocatalyst which can degrade an antibiotic ciprofloxacin at high efficiency of 96.36%, which is promising in the treatment of antibiotics pollution in water.

CONCLUSIONS

In conclusion, the Ag_3PO_4/AgBr nanoparticle was successfully fabricated by a simple precipitation method at room temperature with the help of CTAB to degrade ciprofloxacin. Different proportion of CTAB contributed to different size: with the increasing concentration of CTAB, the size of Ag_3PO_4/AgBr became smaller so that they had larger specific surface area. But too much CTAB might block the reaction between the ions and cations in the solution. When CTAB was added, about 0.8–1.6 g during the fabricating process, the degradation efficiency could be lifted from 50% to 96.36%. The effect research of reaction conditions indicated that the optimum dosage of CTAB was 0.8 g. XRD patterns of Ag_3PO_4/AgBr indicated a high purity of Ag_3PO_4/AgBr samples. UV-visible diffuse reflectance spectroscopy (UV-vis DRS) showed that the absorption spectrum of Ag_3PO_4/AgBr shifted to red dramatically and the compounds have lower band gap compared with the pure Ag_3PO_4 and pure AgBr, making it more effective in the usage of visible light. Radical detection experiments indicated that the h^+ was the major active species in the degradation process. So the enhancement of photocatalytic efficiency of Ag_3PO_4/AgBr composites are strongly dependent on the excellent separation of photogenerated electron-hole pairs through Ag_3PO_4/AgBr heterojunction and a lower band gap. Finally, COD_{Cr} test indicated that ciprofloxacin molecules were partially mineralized under the visible-light irradiation, suggesting the successful degradation of ciprofloxacin in water system. This might be a progress in the study of nanoparticles for degradation of pollutants such as antibiotics in aqueous environment.

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