



# Novel AgCl nanoparticles coupling with PbBiO<sub>2</sub>Br nanosheets for green and efficient degradation of antibiotic oxytetracycline hydrochloride under visible-light irradiation

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## Abstract

In this work, novel Ag/AgCl/PbBiO<sub>2</sub>Br photocatalysts were synthesized via a hydrothermal and in situ photoreaction method. The microstructure, morphology, composition, electrochemical, and optical properties of the synthesized catalysts were investigated by multiple techniques. The obtained Ag/AgCl, PbBiO<sub>2</sub>Br, and Ag/AgCl/PbBiO<sub>2</sub>Br composites were evaluated via degradation of oxytetracycline (OTC) hydrochloride antibiotic under visible-light irradiation. The results show that the Ag/AgCl/PbBiO<sub>2</sub>Br composites are composed of Ag/AgCl nanoparticles (NPs) and PbBiO<sub>2</sub>Br nanosheets. The Ag/AgCl/PbBiO<sub>2</sub>Br (20.4%) composite exhibits the highest visible-light absorption and best photogenerated charge separation efficiency. The photocatalytic degradation experiments show that all Ag/AgCl/PbBiO<sub>2</sub>Br composites exhibit an enhanced degradation activity under visible-light irradiation, and maintain good stability in the photocatalytic process. The Ag/AgCl/PbBiO<sub>2</sub>Br (20.4%) composite has the highest degradation activity, which is 1.82 and 2.11 times higher than that of Ag/AgCl and PbBiO<sub>2</sub>Br, respectively. The enhanced photocatalytic activity of Ag/AgCl/PbBiO<sub>2</sub>Br can be mainly attributed to the fact that the loading of Ag NPs on the surface of the AgCl promotes the separation efficiency of photoinduced charge and enhance the visible-light absorption. Additionally, active species trapping experiments confirm that superoxide radicals ( $\cdot\text{O}_2^-$ ),  $\text{Cl}^0$  and holes ( $\text{h}^+$ ) play a very important role in the degradation process.

## 1 Introduction

Nowadays, the widespread usage of antibiotics has received the increasing attention because they flow into the water system and cause the water pollution [1]. Oxytetracycline (OTC) hydrochloride is one of the very important antibiotics, extensively used in human and veterinary medicine [2].

Worryingly, the most of OTC is only partially metabolized in humans or animals and hardly biologically degraded, ultimately released into lakes and rivers. These antibiotics have harmful effects on water environment and human health [3]. Hence numbers of research attempts have been made in the past decades to eliminate these refractory antibiotics, such as electrochemical treatments [4], photoelectron-Fenton [5] and advanced oxidation treatment [6]. However, most of the methods use expensive oxidants. Therefore, it is indispensable to develop novel visible-light-driven photocatalysts [7], which are environmentally friendly and efficient approach to remove OTC from waters.

PbBiO<sub>2</sub>Br is an n-type visible-light-driven semiconductor and has attracted more and more attention in recent years, owing to its physicochemical stability, highly anisotropic layered structure, and outstanding photocatalytic performance [8–11]. Unfortunately, the photocatalytic activity of bare PbBiO<sub>2</sub>Br is still unsatisfactory owing to its fast recombination rate of photoexcited electron–hole ( $\text{e}^-/\text{h}^+$ ) pairs [12, 13]. To overcome the above mentioned drawback of PbBiO<sub>2</sub>Br and improve the degradation efficiency, constructing semiconductor composites is effective

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in improving the separation efficiency of photoinduced  $e^-/h^+$  pairs. So far, studies have reported on  $g\text{-C}_3\text{N}_4/\text{PbBiO}_2\text{Br}$  [14],  $\text{NbSe}_2/\text{PbBiO}_2\text{Br}$  [15],  $\text{PbBiO}_2\text{Br}/\text{UiO-66-NH}_2$  [16]  $\text{Cu}_2\text{O}/\text{PbBiO}_2\text{Br}$  [17],  $p\text{-Ag}_2\text{O}/n\text{-PbBiO}_2\text{Br}$  [18],  $\text{PbBiO}_2\text{Br}/\text{BiOBr}$  composites [19], and etc. These heterojunction composites were found to exhibit superior photocatalytic activity. Despite many  $\text{PbBiO}_2\text{Br}$ -based materials have been reported, it is still necessary to be committed to the exploitation of more efficient visible-light-driven  $\text{PbBiO}_2\text{Br}$ -based photocatalysts for making the best use of the solar energies.

The surface plasmon resonance (SPR) strategy is widely used in fabricating efficient visible-light-driven photocatalysts [20]. Because of SPR of noble metal nanoparticles (NPs), the absorption range of visible-light region can be expanded, resulting in the enhanced degradation performance of photocatalysts [21]. Recently,  $\text{Ag}/\text{AgCl}$  has been widely considered as a promising photocatalyst due to its being a p-type SPR structure semiconductor [22]. Furthermore,  $\text{Ag}^0$  NPs dispersed on the surface of  $\text{AgCl}$  can not only effectively absorb visible light, but also can accelerate the transfer of photo-carriers. By now, a number of  $\text{Ag}/\text{AgCl}$ -based photocatalysts have been successfully synthesized, such as  $\text{Ag}/\text{AgCl}/\text{NaTaO}_3$  [23], and  $\text{BiVO}_4/\text{MWCNT}/\text{Ag}@/\text{AgCl}$  [24]. These composite photocatalysts exhibited superior photocatalytic performances. To the best of our knowledge, the coupling of  $\text{PbBiO}_2\text{Br}$  nanosheets with  $\text{Ag}/\text{AgCl}$  NPs has not been reported yet. Hence, we expect that the new  $\text{Ag}/\text{AgCl}/\text{PbBiO}_2\text{Br}$  composites not only improve the utilization rate of solar energy, but also enhance photocatalytic ability.

Inspired by previous studies, we have successfully fabricated a series of  $\text{Ag}/\text{AgCl}/\text{PbBiO}_2\text{Br}$  composites by a hydrothermal and in situ photoreaction method. Morphology and microstructure, elements chemical states, optical and electrochemical properties of the  $\text{Ag}/\text{AgCl}/\text{PbBiO}_2\text{Br}$  composites were systematically studied. Their photocatalytic performances were investigated by the degradation of OTC under visible-light irradiation. The possible enhanced photocatalytic mechanism was also proposed.

## 2 Experimental

### 2.1 Preparation of the photocatalysts

$\text{PbBiO}_2\text{Br}$  nanosheets were synthesized via a facile hydrothermal method [17]. Detailed experimental process was given in Supporting Information (S1).  $\text{Ag}/\text{AgCl}/\text{PbBiO}_2\text{Br}$  composites were prepared via a photoreduction method. The preparation process was as follows: 1 mmol of  $\text{PbBiO}_2\text{Br}$  was dispersed in deionized water, stirred for 20 min to form uniform suspension A. Then, 1 mmol  $\text{AgNO}_3$  was added into the suspension A and stirred for 20 min. Subsequently,

1 mmol  $\text{NaCl}$  was transferred into the suspension A under strong stirring for 30 min. The resulting mixture was illuminated under a 500 W xenon lamp for 30 min so that the  $\text{Ag}^+$  NPs on the surface of  $\text{AgCl}/\text{PbBiO}_2\text{Br}$  were reduced to  $\text{Ag}^0$  NPs. Eventually, the precipitate was filtered, rinsed with deionized water and ethanol, and dried at 80 °C for 24 h. The obtained product, in which the mass ratio of  $\text{Ag}$  to  $\text{PbBiO}_2\text{Br}$  was 20.4%, was designated as  $\text{Ag}/\text{AgCl}/\text{PbBiO}_2\text{Br}$  (20.4%).  $\text{Ag}/\text{AgCl}/\text{PbBiO}_2\text{Br}$  (13.6%),  $\text{Ag}/\text{AgCl}/\text{PbBiO}_2\text{Br}$  (40.8%), and bare  $\text{Ag}/\text{AgCl}$  were also obtained with the same conditions by changing the content of  $\text{PbBiO}_2\text{Br}$ .

### 2.2 Characterization and photocatalytic evaluation

The synthesized catalysts were investigated in detail by multiple instruments analyses. The photocatalytic activities of the  $\text{Ag}/\text{AgCl}$ ,  $\text{PbBiO}_2\text{Br}$ , and  $\text{Ag}/\text{AgCl}/\text{PbBiO}_2\text{Br}$  composites were evaluated via the degradation of the antibiotic OTC under visible-light irradiation. Detailed experimental process was given in Supporting Information (S2).

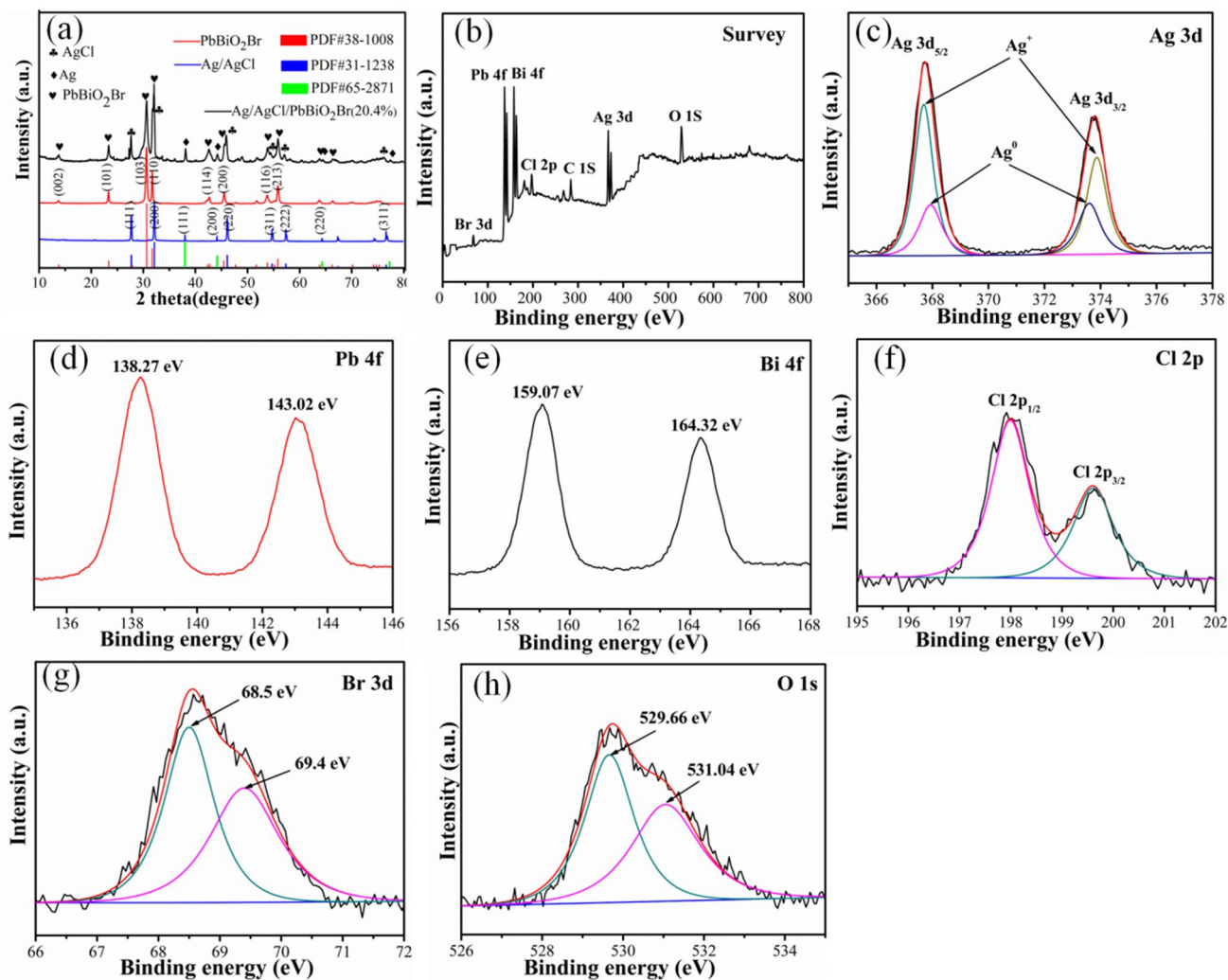
### 2.3 Photoelectrochemical measurements

The electrochemical properties of as-prepared samples were investigated on a electrochemical workstation (CS350H, wuhan sikete instrument Co., Ltd, China) with standard calomel electrode (SCE). Preparation of the working electrodes and detailed experimental process were given in Supporting Information (S3).

## 3 Results and discussion

### 3.1 XRD analysis

The crystal structures of as-synthesized  $\text{PbBiO}_2\text{Br}$ ,  $\text{Ag}/\text{AgCl}$ , and  $\text{Ag}/\text{AgCl}/\text{PbBiO}_2\text{Br}$  (20.4%) composite were analyzed using X-ray diffraction (XRD), as presented in Fig. 1a. It can be seen that the XRD pattern of bare  $\text{PbBiO}_2\text{Br}$  was consistent with the standard spectrum of tetragonal phase  $\text{PbBiO}_2\text{Br}$  (PDF#38-1008). The strong peak located at  $30.6^\circ$  corresponds to the (103) plane of  $\text{PbBiO}_2\text{Br}$ , indicating that the obtained catalyst is well-crystallized [25]. For the  $\text{Ag}/\text{AgCl}$ , the peaks at  $2\theta = 27.7^\circ$ ,  $32.1^\circ$ ,  $46.1^\circ$ ,  $54.7^\circ$ , and  $57.3^\circ$  correspond to the (111), (200), (220), (311), and (222) planes of cubic  $\text{AgCl}$  (PDF#31-1238), respectively [26]. In addition, the diffraction peaks at  $2\theta = 37.9^\circ$ ,  $44.1^\circ$ ,  $64.3^\circ$ , and  $77.2^\circ$  match with the (111), (200), (220), and (311) facets of  $\text{Ag}$  crystal (PDF# 65-2871), respectively [27]. Additionally, as for the  $\text{Ag}/\text{AgCl}/\text{PbBiO}_2\text{Br}$  (20.4%) photocatalyst, all the diffraction peaks correspond to  $\text{PbBiO}_2\text{Br}$  and  $\text{Ag}/\text{AgCl}$ , and no additional crystal phases can be detected, which indicates the formation of  $\text{Ag}/\text{AgCl}/\text{PbBiO}_2\text{Br}$  composites.



**Fig. 1** a XRD patterns of Ag/AgCl, PbBiO<sub>2</sub>Br, and Ag/AgCl/PbBiO<sub>2</sub>Br (20.4%) composite. XPS spectra of Ag/AgCl/PbBiO<sub>2</sub>Br (20.4%) composite; b the XPS survey spectrum, c Ag 3d, d Pb 4f, e Bi 4f, f Cl 2p, g Br 3d and h O 1s

### 3.2 XPS analysis

The elemental valence states of the as-synthesized Ag/AgCl/PbBiO<sub>2</sub>Br (20.4%) were detected by X-ray photoelectron spectroscopy (XPS) technology, and the obtained results are illustrated in Fig. 1. The main peaks in the XPS survey spectrum of Ag/AgCl/PbBiO<sub>2</sub>Br (20.4%) composite (Fig. 1b) correspond to Br 3d, Pb 4f, Bi 4f, Cl 2p, Ag 3d, and O 1s. Figure 1c displays the XPS spectrum of Ag 3d, where the peaks at 367.93 and 373.60 eV are assigned to Ag<sup>0</sup>, and the other two strong peaks at 367.69 and 373.87 eV are ascribed to Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub> of Ag<sup>+</sup> in Ag/AgCl, respectively. This result is consistent with other reports in literatures [28]. In Fig. 1d, the binding energy peaks at 138.27 and 143.02 eV are corresponding to Pb 4f<sub>7/2</sub> and Pb 4f<sub>5/2</sub>, respectively [29]. Figure 1e shows

that the XPS spectrum of Bi element, where the peaks at 157.09 and 164.32 eV are attributed to Bi 4f<sub>7/2</sub> and Bi 4f<sub>5/2</sub>, respectively [30–34], indicating that Bi<sup>3+</sup> ions exist in PbBiO<sub>2</sub>Br. Furthermore, in Fig. 1f, two typical peaks at 199.61 and 197.99 eV can be attributed to Cl 2p<sub>3/2</sub> and Cl 2p<sub>1/2</sub>, indicating that Cl<sup>-</sup> ions exist in AgCl phase [34]. Figure 1g shows the XPS spectrum of Br 3d, where the binding energy peaks at 68.5 and 69.4 eV are corresponding to Br 3d<sub>3/2</sub> and Br 3d<sub>5/2</sub>, respectively [35]. The O 1s XPS spectrum of Ag/AgCl/PbBiO<sub>2</sub>Br (20.4%) composite (Fig. 1h) is composed of fitted peaks at 529.66 and 531.04 eV, which could be attributed to the lattice oxygen of PbBiO<sub>2</sub>Br and surface-adsorbed oxygen species, respectively [36, 37]. From the XPS analysis, it is clear that Ag/AgCl/PbBiO<sub>2</sub>Br is a composite sample composed of Ag/AgCl and PbBiO<sub>2</sub>Br.

### 3.3 Scanning electron microscope (SEM) and EDX analysis

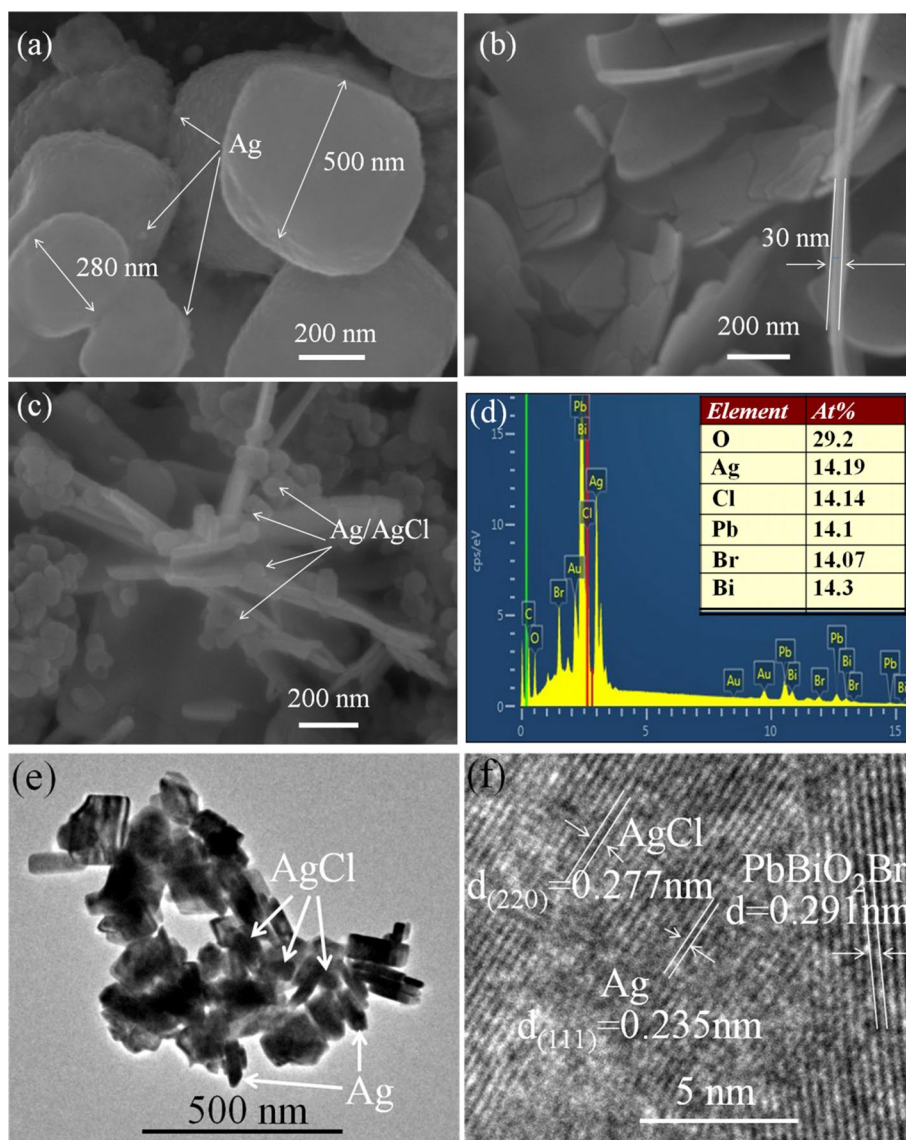
Figure 2 shows the morphologies of the  $\text{PbBiO}_2\text{Br}$ ,  $\text{Ag}/\text{AgCl}$ , and  $\text{Ag}/\text{AgCl}/\text{PbBiO}_2\text{Br}$  (20.4%) composite. Figure 2a reveals that the  $\text{AgCl}$  consists of cubic-like NPs with grain size of 300–500 nm and  $\text{Ag}$  NPs are dispersed on the surfaces of  $\text{AgCl}$  cubes. Figure 2b shows that the as-prepared  $\text{PbBiO}_2\text{Br}$  has a sheet-like morphology with thickness about 30 nm. As seen from Fig. 2c, the  $\text{Ag}/\text{AgCl}$  NPs are attached on the surface of  $\text{PbBiO}_2\text{Br}$  nanosheets. Moreover, we also notice that compared with the pure  $\text{Ag}/\text{AgCl}$ , the particle size of  $\text{Ag}/\text{AgCl}$  in the  $\text{Ag}/\text{AgCl}/\text{PbBiO}_2\text{Br}$  (20.4%) composite undergoes significant change, which could be due to the fact that  $\text{PbBiO}_2\text{Br}$  could influence the surface energy of  $\text{Ag}/\text{AgCl}$  and thus impede their growth. Additionally, energy-disperse X-ray (EDX) spectroscopy analysis of

$\text{Ag}/\text{AgCl}/\text{PbBiO}_2\text{Br}$  (20.4%) composite was carried out, and the obtained result is illustrated in Fig. 2d. From the EDX spectrum, the peaks belonging to  $\text{Ag}$ ,  $\text{Cl}$ ,  $\text{Pb}$ ,  $\text{Bi}$ ,  $\text{O}$ ,  $\text{C}$ ,  $\text{Au}$ , and  $\text{Br}$  are observed ( $\text{C}$  and  $\text{Au}$  element come from the test instrument). The atomic ratio of  $\text{Ag}/\text{Pb}$  equals to 1:1, which is in good agreement with the  $\text{Ag}/\text{Pb}$  atomic ratio of  $\text{Ag}/\text{AgCl}/\text{PbBiO}_2\text{Br}$  (20.4%) composite.

### 3.4 TEM analysis

To further obtain more detailed structure information of  $\text{Ag}/\text{AgCl}/\text{PbBiO}_2\text{Br}$  (20.4%) composite, field emission transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images were carried out. As shown in Fig. 2e, the  $\text{Ag}/\text{AgCl}$  NPs are formed on the surface of  $\text{PbBiO}_2\text{Br}$  nanosheets. From Fig. 2f, it is clearly seen that the lattice fringes of 0.235 and 0.277 nm are corresponding to the (111)

**Fig. 2** SEM images of **a**  $\text{Ag}/\text{AgCl}$ , **b**  $\text{PbBiO}_2\text{Br}$ , and **c**  $\text{Ag}/\text{AgCl}/\text{PbBiO}_2\text{Br}$  (20.4%); **d** EDS spectrum, **e** TEM and **f** HRTEM images of as-prepared  $\text{Ag}/\text{AgCl}/\text{PbBiO}_2\text{Br}$  (20.4%) composite



and (220) planes of Ag and AgCl, respectively [38]. The lattice fringes of 0.291 nm are correlated with the (103) plane of PbBiO<sub>2</sub>Br [39].

### 3.5 Optical properties of the photocatalysts

The optical properties of photocatalysts are very important for their photocatalytic application in the degradation of the antibiotics. Therefore, the optical properties of as-obtained bare PbBiO<sub>2</sub>Br, Ag/AgCl, and different Ag/AgCl/PbBiO<sub>2</sub>Br composites were investigated via ultraviolet–visible diffuse reflectance spectra (UV–Vis DRS) measurement, as shown in Fig. 3a. The bare PbBiO<sub>2</sub>Br exhibits the absorption edge at 500 nm, which is in agreement with the previous results in literatures [17, 40]. It can be seen that Ag/AgCl exhibits a strong absorption in the visible-light region. It is also obvious that the absorption intensities of Ag/AgCl/PbBiO<sub>2</sub>Br composites are stronger than that of bare PbBiO<sub>2</sub>Br in the visible-light regions, which can be attributed to the Ag SPR strategy [41].

### 3.6 FT-IR analysis

Figure 3b shows the Fourier transform infrared spectroscopy (FT-IR) spectra of the samples. For the pristine Ag/AgCl sample, the peak at 1044.1 cm<sup>-1</sup> is attributed to the stretching vibration of Ag–Cl [42]. Furthermore, the stretching vibration of Ag NPs bond can be also observed at 2790.1 and 2908.7 cm<sup>-1</sup> [43]. For pure PbBiO<sub>2</sub>Br, the peaks at 1388.4 and 1600.1 cm<sup>-1</sup> are attributed to the bending vibrations of the Pb–O bond and the Bi–O bond, respectively [44, 45]. The broad absorption bands on the right side from 3250 to 3425 cm<sup>-1</sup> are corresponding to the stretching vibration O–H band by the absorbed H<sub>2</sub>O [46, 47]. As for the Ag/AgCl/PbBiO<sub>2</sub>Br composites, all the absorption peaks are

from Ag/AgCl and PbBiO<sub>2</sub>Br. The analysis results indicate that Ag/AgCl/PbBiO<sub>2</sub>Br are successfully fabricated.

### 3.7 Nitrogen adsorption analysis

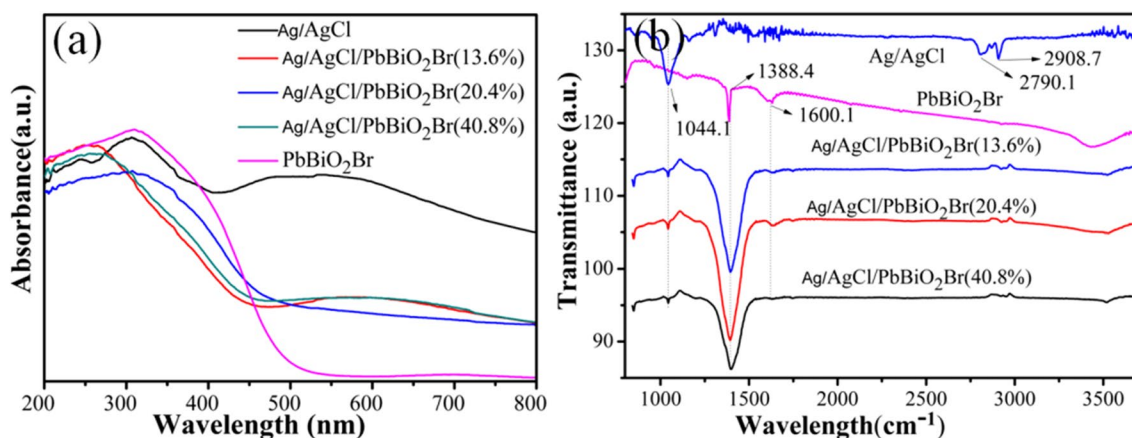
According to the previously reported literature [47–49], the photocatalytic efficiency of the catalyst is largely dependent on its specific surface area, so the Brunauer–Emmett–Teller (BET) specific surface areas of the as-prepared samples were measured using nitrogen adsorption–desorption measurements. The BET specific surface areas of pure PbBiO<sub>2</sub>Br, Ag/AgCl, and Ag/AgCl/PbBiO<sub>2</sub>Br composites are summarized in Table 1. It is found that the BET specific surface area of the Ag/AgCl/PbBiO<sub>2</sub>Br (20.4%) is measured to be 37.16 m<sup>2</sup>/g, which is 3.06 times higher than that of pure PbBiO<sub>2</sub>Br (12.12 m<sup>2</sup>/g). The much larger surface area facilitates the contaminant contact with the catalyst and enhances the photocatalytic performance.

### 3.8 Photocatalytic activity

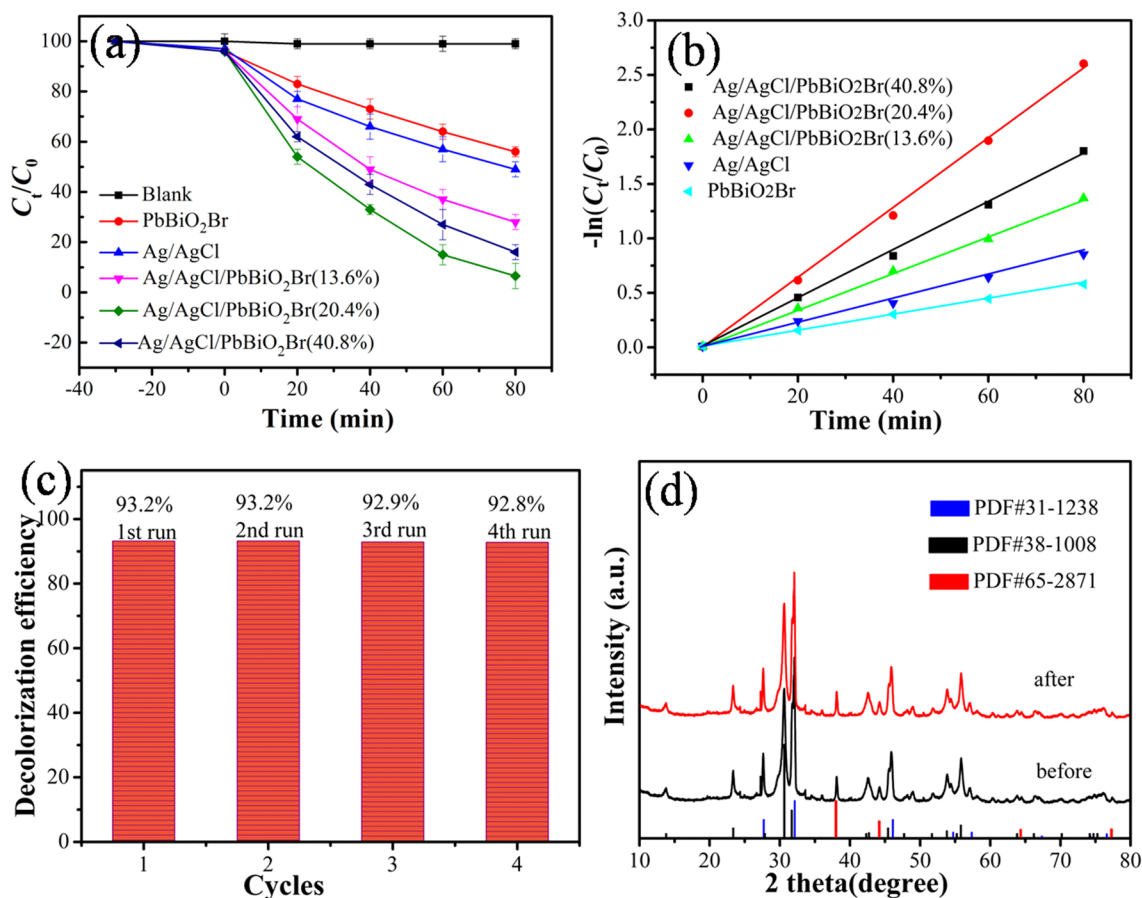
The removal of OTC was used to evaluate the photocatalytic properties of the obtained photocatalysts under visible-light irradiation, and the attained results are given in Fig. 4a. No apparent OTC degradation is detected without photocatalyst under visible-light irradiation, indicating that the direct

**Table 1** BET specific surface areas of the as-prepared samples

Samples	BET(m <sup>2</sup> /g)
Pure PbBiO <sub>2</sub> Br	12.12
Ag/AgCl/PbBiO <sub>2</sub> Br (13.6%)	25.82
Ag/AgCl/PbBiO <sub>2</sub> Br (20.4%)	37.16
Ag/AgCl/PbBiO <sub>2</sub> Br (40.8%)	32.01
Ag/AgCl	26.14



**Fig. 3** a UV–Vis absorption spectra and b FT-IR spectra of bare PbBiO<sub>2</sub>Br, Ag/AgCl and different Ag/AgCl/PbBiO<sub>2</sub>Br composites



**Fig. 4** **a** OTC photodegradation and **b**  $-\ln(C_t/C_0)$  vs. time plots for photodegradation of OTC by the obtained catalysts; **c** Cycling degradation efficiency of  $Ag/AgCl/PbBiO_2Br(20.4\%)$  composite and **d**

XRD patterns of  $Ag/AgCl/PbBiO_2Br(20.4\%)$  composite before and after the recycling photocatalytic experiment

photolysis of OTC can be almost neglected. It can be observed that 44% and 51% of OTC solution is removed within 80 min visible-light irradiation for bare  $PbBiO_2Br$  and  $Ag/AgCl$ , respectively. However, the  $Ag/AgCl/PbBiO_2Br$  composites exhibit enhanced photocatalytic activity in comparison to pure  $PbBiO_2Br$  and  $Ag/AgCl$  under identical experimental conditions. The degradation percentage of OTC solution reaches 72%, 93.2%, and 84% for  $Ag/AgCl/PbBiO_2Br(13.6\%)$ ,  $Ag/AgCl/PbBiO_2Br(20.4\%)$ , and  $Ag/AgCl/PbBiO_2Br(40.8\%)$  composites within 80 min visible-light irradiation, respectively. It is worth noting that the  $Ag/AgCl/PbBiO_2Br(40.8\%)$  photocatalyst has a higher mass ratio of Ag than the  $Ag/AgCl/PbBiO_2Br(20.4\%)$  photocatalyst, however, the photocatalytic activity of the former is lower than that of the latter. The reason may be that Ag NPs are loaded on the surface of the photocatalyst, which not only motivate the SPR, but also promote separation of electrons and holes. However, excessive Ag NPs covering on surface of the  $AgCl$  could inhibit the light absorption and decrease the separation efficiency of  $e^-/h^+$  pairs, thus leading to decreased photocatalytic activity. In addition, to get further insight into the reaction kinetic behaviors, the

photocatalytic degradation rates are calculated using the following equation [50–52]:

$$\ln(C_t/C_0) = K_{app}t \quad (1)$$

where,  $k_{app}$  stands for degradation rates constant [53]. The results are drawn and displayed in Fig. 4b. The obtained rate constants  $k_{app}$  are  $1.06 \times 10^{-2}$ ,  $7.25 \times 10^{-3}$ ,  $1.71 \times 10^{-2}$ ,  $3.25 \times 10^{-1}$  and  $2.21 \times 10^{-1} \text{ min}^{-1}$  for  $Ag/AgCl$ ,  $PbBiO_2Br$ ,  $Ag/AgCl/PbBiO_2Br(13.6\%)$ ,  $Ag/AgCl/PbBiO_2Br(20.4\%)$ , and  $Ag/AgCl/PbBiO_2Br(40.8\%)$ , respectively. It is clear that the rate constant  $k_{app}$  of  $Ag/AgCl/PbBiO_2Br(20.4\%)$  is 3.04 and 4.48 times higher than that of  $Ag/AgCl$  and  $PbBiO_2Br$ , respectively. These results confirm that  $Ag/AgCl/PbBiO_2Br$  composites accelerate the degradation of OTC in photocatalytic progress.

### 3.9 Cyclic experiments

In order to investigate the structural stability and practical application of  $Ag/AgCl/PbBiO_2Br(20.4\%)$  composite,

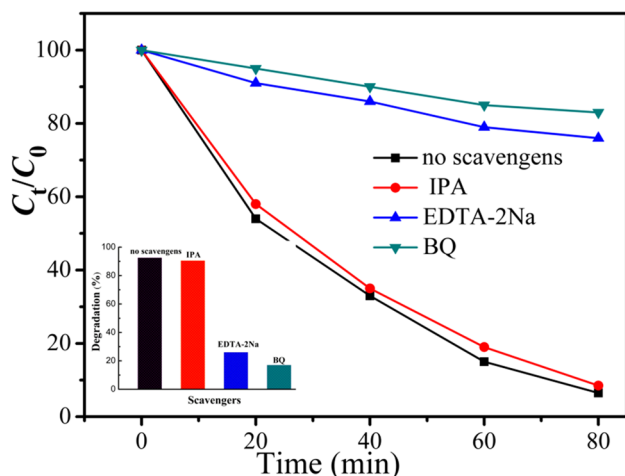
recycling experiments were performed under the same condition, as shown in Fig. 4c. It can be observed that after the 4th run recycle experiment, the removal efficiency of Ag/AgCl/PbBiO<sub>2</sub>Br (20.4%) photocatalyst decreases from 93.2 to 92.8%. This implies that the decrease of the degradation efficiency can be negligible. Furthermore, Fig. 4d exhibits the XRD patterns of Ag/AgCl/PbBiO<sub>2</sub>Br (20.4%) photocatalyst before and after photodegradation recycling. It is clearly observed that all diffraction peaks undergo no change, indicating no any change in crystalline structure. Above results further confirm the stability of the Ag/AgCl/PbBiO<sub>2</sub>Br composites during photocatalytic process.

### 3.10 Possible photocatalytic mechanism

As we all know, superoxide radicals ( $\cdot\text{O}_2^-$ ), hydroxyl radicals ( $\cdot\text{OH}$ ) and holes ( $h^+$ ) are involved in the photocatalytic reaction system as the main radical species [54]. To explore the role of the active species, the radical trapping experiments was implemented by separately adding 10 mM ethylene diaminetetraacetic acid disodium salt (EDTA-2Na), 10 mM

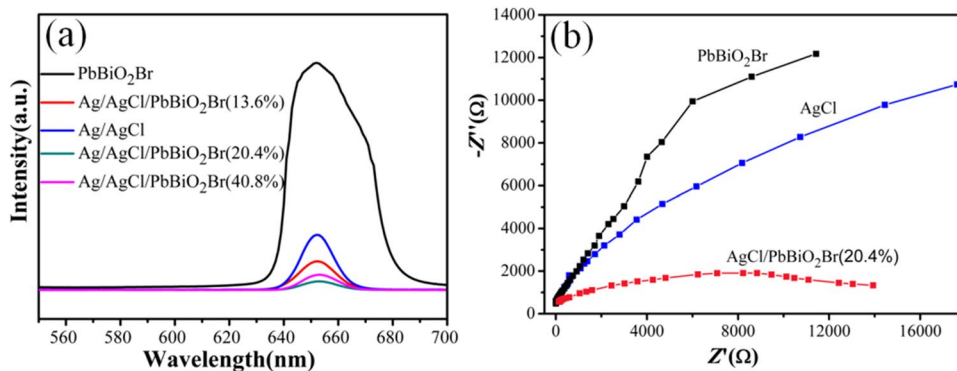
isopropanol (IPA) and 1 mM benzoquinone (BQ) into the photocatalytic reaction system, which act as the  $h^+$ ,  $\cdot\text{OH}$  and  $\cdot\text{O}_2^-$  scavengers, respectively. As depicted in Fig. 5, it is evident that with adding IPA, the degradation rate of Ag/AgCl/PbBiO<sub>2</sub>Br (20.4%) decreases slightly to 90.5%, demonstrating that there are almost no  $\cdot\text{OH}$  radicals generated in the degradation process. However, when adding BQ or EDTA-2Na, the degradation efficiency sharply decreases from 93.2 to 17 and 26%, respectively, demonstrating that  $\cdot\text{O}_2^-$  and  $h^+$  play very important role in the degradation process. Furthermore, in this study, considering that the  $\text{Cl}^-$  could be oxidized by holes to  $\text{Cl}^0$  atoms and the antibiotics OTC could be oxidized [55].  $\text{Cl}^0$  atoms are considered to be another actual active species in the photocatalytic degradation process [56].

Many researches indicate that photoluminescence (PL) emission spectra can be induced by the recombination between photogenerated electrons and holes [57]. The lower the PL emission peaks, the less the recombination of photoexcited charge carriers. Therefore, the charge transfer and recombination processes in the photodegradation experiment can be investigated by PL spectra. Figure 6a shows the PL spectra of bare PbBiO<sub>2</sub>Br, Ag/AgCl, and different Ag/AgCl/PbBiO<sub>2</sub>Br composites in the range of 420–620 nm under excitation at 325 nm, which arise due to the recombination of photogenerated electrons and holes. It is observed that the emission spectrum intensity of bare PbBiO<sub>2</sub>Br is the strongest. However, after the coupling of Ag/AgCl NPs with PbBiO<sub>2</sub>Br nanosheets, the intensity of the PL emission spectra is decreased, indicating that the charge separation rate of Ag/AgCl/PbBiO<sub>2</sub>Br composites is more efficient than that of bare PbBiO<sub>2</sub>Br and Ag/AgCl nanoplates. It is noteworthy that the Ag/AgCl/PbBiO<sub>2</sub>Br (20.4%) composite exhibits the weakest intensity, suggesting that it has the highest separation efficiency of photoexcited charge carriers [58]. In order to further understand the charge transfer in the photocatalytic process. Electrochemical impedance spectroscopy (EIS) measurement was also carried out for the bare PbBiO<sub>2</sub>Br, Ag/AgCl, and Ag/AgCl/PbBiO<sub>2</sub>Br (20.4%) composite. As shown in Fig. 6b, it is found that Ag/AgCl/PbBiO<sub>2</sub>Br (20.4%) composite owns the smallest semicircle



**Fig. 5** The degradation of OTC on the Ag/AgCl/PbBiO<sub>2</sub>Br (20.4%) composite in presence of various scavengers

**Fig. 6** **a** PL spectra (excited at 325 nm) and **b** EIS Nyquist plots of the as-synthesized samples

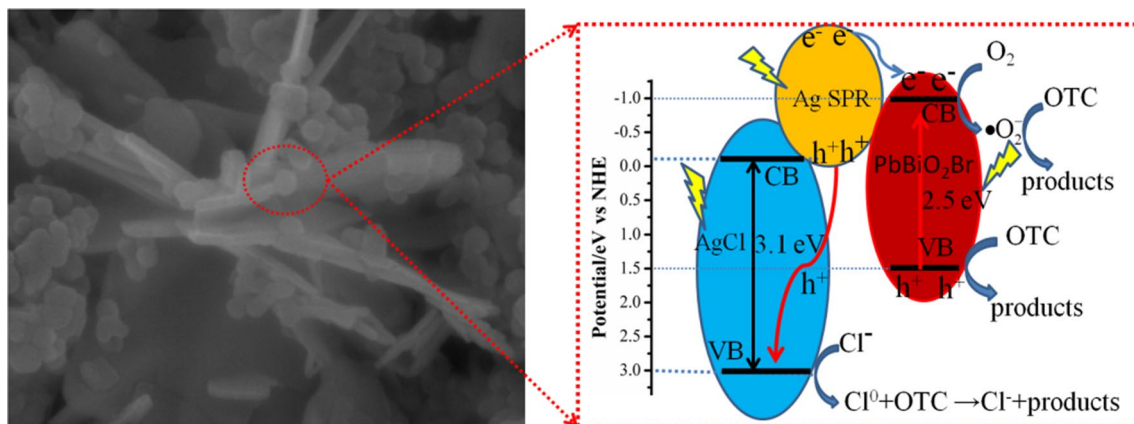
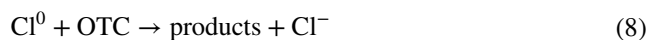
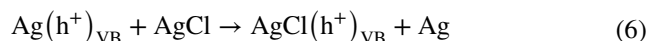
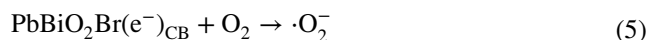
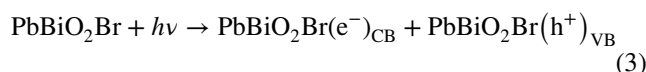
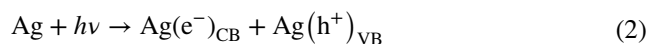


radius. It is commonly recognized that the curvature radius serves as an indicator of charge-transfer resistance, and a smaller semicircle radius implies higher charge transfer efficiency [59, 60].

The positions of the conduction band (CB) and valence band (VB) of obtained  $\text{PbBiO}_2\text{Br}$  are about  $-1.0$  and  $1.5$  eV (vs. NHE), respectively, according to our previously reported results [17, 18]. Furthermore, in the light of the literature, the positions of the CB and VB of the AgCl are located at  $-0.09$  and  $3.16$  eV (vs. NHE), respectively [23, 25].

In the light of above experimental results, a possible photocatalysis mechanism is proposed to explain the charge transfer behaviors of Ag/AgCl/PbBiO<sub>2</sub>Br composite in the photocatalytic process. As shown in Fig. 7, the PbBiO<sub>2</sub>Br and metallic Ag NPs are photoexcited to generate  $e^-/h^+$  under visible-light irradiation (Eqs. 2, 3). The AgCl is difficult to be stimulated under visible-light irradiation due to its broad bandgap. Since the SPR of Ag NPs is energetic enough to the photoexcited electrons and can be easily injected into the  $E_{\text{CB}}$  of AgCl or PbBiO<sub>2</sub>Br (Eq. 4). These accumulated electrons on the  $E_{\text{CB}}$  of AgCl could not reduce oxygen to form  $\cdot\text{O}_2^-$ , due to the  $E_{\text{CB}}$  potential of AgCl ( $-0.09$  eV) more positive than the standard reduction potential of  $E_0(\text{O}_2/\cdot\text{O}_2^-) = -0.33$  eV vs. NHE [61–64]. These accumulated charges could react with  $\text{O}_2$  on the surface of PbBiO<sub>2</sub>Br to form  $\cdot\text{O}_2^-$  due to the  $E_{\text{CB}}$  potential of PbBiO<sub>2</sub>Br ( $-1.0$  eV) more negative than the standard reduction potential of  $E_0(\text{O}_2/\cdot\text{O}_2^-) = -0.33$  eV vs. NHE (Eq. 5). Above radical trapping experimental results verify that the  $\cdot\text{O}_2^-$  is one of the main active species in the photocatalytic process. Meanwhile, the residual  $h^+$  at Ag NPs migrates to the  $E_{\text{VB}}$  of AgCl surface to oxidize the  $\text{Cl}^-$  ion to form  $\text{Cl}^0$  atoms (Eqs. 6, 7). The  $\text{Cl}^0$  atoms are reactive radical species. After that,  $\text{Cl}^0$  atoms

oxidize OTC and hence are reduced to  $\text{Cl}^-$  again (Eq. 8) [65, 66]. Thus, the Ag/AgCl/PbBiO<sub>2</sub>Br can maintain good catalytic performance and stability. On the other hand, from a thermodynamic point of view, the photogenerated  $h^+$  cannot react with  $\text{OH}^-$  or  $\text{H}_2\text{O}$  to produce  $\cdot\text{OH}$  since the VB potential of PbBiO<sub>2</sub>Br is more negative than the redox potentials of  $E^0(\text{OH}^-/\cdot\text{OH})$  (1.99 eV vs. NHE) and  $E^0(\text{H}_2\text{O}/\cdot\text{OH})$  (2.38 eV vs. NHE), indicating that the  $h^+$  can directly oxidize OTC [67–69]. The produced active species ( $h^+, \cdot\text{O}_2^-$ ) can efficiently decompose OTC into intermediate products and finally into  $\text{H}_2\text{O}$  and  $\text{CO}_2$  (Eq. 9). The above discussion suggests that the Ag/AgCl/PbBiO<sub>2</sub>Br composites can improve the separation of photogenerated  $e^-/h^+$ , finally leading to the enhancement of photocatalytic activity.



**Fig. 7** Proposed photocatalytic reaction processes and charge separation of Ag/AgCl/PbBiO<sub>2</sub>Br composites under visible-light irradiation



## 4 Conclusions

In this study, visible-light-driven novel Ag/AgCl/PbBiO<sub>2</sub>Br composites were successfully synthesized through hydrothermal and in situ photoreaction method. The UV–Vis absorption spectra confirm that the as-obtained Ag/AgCl/PbBiO<sub>2</sub>Br composites exhibit remarkable photo-absorption property in the visible-light region as compared to PbBiO<sub>2</sub>Br nanosheets, which could be due to the surface Ag resonance. The Ag/AgCl/PbBiO<sub>2</sub>Br (20.4%) composite exhibits the strongest capacity for degradation of the antibiotic OTC under visible-light irradiation, which can be mainly attributed to strong visible-light absorbance and the efficiently separation of photoexcited charge. The recycling experiments demonstrate that the Ag/AgCl/PbBiO<sub>2</sub>Br composites possess good stability. In addition, active species trapping experiments confirm that  $\cdot\text{O}_2^-$ ,  $\text{Cl}^0$  and  $\text{h}^+$  play an very important role in the degradation process. This work provides a way to design an excellent environmental purification material.

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**Availability of data and materials** All data are fully available without restriction.

## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no competing interests.

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