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Comparison of Ag and AgI-Modified ZnO as Heterogeneous Photocatalysts for Simulated Sunlight Driven Photodegradation of Metronidazole

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Abstract: Ag and AgI-modified ZnO composites (Ag/ZnO and AgI/ZnO) were synthesized in facile ways. The photocatalysts were used for the photodegradation of metronidazole (MNZ) under the irradiation of simulated sunlight. The results of experiments showed that both Ag/ZnO and AgI/ZnO had a specific molar ratio to reach the best performance. Ag/ZnO performed better in the photodegradation of MNZ than AgI/ZnO under the same conditions. The reaction rate constant of AgI/ZnO was less affected by the variation of initial concentration of MNZ or pH values. The main reactive oxygen species of the photocatalytic process are OH, O_2^- and h^+ , but the free radicals which play the most critical part differ in Ag/ZnO and AgI/ZnO. Several intermediates were revealed by LC-MS/MS analysis. The stability of the photocatalysts was evaluated by a series of repeated MNZ photodegradation experiments. The results showed that AgI/ZnO had better stability than Ag/ZnO.

Keywords: Ag/ZnO and AgI/ZnO; composite photocatalysts; metronidazole; reactive oxygen species

1. Introduction

Metronidazole (MNZ) has been widely used as a typical antiprotozoal and antibacterial drug in recent years. It has the potential ability to inhibit the growth of the anaerobic bacteria [1,2]. Residues of MNZ in the environment could cause animal-derived food contamination [3]. In addition, with its neural toxicity, MNZ has the potential to harm human body [4]. It was reported that the maximum concentration of MNZ was at 9400 ng/L and 127 ng/L, respectively in hospital wastewater [5] and the wastewater treatment plants [6]. As a persistent pollutant, MNZ cannot be easily eliminated by the traditional water treatment processes [7,8]. This may lead to a potential MNZ accumulation in the water environment [9,10].

Plenty of research has been conducted [11–17] to study the removal of MNZ in water environment. Among them, photocatalysis has attracted much interest due to its eco-friendly property of utilizing solar energy. $CuBi_2O_4/CuO$ heterojunctions [18], UV/TiO₂ [19], Ag-doped ZnO [20], Fe₂TiO₅ [21], etc. are some recent studies which are based on the photodegradation of MNZ. As an alternative of well-applied photocatalyst TiO₂, zinc oxide (ZnO) has drawn much attention owing to its extraordinary properties of low cost, innocuity, appropriate bandgap energy and exciton binding energy [22,23]. In some studies, ZnO exhibited even more photoactivity than TiO₂ for the photodegradation of organics [24]. However, the photocatalytic capability of ZnO is restricted since the recombination of photoelectron–hole pairs and relatively low quantum efficiency [25]. One of the most effective methods to compensate for the defects of ZnO in photocatalysis is the modification with silver (Ag) or silver halide (AgX, X = Cl, Br, I). Ag nanoparticles have strong absorption of the visible light,

narrow bandgap and can improve electron transport [26]. When incorporated with semiconductor materials, Ag nanoparticles can perform functional abilities of promotion of interfacial charge-transfer, due to its high Schottky barrier at the semiconductor interface [27–29]. Meanwhile, as photosensitive materials, silver halides absorb photons and generate electron–hole pairs [30]. Comparing with AgCl and AgBr, AgI has a smaller band gap [31]. Thus, AgI may have more excellent application prospects in photocatalysis. To date, as we know, there have already been plenty of studies that utilize Ag, AgI and ZnO composite materials to eliminate micropollutants in water, most target compounds of the studies are chosen to be dyes [32–35] and phenol [23,35,36], etc. However, few have focused on the degradation of refractory antibiotics, such as MNZ. By conducting several MNZ photodegradation experiments under simulated sunlight, the aim of this research is to compare the differences between the photocatalytic performance of Ag/ZnO and AgI/ZnO composites as catalysts. To take a step further, the structural distinction of the two composites were investigated and the different reaction mechanism which led to the differences of photocatalytic performances was discussed and illustrated. Finally, a possible degradation pathway of MNZ was proposed on the basis of LC–MS/MS results.

2. Results and Discussion

2.1. Structure and Composition of Ag and AgI-Modified ZnO Photocatalysts

2.1.1. XRD

The XRD results of Ag/ZnO and AgI/ZnO photocatalysts are shown in Figure 1. In both patterns, ZnO displays strong characteristic diffraction peaks at 31.75° , 34.40° , 36.24° , 47.52° , 56.57° , 62.83° , 67.90° , which match to the (100), (002), (101), (102), (110), (103) and (112) planes of the crystalline structure of ZnO, respectively. Among these, (100), (002) and (101) planes are the Wurtzite structure of ZnO (JCPDS NO. 36-1451) [37]. As shown in Figure 1a, diffraction peaks at 38.05° , 44.26° and 64.43° , referring to the (111), (200) and (220) planes of Ag, respectively. These planes match the standard Ag pattern (JCPDS NO. 04-0783) [37]. On the other hand, in Figure 1b, diffraction peaks at 22.39° , 23.71° , 25.31° , 39.20° , 43.45° , 46.33° are corresponding to the (100), (002), (101), (110), (103) and (112) planes of the hexagonal β -AgI phase (JCPDS No. 09-0374) [30]. Moreover, there are neither other impure phases nor changes of all diffraction peaks observed in both graphs, suggesting that the materials have high crystallinity and good crystal form.

2.1.2. XPS

In order to verify the chemical composition and elemental valent state of the photocatalysts Ag/ZnO and AgI/ZnO, XPS was performed; the results are shown in Figures 2 and 3. Figures 2a and 3a are the Zn 2p spectra, the two peaks are located at 1041.3 and 1018.2 eV, 1044.7 and 1021.6 eV, respectively. These results all refer to Zn 2p_{1/2} and Zn 2p_{3/2}, indicating that the form of Zn is Zn²⁺ [38]. Figures 2b and 3b are the O 1s spectra, the feature peaks are 526.9 eV and 530.4 eV, which are related to the lattice oxygen of nanocomposite (the bond of Zn–O). Figure 2c is the spectrum of Ag 3d of Ag in Ag/ZnO, the two peaks are at 370.1 eV and 364.1 eV, with a gap of 6.0 eV, which is assigned to the metallic Ag⁰ species [39]. Figure 3c shows the spectrum of Ag 3d and the two peaks are located at 373.8 eV and 367.8 eV, which should be attributed to Ag 3d_{5/2} and Ag 3d_{3/2}, belonging to Ag⁺ [40]. Figure 3d is the I 3d spectrum, the two peaks at the binding energy of 630.6 eV and 619.1 eV refer to I 3d_{5/2} and I 3d_{3/2} of I[−] [41]. Consequently, all these results confirm the heterojunction structure of Ag/ZnO and AgI/ZnO.

Figure 1. XRD patterns of different Ag/ZnO and AgI/ZnO photocatalysts in the range 10–80°. (a) Ag/ZnO, (b) AgI/ZnO.

2.2. Optical Properties of Ag and AgI-Modified ZnO Photocatalysts

2.2.1. UV-Vis Diffuse Reflectance Spectra

Figures 4 and 5 show the UV-vis DRS spectra and $(\alpha h\nu)^2$ versus energy ($h\nu$) plots of the photocatalysts. All photocatalysts show significant absorption in the UV range. This is due to ZnO's properties as a semiconductor [42]. The absorption edge of pure ZnO is around 400 nm. After being modified with silver, the catalysts' absorption range expands significantly to the visible light region, with the edge of approximately 500 nm. This could be attributed to the surface plasma absorption of Ag [43]. The red shift of the resonance peak occurs more obviously when the size of the nanoparticles gets larger, so the absorption peak of Ag/ZnO (100:1) at 450 nm is due to the SPR effect of Ag particles with the size at around 14 nm (related data are shown in TEM images). When being modified with AgI, the catalysts have border light absorption in the visible light region than bare ZnO, and the absorption

edge is at about 415 nm. Moreover, as the contents of Ag and AgI increase, the light absorption in the visible light area also increases.

Figure 2. XPS spectra of Ag/ZnO (100:1). (a) Zn 2p, (b) O 1s, (c) Ag 3d.

Figure 3. *Cont.*

Figure 3. XPS spectra of AgI/ZnO ($X = 0.4$). (a) Zn 2p, (b) O 1s, (c) Ag 3d, (d) I 3d.

Figure 4. (a) UV-vis spectra and (b) plots of $(\alpha h\nu)^2$ versus energy ($h\nu$) of all prepared photocatalysts Ag/ZnO.

Figure 5. (a) UV-vis spectra and (b) plots of $(\alpha h\nu)^2$ versus energy ($h\nu$) of all prepared photocatalysts AgI/ZnO.

In order to determine the band gap energy of the photocatalysts, based on the Kubelka–Munk function, the relationship of $(\alpha h\nu)^2$ and ($h\nu$) was plotted and shown in Figures 4b and 5b. The results show that the band gaps of ZnO in the two photocatalysts are 3.00 eV and 3.19 eV, respectively. This can be classified as the near monodispersed ZnO microrods, which is consistent with the previous literature [44]. The band gaps of Ag/ZnO (100:0.5, 100:1, 100:2) and AgI/ZnO ($X = 0.1, 0.2, 0.4$) are 3.07 eV, 3.05 eV, 3.05 eV and 2.80 eV, 2.79 eV, 2.78 eV, respectively. The results show that Ag has little effects on the band gap of ZnO. However, with the deposition of AgI, the band gaps of composites become smaller, indicating the modification of ZnO by AgI can enhance the light absorption, so that photocatalysts can produce electron–hole pairs more effectively, the recombination of photoelectron and hole is inhibited. In addition, there are clearly two steps at the curves of AgI/ZnO in Figure 5b, the curves at around 2.80 eV and 3.10 eV are attributed to AgI and ZnO in the composites, respectively, since the band gap values are typical for AgI and ZnO.

2.2.2. PL Spectra

PL spectra can reveal the generation, migration and recombination processes of photoelectron–hole pairs. The results are illustrated in Figure 6. Due to the recombination of photoelectron–hole pairs, the decrease of the intensity of PL spectra commonly indicates the increase of catalytic performance. As displayed in Figure 6a, Ag/ZnO (100:1) shows the minimum PL intensity; but for Ag/ZnO (100:0.5) and Ag/ZnO (100:2), PL intensity is mostly the same. PL intensity depends on the Ag concentration. With appropriate amount of Ag content, more metal sites that accept electrons can be formed under light excitation, leading to the enhancement of separation effects of the photoelectron–hole pairs [45]. Thus, the PL intensity decreases. However, with much higher silver concentration, the nanoparticles tend to aggregate and form clusters, eventually cover the surface of ZnO. This process may hinder the heterojunction structure from utilizing light energy and reduce the transportation of electron [46], thus the PL intensity rises. For AgI/ZnO, as displayed in Figure 6b, in the range of 200–800 nm, PL intensity decreases with the increase of silver content. Indicating that the presence of AgI quenches PL intensity, since the electron transfer becomes more efficient on the surface of the heterojunction as the content of AgI increases.

Figure 6. PL spectra of (a) Ag/ZnO, (b) AgI/ZnO.

2.3. Morphology of Ag and AgI-Modified ZnO Photocatalysts

2.3.1. TEM

The surface morphology and structure of the composites was observed by TEM and SEM. As shown in Figure 7, ZnO remains in good shape after Ag deposition. The dark-colored dots on the surface of ZnO in the images refer to Ag particles. Figure 8 shows that AgI particles are distributed on ZnO surfaces uniformly. The particle size of Ag and AgI were also determined. As shown in Figures 7c and 8c, the average size of the as-selected Ag and AgI particles are 13.63 nm and 13.69 nm, respectively.

Figure 7. TEM images of Ag/ZnO (100:1), (a) 100 nm, (b) 50 nm, (c) 20 nm.

2.3.2. SEM and EDS Mapping

As illustrated in Figure 9a–c, the presence of element Ag, Zn and O is confirmed in Ag/ZnO (100:1), element Ag is uniformly distributed within the photocatalysts. Meanwhile, Figure 10a–d reveal that AgI/ZnO ($X = 0.4$) possesses the elements of Ag, I, Zn and O. SEM results are shown in Figures 9a–c and 10a–d. In these images, rodlike ZnO shows good geometry, Ag and AgI particles are well dispersed on the surface, following the EDS results.

Figure 8. TEM images of AgI/ZnO (X = 0.4). (a) 100 nm, (b,c) 50 nm.

Figure 9. (a–c) EDS mapping of Ag/ZnO (100:1); (d–f) SEM images of Ag/ZnO (100:1).

Figure 10. (a–d) EDS mapping of AgI/ZnO ($X = 0.4$); (e–g) SEM images of AgI/ZnO ($X = 0.4$).

2.4. The Photodegradation of Metronidazole under Simulated Sunlight Irradiation

2.4.1. The Effect of Ag and AgI Loading

The MNZ degradation experiments were conducted to evaluate the performance of photocatalysts Ag/ZnO and AgI/ZnO under simulated sunlight irradiation. The tests were carried out in a 100 mL reaction vessel, with MNZ solution of 2 mg L^{-1} and catalysts dosage of 100 mg. The results are shown in Figure 11. It can be found in Figure 11a that the MNZ cannot be completely degraded without any catalysts after 90 minutes' irradiation of simulated sunlight, only 53.4% is removed. When pristine ZnO and Ag/ZnO (100:2) are used to be the photocatalysts, 91.4% of the MNZ can be eliminated in 30 min. However, with the presence of photocatalyst Ag/ZnO (100:0.5) and Ag/ZnO (100:1), the MNZ is all removed also in 30 min. This improvement is probably due to the enhancement of photocatalytic activity by Ag deposition, which can be approved by the various characterization mentioned previously. The Ag/ZnO (100:1) catalyst showed the highest performance. It reveals the fact that the increase in catalytic efficiency is not merely positively correlated with the content of silver [47]; there is an optimal value. This can be interpreted by the fact that a specific amount of noble metal may become the center for the capture of photoelectrons, but an excess amount of noble metal can also be the core of promoting the recombination of photoelectrons and hole pairs, resulting in a weakened catalytic effect [48].

Figure 11b shows the degradation of MNZ with different AgI/ZnO photocatalysts under simulated sunlight. In 30 min, 50.3%, 63.3% and 67.1% of MNZ can be removed by AgI, AgI/ZnO ($X = 0.1$), AgI/ZnO ($X = 0.2$) and AgI/ZnO ($X = 0.4$), respectively. Compared to bare AgI, the degradation efficiency of MNZ is improved when combined with ZnO. It should be noted that efficiency increased with the AgI content. The enhancement can be attributed to the heterojunction structure of AgI and ZnO, which can increase not only the light adsorption, but also the generation and transportation of photoelectron and hole pairs.

To explore the kinetics of photocatalytic reactions, the pseudo-first-order apparent reaction rate constants (k) were calculated according to the graphs of reaction time versus $\ln(C_t/C_0)$ and are shown in Figure S5. According to the results, the photocatalytic degradation of MNZ follows the pseudo-first-order kinetics ($-dC/dt = kC$) [49]. The rate constants of Ag modified ZnO catalysts are approximately ten times higher than that of MNZ photodegradation without catalysts. In contrast, the rate constants of AgI/ZnO are almost four times higher than that of non-catalyst MNZ photodegradation, 1.3 times higher than that of MNZ photodegradation with AgI. These results confirm that the modification of ZnO can significantly enhance the photocatalytic activity of the catalysts. Overall, the Ag/ZnO catalysts perform better than AgI/ZnO catalysts.

Figure 11. Photocatalytic degradation of MNZ under simulated sunlight with (a) Ag/ZnO, (b) AgI/ZnO, of MNZ.

2.4.2. Initial Concentration of MNZ

The influence of initial concentration is displayed in Figure 12. In MNZ photodegradation processes with both Ag/ZnO and AgI/ZnO as photocatalysts, as the initial concentration of MNZ increases, the degradation efficiency tends to decrease. Since the generation and transfer of active groups is the main factor controlling the rate of photocatalytic degradation, the activity sites on catalyst surface will gradually be occupied by target organics to reach a saturation point and the active groups in contact with MNZ are also reduced accordingly. Moreover, a high concentration of MNZ leads to the formation of more intermediates. The intermediates will compete with MNZ for active

groups, resulting in a decrease in the photocatalytic degradation of MNZ. Figure S6a,b shows the pseudo-first-order apparent reaction rate constants (k) of each reaction. With the initial concentration of MNZ increases from 0.5 mg/L to 10 mg/L, the k values of Ag/ZnO decrease from 0.45 min^{-1} to 0.057 min^{-1} ; whereas the k values of AgI/ZnO decreases from 0.034 min^{-1} to 0.02 min^{-1} .

Figure 12. Effects of initial concentration on MNZ photodegradation under simulated sunlight with (a) Ag/ZnO (100:1) and (b) AgI/ZnO (X = 0.4).

Overall, for both photocatalysts, the initial concentration shows noticeable effect on the enhancement for MNZ photodegradation. The variation of initial concentration has bigger impact on Ag/ZnO than on AgI/ZnO, the highest k value (when $C_0 = 0.5$ mg/L) is around eight times than the lowest k (when $C_0 = 10$ mg/L), while that of AgI/ZnO is 1.7 times.

2.4.3. pH

In photocatalytic reactions, pH value plays an important role. To determine how pH affects the surface charge of photocatalysts, Zeta potential was measured under different pH conditions; the results are shown in Figure S3. It can be found that the Zeta potential of Ag/ZnO (100:1) is 7.12. For AgI/ZnO ($X = 0.4$), the isoelectric point is 2.38. The initial pH was adjusted to 2, 4, 8, 10 $\times$ 0.1 M H_2SO_4 and NaOH solution in the experiments. The results can be observed in Figure 13a,b, the pseudo-first-order apparent reaction rate constants are calculated and plotted in Figure S7a,b. When using Ag/ZnO (100:1) as catalysts, the reaction is immensely contained when the pH is 2 and the MNZ degradation rate constant (k) is the lowest. Moreover, k (pH = 8) > k (pH = 4) > k (pH = 10). This is because of the changes in the charges of MNZ and the charges on the surface of the catalysts under different pH conditions. According to previous research, the pK_a of MNZ is 2.55 [50], therefore when pH is below 2.55, both MNZ and Ag/ZnO are positively charged, which reduces MNZ's adsorption capacity on the catalysts' surface and causing a decrease in the degradation rate. When pH is at 2.55–7.12, the catalyst surface is still positively charged, but MNZ becomes negative and the adsorption of MNZ on catalyst surface becomes stronger, thus promoting the photolysis degradation of MNZ. When pH is higher than 7.12, both MNZ and Ag/ZnO are negatively charged, the rate of photodegradation is not greatly affected in such conditions. The $-OH$ generation will be facilitated when OH^- massively exists. Thus, the reaction rates will increase, the effects of electrostatic rejection will be weakened. As a result, the photocatalytic reaction efficiency reach maximum at pH = 8. When the pH is further increased to 10, the electrostatic repulsion becomes more significant, so the reaction rates decrease. Similarly, for AgI/ZnO ($X = 0.4$), the photodegradation efficiency is greatly inhibited when pH is 2. However, when the pH gradually increases to greater than 2.38, but less than 2.55, the catalyst and MNZ are oppositely charged. Therefore, the photocatalytic reaction efficiency will be enhanced. When pH is greater than 2.55, both MNZ and AgI/ZnO will be negatively charged, likewise, the mass generation of $\cdot OH$ counteracts with the decrease of degradation rate causing by electrostatic repulsion.

In general terms, pH has a significant effect on the MNZ photodegradation with Ag/ZnO and AgI/ZnO under simulated sunlight. The reaction is significantly inhibited in acidic environments due to electrical rejection. Only under this circumstance, AgI/ZnO performs similarly as Ag/ZnO, but as pH grows higher, Ag/ZnO performs much better than AgI/ZnO.

2.5. Mechanism of Photocatalytic Reactions

2.5.1. Validating the Presence of Reactive Oxygen Species

The presence of the reactive oxygen species were validated by quenching experiments. The common reactive oxygen species and their quenchers are OH and isopropanol (10 mM), O_2^- and benzoquinone (0.5 μM), photogenerated holes (h^+) and EDTA disodium (5 mM), 1O_2 and sodium azide (0.5 μM) [39], respectively. Figure 14 shows the results of the quenching experiments. It can be seen from Figure 14a that the presence of isopropanol and EDTA significantly inhibited the photocatalytic activity of Ag/ZnO. The effects of benzoquinone and sodium azide were minimal, indicating that OH are the main reactive oxygen species. Figure 14b shows that the quenchers suppressed the photocatalytic activity of AgI/ZnO to different extent. Among them, isopropanol has the most apparent inhibition effect. Hence, OH plays a major role, h^+ and O_2^- are secondary. To further determine the main reactive oxygen species, EPR analysis was conducted. As Figure 15 displays, Ag/ZnO patterns show the four characteristic peaks of OH with significant intensity, implying the existence and abundance of OH . Meanwhile, though the OH pattern of AgI/ZnO also shows the characteristic peaks, the baseline is not

smooth enough, revealing that the intensity is not as good as that of Ag/ZnO. For the O_2^- pattern of Ag/ZnO, the feature peaks are not clear enough and the intensity is insufficient. The O_2^- pattern of AgI/ZnO is much more defined than that of Ag/ZnO. This suggests that O_2^- plays a more critical role in the photocatalysis with AgI/ZnO. These results all correspond to quenching experiments.

Figure 13. Effect of initial pH for MNZ photodegradation by (a) Ag/ZnO (100:1) and (b) AgI/ZnO (X = 0.4) as catalysts.

Figure 14. Effects of different quenchers for the photodegradation of MNZ under simulated sunlight irradiation with (a) Ag/ZnO (100:1) and (b) AgI/ZnO (X = 0.4).

2.5.2. Proposed Photocatalytic Mechanism

For Ag/ZnO, as an n-type semiconductor, the work function (ϕ_s) of ZnO is 5.2 eV [37], the band gap is around 3.2 eV, the conduction band (CB) and valence band (VB) are -4.19 eV and -7.39 eV (vs. AVS), respectively [51]. It is well known that Ag as a noble metal is also a good conductor, its CB overlaps with VB, so it contains many free electrons and the work function (ϕ_m) of Ag is 4.26 eV [52]. At the time Ag and ZnO contact with each other, free electrons start to transfer. Since $\phi_m < \phi_s$, electrons transfer from Ag to ZnO until the Fermi levels of Ag ($E_{F,m}$) and ZnO ($E_{F,s}$) are at the same level. This results in the formation of accumulation layer, where the electrons accumulate in the space charge region [53]. This process can be described as:

Figure 15. EPR patterns of OH and O_2^- in the photodegradation of MNZ under simulated sunlight irradiation with Ag/ZnO (100:1) and AgI/ZnO ($X = 0.4$).

Eventually, the energy band edges of ZnO shift due to the charge transfer and band bending happens. The proposed scheme of band structure and photocatalytic mechanism for Ag/ZnO under the irradiation of simulated sunlight is displayed in Figure 16a. When the catalysts are under the radiation and receiving energy higher than band gap of ZnO, the electrons on VB will be excited and transferred to CB and the same amount of h^+ will be generated on the VB, thus the photoelectron–hole pairs are formed. The O_2 molecules in water can trap the photoelectrons on Ag and CB of ZnO and transfer to O_2^- . The h^+ on VB of ZnO can react with OH^- to generate OH. Furthermore, the defects at the interface of Ag and ZnO can also restrain the recombination process by transferring the electrons to organic matters in solution [37]. The active oxygen species and h^+ can all react with MNZ and decompose it. Ag^+ will absorb photoelectrons and be reduced to Ag. Thus, the catalysts remain stable. The rest of the photocatalytic process can be described as:

As for AgI/ZnO, the band gap of AgI is around 2.79 eV, the CB and VB are -0.42 eV and 2.37 eV, respectively [54,55]. The CB and VB of ZnO are -0.34 eV and 2.86 eV (vs. NHE), respectively [56]. Figure 16b illustrates the proposed photocatalytic mechanism of AgI/ZnO. After contact, AgI and ZnO will become heterojunction structure. Under the radiation of simulated sunlight, photoelectrons on CB of AgI can easily transfer to CB of ZnO, since CB_{AgI} is more negative than CB_{ZnO} . The potential energy of O_2 / O_2^- (-0.33 eV [57]) is less negative than that of AgI and ZnO, so O_2 molecules in water can capture the electrons on CB of AgI and ZnO to generate O_2^- . The potential energy of $\cdot OH / OH^-$ (2.38 eV) is higher than VB energy of AgI, thus the h^+ on VB of AgI cannot oxidize OH^- to OH, instead,

it can directly react with MNZ molecules [58]. On the other hand, the potential energy of $\cdot\text{OH}/\text{H}_2\text{O}$ (2.72 eV) is lower than the VB energy of ZnO, so the h^+ on the VB of ZnO will react with H_2O molecules to produce $\cdot\text{OH}$ [29]. The photocatalytic process can be described as:

Figure 16. Proposed band structure and photocatalytic mechanism of (a) Ag/ZnO [57], (b) AgI/ZnO.

According to former experiment results, under the irradiation of simulated sunlight, Ag/ZnO performs much better in the photodegradation of MNZ than AgI/ZnO as the photocatalyst. The reason is evident through the proposed photocatalytic mechanism. OH plays a key role in the photodegradation of MNZ. Owing to the existence of an accumulation layer [59], the photoelectron transmission process from ZnO to Ag is boosted, so that the recombination of photoelectron–hole pairs is reduced in Ag/ZnO, thus the OH generation is promoted. Moreover, the surface plasmon resonance (SPR) of Ag also improves the utilization of light energy and the efficiency of electronic transmission [39]. Noticeably, as shown in Figure 16b, since the Fermi levels of AgI and ZnO are close to their VB, comparing to Ag/ZnO, when the electronic transfer of the two interfaces is balanced, the direction of band bending in AgI and ZnO is opposite, resulting in discontinuous energy edges [57,58]. This is unfavorable not only to the transfer of photoelectron–hole pairs, but also to the mass generation of OH. To conclude, the structural distinctions of Ag/ZnO and AgI/ZnO lead to differences in their ability to produce free radicals, which is why the photocatalysis capabilities of the two catalysts are different.

2.6. Identification of Possible Intermediates during Photocatalytic Degradation

To determine the main intermediates during the photodegradation of MNZ, LC–MS/MS analysis was conducted. The mass spectrum of MNZ produced a molecular ion at m/z 171 and the intermediates of MNZ photodegradation were determined at m/z 184, 149, 121, 158, 98, 142. Figure 17 shows the possible photodegradation pathway of MNZ, which is based on the LC–MS/MS results and reported MNZ degradation by hydroxyl radicals [3,59–61]. The images of TOC removal are shown in Figure S4, the TOC removal rates are nearly 50% in the process of MNZ photodegradation under simulated sunlight.

Figure 17. Degradation pathway of MNZ during the reaction. MNZ $C_0 = 2 \text{ mg L}^{-1}$, photocatalyst dosage = 0.1 g L^{-1} .

2.7. Stability of the Photocatalysts

To investigate the stability of Ag/ZnO (100:1) and AgI/ZnO ($X = 0.4$), three-time cycling experiments of MNZ photodegradation were conducted. As shown in Figure 18a, there is a slight decline of the efficiency after the first run. It takes more time to get 100% degradation rate. Figure 18b shows the XRD patterns of Ag/ZnO (100:1) before and after the reaction. The characteristic peaks of Ag and

ZnO are not changed, but the intensity of Ag has a small decrease. The results of ICP-MS test show that the Ag^+ concentration of the reaction system increases from 0.0 to 62.9 ppb after the first run, confirming that it was the leaching of Ag content which caused the decline of photocatalytic efficiency. As for AgI/ZnO ($X = 0.4$), it can be found in Figure 18c that degradation rate generally remains at the same level, the XRD patterns in Figure 18d also displays no changes. Furthermore, the results of the ICP-MS test show that the concentrations of Ag^+ before and after the reaction are 1.2 ppb and 1.5 ppb, respectively, which is negligible. These results suggest that AgI/ZnO is more stable than Ag/ZnO.

Figure 18. Cont.

Figure 18. (a,c) Circling runs of MNZ photodegradation in the presence of the photocatalysts Ag/ZnO (100:1) and AgI/ZnO ($X = 0.4$); (b,d) XRD patterns of photocatalysts Ag/ZnO (100:1) and AgI/ZnO ($X = 0.4$) before and after MNZ photodegradation under simulated sunlight irradiation. MNZ's initial concentration is 2 mg L^{-1} , photocatalyst dosage is 0.1 g L^{-1} .

3. Materials and Methods

3.1. Materials

Metronidazole (MNZ, analytical reagent) was obtained from Sigma-Aldrich (St. Louis, MO, USA). Silver nitrate (AgNO_3 , analytical reagent), sodium hydroxide (NaOH , analytical reagent), ethanol absolute ($\text{CH}_3\text{CH}_2\text{OH}$, analytical reagent), sodium chloride (NaCl , analytical reagent), sodium sulfate (Na_2SO_4 , analytical reagent), sodium nitrate (NaNO_3 , analytical reagent) and sodium humate were purchased from Sino-pharm Chemical Reagent Corp (Shanghai, China). Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, analytical reagent) and potassium iodide (KI , analytical reagent) were purchased from CNW Technologies GmbH (Dusseldorf, Germany).

3.2. Preparation of the Catalysts

Ag/ZnO photocatalysts with different molar ratios of Ag and Zn (named as Ag/ZnO 100:1, etc.) were synthesized by a hydrothermal method [61]. AgI/ZnO photocatalysts with different molar ratios of ZnO and Ag (named as AgI/ZnO $X = 0.1$, etc.) were synthesized by a coprecipitation method. The details of preparation methods are described in the supporting information file.

3.3. Characterization

X-ray diffraction (XRD, Bruker D8 Advance X-ray diffractometer equipped with $\text{Cu-K}\alpha$ radiation. $\lambda = 1.5406 \text{ \AA}$, the scanning rate is $10^\circ \text{ min}^{-1}$ and 2θ range is from 10° to 80° .) was used to examine the crystal structure of the photocatalyst. X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos Supra instrument (Kratos Analytical, Manchester, UK) with monochromatic Al radiate (1486.7 eV , 150 W), to confirm surface composition and chemical bonds of the photocatalysts. UV-vis diffuse reflectance spectra (UV-vis DRS) were operated by UV-2550 spectrophotometer, Shimadzu, Japan. The photoluminescence spectroscopy (PL) of photocatalysts was tested on Edinburgh Instruments FLS980. Transmission electron microscopy (TEM) observation was performed by FEI Tecnai G2 F20 S-Twin. The zeta potential was measured by nano particle potentiometer: Malvern Zetasizer Nano ZS90. The possible silver ion stoic in the reaction system was detected by inductively coupled plasma mass spectrometry (ICPMS): Agilent 7700, USA. Electron spin resonance (EPR) spectra were performed on Bruker JES FA200.

3.4. Evaluation of Photocatalytic Activity

The photocatalytic activity was assessed by the degradation of MNZ under simulated sunlight irradiation. The light source was a 300 W Xenon lamp (PLS-SXE 300, Beijing Perfectlight Technology Co., Ltd. China). The light intensity of the reaction system surface was 100 mW cm^{-2} . Typically, 100 mL MNZ solution with a concentration of 2 mg/L was added to a quartz reactor, 100 mg of the catalysts were added and mixed. During the experiment, when illuminated, water circulation was enabled to keep the reaction system at room temperature (25°C). The samples were taken with disposable syringes every five minutes. When the effects of influencing factors were examined, the factors to be studied were changed while the others were controlled. A three-cycle experiment was conducted to evaluate the stability of the photocatalysts. The used catalysts were collected after each cycle by filtering of $0.45 \mu\text{m}$ polyether sulfone membranes, then washed and dried for the next cycle. The possible silver ions emission was detected by ICPMS.

3.5. Evaluation of Reactive Oxygen Species

There are several typical free radicals which are functional in photocatalysis: $\text{OH}^\bullet$ [36,37], $\text{O}_2^{\bullet-}$, $^1\text{O}_2$ and h^+ [38]. A series of quencher experiments were conducted to determine which reactive species play a part in photodegradation. Isopropanol (10 mmol L^{-1}) was selected as the quencher for $\text{OH}^\bullet$, while benzoquinone ($0.5 \mu\text{mol L}^{-1}$) for $\text{O}_2^{\bullet-}$, sodium azide ($0.5 \mu\text{mol L}^{-1}$) for $^1\text{O}_2$ and EDTA disodium ($0.5 \mu\text{mol L}^{-1}$) for h^+ . Moreover, the results were further verified by electron paramagnetic resonance spectrometer (MiniScope MS-5000, Magnettech, Germany).

3.6. Analytical Methods

The concentration of MNZ was measured by high-performance liquid chromatography (HPLC, Agilent 1200) with a diode array detector (DAD), using a C18 column (Athena C18-WP, $100 \text{ \AA}$, $4.6 \times 250 \text{ mm}$, $5 \mu\text{m}$, CNW) at the wavelength of 318 nm. The mobile phases consisted acetonitrile and water. The byproducts during the degradation of MNZ was distinguished by LC-MS/MS (TSQ Quantum, Thermo Fisher Scientific). The mobile phases consisted acetonitrile and water with ammonium acetate and formic acid [4].

4. Conclusions

A series of Ag/ZnO and AgI/ZnO composites were successfully prepared by hydrothermal method and coprecipitation method, respectively. The deposition of Ag and AgI enhanced the photocatalytic activity of ZnO without changing its surface property and crystalline structure. Ag/ZnO (100:1) and AgI/ZnO ($X = 0.4$) have the best photocatalytic activity among all Ag/ZnO and AgI/ZnO composites, respectively. Under the same conditions, Ag/ZnO (100:1) performed better than AgI/ZnO ($X = 0.4$), the reaction rate constant of Ag/ZnO (100:1) is 3.25 times higher. The main drawback of Ag/ZnO is that it can be easily affected by the changes of reaction conditions. The efficiency of Ag/ZnO decreases after the reaction is because of the leaching of Ag^+ . AgI/ZnO is more stable. The main reactive oxygen species of the photocatalytic process are $\text{OH}^\bullet$, $\text{O}_2^{\bullet-}$ and h^+ . In Ag/ZnO system, $\text{OH}^\bullet$ and h^+ play the leading role, $\text{O}_2^{\bullet-}$ has a minor effect. In AgI/ZnO, system $\text{OH}^\bullet$, $\text{O}_2^{\bullet-}$ and h^+ contribute to the photocatalytic process to a similar extent. Structural differences lead to the discrepancy between two catalysts. Ag/ZnO is a metal-semiconductor structure. With the SPR of Ag and defects on the interface of Ag and ZnO, the catalytic capability is enhanced. AgI/ZnO is a typical heterojunction structure, but the electron transportation is weaker than that of Ag/ZnO due to the discontinuous energy edges, resulting in the disparity of catalytic capability.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/9/1097/s1>, Figure S1: Kinetic analysis of photocatalytic degradation of MNZ with (a) Ag/ZnO, (b) AgI/ZnO. Figure S2: Kinetic analysis of photocatalytic degradation of MNZ in different initial pH conditions with (a) Ag/ZnO, (b) AgI/ZnO. Figure S3: Effect of pH on the Zeta potential and isoelectric point of (a) Ag/ZnO (100:1), and (b) AgI/ZnO ($X = 0.4$). Figure S4: TOC removal by Ag/ZnO (100:1) and AgI/ZnO ($X = 0.4$). Figure S5: The pseudo-first order apparent

reaction rate constants (k) of different catalysts. Figure S6: The pseudo-first order apparent reaction rate constants (k) of MNZ photocatalytic degradation with (a) Ag/ZnO (100:1) and (b) AgI/ZnO (X = 0.4) under conditions of different initial MNZ concentrations. Figure S7: The pseudo-first order apparent reaction rate constants (k) of MNZ photocatalytic degradation with (a) Ag/ZnO (100:1) and (b) AgI/ZnO (X = 0.4) under different initial pH conditions.

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