Two dimensional Z-scheme AgCl/Ag/MnTiO$_3$ nano-heterojunctions for photocatalytic degradation performance enhancement

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Abstract: The AgCl/Ag/MnTiO$_3$ heterojunction was synthesized by two steps, the MnTiO$_3$ nanowires were first prepared by electrospinning, and then Ag/AgCl was loaded onto MnTiO$_3$ by photodeposition. It can be seen that the AgCl/Ag/MnTiO$_3$ heterojunction is successfully synthesized and proved by XPS and SEM. The absorption band of the AgCl/Ag/MnTiO$_3$ heterojunction exhibits a red shift indicating an increase absorption in sunlight. Compared with pure MnTiO$_3$, the AgCl/Ag/MnTiO$_3$ heterojunction exhibits a better photocatalytic degradation rate of about 8 times, which is attributed to the AgCl/Ag could accelerate the transfer of photogenerated electrons and promote separation of electron-holes efficiently.

1. Introduction

Due to the increasing environmental pollution and the scarcity of water resources, in recent years, a great deal of researches have been carried out on reducing water pollution and cleaning contaminated water sources [1, 2]. There, the semiconductor photocatalyst, with excellent photocatalytic performance, is regarded as the effective method for degrading toxic organic pollutants in wastewater and wastewater, and has attracted lots of attentions. Up to now, series of semiconductors have been reported, which can efficiently mine the organic pollutants form into harmless and non-polluting substances [3, 4], including the TiO$_2$, ZnO, CdS, etc..

Among these, the ilmenite structure MnTiO$_3$, with the wide band gap (3.1 eV) and a nti ferromagnetic properties [5], can be used as the ideal photocatalyst for degradation of pollutants in water due to its strong absorption [6] in the visible region and suitable band gap [7, 8], so there are lots of preparation methods of manganese titanate have been reported, including oxidation reaction [9], hydrothermal method [10], sol-gel method [11], etc.. As known, the electrospinning method is a decent method to control the morphology of the nano-material, including the TiO$_2$ nanotubes, ZnO nanospheres, etc.. However, there are few reports about the preparation of MnTiO$_3$ by electrospinning. So in this study, the method of electrospinning is used as the ideal way to prepare MnTiO$_3$ [12].

However, due to the wide band gap, the photocatalytic performance of the MnTiO$_3$ is expected to be improved, and lots of ways have been reported. Especially the heterojunction modification, with the easy preparation and low cost, is popular in current researches. There, the AgCl modification, with high quantum yield and concomitant AgCl/Ag structure, is widely used in the field of photocatalytic degradation, because such structure could enhance the stability and catalytic efficiency efficiently [13, 14]. Nowadays, the structure and photocatalytic activity of AgCl/Ag semiconductor heterojunctions...
have been a hot topic, such as, Zhao, Zhou and Lu et al. improve the adsorption capacity and the separation efficiency of photogenerated carriers to enhance the photocatalytic performance by loading the AgCl nanotubes on the BiOCl nanosheets [15], Yang, Hu and Guo's research group improve the photocatalytic degradation of organic pollutants by preparing AgCl/Ag/TiO$_2$ ternary heterostructure nanocomposites [16]. McEvoya, Cuib and Zhang have reported a new composite photocatalyst of AgCl/Ag activated carbon with good photocatalytic activity for MO and phenol under visible light [17], and so on. These above researches indicate that the AgCl/Ag owns great prospects in photocatalytic degradation.

In this work, we prepared the AgCl/Ag/MnTiO$_3$ heterojunction by electrospinning and photodeposition. The results show that the AgCl/Ag/MnTiO$_3$ heterojunction exhibits remarkable photocatalytic degradation enhancement under the illumination. In addition, a simple detection and mechanism study of the nano-heterojunction has been carried out.

2. Material and Methods

2.1. Materials

Manganese (II) acetate tetrahydrate (Mn(CH$_3$COO)$_2$·4H$_2$O), tetrabutyl titanate (Ti(OC$_4$H$_9$)$_4$) and polyvinylpyrrolidone (PVP, Mw=1300,000) were purchased from MACKLIN. Methyl alcohol (CH$_3$OH) and glacial acetic acid (CH$_3$COOH) were purchased from Hangzhou Gaojing Fine Chemical Industry Co.Ltd. All the chemicals are analytical grade and Deionized (DI) water was used throughout the experiments.

2.2. Methods

2.2.1. Synthesis of AgCl/Ag/MnTiO$_3$ nano-heterojunction. The synthesis of AgCl/Ag/MnTiO$_3$ nano-heterojunction is divided into two major steps. The first is to synthesize MnTiO$_3$ by electrospinning. Typically, 1.13 g of Ti(OC$_4$H$_9$)$_4$ and 0.81 g of Mn(CH$_3$COO)$_2$·4H$_2$O were dissolved in a mixture of 10 mL methyl alcohol and 2 mL of acetic acid and stirred for 1 h to obtain a clear solution at room temperature. Then, 0.8 g of PVP was added to the solution stirred vigorously for 8 h to get a homogeneous mixture. Add the well-mixed solution to a 20ml syringe equipped with a needle of 22-gauge stainless steel. A high voltage power supply was used to provide a voltage of 15 kV to the needle tips and the rotating drum collector (Electrospinning machine model, WL-2C, Beijing Zhiye Ion Technology Co. Ltd.). The flow rate of the solution was fixed at 1.0 mL/h. The nanofibers obtained by spinning were initially dried in a vacuum furnace at 80 °C for 12 h. The fibers were calcined at 1000 °C for 2 h at a heating rate of 5 °C/min in air.

AgCl was loaded onto the previously prepared MnTiO$_3$ by a chemical deposition-photo reduction process. Specific steps are as follows: 0.10 g of MnTiO$_3$ was added in 15 mL of deionized water with ultrasonicated for 5 min. Then, different volumes of 0.05 M silver nitrate solution were added to the solution and stirred vigorously for 1 hour. Subsequently, adding the same amount of 0.05 M hydrochloric acid as the above silver nitrate solution to the solution. After stirring in the dark for 1 h, the solution was irradiated under a 500 W xenon lamp for 20 min. The precipitate was washed twice by water and ethanol. The precipitate was dried for 8 h at 80 °C. Samples with silver nitrate solution of 100 mL, 200 mL and 300 mL were labeled as MTO-Ag-1, MTO-Ag-2, MTO-Ag-3, respectively. Pure MnTiO$_3$ was recorded as MTO.

2.2.2. Characterization. The phase composition of the as-prepared samples were examined by X-ray power diffraction (XRD, Bruker D8 Discover) using Cu Kα (λ = 1.5406 Å) radiation at 40 kV and 40 mA. The micromorphology were characterized by scanning electron microscopy (FESEM Hitachi S-4800). The UV–vis diffuse reflectance spectra were obtained by the UV–vis spectrophotometer (Hitachi-U3900). Photoluminescence (PL) measurements were recorded by using a spectrofluorimeter (Hitachi F-7000) with an excitation wavelength at 320 nm.
2.2.3. Photocatalytical degradation of dye. Photocatalytic activities were evaluated by the degradation of RhB under simulative visible-light irradiation using a 500 W Xenon lamp. The concentration of the RhB solutions was determined indirectly by UV–vis spectroscopy. In a typical adsorption test, 50 mg of the samples were added into 100 mL RhB aqueous solution with an initial concentration of 10 mg·L⁻¹. In the photocatalytic activity test, about 5 mL of mixture was collected in every 20 min to measure the change of RhB concentration. Before the beginning of each cycle, fresh RhB solution would be used in order to keep the same initial concentration.

3. Results and Discussion

3.1. XRD & UV

![XRD and UV spectra](image)

Figure 1. XRD(left) and UV(right) diagram of MnTiO₃ and AgCl/Ag/MnTiO₃. The XRD patterns of AgCl/Ag/MnTiO₃ modified by different amount of AgCl/Ag are shown in Figure 1(left). It can be seen that pure MnTiO₃ and MnTiO₃ loaded with AgCl/Ag exhibit obvious diffraction peaks of the MnTiO₃ in the XRD diagram, where the diffraction peaks at 2θ=23.51°, 32.05°, 34.72°, 39.80°, 48.11°, 52.30°, 55.31°, 60.80°, 62.51° could be match with (012), (104), (110), (113), (024), (116), (018), (214), (300) crystal planes of the MnTiO₃. As the AgCl/Ag loading increases, the new diffraction peaks appear and the intensity of the diffraction peaks increases. The diffraction peaks at 2θ=29.39°, 33.01°, 57.01° are the characteristic peaks of AgCl, which correspond to (111), (200) and (222) crystal faces of the AgCl, and the diffraction peak at 2θ=36.34° corresponds to the (111) crystal plane of the cubic phase Ag. Due to the small amount of Ag, the corresponding diffraction peak in XRD is not obvious.

The photocatalytic performance of semiconductor materials depends largely on its light absorption capacity. In order to determine the photoelectric properties of pure MnTiO₃ and different proportions of AgCl/Ag/MnTiO₃, the UV diffuse reflectance spectroscopy is performed on different samples, and is shown in Figure 1(right). It can be clearly seen from the figure that with the amount of AgCl/Ag increases, the absorption of light by the heterojunction is red-shifted. The absorption edge of pure MnTiO₃ is located at around 380 nm, and the absorption edge of AgCl/Ag/MnTiO₃ heterojunction with the highest loading is located at 500 nm, which indicates that the AgCl/Ag/MnTiO₃ nano-heterostructure exhibits better visible light response than pure MnTiO₃, and is beneficial to improve photocatalytic degradation efficiency.
3.2. SEM

Figure 2. SEM image of MnTiO₃ and AgCl/Ag/MnTiO₃.

The morphology of MnTiO₃ and Ag/AgCl/MnTiO₃ nanoheterojunctions is shown in Figure 2. Figure 2a is SEM diagrams of MnTiO₃. As shown, we can intuitively see that the MnTiO₃ nanowires have a diameter of about 150 nm and the surface is not smooth. Figures 2b-2d are SEM diagrams of AgCl/Ag/MnTiO₃ nanoheterojunctions. It is obviously that many small particles with diameters of about 20 nm on the surface of MnTiO₃ are AgCl/Ag particles.

3.3. PL

Figure 3. PL diagram of MnTiO₃ and AgCl/Ag/MnTiO₃.

The PL measurement of photocatalysts is an effective means of evaluating the separation efficiency of photogenerated electron-hole pairs. Figure 3 shows a comparison of PL of pure MnTiO₃ and AgCl/Ag/MnTiO₃-X (X=1,2,3). It can be clearly seen that the peak of AgCl/Ag/MnTiO₃-X is lower than that of MnTiO₃, and the peak intensity of AgCl/Ag/MnTiO₃-2 is the lowest, which indicates that the AgCl/Ag/MnTiO₃-2 owns the highest photo-generated carrier separation efficiency and more efficient charge transfer.

3.4. Photocatalytic performance

Figure 4. Photocatalytic degradation of MnTiO₃ and different amounts of AgCl/Ag/MnTiO₃.
Figure 4 shows the photocatalytic degradation properties of AgCl/Ag/MnTiO₃ heterojunctions with different ratios and pure MnTiO₃. As seen, the pure MnTiO₃ (MTO) shows a weak degradation rate, and the degradation rate of AgCl/Ag/MnTiO₃ heterojunctions increase with the increasing loading ratios. The degradation rate of RhB by pure MnTiO₃ is 10% with in 2 h, while the degradation rate of AgCl/Ag/MnTiO₃-2 is 80%, which is 8 times that of pure MnTiO₃. The degradation rates of AgCl/Ag/MnTiO₃-1 and AgCl/Ag/MnTiO₃-3 in 2 h were 42.5% and 60%, respectively. It is worth noting that the degradation rate of RhB by AgCl/Ag/MnTiO₃-2 is higher than that of AgCl/Ag/MnTiO₃-3. Combined with PL analysis, AgCl/Ag/MnTiO₃-2 showed the lowest peak intensity of PL, indicating that electron-hole separation is more effective and more favorable for photocatalytic degradation. The results of photocatalytic degradation are consistent with the results of PL detection.

4. Conclusions
In this work, we prepared MnTiO₃ by electrospinning method, and then successfully prepared AgCl/Ag/MnTiO₃ photocatalytic heterojunction by photodeposition. Compared with pure MnTiO₃, photocatalytic degradation performance of AgCl/Ag/MnTiO₃ has been greatly improved. Such result is mainly ascribed to the formation of a good heterostructure between the AgCl/Ag and MnTiO₃, which makes it owns better visible light response capability, and more efficient photon transfer to achieve rapid separation of photogenerated electron-holes.

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