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Study on preparation and sunlight photocatalytic activity of porous coupled ZnO/TiO_2 photocatalyst

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Porous ZnO/TiO_2 photocatalyst was prepared from porous TiO_2 coupling with ZnO by marinating method. The photocatalytic activity was investigated by photocatalytic degradation of bromamine acid aqueous solution in the sun. The effects of ZnO adulterant proportion, the initial concentration of the bromamine acid aqueous solution and different light sources on the activity of the photocatalyst were discussed. The results suggest that in the sun, when the ZnO adulterant proportion was 1%, the activity of the porous ZnO/TiO_2 photocatalyst was satisfying and superior to that of the porous TiO_2. When the initial concentration of the bromamine acid aqueous solution was lower than 100mg/L, the result of photocatalytic degradation was better. The removal rate of chroma reached almost 100% and the removal rate of TOC over 75%. The photocatalyst had a better activity under the sunlight than the UV light.

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Keywords: Sunlight, Porous ZnO/TiO_2, Photocatalytic degradation, Photocatalytic activity

1. Introduction

The technology of semiconductor photo catalytic oxidation has many advantages, such as simple reactor, mild reaction condition, complete mineralization of organic pollutants leaving no secondary pollution, etc [1, 2]. Moreover, solar energy may be directly used in the technology for potocatalytic oxidation and reduction reaction catalyzed by modified photocatalysts, which make it a greater value for development. Among a lot of photocatalysts, TiO_2 is a research focus because of the merits of anti-chemistry, anti-glossy corrosion, steady character, innocuous, high catalytic activity and rapid reaction rate. But TiO_2 belongs to a wide band gap material, with the band gap of 3.2 eV. It can only absorb the ultraviolet part of the sun, with a lower solar energy utilization ratio. It generally requires the ultraviolet illuminant to stimulate TiO_2, which limits the practical application of photo catalyst [3]. Semiconductor coupling is an effective way to improve the photo catalytic efficiency. By coupling with semiconductors of different energy levels, the TiO_2 photo catalyst' s absorption spectra of sunlight in the visible range can be broadened, leading to the extension of the scope of photo catalyst application and sunlight utilization.

Some semiconductors such as CdS, CdSe, and HgS are usually used as the adulterant constituent to modify TiO_2 at present, but these materials easily produce secondary pollution. Porous coupled ZnO/TiO_2 photo catalyst which can be in response to visible light with a high photo catalytic activity was prepared by coupling porous TiO_2 with proper ZnO aiming at the problems above. And in the sun, the photodegration experiment of organic pollution solution was carried out with the porous ZnO/TiO_2 photo catalyst and the degradation result is satisfying.

2. Experimental details

2.1 Main reagents and instruments

Main reagents: Butyl titanate; Glacial acetic acid; Anhydrous ethanol, Tetraethyl orthosilicate, zinc nitrate, sodium hydroxide

Main instruments: Shimadzu V_{CPH}TOC Analyzer; 722 Grating spectrophotometer; BDX3300X-ray diffractometer

2.2 Experimental method

2.2.1 The preparation of porous oxide titanium

Tetraethyl orthosilicate, and anhydrous alcohol were dissolved in distilled water according to a certain proportion in a reaction vessel and refluxed for 2h to obtain SiO_2 sol. Butyl titanate, anhydrous alcohol, glacial acetic acid, and distilled water were mixed according to a certain proportion to form TiO_2 sol. Then SiO_2 and TiO_2 sol were mixed in the proportion of 1:5 and stirred for about 8h to form a mixed SiO_2-TiO_2 gel. and aged for more than 12h. Then the SiO_2-TiO_2 gel was dried in the oven at 110℃ for 12 hours followed by being calcined at 500℃ for 2h. After that, it was immersed in saturated

NaOH solution for certain time and washed by distilled water until the filtrate became neuter. The porous oxide titanium was prepared after being milled and sieved (300 meshes).

2.2.2 The preparation of porous coupled ZnO/TiO_2 photo catalyst by marinating

Porous oxide titanium was fully mixed with the zinc nitrate solution in a certain proportion to couple ZnO with porous TiO_2. After being dried, the coupled porous TiO_2 was calcined for 0.5 hours at 500℃ to prepare the porous ZnO / TiO_2

2.2.3 Evaluation of photo catalytic activity

In order to evaluate the photo catalytic activities, the porous coupled ZnO /TiO_2 photo catalyst was used to degrade the dye intermediate bromamine acid aqueous solution under the sunlight. The absorbance (A) and the content of total organic carbon (TOC) in the water sample were measured. The activities of the photo catalyst were evaluated by the removal rate of chroma and total organic carbon.

3. Results and discussion

3.1 Preparation and characterization of the photo catalyst

In the process of the photo catalyst preparation, some factors such as ZnO adulterant proportion, calcining temperature and time will affect the physical and degradation properties of the photo catalyst. This paper mainly discussed the effects of ZnO adulterant proportion on the photo catalytic activity compared with that of porous oxide titanium.

3.1.1 The effects of ZnO adulterant proportion on the activity of the photo catalyst

30 mg/L bromamine acid aqueous solutions were degraded by photo catalysts with different ZnO adulterant proportions to examine the effect of ZnO adulterant proportion on the activity of the photo catalyst (the dosage of the photo catalyst was 3g/L and the degradation time was 5h). The experiment results are shown in Fig. 1.

Fig. 1 showed that the removal rate of the bromamine acid aqueous solutions changed with the increase of the ZnO adulterant proportion. When the ZnO adulterant proportion reached to 1%, the degradation of the bromamine acid aqueous solution achieved the best. The removal rate of chroma and TOC of bromamine acid aqueous solution reached 99.28% and 93.32% respectively.

Interlaced band position exits between ZnO and TiO_2. When excitated by the sunlight, the electrons photogenerated by ZnO are easily transferred to the conduction band of TiO_2, and the holes promoted from the valence band of TiO_2 to that of ZnO. Thus the compound probability of the carries reduced and the activity of the photo catalyst was improved. But when the ZnO adulterant proportion was lower, the photogenerated electrons and holes cannot be separated effectively and the activity of the photo catalyst became lower. When the ZnO adulterant proportion was higher, the active centers of the photo catalyst surface decreased, thus the absorption ability of the sun reduced [4, 5]. Furthermore, the photo catalyst belongs to porous structure, and more adulterant ZnO would make redundant ZnO deposited on the holes. Thus the holes would be built up and the absorption of the sun was blocked, which reduced the activity of the photo catalyst.

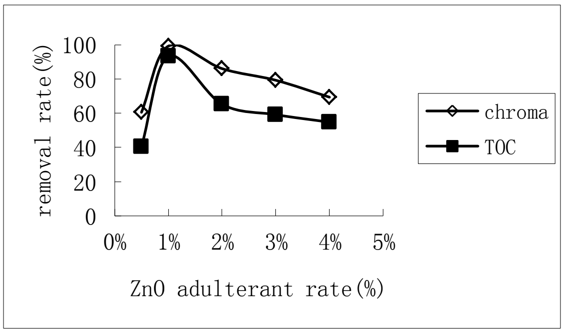

Fig. 1. The effects of ZnO adulterant proportion on the degradation activity of the photo catalyst.

3.1.2 The comparison between porous coupled ZnO /TiO_2 photo catalyst and the porous TiO_2

The bromamine acid aqueous solution were degraded by porous coupled ZnO /TiO_2 photo catalyst and the porous TiO_2 respectively, (the dosage was 3g/L). The experiment results are shown in Fig. 2.

Fig. 2 showed that the activity of the ZnO /TiO_2 photo catalyst was superior to that of the porous TiO_2. After the degradation for 3h, the removal rate of chroma of bromamine acid aqueous solution degraded by ZnO /TiO_2 photo catalyst could reach 100%, but only 77.14% by the porous TiO_2 photo catalyst. ZnO and TiO_2 have similar band gap (Eg=3.2 eV) and interlaced band position. The conduction band and valence band position of the ZnO are both slightly higher than those of TiO_2. The electrons of the conduction band of the TiO_2 could be captured by the electron traps such as molecule oxygen and the holes of the ZnO valence band could be captured by the hole traps such as OH^- [6,7]. Coupling TiO_2 with ZnO developed the light response range to some tune, and improved the utilization ratio of solar energy. There is 4% UV light in the sunlight and the excitation energy is enough to make band promotion of the TiO_2 and ZnO take place simultaneously [8]. Because of the differences in the energy level, photogenerated electrons assembled on the conduction band of the TiO_2, and the holes assembled on the valence band of ZnO. So the photon-generated carriers were separated and the quantum efficiency was improved, thus the photo catalytic efficiency was improved.

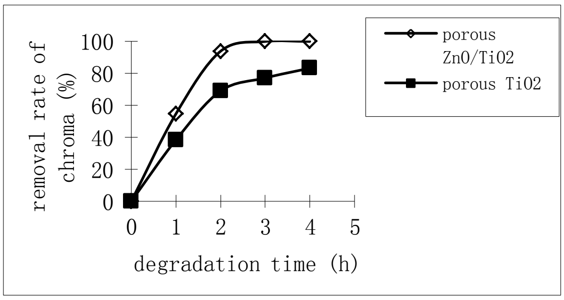

Fig. 2. Comparison of the degradation activity of porous coupled ZnO/TiO_2 with that of porous TiO_2.

3.1.3 The XRD characterization of the photo catalyst

Porous coupled ZnO /TiO_2 photo catalyst and pure TiO_2 A101 were characterized by XRD. The XRD patterns are shown in Fig. 3. Comparing the porous TiO_2 adulterated by ZnO with the pure TiO_2 A101, it can be seen that they have the entirely same positions of the characteristic peak 2θ angle, which indicates that when the photo catalyst was calcined, ZnO came into the inside of the TiO_2 crystal lattice, dedicating to the formation of the crystal. And compared with the diffraction peaks of the A101 TiO_2, the diffraction peak intensity of the porous ZnO /TiO_2 reduced significantly and the peaks widens and overlaps (which could explain that part Zn ions came into the gaps of the TiO_2 crystal lattice and disturbed the crystal process of TiO_2 when the TiO_2 was calcined at the high temperature, so that its crystallinity was not good enough and defects occurred [9].

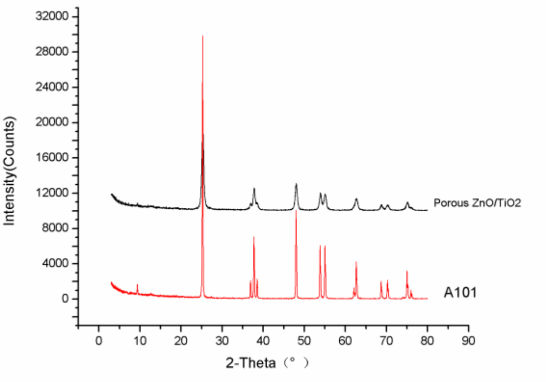

Fig. 3. XRD patterns of porous coupled ZnO/TiO_2 and porous /TiO_2 (red line).

3.2 Photocatalytic degradation capability of Porous coupled ZnO /TiO_2 photocatalyst on the organic contamination

Many factors could affect the degradation results of the bromamine acid aqueous solution, such as the adsorption quantum of the photocatalyst, light sources, the property of bromamine acid aqueous solution including the initial concentration, the chroma of the solution, pH, the content of the salt and so on. This paper mainly discussed the effects of the initial concentration of the bromamine acid aqueous solution and different light sources on the degradation.

3.2.1 The effects of the initial concentration of the bromamine acid aqueous solution on the degradation capability

The bromamine acid aqueous solutions with the initial concentrations of 10 mg/L, 30 mg/L, 50 mg/L, 80 mg/L, 100 mg/L and 150 mg/L were degraded by porous ZnO /TiO_2 photocatalyst under the sunlight respectively. The dosage of the photo catalyst was 2g/L and the degradation time was 5h. The experiment results are shown in Fig. 4 and Fig. 5.

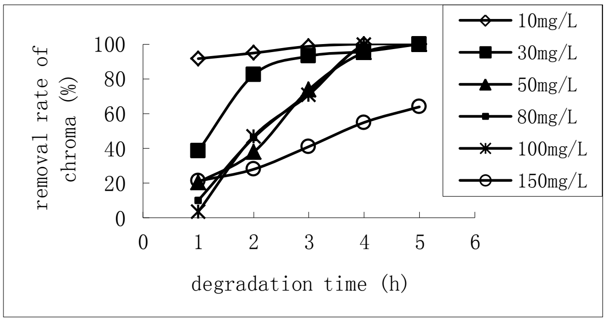

Fig. 4. The effects of the initial concentration of the bromamine acid aqueous on the removal rate of chroma.

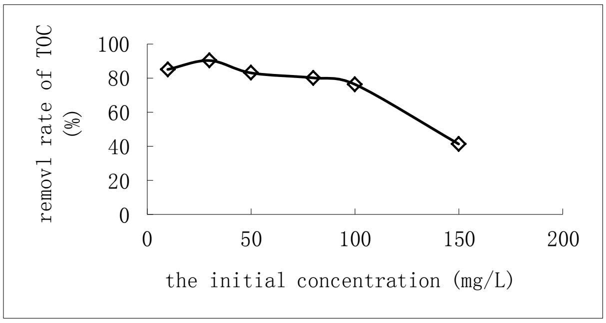

Fig. 5. The effects of the initial concentration of the bromamine acid aqueous on the removal rate of TOC.

It can be seen from Fig. 4 and Fig. 5 that the photo catalytic degradation efficiency decreased with the increase of the initial concentration of the bromamine acid aqueous solution. When the initial concentrations were lower than 100 mg/L, the removal rate of chroma reached 100%, and the removal rate of TOC was higher than 75%. While, 63.88% for the removal rate of chroma and 41.45% for the removal rate of TOC were obtained when the initial concentration reached150 mg/L. According to the photo catalytictheory, the key photo catalytic reaction occurred on the surface of the TiO_2. When the bromamine acid aqueous reached a certain concentration, the active sites on the surface of the photo catalyst were fully occupied and the increase of the concentration would not increase the contamination concentration which was adsorbed on the surface of the photo catalyst, so that the degradation rate decreased. Besides, owing to chroma of the dye itself，the light transmission in the waste water would be affected when the concentration was higher. The concentration of the dye degraded effectively is about 50 mg/L for general photo catalytic degradation reaction, while owing to the larger surface area of the porous coupled ZnO /TiO_2 photo catalyst, it can effectively degrade 100 mg/L bromamine acid aqueous solution, which enlarges the degradation concentration range of the photo-catalytic reaction to some extent.

3.2.2 The effect on the degradation of the bromamine acid aqueous solution under different light sources

30mg/L bromamine acid aqueous solutions were degraded under the sun and the UV light respectively with the dosage of 2g/L for the photo catalyst. The experiment results are shown in Fig. 6.

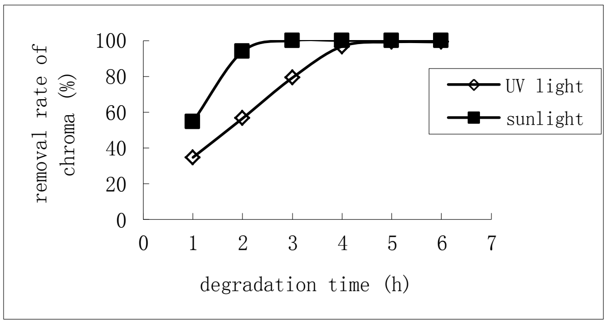

Fig. 6. Comparison of the degradation results of the bromamine acid aqueous solution under different light sources.

Fig. 6 showed that under the sunlight, the bromamine acid aqueous solution had a better degradation result than that under the UV light. When the degradation time was 3h, under the sun, the removal rate of chroma of the bromamine acid aqueous solution reached 100%, but only 79.18% under the UV light. When the time was 5h, under the UV light, the removal rate of chroma could also reached 100%. It indicates that better degradation results can be reached both under the sun and under the UV light, and it has a higher utilization rate of the solar energy under the sun with a better degradation result.

3. Conclusion

Porous ZnO/TiO_2 photo catalyst was prepared from Porous TiO_2 coupled with ZnO by marinating method and some factors acting on the degradation efficiency were discussed.

When the ZnO adulterant proportion reached 1%, the activity of the photo catalyst was superior to that of other photo catalyst mentioned above. The removal rate of chroma and TOC of bromamine acid aqueous solution reached 99.28% and 93.32% respectively. What’s more, the degradation results were also affected by the initial concentration of the bromamine acid aqueous. When the initial concentration was lower than 100mg/L, the removal rate of chroma could reach 100%, which enlarged the degradation concentration range of the photocatalytic reaction to some extent. And under the sunlight, the photo catalyst had a better activity than that under the UV light, improving the utilization ratio of the solar energy.

Acknowledgements

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