Fabrication of translated metal doped TiO2 composites and its photocatalytic degradation toward the ammonia nitrogen compounds in farm wastewater

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Abstract: TiO_2 and TiO_2 doping translated metal composites, including Cu, Co, Ni, Ag, Au elements, were prepared by sol-gel method by using tetrabutyl titanate and different metal salts as raw materials. The TiO_2 and its composites were characterized by means of UV-vis, FTIR, and fluorescence spectrometry, etc. Furtherly, photocatalytic degradation properties of TiO_2, Cu/TiO_2, Co/TiO_2, Ni/TiO_2, Ag/TiO_2 and Au/TiO_2 on ammonia-nitrogen compounds in farm wastewater were studied under simulated sunlight. The results showed that the translated metal doped TiO_2 composites had higher photocatalytic degradation rate than pure TiO_2, among which, the degradation rate of Ag/TiO_2, Au/TiO_2 and Ni/TiO_2 reached to 30.3%, 29.9%, and 26.9%, respectively, and those of Cu/TiO_2 and Co/TiO_2 were 25.0% and 26.3%, respectively. Photocatalytic degradation conditions of ammonia nitrogen compounds were investigated by using Ag/TiO_2 as photocatalyst. It was found that the degradation rate of ammonia nitrogen compounds could reach 37.5% when the initial concentration was 0.07 g/L, the time was 180 min, and the dosage of catalyst was 0.10%. Additionally, in comparison with natural sun light as the light source, the degradation efficiency of the catalyst was still reach 32.6%, which indicated the perfect application prospect in the treatment of farm wastewater.

Keywords: TiO_2; Farm wastewater; Photocatalytic; Ammonia nitrogen compounds

Photocatalytic degradation of organic pollutant based on semiconductors materials as photocatalyst is one of most active and promising research directions due to semiconductors such as TiO_2, ZnO, Ag_3PO_4 are low-cost, stable, nontoxic and environmental friendly[1-4]. Moreover, the operation condition of photocatalytic degradation to organic pollutant is high efficient and mild.

Titanium dioxide (TiO_2) possesses perfect photoelectric properties, high chemical stability, low cost and safety toward both humans and the environment, which is widely applied in many yields as catalyst, coating, plastic, and so on[1, 5-7]. Particularly, TiO_2 as photocatalyst can decompose the organic compound that, recently, becomes popular research directions. However,

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narrow light response range only to ultraviolet limits the utilization efficiency of actual sunlight. Further, the recombination rate of hole and electron induced electron-hole pairs of TiO_2 photocatalytic system that seriously affects the photocatalytic rate. In order to improve the photocatalytic activity as well as the response into visible-light region, TiO_2 doping with transition metals has been widely investigated [8-11]. Usually, the metal selective doping is one of the common approaches to enhance the phtocatalytic efficiency of the catalyst. A series of titania-metal composites (mainly including noble metals and noble/transition metal ions) have been used in order to increase the efficiency of the photocatalytic process[12-15].

Bear these perspectives in mind, the present work pays special attention to synthesize translated metal (Cu, Co, Ni, Ag, and Au) doped TiO_2 composites by hydrothermal method. Then the photocatalytic degradation properties of as-prepared translated metal doped TiO_2 composites on ammonia nitrogen compounds in farm wastewater are investigated in the simulated sunlight and actual sunlight.

1. Experimental

1.1 Chemicals

Tetrabutyl titanate was supplied by Tianchen chemicals, China; Copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), cobaltous nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), and silver nitrate ($AgNO_3$) were obtained from Tianjin Kaitong chemicals Co., Ltd, China; methyl orange was supplied by Sinopharm chemicals reagent Co., Ltd, China. Other reagents are of analytical grade.

1.2 Preparation of TiO_2 and translated metal doped TiO_2 composites

TiO_2 and translated metal doped TiO_2 composites were prepared readily by hydrothermal synthesis method [11]. Firstly, proper amount of tetrabutyl titanate (2 mL) was added into 20 mL absolute ethanol in a three-neck flask, and then stirred for 30 min under magnetic stirring. Subsequently, the above solution was transferred into hydrothermal reactor of 30 mL under 210 ºC for 24 h, then washed by distilled water and absolute ethanol for 3 times, respectively, followed to heat at 80 ºC for 24 h thereby affording TiO_2 nanoparticles. Translated metal doped TiO_2 composites were obtained by the same synthesis process, the atomic ratio of metal ions (Co^{2+}, Ni^{2+}, Ag^{+}, Au^{+}, and Cu^{2+}) doping TiO_2 was 2.0 at% and the samples were noted as Co/TiO_2, Ni/TiO_2, Ag/TiO_2, Au/TiO_2, Cu/TiO_2, respectively.

1.3 Characterization of TiO_2 and translated metal doped TiO_2 composites

UV-vis absorption spectrum of TiO_2 and translated metal doped TiO_2 composites were measured over a wavelength range of 200-800 nm with a Cary 100 spectrophotometer. Fluorescence spectrometry (F-2700, Hitachi Company, Japan) was utilized to evaluate the fluorescence properties of TiO_2 and translated metal doped TiO_2 composites at the range of the wavelength of 220-730 nm. The infrared spectrum of the samples of TiO_2 and translated metal doped TiO_2 composites were recorded inside KBr pellets on Fourier Transform Infrared Spectrometer (FTIR/Avatar360, Nicolet, American).

1.4 Testing of photocatalytic degradation properties of TiO_2 and translated metal doped TiO_2 composites toward ammonia nitrogen compounds

The photocatalytic degradation performance of TiO_2 and translated metal doped TiO_2 composites were measured by monitoring the decomposition of ammonia nitrogen compounds at simulated solar light or actual solar light. Typically, 0.05 g catalyst and 50 mL farm wastewater were added in a breaker of 100 mL, then the solution was magnetically stirred for 1 h to achieve adsorption saturation before illumination. Following this, the photocatalytic degradation reaction of ammonia nitrogen compounds was carried out via the exposure of simulated solar light or actual solar light, and the temperature of the reaction system was kept at room temperature by using a constant temperature circulating pump. After a half hour, 2 mL aqueous solution was taken out, centrifuged to test the content of the residual ammonia nitrogen compounds by using UV-vis adsorption spectrum at the main adsorption peak of 420 nm.

2. Results and discussion

2.1 The photo of standard curve of ammonia nitrogen compounds

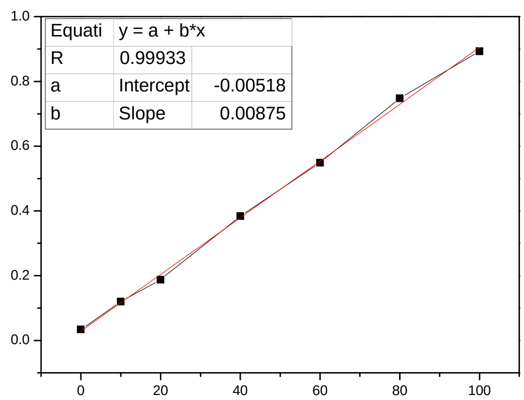

Fig.1 Standard curve of ammonia nitrogen compounds

The standard curve of ammonia nitrogen compounds was drew according the Chinese standards of water quality (Determination of ammonia nitrogen-Nessler's reagent spectrophotometry, No: HJ 535-2009)[16], as shown in Fig.1. As-obtained standard curves had perfect linear relationship coefficient (R) of 0.99933 that was consist with relative testing requirements, which could be used for evaluating the content of ammonia nitrogen compounds in farm wastewater.

2.2 Charaterization of TiO_2 and translation metal doped TiO_2 composites

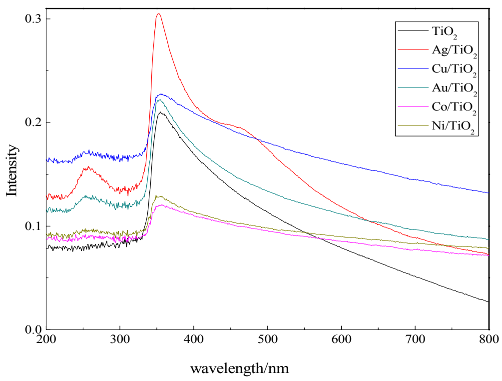

Fig.2 UV curves of TiO_2 and its composites

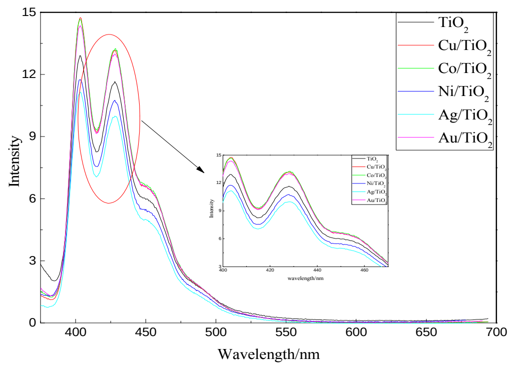

Fig.3 Fluorescence spectra of TiO_2 and its composites

UV curves of TiO_2 and its composites were shown in Fig.2. It can be seen that the adsorption peaks were emerged at 350 nm, however, that of TiO_2 obviously decreased with increasing wavelength. Particularly, the adsorption intensity of TiO_2 was lowest in all translated metal doped TiO_2 composites. The possible reason was owned to the lower electrode potential of translated metal and its ions that was apt to extend the light response range thereby improving the photocatalytic rate. Moreover, the adsorption peaks of Ag/TiO_2 composites appeared two peaks at 350 nm and 450 nm, respectively, that may be concluded from the perfect adsorption of light and led to high photocatalytic degradation rate toward organic pollutants[17].

Another important factor on photocatalytic degradation of organic pollutants is the recombination rate of holes and electrons of photocatalyst. The electron recombination rates of the photocatalysts were characterized by fluorescence spectrometry, the results of which are shown in Fig. 3. Among the emission intensities observed, that of Ag/TiO_2 was the lowest. This result revealed that Ag/TiO_2 had a low electron recombination rate, which enhanced its photocatalytic degradation abilities, which was agreement with experimental result[18].

Translated metal doped TiO_2 to form based TiO_2 composites affect the crystallization structure of TiO_2. Fig.4 indicated the FTIR spectra of TiO_2 and its composites, as seen from Fig.4

that those absorption peaks at 3400 cm^{-1} belonged to the adsorption peaks of hydroxyl groups (·OH) on the surface of TiO_2. Additionally, that at 2925 cm^{-1} and 2850 cm^{-1} represented methyl and methylene (·CH_3 and ·CH_2), and that at 1700 cm^{-1} was the adsorption peak of carbonyl groups (C=O), these peaks were own to residue of the organic chians of tetrabutyl titanate[12-14, 17]. However, the FTIR relative intensity of Ag/TiO_2 and Au/TiO_2 at the rang of 1000-400 nm were stronger than that of TiO_2, the main reason may be the strong adsorption properties of Ag and Au to light, which enhanced the intensity of response light of photocatalyst thereby improving photocatalytic degradation rate.

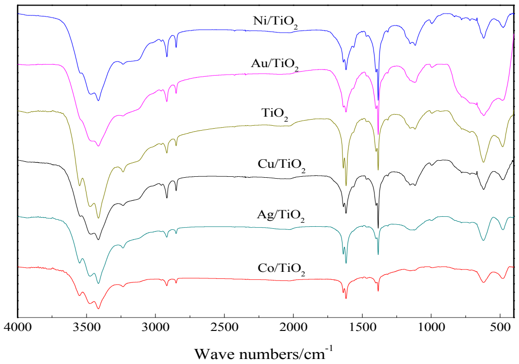

Fig.4 FTIR spectra of TiO_2 and its composites

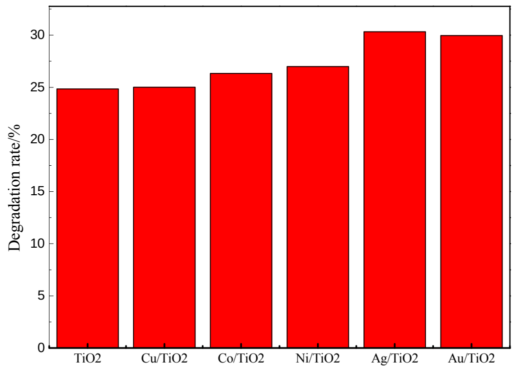

Fig. 5 Photocatalytic degradation rate of TiO_2 and its composites toward ammonia nitrogen compounds

2.3 The photocatalytic degradation properties of TiO_2 and its composites on ammonia nitrogen compounds

2.3.1 The effect of doped translated metal on the photocatalytic degradation properties of TiO_2

The photocatalytic degradation properties of TiO_2, Cu/TiO_2, Co/TiO_2, Ni/TiO_2, Ag/TiO_2, and Au/TiO_2 for ammonia nitrogen compounds were shown in Fig.5. It can be seen that TiO_2 doped translated metal displayed better photocatalytic degradation performance toward ammonia nitrogen compounds under simulated sunlight in 120 min, particularly, Ag/TiO_2 and Au/TiO_2 indicated higher degradation rate that improved 22.1% and 20.7%, respectively, in comparison with that of TiO_2. The main reason owned to the light enhancement effect of Ag and Au that was apt to increase the light response range of TiO_2, thereby improving the photocatalytic degradation rate to ammonia nitrogen compounds even to other organic pollutants[8-9]. Among these photocatalyst, Ag/TiO_2 possessed best photocatalytic degradation properties on ammonia nitrogen compounds, thus, we chose Ag/TiO_2 as photocatalyst to investigated the suitable conditions for photocatalytic degradation of organic pollutants.

2.3.2 The effect of the initial concentration of ammonia nitrogen compounds on degradation rates

The certain amount of farm wastewater with ammonia nitrogen content of 1.75 g/L was add to volumetric flask of 100 mL and then diluted to scale line by adding distilled water, thereby the farm wastewater with different concentration was gained. Furthermore, the photocatalytic degradation rates of the farm wastewater were conducted by using Ag/TiO_2 as photocatalyst under simulated sunlight in 180 min where the samples was tested per 30 min, the results were shown in Fig.6. The farm wastewater with the initial concentration of 0.07 g/L possessed highest degradation rate, which showed that the fit concentration of farm wastewater was 0.07 g/L.

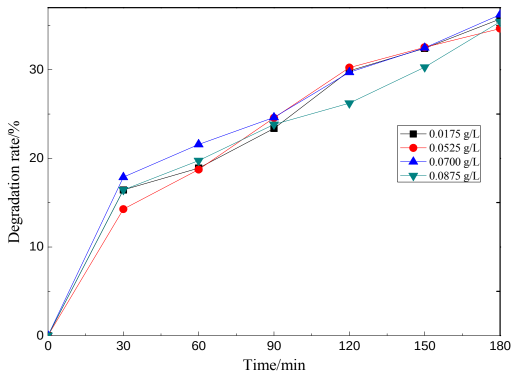

Fig. 6 The effects of the concentration of farm wastewater on the degradation rate

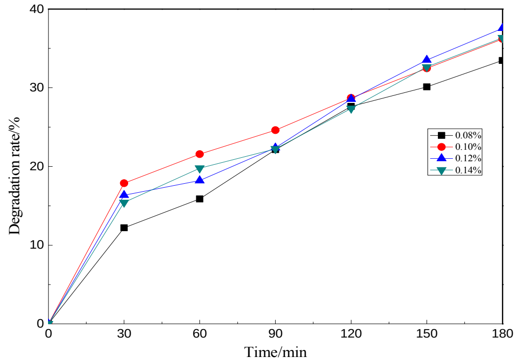

Fig.7 The effects of photocatalyst dosage on degradation rate

2.3.3 The effect of amount of catalyst on catalytic property

The influence of amount of photocatalyst on photocatalytic degradation performance of Ag/TiO_2 was also studied by degrading ammonia nitrogen compounds, as seen in Fig.7. With the increasement of photocatalytic time, the photocatalytic degradation rates gradually increased. The highest degradation rate reached to 37.5%, as compared with the result of the similar literatures, the catalyst has better catalytic activity.

2.3.4 The effect of irradiation conditions on the photocatalytic properties of photocatalyst

Furthermore, the irradiation conditions also affected the photocatalytic degradation properties of photocatalyst on ammonia nitrogen compounds[11-12], as seen in Fig.8. In comparison with the catalytic degradation rate under different illumination conditions by using Ag/TiO_2 as photocatalyst, the results showed that the degradation rate of ammonia nitrogen compounds was very low without illumination, which might be caused by adsorption. The degradation rate of ammonia nitrogen compounds under simulated sunlight was 37.5%, that under actual sunlight was 32.6% whereas under no light photocatalyst only indicated adsorption property thereby led to the lowest elimination rate of ammonia nitrogen compounds.

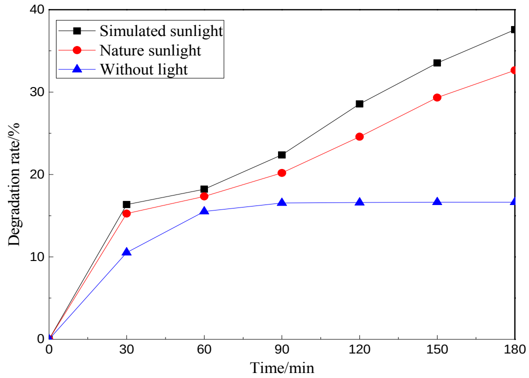

Fig. 11 Effect of different light on degradation rate of catalyst

3. Conclusion

TiO_2 and TiO_2 doping translated metal composites were prepared by hydrothermal method. The spectral properties of as-prepared TiO_2 and its composites were studied by means of UV-vis, FTIR, fluorescence spectrometry. The results showed that translated metal doped TiO_2 could improve the light response range and decrease the recombined rate of electron-hole, thereby raising the photocatalytic degradation rate of TiO_2 toward ammonia and nitrogen compounds in farm wastewater. The results, photocatalytic degradation properties of TiO_2, Cu/TiO_2, Co/TiO_2, Ni/TiO_2, Ag/TiO_2 and Au/TiO_2 on ammonia-nitrogen compounds in farm wastewater, also displayed that translated metal doped TiO_2 composites had higher photocatalytic degradation rate than pure TiO_2. additionally, in comparison with he effect of irradiation conditions on the photocatalytic properties of photocatalyst, it was found that as-fabricated photocatalyst also had perfect photocatalytic degradation performance to ammonia nitrogen compounds under natural light, and degradation rate reached to 32.6% in 180 min, these showed perfect application respect in actual treatment of farm wastewater.

Acknowledgments

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