



Preparation and Photocatalytic Performance Study of TiO₂ Coating on Cenospheres†

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TiO₂ coating on cenospheres was prepared by sol-gel method. The better preparation conditions of TiO₂ photocatalysts coating on cenospheres to get a high catalytic activity were investigated. Their phase, microstructure were characterized by using X-ray diffractometry and scanning electron microscopy. Photocatalytic properties were investigated by UV-visible photometer. The results show that TiO₂ coating on cenospheres with high catalytic activity is obtained with cenospheres pretreated by concentrated sulfuric acid and samples calcined at 600 °C for 3.5 h. Methylene blue was used as target contaminants and the maximum degradation rate reach 60.83 %. It may be the adsorption of methylene blue by cenospheres and the high specific surface area of TiO₂ lead to the high degradation rate.

Keywords: TiO₂, Cenosphere, Sol-gel method, Microstructure, Photocatalytic properties.

INTRODUCTION

Water pollution is a serious environmental problem nowadays. A lot of works have been done in photocatalytic technology. As one of the most advanced oxidation technology^{1,2}, photocatalytic technology is effective using photo-generated strong oxidants to turn the organic pollutants to H₂O and CO₂ and other small molecule. Mahyar *et al.*³ and Ying *et al.*⁴ prepared TiO₂ particles with sol-gel method and discuss the influence of solvent type, pH of sol and the calcination temperature on characteristics and photocatalytic activity of TiO₂ nanoparticles. In the field of waste water treatment, the reported carrier^{5,6} include activated carbon, zeolite, ceramics, glasses, aluminium plate, expanded perlite *etc.* Among them the activated carbon becomes the most commonly used carrier due to its large specific surface area and high absorption capacity. But the price of activated carbon is expensive relatively and this can increase the cost of waste water treatment. Cenospheres are hollow and lightweight spherical particles can float on water, its mainly chemical composition are Al₂O₃ and SiO₂⁷. Cenospheres draw attention for its excellent performance in many aspects. On the other hand, the pretreatment to the cenospheres have good effect to improve the adsorption of cenospheres⁸⁻¹⁰. In this paper, cenospheres obtained from the fly ash was used as the carrier, butyl titanate as the precursor and then successfully prepared catalysts of TiO₂ coating on cenospheres.

EXPERIMENTAL

Cenospheres was sieved out by using a griddle with 80 mesh in order to get smaller and uniform size distribution particles from those uneven size distribution cenospheres, then those chosen cenospheres were put into deionized water and stirred for 10 min, chose those cenospheres floating on water and drying. Put them into the 70 % concentrated sulfuric acid solution and stirred for 0.5 h and then insulated in water bath of 75 °C for 3.5 h. Rinsed with deionized water to neutral, then achieved the cenospheres with acid-treated.

10 mL butyl titanate and 25 mL ethanol were mixed in beaker and stirred for 0.5 h to get a uniform solution, put 5 g pre-prepared cenospheres into the solution and continued stirring for 1 h to get the mixture marked as A; 5 mL (or 4 mL) deionized water and 25 mL ethanol were mixed to get the solution marked as B. Solution B was slowly add dropwise to the mixture A. Some experiments need to added with the mixed solution 1 mL KH550 and 1 mL H₂O. Added a small amount of nitric acid to control the pH at 3.0-3.5, continued stirring for 1.5 h. Then, left for 12 h at room temperature and finally calcined in a muffle furnace for 3.5 h at appropriate temperature after drying. Finally the photocatalyst of TiO₂ coating on cenospheres was achieved. All reagent used are grade AR and bought from China National Pharmaceutical Group Corporation.

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Prepare 20 mg/L methylene blue solution in beaker as target contaminants in the photocatalytic degradation experiment, stirred the solution for 0.5 h, took appropriate amount solution as the sample for absorbance test. Then added 0.15 g photocatalyst prepared to the solution and at the same time opened the UV light. Took sample per 1 h. The samples were centrifuged at the speed 6000 rpm to precipitate the catalyst. Then use UV-visible photometer to measure the absorbance A at the maximum absorption wavelength for methylene blue solution in 665 nm. Calculated degradation rate through the following formula:

$$D (\%) = \frac{(A_0 - A_t)}{A_0} \times 100 \%$$

where D is the degradation rate (%), A_0 is the absorbance before the photocatalyst added in, A_t is the absorbance when experiment ended.

The phase of samples was identified by X-ray diffraction analyzer using $\text{CuK}\alpha$ radiation (XRD-6000, Shimadzu). The morphology of cenospheres and the photocatalyst were observed by scanning electron microscope (SEM, Hitachi S-4800, Japan). High pressure mercury lamp used in the photocatalytic test is 175 W, dominant wavelength 365 nm. Ultraviolet-visible spectrophotometer is type 752 made by spectrum Shanghai.

RESULTS AND DISCUSSION

Phase of TiO_2 coating on cenospheres: Fig. 1 shows XRD patterns of the cenospheres and samples obtained in different conditions. It is found in (a) and (b) that the major phase of cenospheres are Al_2O_3 , SiO_2 and mullite. Diffraction peaks referred to Fe_2O_3 and MgO are not observed in (b) as it was pretreated by concentrated sulfuric acid, which indicates that cenospheres with less impurities by acid treating is achieved. There are also some miscellaneous peaks in the XRD patterns in (a), (b), it is because the cenospheres is a product of fly ash.

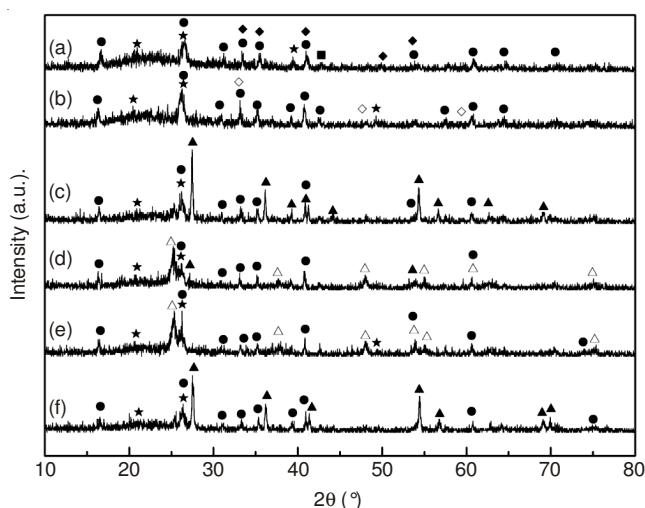


Fig. 1. XRD patterns of cenospheres (where \star - SiO_2 , \bullet - $\text{Al}_6\text{Si}_2\text{O}_{13}$, \blacklozenge - Fe_2O_3 , \blacksquare - MgO , \odot - $\text{Ca}_3(\text{AlO}_3)_2$, \blacktriangle - TiO_2 (Rutile), \blacktriangledown - TiO_2 (Anatase). a-cenospheres without acid treatment; b-cenospheres with acid treatment; c-condition of 650 °C calcined, cenospheres without acid treatment and without KH550 added; d-condition of 650 °C Calcined, cenospheres acid treated and KH550 added; e-condition of 550 °C calcined, cenospheres without acid treatment and KH550 added; f condition of 550 °C calcined, cenospheres acid treated and without KH550 added)

It is found in (c) that the major phase of sample calcined at 650 °C is rutile, which indicates that the phase transition has been completed. It can be seen in (d) that the major diffraction peaks are identified to be anatase and a small amount of rutile as it was added with KH550. Maybe the KH550 added can inhibit the crystal transition in high temperature. On the other hand the sample in (d) showed has a higher degradation rate than that sample showed in (c), which means that the mixture of anatase and rutile have the highest photocatalytic effect¹¹ was indicated.

It can be seen in (e) that the TiO_2 is anatase and that in (f) is rutile. Although the catalytic effect of anatase is better than that of rutile, the catalytic effect of sample with cenospheres acid pretreated is better. Even so, this sample has low photocatalytic efficiency due to the rutile crystal.

Microstructure of TiO_2 coating on cenospheres: Fig. 2 shows SEM images of samples prepared in different conditions. Firstly, the surface of cenospheres without acid treatment is smooth relatively and there are few small holes (Fig. 2(a)), but with the treatment of concentrated sulfuric acid, the number of holes on surface increase obviously, also the holes become larger in Fig. 2(b) and these pretreated cenospheres have high adsorption of methylene blue. So the concentrated sulfuric acid has a significant treatment effect to cenospheres is indicated.

Fig. 2(c,d) show typical images of a thin, transparent and white TiO_2 parcel layer coating on the surface of the cenospheres. The parcel layer has crack and the edge of parcel layer turn up, there are TiO_2 particle agglomeration in some areas. There are not only TiO_2 parcel layer coating on the surface of the cenospheres but also TiO_2 particles filling in the holes on surface of those cenospheres in Fig. 2(e,f). The TiO_2 parcel layer is maldistribution. So the specific surface area of TiO_2 decrease and this lead to the lower photocatalytic efficiency. The large specific surface area lead to the increasing of reaction area and it is also conducive to the adsorption of target contaminants¹² is indicated; one can see that the TiO_2 parcel layer on surface has a more closely integrate with cenospheres in Fig. 2(g,h) than that showed in Fig. 2(c,d), because the coating is more evenly and the edge of parcel layer is not turn up. There are also some TiO_2 particles loaded on the surface of TiO_2 parcel layer. Thus, TiO_2 coating on cenospheres with high photocatalytic efficiency can be obtained.

Photocatalytic test results analyses: the absorbances of methylene blue solution tested by ultraviolet-visible spectrophotometer in the wavelength 665 nm are showed in Fig. 3.

Fig. 3 shows that the methylene blue is gradually degraded. The calculated photodegradation rates are 14.93, 3.44, 6.82, 2.85, 11.04, 12.77, 15.85 and 3.40 %, respectively.

In the investigated three factors, calcination temperature has the maximum impact to the experiment according to the results of intuitive analysis of orthogonal experiment. Cenospheres with acid-treated or not also has a high effect to the experimental result but it is less than that of calcination temperature; otherwise KH550 added or not has a little effect. This experiment shows that the better condition to get the high photocatalytic activity are calcination temperature of 600 °C and cenosphere with acid treated.

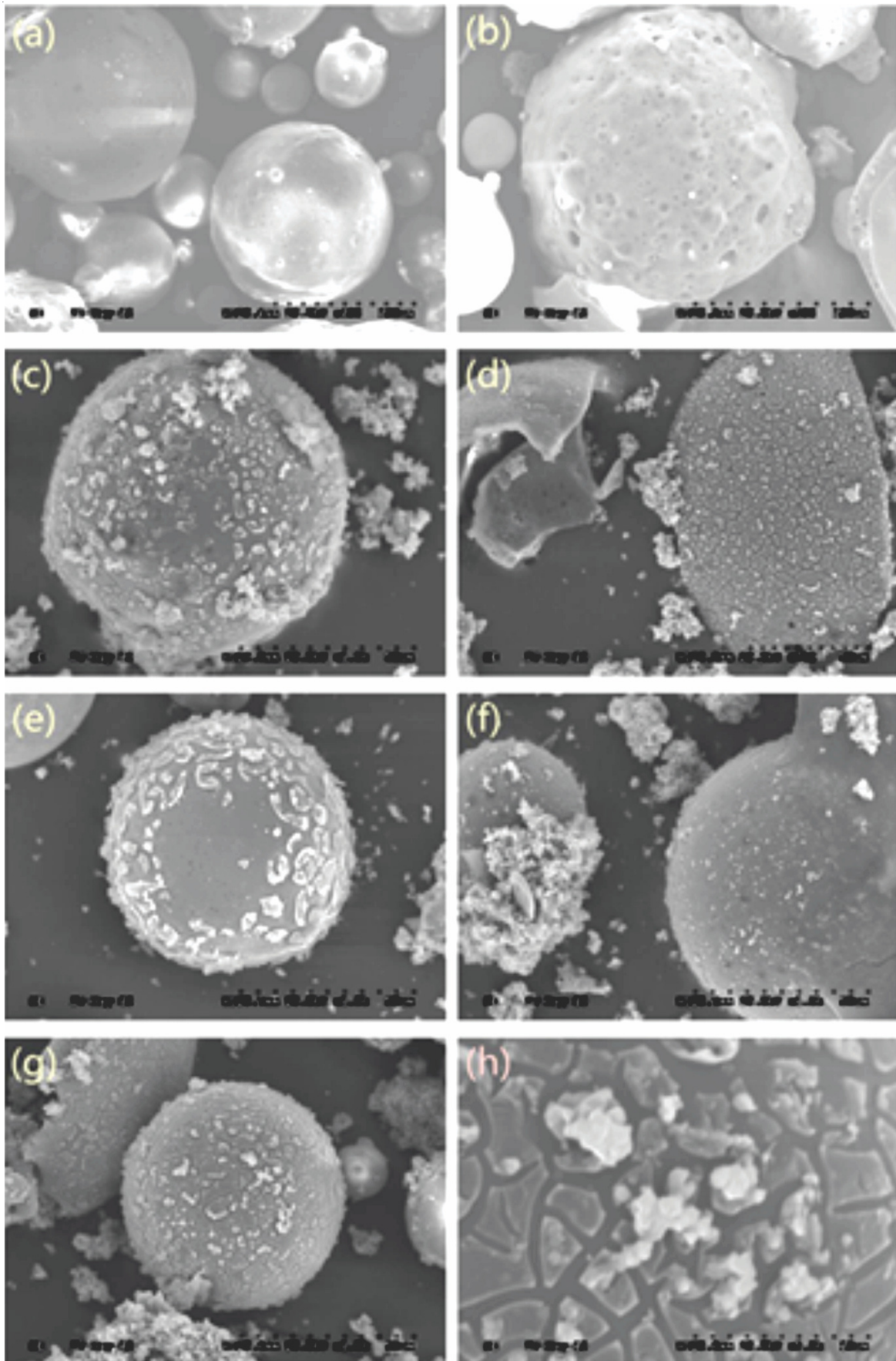


Fig. 2. SEM images of the cenospheres and TiO₂ coating on cenospheres (a-cenospheres without acid treatment; b-cenospheres with acid treated; c, d-450°C calcined, with acid treated, without KH550 added; e,f-600°C calcined, without acid and KH550 added; g,h-650°C calcined, with acid and KH550 added)

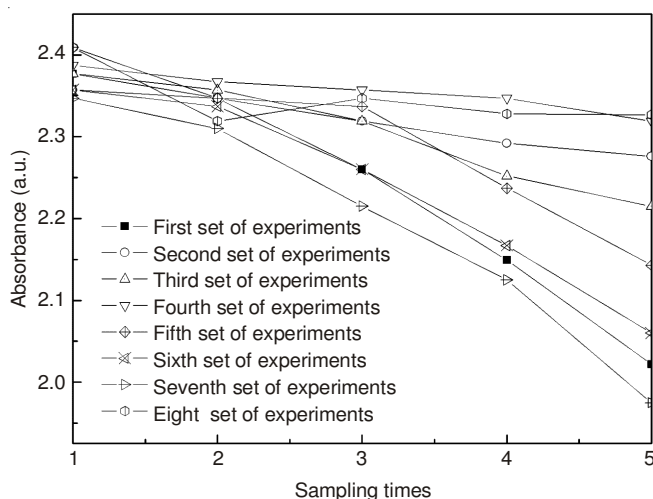


Fig. 3. Absorbance curve of different sets of experiment

With the better condition above, another three group of experiments were added. One of them change the order of KH550 added. That was adding the KH550 to the mixture A, not after B added into A. The absorbance of methylene blue solution tested showed in Fig. 4.

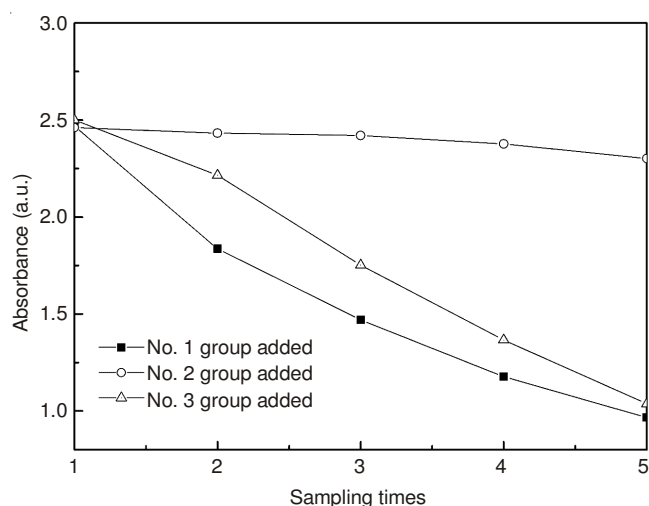


Fig. 4. Absorbance curve of different group of experiment added (No. 1-KH550 added after solution B added into mixture A, but the acid is dilute nitric acid of 1.5 mol/L; No. 2-KH550 added to mixture A; No. 3-KH550 added after B added into A)

The degradation rates calculated from above are: 60.83, 7.25 and 58.52 %. The degradation rate of the first group is the biggest, maybe it is because of the increasing water brought in by dilute nitric acid, so the proportion of water and butyl titanate is so important to the result. But the result of the first group is not very higher than that of the third group, indicates

that the proportion of water and butyl titanate (1:2) used before is appropriate. However the result of the second group is much lower so that the order KH550 added has no effect in improving the degradation rate and even decreases the rate is indicated.

Conclusion

This experiment successfully coat the TiO₂ parcel layer onto the surface of cenospheres and achieve samples with good photocatalytic efficiency by improve the preparation conditions using sol-gel method. The calcination temperature and the pre-treatment to cenospheres play very important role to get a photocatalyst with high photocatalytic efficiency. They are also the key conditions in the process of preparation the sample. The calcination temperature mainly affects the crystalline phase transition of TiO₂ and the transition is restrained by other additive such as KH550. The proportion of water and butyl titanate is another important condition in this experiment, the proportion 1:2 used is indicated to be appropriate. The better condition of this preparation are: pH 3.0-3.5; with calcination temperature of 600 °C; proportion of water and butyl titanate is 1:2 and cenospheres be pretreated.

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