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# Study on Preparation and Photocatalytic Activity of Nano-$TiO_2$/Precipitated Silica Composite Material

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**Abstract.** Using precipitated silica as the carrier, a kind of composite photocatalyst was prepared through hydrolysisde positing method. The obtained composite material was characterized by XRD, SEM, TEM, FT-IR. Based on the experimental results and analysis of characterization, the preparation mechanism of composite powder material was studied. The photocatalytic degration experiment of Rhodamine-B indicates that the precipitated silica is an ideal carrier of the $TiO_2$,and the photocatalyst can combine with the silica tightly. The photocatalytic activity of the obtained composite material is stabilize and constant.

## Introduction

The photocatalysis technology began to be applied in environmental protection from 1976[1,2].The research on the photocatalytic degradation of organic contaminants was very active in recent ten years. Photocatalytic performance is one of the unique properties of semiconductor materials. As a semiconductor material, nano-$TiO_2$ has a good photocatalytic activity. However, the photocatalytic material $TiO_2$ prepared by chemical methods is usually ultra fine powder. As a result, the problems of poor dispersion, difficult recovery, poor absorption will become very serious if it was used directly. In order to solve these problems, glass, stainless steel, silicon, organic and some non-metallic minerals [4,5,6,7,8,9,10,11] were used as nano-$TiO_2$ carrier in order to achieve practical purposes[12,13]. Using the raw material precipitated silica as carrier, a kind of composite photocatalyst of nano-$TiO_2$ was prepared by means of hydrolysis–depositing method.

## Experiments

**Materials used.** The precipitated silica used as the carrier material was obtained from Guangzhou, China. Precipitated silica is a kind of amorphous silica and its formula is $SiO_2 \cdot nH_2O$. The precipitated silica has many good characters to be the carrier material as follows: porosity, good chemical stability, high temperature resistance, high insulating and so on. The relative density of the carrier material is about 2.45g/cm$^3$. The size of the particles ranges from 10nm to 1000nm.

**Methods.** The specific preparing process of the composites is shown in Fig.2-1. First, the precipitated silica as the carrier material and a certain percentage of water were put into the flake to prepare the original pulp, which was under the condition of ice water bath in order to get a low temperature. Then a certain amount of concentrated hydrochloric acid was put into the pulp after the feed had been well stirred. Second, a certain amount of $TiCl_4$ solution was dropped into the pulp by Constant Flow Pump (CFP) with a set dropping velocity. Then a certain amount of ammonium sulphate solution was been dropped into the pulp after a certain time. 10 minutes of stirring was set to ensure the uniformity of the pulp. Third, the temperature of the bath water was heated up to a certain degree. Additionally, sufficient $NH_3 \bullet H_2O$ with a specific concentration was dropped into the pulp by CFP until the pH of the pulp reached to a certain degree. Then maintain the condition and react for a certain period of time. The product was been filtered and washed to remove $Cl^-$ and some other ions. Finally, the composites were dried under 105℃ for 1 h and calcined under the stationary temperature. Thus the product was prepared.

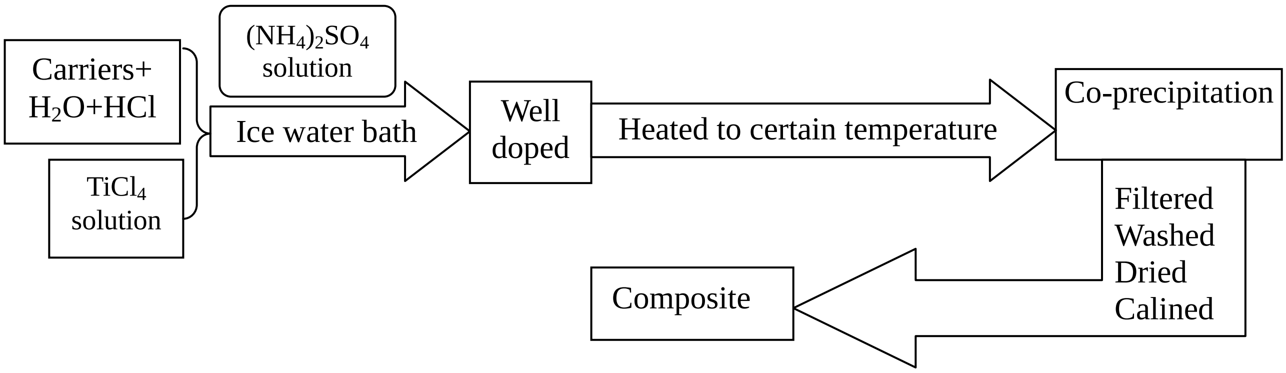



Fig. 1 The flow sheet of preparing nano-$TiO_2$/ mineral composite

The photocatalytic activity of the composite material was evaluated by using Rhodamine-B and ultraviolt light as pollutant and irradiation source, respectively. The photocatalytic discoloration of Rhodamine-B was conducted in a 1000mL glass reactor at room temperature. The 100-400W 2.5-4KV lamp was located at about 15 cm above the solution. The concentration of Rhodamine-B was maintained at 10mg/L. 100mL of the Rhodamine-B solution and 0.1g of the photocatalyst were placed in the reactor before irradiation. At regular time intervals of irradiation, the discoloration ratio, i.e. the removal degree of color at the $L_{max}$ of the Rhodamine-B solution (562 nm)was calculated using $D_R$ (%) = $(C_0 - C_t)/C_0 \times 100$, where $C_0$ is the initial concentration of the Rhodamine-B waste water and $C_t$ the concentration at irradiation time t. In order to evaluate the adsorption of Rhodamine-B on the photocatalysts, experiments were run under the same condition without UV irradiation which was used as blank tests. The measurement of Rhodamine-B concentrations and calculation of Rhodamine-B adsorption ratios were conducted using the mentioned method.

The crystal structures of the samples were determined by XRD (X'Pert PRO MPD, Panalytical, Netherlands) using copper radiation (Cu Kα) at 40KV, 30mA over the 2θ range 10°-70°. The infrared spectrometer is from the United States Bruker. The resolution in the test is $4cm^{-1}$, and the scan number is 16. The tabletting is KBr. The profiles of the samples were observed by SEM which is from the English Cambridge company. The secondary electron resolution is 1.0nm (20kV) and 5.0nm(10kV),and the magnification times is 10-450000.The morphology and structure are obtained from TEM (JEM-2100, NEC).

## Results and Discussion

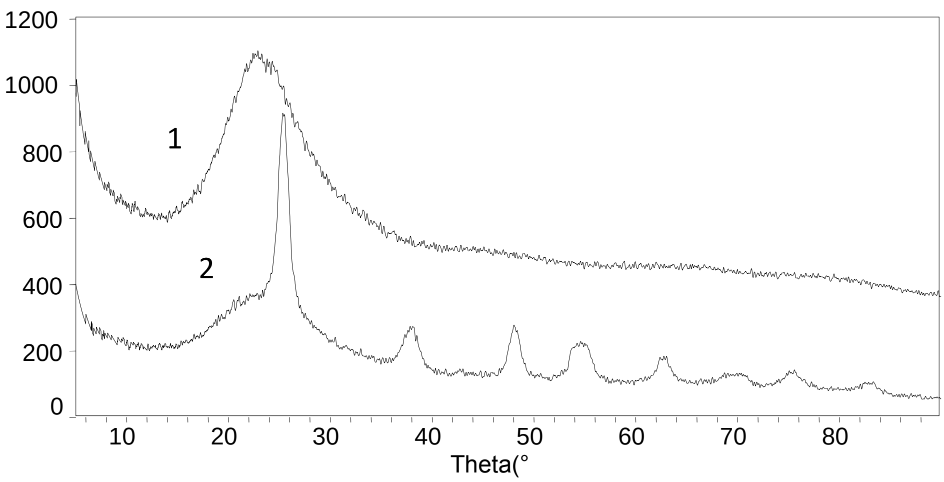



Fig. 2 X-Ray diffraction spectrogram of precipitated silica and nano-$TiO_2$/precipitated silica composite material

**X-Ray Diffraction.** Figure 2 shows X-Ray diffraction patterns of precipitated silica and nano-$TiO_2$/porous silica composite material. Curve 1 is the spectrogram of precipitated silica and curve 2 is the spectrogram of nano-$TiO_2$/ precipitated silica composite material. No peak of $TiO_2$ can be found in curve 1, so there is no $TiO_2$ existed in the carrier material. Five distinctive $TiO_2$ peaks can be found at 2θ of 25.28, 7.93, 48.38,53.89, 55.29 in curve 2. Corresponding to the crystal planes of (101), (004), (200), (105), (211) of the anatase phase of $TiO_2$ (JCPDS 78-2486), respectively. This result indicates that $TiO_2$ exists in the form of anatase phase. As expected, no rutile phase can be found in the samples, which is beneficial to photocatalytic activity of the composite catalysts.

**Infrared Spectroscopy.** Figure 3 is infrared spectrogram of precipitated silica and nano-$TiO_2$/precipitated silica composite material. From curve 1 of the figure, the bands at 1635.3cm$^{-1}$and 3438.5cm$^{-1}$corresponds with vibrations of $^-$OH and H-O-H which means that there are a lot of hydroxide radicals and absorbed water on the surface of the precipitated silica and the composite material, respectively; The absorption peaks at 542.9cm$^{-1}$, 816.3cm$^{-1}$, 1105.0cm$^{-1}$ are caused by stretching vibrations of Si-O-Si. The peaks mentioned above do not change greatly in curve 2. However, because $TiO_2$ is coated on the surface of the precipitated silica particle, the absorption peak of Si-O-Si becomes weaker. From the comparison of curve 1 and 2, it can be clearly seen that there are tiny vibrations at 500-700cm$^{-1}$ in curve 2. The absorption peaks at 473-659cm$^{-1}$are the characteristic absorption peaks of $TiO_2$ which is caused by the vibrations of [$TiO_6$]. The weak peak at 966.2cm$^{-1}$ is attributed to Ti-O-Si. The fact indicates that there are new bonds formed among Ti, O and Si in the nano-$TiO_2$/ precipitated silica composite material.

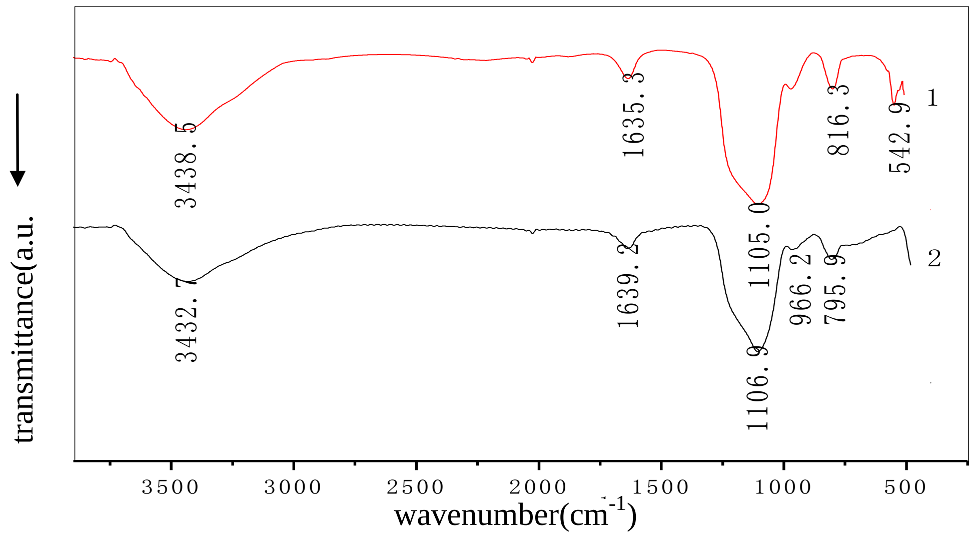
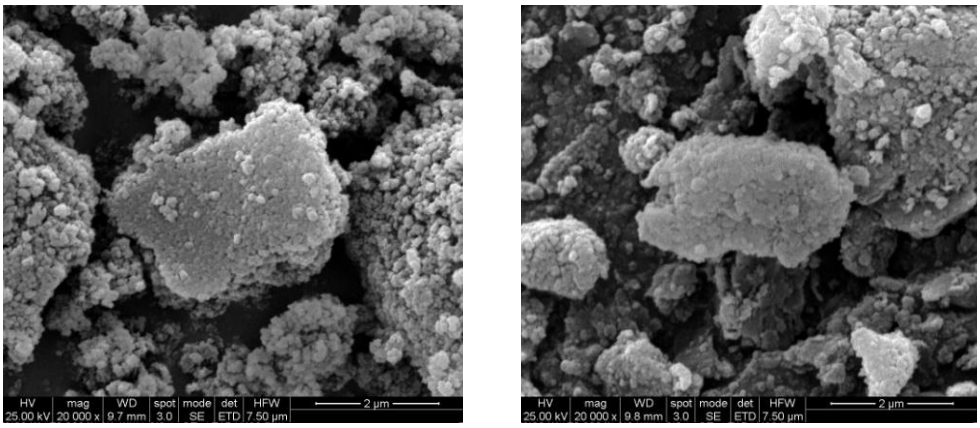


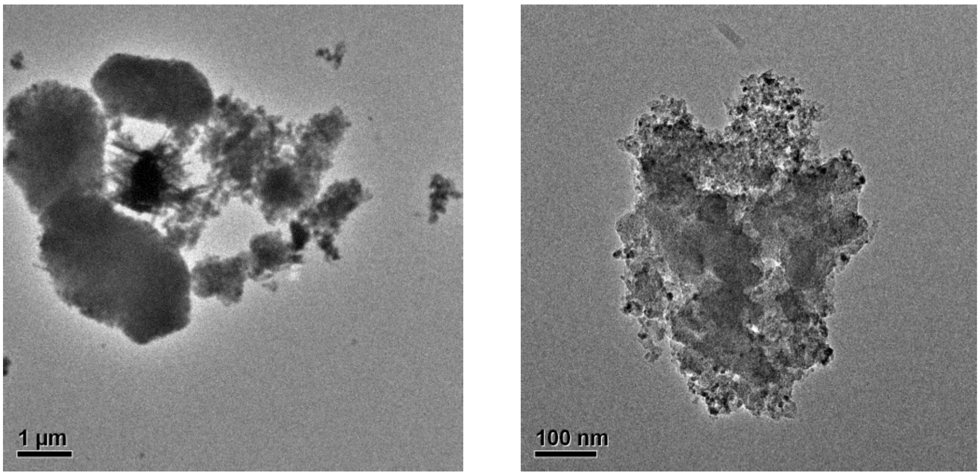

Fig. 3 Infrared spectrogram of precipitated silica and nano-$TiO_2$/precipitated silica composite material

**Sample morphology (SEM and TEM).** Figure 4 is SEM photographs of the precipitated silica and the nano-$TiO_2$/precipitated silica composite material. Figure 3-3(a) shows that large numbers of cracks are formed for the accumulation of the precipitated silica particles. Figure 3-3(b) shows that the $TiO_2$ particles' diameters are 50nm which were loaded uniformly on the surface and recesses of precipitated silica. This microstructure is very important to improve the active sites of photo-catalytic reaction and photo-catalytic efficiency. Figure 3-3 is TEM photographs of the precipitated silica and the nano-$TiO_2$/precipitated silica composite material. Comparing the two images, every black core is surrounded by a thin film in the figure 3-4(b). Figure 3-5 and table 3-1 are the EDX spectrum information, which show that there is no element Ti in the carrier material, but the weight percentage of element Ti is relevant high in composite material, which also consist of high weight percentage of element Si and element O. So it can be inferred that the thin films is $TiO_2$ layers and $TiO_2$ loaded on the surface of the precipitated silica. Also, from the image figure 3-4(b), there is a certain amount of element Si in the $TiO_2$ layer, indicating that maybe the load is not a pure physical process but $TiO_2$ particles which enter into a certain depth below the surface of the carrier material are bonded with $SiO_2$ and maybe the bond Ti-O-Si is formed.



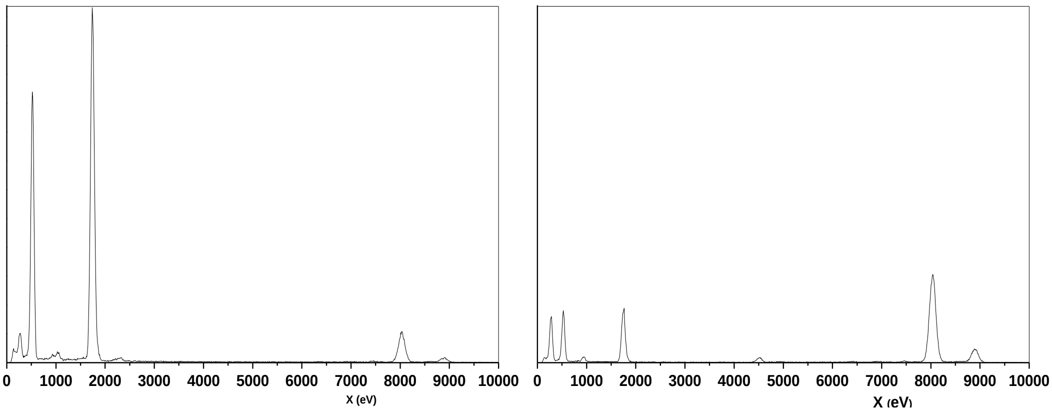

(a) (b)

Fig. 4 SEM photographs of the porous silica and the nano-$TiO_2$/ precipitated silica composite material.




(a) (b)

Fig. 5 TEM photographs of the precipitated silica and the nano-$TiO_2$/precipitated silica composite material




(a) (b)

Fig.6 EDX spectrum of the precipitated silica and the nano-$TiO_2$/precipitated silica composite material

Table 1 EDX spectrum data of the precipitated silica and the nano-$TiO_2$/precipitated silica composite materia

(a)

| Element | Weight(%) | Atomic(%) |
|---|---|---|
| C(K) | 7.9 | 13.33 |
| O(K) | 43.89 | 55.61 |
| Na(K) | 0.71 | 0.62 |
| Si(K) | 37.73 | 27.23 |
| S(K) | 0.21 | 0.13 |
| Cu(K) | 9.54 | 3.04 |

(b)

| Element | Weight(%) | Atomic(%) |
|---|---|---|
| C(K) | 24.31 | 49.86 |
| O(K) | 13.84 | 21.31 |
| Si(K) | 9.5 | 8.34 |
| Ti(K) | 1.38 | 0.71 |
| Fe(K) | 0.22 | 0.09 |
| Cu(K) | 50.71 | 19.65 |

## Conclusion

According to a series of orthogonal and single factor experimental results，the optimal experimental conditions were selected and the decolorization of Rhodamine-B of composite material under the optimum conditions was over 95%.It reached the experimental purposes.

Using spectrum silica as the carrier and $TiCl_4$ as the precursor, $TiO_2$ particles were uniformly loaded on the surface of the spectrum silica through hydrolysis-precipitation method. After calcination, nano-anatase $TiO_2$, the diameter of which was about 15nm, was obtained. The infrared spectrogram results showed that the nano-$TiO_2$ particles were loaded on the surface of the carrier material chemically, because there were new chemical bonds Ti-O-Si formed. The SEM and TEM images showed that the carrier particles were loaded with the nano-$TiO_2$, and the uniformity of loading was good. It has a good bleaching effect to the pollutant Rhodamine-B in the water, overcoming the application problems using the nano-$TiO_2$ directly in the sewage plant.

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