Preparation, Characterization and Photocatalytic Activity of Ag/TiO$_2$ Nanoparticle Semiconductor Catalysts

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Abstract. A series of Ag-doped TiO$_2$ powder photocatalysts were prepared by the sol-gel method. The phase structure and morphology of the samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The persistent organic pollutant sodium pentachlorophenol ate (PCP-Na) was selected as the target pollutant, and the photocatalytic property of the material Ag/TiO$_2$ was evaluated by PCP-Na degradation rate. It was found that the calcination at 450 °C was conducive to form the anatase structure with high catalytic activity, and the catalytic activity was higher when the silver mole fraction of Ag/TiO$_2$ was 0.50%. The influence of Ag/TiO$_2$ dosage, hydrogen peroxide volume, silver mole fraction and PCP-Na initial concentration was investigated by the single factor experiment.

1. Introduction

At present, the semiconductor photocatalyst is the most widely used in photocatalyst. Among the semiconductor photocatalyst, the TiO$_2$ semiconductor shows the characteristics of stable performance, non-toxic, high activity, low cost, and strongly absorbing proton or electronic ability, and has the leading position in the semiconductor catalyst. [1] However, TiO$_2$ still has some limits in the practical application. The band gap of TiO$_2$ is 3.2 eV, which can only be excited by a shorter wavelength of ultraviolet light ($\lambda$ <387 nm), which takes less than 10% of the ground solar spectrum, therefore the utilization of solar radiation is low. [2] Moreover, the photo-generated electrons and holes are easily recombined, resulting in a lower quantum efficiency of the absorbed light. In order to overcome the defects, lots of methods have been made on the modification of TiO$_2$. [3-6] The method of modifying TiO$_2$ mainly includes doping with non-metallic elements, doping with transition metal elements, doping with rare earth metal elements, depositing precious metals, compositing semiconductor materials, organic dye photosensitization and so on. The purpose of modification includes broadening the wavelength range of light response, facilitating the effective separation of photo-generated charge and suppressing carrier recombination to improve the efficiency of light quantum and the stability of TiO$_2$.

In this paper, a series of Ag-doped TiO$_2$ powder photocatalysts were prepared with tetrabutyl titanate and silver nitrate as raw materials by the sol-gel method. It is hoped to broaden the wavelength range of the response of TiO$_2$ to the excitation light and improve the quantum efficiency of the absorbed light. PCP-Na was used as a target pollutant, the photocatalytic degradation of PCP-Na was investigated with
Ag/TiO₂ powder, and the photocatalytic property of Ag/TiO₂ was evaluated by PCP-Na degradation rate, which provided the theoretical and experimental basis for the TiO₂ photocatalytic degradation phenol wastewater.

2. Experiment part

2.1. Reagents and instruments
Tetrabutyl titanate; glacial acetic acid; silver nitrate; anhydrous ethanol; hydrogen peroxide; PCP-Na. They are all analytical pure, all of the test water is distilled water.

X-15A self-coloring UV lamp (US Specronics (sp.), D8 ADVANCE X-ray diffractometer (Brooks AXS Co., Ltd.), Quanta 600 FEG field emission scanning electron microscope (USA FEI), WFZ-26A UV-Vis spectrophotometer (Tianjin Optical Instrument Factory) and so on.

2.2. Preparation of Ag/TiO₂ catalyst
Under the vigorous stirring, 2 mL of tetrabutyl titanate was added to 10 mL of absolute ethanol and named as solution A; 20 mL of absolute ethanol, 1.3 mL of distilled water and 5 mL of glacial acetic acid were mixed and stirred to obtain solution B. After vigorous stirring, solution A was added to solution B (modified with a certain concentration of silver nitrate solution instead of distilled water), stirring was continued for 1 h, then placed in air and aged to obtain a pale yellow solid gel; The solid gel was dried in air for 72 h, then put in the thermostat at 90 °C and dried for 12 h to obtain solid dry gel. Grinding the dry gel with agate mortar, and then placed in the muffle furnace firing at a certain temperature for a certain time to obtain Ag/TiO₂ powder.

2.3. Determination of PCP-Na - Ultraviolet spectrophotometry
Determination wavelength was 251 nm. The relationship of absorbance and PCP-Na concentration was shown in equation (1).

\[
A = 0.02894c + 0.0054
\]

2.4. PCP-Na degradation test
0.050 g of Ag/TiO₂ with silver mole fraction of 0.50% was put into a 250 mL beaker (Φ = 8.0 cm), add 50 mL of 50 μg/mL PCP-Na solution, then add 2 mL of hydrogen peroxide (1:100 by volume). Place in the magnetic stirrer and stir well for 5 minutes; open the UV lamp (lamp was above the liquid surface for 12 cm) for the photocatalytic degradation. And the photocatalytic degradation was continued for 2.5 h. After centrifugation at high speed, the supernatant was used to measure the remaining PCP-Na concentration in the degradation solution by UV spectrophotometry. The degradation rate of PCP-Na was calculated according to formula (2), and the degradation ability of the catalyst was characterized with degradation rate.

\[
\phi = \frac{c_0 - c}{c_0} \times 100\%
\]

Where: \( \phi \) is the degradation rate; \( c_0 \) is the initial concentration, μg/mL; \( c \) is the residual concentration of the solution after degradation, μg/mL.

3. Results and discussion

3.1. Structural characterization of Ag/TiO₂

3.1.1. XRD analysis. Figure 1 showed the X-ray diffraction patterns of Ag/TiO₂ with silver mole fraction of 0.5% after calcination at 450 °C and 650 °C respectively.
Figure 1. XRD of Ag/TiO$_2$ with silver mole fraction of 0.50% calcined at different temperature a. 450 °C; b. 650 °C

Compared with the X-ray standard card, when the calcination temperature is 450 °C, the sample exists in the composite phase of anatase and rutile phase and mainly exists in the anatase phase; When the calcination temperature is 650 °C, most of the sample is converted to rutile phase. It can be deduced that the Ag/TiO$_2$ powder would change from the anatase structure to the rutile structure with the increase of the calcination temperature. The higher the temperature is, the greater the configuration ratio of the rutile phase is. Among the two main crystal forms of TiO$_2$, anatase-type TiO$_2$ has more surface-adsorbed oxygen than the rutile-type, and the rutile-type photocatalytic oxidation activity is much less than the anatase-type. [7] To obtain a higher TiO$_2$ catalytic activity, the calcination temperature was chosen to be 450 °C.

3.1.2. SEM analysis. Figure 2 showed the morphology of the pure TiO$_2$ and Ag/TiO$_2$ with silver mole fraction of 0.50% after calcination at 450 °C. Figure 6 showed the morphology of the Ag/TiO$_2$ with silver mole fraction of 0.50% after calcination at 450 °C and 650 °C.

Figure 2. SEM of pure TiO$_2$ and Ag/TiO$_2$ with silver mole fraction of 0.50% calcined at 450°C pure TiO$_2$ powder; b. Ag/TiO$_2$ with silver mole fraction of 0.50%

It can be seen from Figure 2 that the surface of Ag/TiO$_2$ powder is very smooth and relatively dense. Compared with pure TiO$_2$, since the amount of silver loaded is small and the degree of dispersion on the surface is high, there is no silver reunion phenomenon on the surface.
Figure 3. SEM of Ag/TiO$_2$ with silver mole fraction of 0.50% calcined at different temperatures
c. 450 °C; d. 650 °C

From Figure 3, When the sample calcination temperature at 450 °C, because the heat treatment
temperature is relatively low, the degree of crystallization is not very well, the sample particles are
unclear, the edge is blurred (as is shown in Figure c). With the calcination temperature rising to 650 °C,
the SEM image is clearer, the particle size is slightly spherical, and the particle size distribution is
relatively uniform, significantly larger than the diameter of the sample prepared at 450 °C.

3.2. Effect of calcination temperature on catalytic activity

Figure 4. Effect of calcination temperature on degradation rate

The effect of calcination temperature on the degradation rate of PCP-Na was observed at Ag/TiO$_2$
with silver mole fraction of 0.50% and 1.00%. The results were shown as Figure 4.

It can be seen from Figure 4 that different calcination temperatures have a great influence on
photocatalytic property. The highest photocatalytic efficiency of PCP-Na solution was 88.71%, when
the calcination temperature was 450 °C. It can be seen that the temperature is low, the sample may not
form a complete crystal form, the light is not conducive to stimulate the photo-generated electrons and
photo-generated holes on the catalyst surface, so the activity is low; when the temperature is high, the
photocatalyst internal pores would reduce, which lead to the decrease of the photoactive center. What
is more, when the temperature is high, and the anatase phase would transform into rutile phase, the
bandgap will reduce. The probability of recombination between photo-generated electrons and photo-
generated holes will increase, leading to a decrease in catalytic activity.

3.3. PCP-Na photocatalytic single factor experiment

3.3.1. Effect of silver content on degradation rate. The effects of different silver mole fraction of
Ag/TiO$_2$ nanoparticles on the degradation rate of PCP-Na were investigated. The result was shown in
Figure 5.

It can be seen from Figure 5, with the increase of silver mole fraction, PCP-Na degradation rate
increased first and then decreased. When the mole fraction of Ag/TiO$_2$ nanoparticles was 0.50%, the
The degradation rate of PCP-Na was 87.8% and the photocatalytic efficiency was the highest. This is because the silver is doped into the TiO₂ powder, the Fermi level of silver is lower than the Fermi level of TiO₂, this would lead the metal contact with the semiconductor, and the electrons are generated on the TiO₂ under the irradiation of ultraviolet light, which will diffuse to the silver, which reduces the recombination probability of the photo-generated electrons and the photo-generated holes and increases the hole concentration on the TiO₂ surface, and the degradation rate will improve. When the amount of doped silver is excessive, the surface of the TiO₂ photocatalyst is excessively covered with metal Ag⁺, and the effective area of the photocatalyst is reduced, resulting in a decrease in the number of electrons generated by photoexcitation.

**Figure 5.** Effect of different silver mole fraction of Ag/TiO₂ nanoparticles on degradation rate

**Figure 6.** Effect of Ag/TiO₂ dosage on degradation rate

**Figure 7.** Effect of hydrogen peroxide volume on degradation rate
3.3.2. Effect of Ag/TiO₂ dosage on degradation rate. The effect of Ag/TiO₂ dosage on the degradation rate of PCP-Na were investigated by Ag/TiO₂ with silver mole fraction of 0.50%. The result was shown in Figure 6.

The concentration of hydroxyl groups in water plays a very important role in the photocatalytic oxidation process. When the amount of catalyst is gradually increased, the production rate of hydroxyl groups in water will be greatly improved, which is conducive to degradation. However, when the catalyst exceeds a certain amount, the excess catalyst will hinder the effective irradiation of ultraviolet light, resulting in a decrease in the absorption efficiency of light and a decrease in the catalytic efficiency.

3.3.3. Effect of H₂O₂ volume on degradation rate. The effect of hydrogen peroxide volume on the degradation rate of PCP-Na were investigated. The result was shown in Figure 7.

Under the ultraviolet light irradiation, hydrogen peroxide can produce stronger oxidation capacity •OH, it would improve the photocatalytic efficiency. During the reaction, when the amount of hydrogen peroxide is relatively small, it mainly acts as an electron capture agent, but when hydrogen peroxide volume exceeds a certain limit, the hydroxyl radicals would reduce due to its own free radical elimination effect.

3.3.4. Effect of initial concentration of PCP-Na on degradation rate. The effect of initial concentration of PCP-Na on PCP-Na degradation rate were investigated. The result was shown in Figure 8.

The initial concentration of pollutants is high, the amount of catalyst is constant and the amount of pollutants which can be degraded is limited, the more the total is, the smaller the degradation rate is.

4. Conclusion
A series of Ag-doped TiO₂ powder photocatalysts were prepared by sol-gel method, and the structure and morphology of the catalysts were characterized. Selecting the persistent organic pollutant PCP-Na as the target pollutant, the catalytic performance of Ag/TiO₂ was evaluated.

Silver content and calcination temperature have an effect on the catalytic activity of Ag/TiO₂ catalyst. The calcination at 450 °C is more favorable for the formation of anatase structure with high catalytic activity. Under the experimental conditions, when the silver mole fraction of Ag/TiO₂ was 0.50%, the catalytic activity of Ag/TiO₂ is high.

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