



## Preparation and Photocatalytic Performance of Nano-TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> Composites

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Nano-TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> composites were prepared by sol-gel method when the γ-Al<sub>2</sub>O<sub>3</sub> was employed as support. The structure, surface information and specific surface area of composites were characterized by X-ray diffraction, scanning electron microscopy and N<sub>2</sub> adsorption. The photocatalytic performance of composites were appraised using phenol solution as the model pollutant. The result indicated that TiO<sub>2</sub> was successfully loaded on the surface of γ-Al<sub>2</sub>O<sub>3</sub> and the particle size of TiO<sub>2</sub> increased with the increase of calcination temperature. Influence of calcination temperature, dosage of the composite on the photocatalytic performance were investigated. When the dosage of composites which were calcined at 500 °C was 3 g/L, we found that the degradation rate of phenol solution reached the maximum 45.6 %. After three cycles, the degradation rate of phenol solution decreased about 25 %.

**Key Words:** TiO<sub>2</sub>, Aluminum oxide, Composites, Phenol, Photodegradation.

### INTRODUCTION

As a deep oxidation process, photocatalytic oxidation reaction has received great attention in organic wastewater treatment technology<sup>1</sup>. It has the following advantages: (1) the harmful substances decompose completely, without secondary pollution; (2) operate at atmospheric pressure, reducing the operating difficulties; (3) reduce the consumption of energy and raw materials, needs little light and other substance; (4) achieve the purpose of disinfection, bleaching, deodorization; (5) photocatalyst is available at low cost, non-toxic, stable, reusable, *etc.*

TiO<sub>2</sub> semiconductor is a new type of highly efficient photocatalyst with strong oxidation ability and decompose environmental harmful organisms into CO<sub>2</sub> and H<sub>2</sub>O in a certain energy light conditions. In most of the earlier studies, TiO<sub>2</sub> powder was mixed with the solution, stirred by ventilation (typically air or oxygen) or mechanical directly, mixing with photolysis sufficiently, after that, TiO<sub>2</sub> suspended in the solution, known as suspension system. The system is simple and convenient, but contact with light hydrolyzate fully, generally, has a higher photolysis efficiency; while the TiO<sub>2</sub> particles in the suspension system were so small that the shortcomings such as difficult to recycle, easy to poisoning, limited its practical application. Therefore, the preparation of supported nano-TiO<sub>2</sub> photocatalyst is imperative. In recent years, people have carried out some research work on TiO<sub>2</sub> immobilization and used different materials such as slides<sup>2</sup>, PVC pipe<sup>3</sup>,

metal<sup>4</sup> as a carrier of TiO<sub>2</sub> composite photocatalyst and achieved satisfactory results.

In present study, we prepared nano TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> composites with sol-gel method using γ-Al<sub>2</sub>O<sub>3</sub> as the carrier. The as-prepared samples were analyzed by X-ray diffraction and scanning electron microscope. Phenol was used as a probe to evaluate the photocatalytic activity of the nano TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. The influence of calcination temperature and composites dosage to its photocatalytic properties were also studied.

### EXPERIMENTAL

Titanium acid butyl ester (chemical pure) was obtained from Tianjin ShenTai Chemical Reagent Co. Glacial acetic acid (Analytical reagent) was supplied by Beijing Chemical plant. Phenol (analytical reagent) was purchased from Tianxin Fine Chemical Development Center. γ-Al<sub>2</sub>O<sub>3</sub> (industrial pure) was produced by China Research Institute of Daily Chemical Industry.

**Preparation of nano-TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>:** Firstly, γ-Al<sub>2</sub>O<sub>3</sub> was grinded into small particles. Then, particles between 0.2-0.3 mm were screened out and washed repeatedly with deionized water. The as-prepared sample was dried and calcined at 120 °C for 3 h.

A solution was prepared by adding 15 mL anhydrous ethanol, 1 mL glacial acetic acid which was used as hydrolysis inhibitor and 10 mL titanium acid butyl ester into 100 mL beaker, respectively, stirred for 10 min. Then a certain quality of γ-Al<sub>2</sub>O<sub>3</sub> carrier was added into solution A with continued

agitation for 0.5 h; In addition, trace deionized water was dripped into 15 mL anhydrous ethanol, then concentrated nitric acid was added to adjust pH to about three getting B solution. Then solution B was dripped into A with continuous agitation for 2 h. And then filtered, the composite obtained will be dried at 60 °C for 2 h, then the nano-TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> was obtained after the dried product was calcined for 2 h at different temperatures.

**Characterization of nano-TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>:** To determine the composition of nano-TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> X-ray diffraction was carried out using a Rigaku D/MAX-RB diffractometer with CuK<sub>α</sub>. A continuous scan mode was used to collect the diffraction with a speed of 6° (2θ)/min between 20° and 80°. The accelerating voltage and the applied current were 40 kV and 100 mA, respectively. Scanning electron microscope (SEM, JSM-35C) was employed to detect the surface morphology of γ-Al<sub>2</sub>O<sub>3</sub> and nano-TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. The surface area was obtained from nitrogen adsorption isotherm by the Brunauer-Emmett-Teller (BET) method using in a Micromeritics ASAP2010 sorptometer at 77 K.

**Evaluation of photodegradation of nano-TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>:** Photocatalytic reaction marched in homemade colourless transparent pyrex glass reactor (250 mL) followed by mechanical stirring and the illumination area of 34.2 cm<sup>2</sup>. Aqueous suspensions (100 mL) containing the phenol (10 mg/L) and the photocatalysts were added in a reactor followed by dark treatment for 0.5 h, in order to get the adsorption equilibrium of the phenol solution on the surface of TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. Then a 500 W high-pressure xenon lamp (>380 nm) was used as the irradiation source and light and liquid level distance is about 70 cm. 5 mL phenol solution were taken and analyzed with UV-VIS spectrophotometer (UV-1600, Beijing Rayleigh Analytical Instrument Corp) every 0.5 h. The concentration of phenol was in proportion to the light absorbance at 269 nm according to Beer-Lambert law and so the photodegradation rate could be calculated as the following equation.

$$\text{Degradation rate (\%)} = \frac{C_0 - C}{C_0} \times 100\% = \frac{A_0 - A}{A_0} \times 100\% \quad (1)$$

Formula C<sub>0</sub>, C, respectively for phenol solution of the initial concentration and final concentration; A<sub>0</sub>, A respectively for the initial absorbance and final absorbance.

## RESULTS AND DISCUSSION

**Structure characterization of nano-TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> composites:** The XRD patterns of prepared TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> composites in different calcination temperature are shown in Fig. 1. When the calcination temperature is 400 °C, diffraction peaks at 2θ = 25.2° was observed corresponding to the (101) crystal face of anatase TiO<sub>2</sub>, it suggested that its degree of crystallinity is not high because of the wider diffraction peak and smaller intensity of the diffraction peak. It showed that in 400 °C the structure of TiO<sub>2</sub> begin transformation from amorphous to anatase. When the calcination temperature is 500 °C and 600 °C, diffraction peak becomes very sharp at 2θ = 25.2° and obvious diffraction peaks at 2θ = 37.8, 47.9 and 62.7° were observed corresponding to the (004), (200) and (204) crystal faces of TiO<sub>2</sub> anatase, respectively. As the temperature rises,

anatase peaks became more acute, which indicate that more and more regular crystal forms with continue growing of grain sizes. The diffraction peak of rutile TiO<sub>2</sub> was observed at 2θ = 27.4 suggested that TiO<sub>2</sub> begin to change from anatase to rutile. When the calcination temperature is 700 °C, diffraction peaks at 2θ = 27.4, 36.1, 41.3, 54.4 and 56.6° were observed corresponding to the (110), (101), (111), (211) and (220) crystal faces of rutile TiO<sub>2</sub>, respectively. It indicated that when calcination temperature is 700 °C TiO<sub>2</sub> converted to rutile completely without appearance of anatase TiO<sub>2</sub> diffraction peaks. The crystal sizes (d = 11.4, 19.1 and 22.9 nm) of the nano-particles in different calcination temperatures (400, 500 and 600 °C) could be estimated by Debye-Scherrer equation,  $d = k\lambda/(\beta\cos\theta)^5$ , according to the peak width of 25.2° for TiO<sub>2</sub> in XRD pattern and the size (d = 57.6 nm) in 700 °C could be estimated according to 2θ = 27.4°.

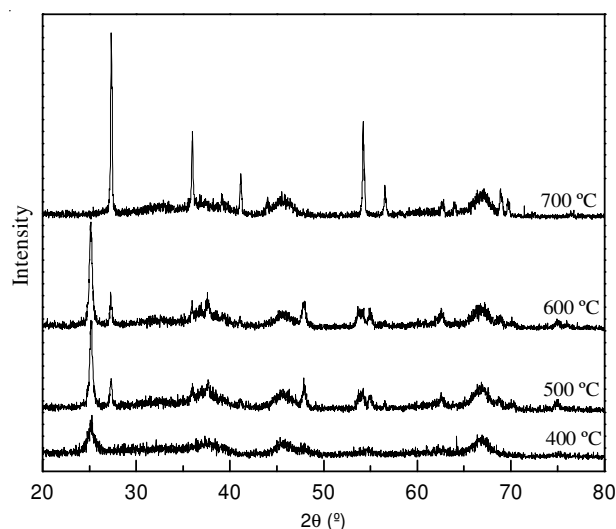


Fig. 1. XRD patterns of nano-TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> composites at different heat-treated temperatures

**Surface morphology of nano-TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> composite:** Fig. 2 shows the surface micrograph of nano-TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> composites prepared in different calcination temperature. It can be seen that compared γ-Al<sub>2</sub>O<sub>3</sub>, the TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> composite prepared in 400 °C and 600 °C covered the surface of γ-Al<sub>2</sub>O<sub>3</sub> with uneven layer of materials. Since γ-Al<sub>2</sub>O<sub>3</sub> carrier channels decrease, combined with XRD results, it can be seen that TiO<sub>2</sub> has been adsorbed on the surface of the carrier successfully. It still can be seen that TiO<sub>2</sub> films of the composite prepared in calcination temperature 600 °C are denser than that in 400 °C. This may be due to reason that 600 °C TiO<sub>2</sub> crystallization is good and grain growth are caused by law.

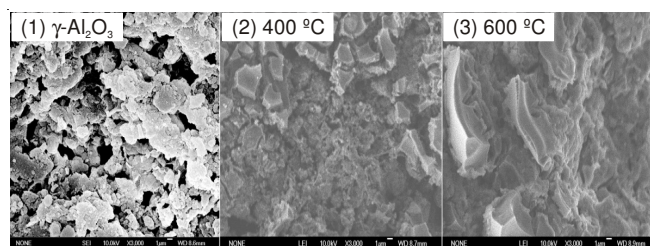


Fig. 2. SEM images of TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> composites were prepared at different heat-treated temperatures

**Surface area of nano- TiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composite:** Table-1 showed the surface area of composite prepared in different calcination temperatures, it can be seen that the specific surface area of the complex after loaded are less than that of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (152.63 m<sup>2</sup>/g), for the surface and pores of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were covered by TiO<sub>2</sub> partially. It can also be seen that along with the calcination temperature increasing specific surface area has the trend of decrease, this may be due to that with increasing of calcining temperature, TiO<sub>2</sub> crystallization tend to be perfect, caused by the grain growth, which is consisted with XRD results.

Calcination temperature (°C)	Specific surface area (m <sup>2</sup> /g)
400	148.42
500	139.13
600	122.65
700	103.49

### Photocatalytic activity of TiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composite

**Effect of heat-treated temperature on degradation rate:** 0.3g TiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composites calcined for 2 h under different calcination temperatures were dispersed in phenol solution under ultraviolet irradiation for 4 h, the degradation rate of phenol with calcination temperatures was shown in Fig. 3.

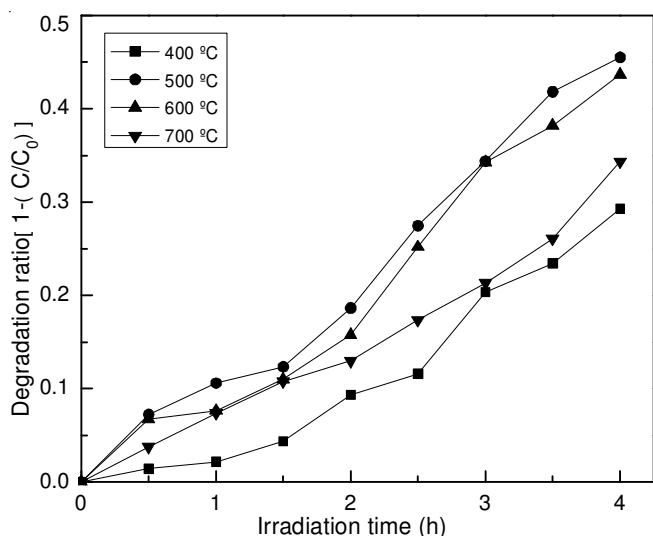


Fig. 3. Effect of different heat-treated temperatures on photodegradation of phenol

As shown in Fig. 3, the phenol degradation first increases and then decreases with the calcination temperature increases and the maximum appeared at 500 °C. This is because TiO<sub>2</sub> crystal type played an important role on the catalytic activity and the crystal type of TiO<sub>2</sub> was determined by calcination temperature. There are three crystal types in TiO<sub>2</sub>: anatase, rutile and plate titanium ore and just like reported, anatase activity is the most powerful, rutile only small activity and plate titanium ore no active<sup>6</sup>. It has reported that in the literature<sup>7,8</sup>, when a small amount of rutile type was mixed in anatase, the photocatalytic activity was higher. When the calcination

temperature was 400 °C, degradation efficiency of phenol solution was low because of no complete anatase TiO<sub>2</sub>. While the calcination temperature increased to 500 °C, 600 °C, complete anatase TiO<sub>2</sub> was formed with little rutile form, which improved the degradation efficiency of phenol solution. The catalytic properties of TiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> calcined at 600 °C was lower than that at 500 °C, because of that TiO<sub>2</sub> grain size, specific surface area decreases with the calcination temperature increases. When the calcination temperature reaches 700 °C, because TiO<sub>2</sub> were basically transformed into rutile, which has poor photocatalytic properties, degradation efficiency of phenol solution was reduced.

**Effect of dosage of complexes on photodegradation of phenol:** When the concentration of phenol solution of 10 mg L<sup>-1</sup>, the irradiation time under UV was 4 h, calcinations temperature of 500 °C, effect of dosage of TiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> complexes on photodegradation of phenol was shown in Fig. 4.

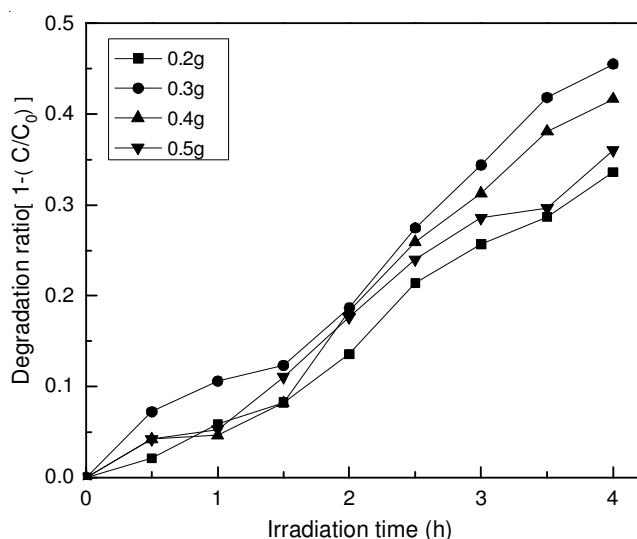


Fig. 4. Effect of different TiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composite dosage on photodegradation of phenol

It can be seen from Fig. 4 that degradation rate of phenol solution was increased and then decreased with the increase of the amount of TiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> complex and when the dosage of TiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was up to 0.3 g the highest photodegradation rate of phenol (45.6 %) could be obtained in the experiments. When a further increase in the amount of complex, the degradation rate of phenol solution showed downward trend. This is because photocatalytic reaction was carried out on the catalyst surface, the catalyst increases in the circumstance of a certain concentration of phenol solution, provided more reaction active sites. Therefore, reactive groups generated by illumination had also increased<sup>9</sup>. Consequentially, photocatalytic reaction rate increased. Further increase of catalyst provided a sufficient number of reactive sites and made the reaction reach saturation<sup>10</sup>. Continued increase of the catalyst caused decline of light efficiency and fall of the degradation rate of phenol solution, due to the shielding and scattering effect of catalyst to light.

**Blank and contrast experiment:** In the photocatalytic degradation process of TiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composite, changes of phenol concentration was not only related to photocatalytic degradation but other factors, such as the complex adsorption,

the light degradation of phenol solution, *etc.* Therefore the blank experiment (only light without catalyst) and adsorption experiment (only catalyst without light) were studied, then contrasted with photocatalytic degradation of performance in the presence of catalyst and light at the same time, in addition, contrasted with the unloaded nano-TiO<sub>2</sub> and the result was shown in Fig. 5.

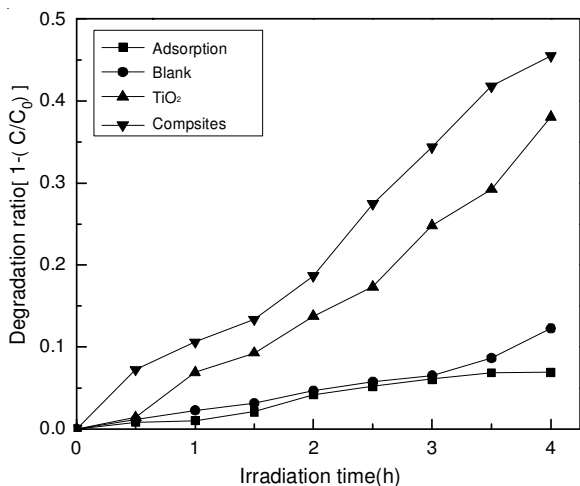


Fig. 5. Effect of different conditions on photodegradation phenol

It can be seen from adsorption curves in Fig. 5, that the concentration of phenol solution changes little in the presence of only catalyst without illumination conditions. Blank test curves in the Fig. 5 showed that after 4 h, the degradation rate of phenol solution is 12.3 % with only ultraviolet light irradiation and no catalyst, which proves that the solution adsorbed ultraviolet light with a certain degree and in the solution occurred photochemical reaction, so that a certain degree of degradation of phenol solution has occurred. It can also be seen from the Fig. 5 that the phenol solution was added complexes enables rapid degradation under the conditions of UV irradiation, after 4 h the degradation rate of phenol solution is up to 45.6 %. It indicate that photocatalyst have a significant photocatalytic activity under UV irradiation conditions and can get degradation of phenol solution in a short time. As can be seen from TiO<sub>2</sub> photocatalytic degradation curve in the Fig. 5 that the degradation rate of the loaded is higher than that of the unloaded, one reason may be caused by the adsorption between TiO<sub>2</sub> and carrier  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which is conducive to the separation of electrons and holes and to increase the adsorption of reactants and the photocatalytic activity of TiO<sub>2</sub>. Another reason may be due to the formation of a gradient interface between TiO<sub>2</sub> and carrier  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by interdiffusion. Moreover, electric double layer is formed, which reduces the recombination probability of electrons and holes, so that the photocatalytic properties of the composite get improved<sup>11</sup>.

**Effect of recycle time of TiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composites on the degradation rate of phenol solution:** TiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composite was recovered, washed, dried at 100 °C and then re-used in the photocatalytic reaction after the light degradation test to study life of the composite. The recycle time of TiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composites on the degradation rate of phenol solution was shown in Fig. 6.

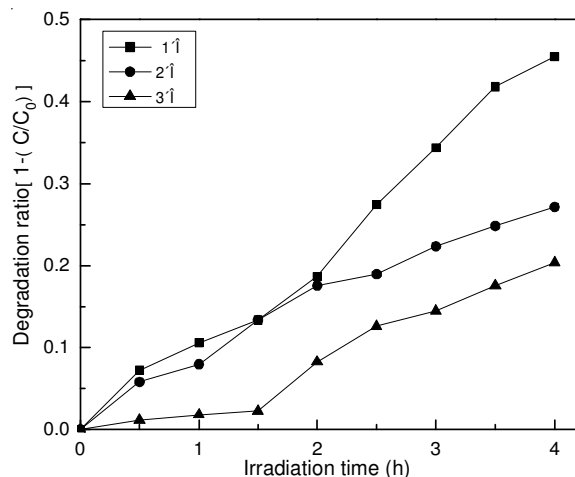


Fig. 6. Curves of recycle time of TiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composites on the degradation rate of phenol solution

As is shown in Fig. 6, reused TiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> complex decreased photocatalytic efficiency of the phenol solution. The degradation rate of phenol diminished about 25 % after three cycles. This phenomenon may be explained by partial loss of TiO<sub>2</sub> from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> carrier or may be that the adsorption sites in the active sites of oxygen and water molecules were occupied by that of reactants and intermediates, bringing the reduce of negative oxygen ions and hydroxyl radicals. In addition, even if the adsorbed reactants and intermediates accept the electron-hole pairs can not immediately redox or form strong oxidizing group that can carry out the oxidation-reduction reaction effectively, accordingly, affected the occurrence of photocatalytic reaction. The reactive sites gradually being occupied by adsorption, led to gradually inactivation of photocatalytic reaction agent.

## Conclusion

In this study, nano-TiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composites were prepared by sol-gel method. The degradation of phenol solution first increases and then decreases and the highest photocatalytic properties that after 4 h under UV irradiation, the degradation of phenol solution was 45.6 % were obtained, when the calcination temperature of 500 °C and complexes dosage of 3 g/L.

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