

## Preparation of the 2,4-dichlorophenol solution of Ce-doped TiO<sub>2</sub> and its photocatalytic activity

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**Keywords:** doped, 2,4-dichlorophenol, photodegradation, cerium, TiO<sub>2</sub>

**Abstract.** Ce doped TiO<sub>2</sub> catalyst was synthesized by sol-gel method. This gel was dried at 70 °C during 2 hours and afterwards was calcined at 500 °C for 4 h. Then, the anatase TiO<sub>2</sub> catalyst power were obtained. The 0.3wt% Ce/TiO<sub>2</sub> catalyst is efficient and stable catalyst for the photodegradation on the 2,4-DCP solution. At the experimental conditions of initial 2,4-DCP solution at 10 mg/L, UV lamp at 20 W, catalysts concentration at 0.5 g/L, the mineralization ratio at 98.14 % could be achieved after 600 min of photodegradation reaction. And the Ce/TiO<sub>2</sub> catalyst also showed photodegradation ability on 2,4-DCP under simulate solar light, the mineralization ratio at 55.23 % could be achieved after 600 min of solar photodegradation reaction.

### Introduction

As intermediates of the chlorophenol solvent, pesticide and pharmaceutical, 2,4-Dichlorophenol (2,4-DCP) is widely used in the field of industrial and agricultural production, mainly used for synthetic Eby phosphorus (epbp) poison grams powder, nitrofen (2,4-D) and lattice Fenpyroximate and drug sulfur two chlorophenols etc.. In 2, 4-dichlorophenol use and production process, due to the stability of phenolic and toxicity to produce organic wastewater is difficult to be degraded. The results on the environment caused great harm to the [1]. Chlorophenol organic matter is environmental endocrine disruptors, it will be growth inhibited the growth of organisms and human body, which would have detrimental effects [2] of their reproductive system. Amendment that U. S. environmental protection agency in 1977 promulgated the "clean water" case clearly defined strictly limit 2, 4-dichlorophenol [3]. Phenolic compounds are well known for high salinity, acidity, chemical oxygen demand(COD) and low biodegradability. In addition, they have low volatilities and easily form azeotropes and eutectics. Removal of these Phenol and phenolic compounds is a very crucial step. Due to these harmful effects, the removal of phenol from industrial wastewater is of great importance[4–8]. However, the reclamation of polluted areas from organic pollutants such as phenol is difficult because they can't be easily transformed into the non-toxic elements[9]. Therefore, conventional biological treatment methods using activated sludge have been used for the removal of high concentration of phenolic compounds from industrial wastewater. .

Titanium dioxide has been widely employed, thanks to its outstanding photocatalytic activity, ready availability, low toxicity, inertness, low cost and high stability compared to other semiconductors. Moreover, TiO<sub>2</sub> shows high efficiency in the complete mineralization of various toxic and bio-recalcitrant organic compounds such as organochloride compounds, organic acids, pesticides, herbicides, and dyes. Titania attracts the attention of international scholars because of higher photocatalytic activity, hard oxidizability, stabilized characteristic, anti-erode and non-toxic properties.

It has been widely applied in paints, photocatalysts, chemical fibers, ceramic pigments and inorganic filler[10–13].

Among the existing processes to decompose the organic compounds, photocatalytic oxidation process coupled with  $\text{TiO}_2$  showed higher efficiency compared to other similar photocatalysts. The amount of research work on semiconductor photoenergy processes has grown exponentially. A number of devices using  $\text{TiO}_2$  for solar energy conversion, such as solar cells or photocatalytic systems have been developed for the recent years[14–16]. This semiconductor has been widely considered as photocatalyst due to its high photocatalytic activity, photostability, and non-toxicity. However, because of the relatively high intrinsic band gap of anatase  $\text{TiO}_2$  (3.2 eV), only 4% of the incoming solar energy on the earth's surface can be utilized. On the other hand, the hole and electron excited by UV light can recombine easily, which will reduce the efficiency of photons. It has been one of the most challenging topics to reduce the band gap to produce visible-light photocatalysis and suppress the recombination of hole-electron pairs. The limitation of  $\text{TiO}_2$  can be overcome by modifying its electronic structure and hence improving its photocatalytic activity[17–19]. Therefore, to extend the reaction into the visible light of the range, considerable efforts have been made to extend the photoactivity of titania-based systems, using doping or co-doping with noble metal, transition metal, rare earth metal and other metals[20–21].

In this study, Ce doping  $\text{TiO}_2$  catalyst were synthesized by sol-gel method. Then the structure and photocatalytic activity on the 2,4-DCP solution of the Ce/  $\text{TiO}_2$  catalyst were study.

## Experiment

### Catalyst preparation

The catalysts were prepared by the sol-gel method. All the employed reagents were of analytical grade and were used without further purification treatment. Undoped  $\text{TiO}_2$  particles were prepared using n-Butyl titanate as the alkoxyde precursor. In the first step, 5.3 ml of n-Butyl titanate were dissolved in 4.5 mL of ethanol and magnetically stirred. The following step was the addition of nitric acid until the pH reached a value of 2 in order to prevent the precipitation of the corresponding hydroxide.

Then, the above prepared solution was heated up to 50 °C and 1 mL of distilled water were dropped to the solution inducing the gelation. In this way, the undoped  $\text{TiO}_2$  precursor gel was obtained. Then the gel was dried at 70 °C of 2 hours and afterwards was calcined at 500 °C during 4 h.

For the doped particles, the same procedure was followed. In the case of Ce- $\text{TiO}_2$  particles, the precursor reagent for Ce doping was cerous sulfate ( $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ ) that was added directly to the initial n-Butyl titanate solution with the hydrolysis water. Two samples with calculated concentration of 0.1% and 0.5% per weight were prepared.

### Characterization of catalyst

These prepared catalysts were characterized by thermogravimetric analysis (TGA) with a TGA/SDTA 851e (Mettler-Toledo, Switzerland) with a flow of 20 mL/min  $\text{N}_2$  flow under a heating rate of 20 °C/min. X-ray diffraction (D/Max-2400, Philips, Holland) was used to analyze the crystal phase of the catalysts. UV-visible diffuse reflectance spectra (DRS) of the  $\text{TiO}_2$  and Ce/ $\text{TiO}_2$  were recorded by Lampda 850 (PE, American).

### Photodegradation performance of catalyst under UV irradiation

Photodegradation performance of the different catalysts were evaluated for 2,4-DCP solution under the UV irradiation. A monochromatic 365 nm UV light with a power of 20 W in a dark chamber was used. A solution of 2,4-dichlorophenol(2,4-DCP) with an initial concentration of 10 mg/L was used in order to evaluate the efficiency in the decomposition of the 2,4-DCP solution. The catalysts (concentration: 0.5 g/L) were dispersed in darkness through magnetic stirring during 120 min until the adsorption-desorption equilibrium was reached. Once the adsorption-desorption equilibrium was reached, the solution was subjected to the UV and the mineralization ratio of the 2,4-DCP at different

times was determined by COD value. The COD value was determined using the dichromate titrimetric standard method.

### Photodegradation performance of catalyst under simulate solar light

Photodegradation performance of the different catalysts were evaluated for 2,4-DCP under the solar light. A fluorescent lamp of 60 W was used. A solution of 2,4-dichlorophenol(2,4-DCP) with an initial concentration of 10 mg/L was used in order to evaluate the efficiency in the decomposition of the 2,4-DCP solution. The catalysts (concentration: 0.5 g/L) were dispersed in darkness through magnetic stirring during 120 min until the adsorption-desorption equilibrium was reached. Once the adsorption-desorption equilibrium was reached, the solution was subjected to the UV and the mineralization ratio of the 2,4-DCP at different times was determined by COD value. The COD value was determined using the dichromate titrimetric standard method.

## Results and discussion

### Characterization of TiO<sub>2</sub> particles

Prior to calcination, the amorphous powder was subjected to thermogravimetric analysis to estimate the calcination temperature. The analysis was carried out using thermal gravimetry analyzer from temperature 30–600°C and the results were presented in Fig. 1.

From the curve B, it can be seen that the thermal weight loss could be divided into four stages. The first stage was belong to the period while the calcination temperature was lower than 220°C. During this period, the weight loss was just about 5%, which were subjected to the volatile components of the sample, such as the water, ethanol, etc.

The second stage was from 220°C to 250°C. During this stage, the speed of the weight losing was faster than the speed of the first stage. The weight loss of this stage may be corresponded to the combustion and carbonization of organic and organic polymer in the gel.

In the third stage, the heat temperature was from 250°C to 420°C. During this stage, the speed of the weight losing was low, And the lossing weight was corresponded to some material which can not fixed in the gel structure.

After the heat temperature reached 420°C, the thermal weight losing curve tends to be flat, which indicates that the residual component had been almost removed.

Therefore, heat treatment of the amorphous powder above 400°C for 4 h was able to completely remove the organic entity from the sample and provide enough time to make the crystal struture transformation of TiO<sub>2</sub>.

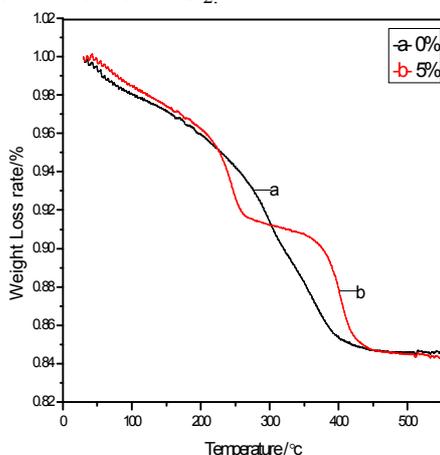


Fig.1. TGA thermogram for (a) TiO<sub>2</sub>, (b) 0.3% Ce doped TiO<sub>2</sub>.

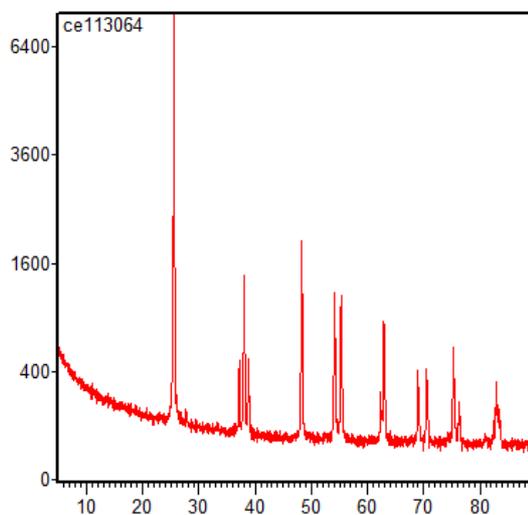


Fig.2. XRD patterns of 0.3% Ce/TiO<sub>2</sub> (calcined temperature at 500°C for 4 h).

### X-ray diffraction studies of the Ce/TiO<sub>2</sub> catalyst

Fig. 2 represents the XRD patterns of 0.3% Ce/TiO<sub>2</sub> catalyst calcined at 500 °C. The peaks at 2θ=25.4°, 37.9°, 48.1°, 53.9°, and 55.2° are attributed to the diffractions of the anatase TiO<sub>2</sub> phase (PDF NO 841286).

Just because TiO<sub>2</sub> in the anatase phase, there are many defects and dislocations, which can generate more oxygen vacancies to capture electrons. So it is suitable for photodegradation of some toxic organics. Therefore, the calcination temperature of the amorphous powder was 500 °C for 4 h was used in the follow experiments.

### UV-vis analysis

The UV-vis diffuse reflectance spectra of the TiO<sub>2</sub> and 0.3% Ce/TiO<sub>2</sub> is shown in Fig. 3. The pure TiO<sub>2</sub> can only absorb UV light ( $\lambda \leq 420$  nm). The light absorption edges of 0.3% Ce/TiO<sub>2</sub> move remarkably to the high wavenumber, the absorption intensity of visible light ( $\lambda > 400$  nm) is also obviously stronger than that of neat TiO<sub>2</sub> catalyst. It can be inferred that Ce-doped TiO<sub>2</sub> exhibits a higher light absorption both in the visible and ultraviolet ranges than neat TiO<sub>2</sub> power.

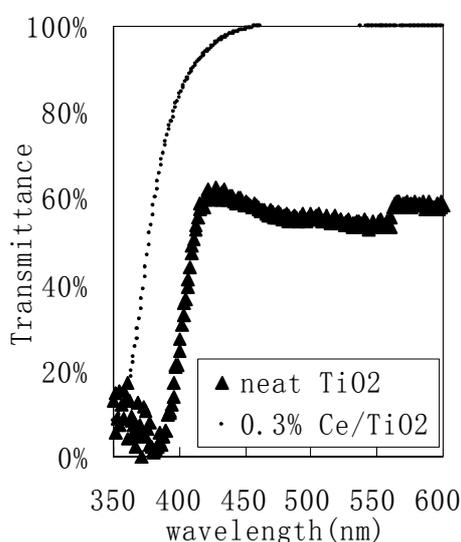


Fig. 3 UV-visible diffuse reflectance spectra of different samples

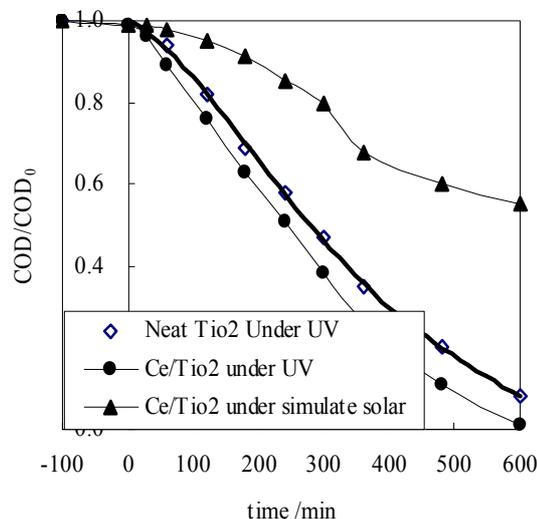


Fig. 4 Photodegradations performance of neat TiO<sub>2</sub> and 0.3% Ce/ TiO<sub>2</sub> under UV irradiating or simulate solar lighting on the 2,4-DCP solution

### Photodegradation performance of catalyst under UV irradiation and simulate solar light

Photodegradation performance of the different catalysts under UV and solar light were evaluated for 2,4-DCP solution. The results were showed on the Fig. 4. With the increase of irradiating time, the concentration of 2,4-DCP solution were all decreasing. The mineralization ratio at 87.63 % was achieved by the neat TiO<sub>2</sub> catalyst under UV irradiating for 600 minutes. And the mineralization ratio at 98.92 % was achieved by the 0.3% Ce/TiO<sub>2</sub> catalyst under UV irradiating for 600 minutes. This improved that 0.3% Ce/TiO<sub>2</sub> catalyst showed better photodegradation ability on 2,4-DCP solution under UV irradiating. It was also indicated that Ce doped on the TiO<sub>2</sub> could enhance photodegradation ability on 2,4-DCP solution under UV irradiating.

The mineralization ratio at 54.02 % was achieved by the 0.3% Ce/TiO<sub>2</sub> catalyst under simulate solar irradiating for 600 minutes. Though the mineralization ratio of 0.3% Ce/TiO<sub>2</sub> catalyst under simulate solar was lower than the mineralization ratio of 0.3% Ce/TiO<sub>2</sub> catalyst under UV, But it can proved that 0.3% Ce/TiO<sub>2</sub> catalyst have photodegradation ability on 2,4-DCP solution under solar light. And Ce atoms which were doped inside crystal of Ce/TiO<sub>2</sub> could influence the band gap of crastal. This result also was showed by the UV-vis diffuse reflectance spectra.

## Conclusion

Ce doped TiO<sub>2</sub> particles were synthesized by sol-gel method. The structure and photocatalytic activity of the Ce/TiO<sub>2</sub> were study. Under calcinations at 500 °C for 4 h, monophasic anatase structure were obtained. The 0.3 wt% Ce/TiO<sub>2</sub> catalyst behaves as efficient catalyst for the photodegradation of phenol solution. At the experimental conditions of phenol initial concentration at 10 mg/L, catalyst dosage of at 0.5g/L, the mineralization ratio at 98.14 % could be achieved after 600 min of photodegradation reaction. And the Ce/TiO<sub>2</sub> catalyst also showed photodegradation ability on 2,4-DCP under simulate solar light, the mineralization ratio at 55.23 % could be achieved after 600 min of solar photodegradation reaction.

## Acknowledgment

This research was supported by the funding (grant number :JB12023) from Fujian Province Education Department, the funding (grant Number: 2014-4-41) from the National Natural Science Foundation of China (grant number: 31070495), and the 948 Project of the State Forestry Administration, People's Republic of China and under project.

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