

Photocatalytic Characteristic of Fe-doped TiO₂ with Phenol

Jingzheng,Weng^{1,2,a}, Kaikai,Zhang²,Jiewei,Huang², Feng,Gao²,Lihui,Chen¹,
Renhui,Qiu^{1, b,*}

¹College of Material Engineering,Fujian Agriculture and Forestry University, Fuzhou, Fujian
Province 350002, China

²College of Materials Science and Engineering ,Fujian Normal University ,Fuzhou, Fujian Province
350007,China

^ajackyweng@vip.163.com, ^brenhuiqiu@fafu.edu.cn

Keywords: doping, phenol, photodegradation, Fe, TiO₂

Abstract. Fe doped TiO₂ particles were synthesized by sol-gel method. This gel was dried at 70 °C during 2 hours and afterwards was calcined at 450 °C during 4 h. Under calcinations at 450 °C (4 h), catalyst particle with an average diameter around 59 nm and monophasic anatase structure were obtained. The 0.3wt% Fe/TiO₂ catalyst behaved as efficient and stable catalyst for the photodegradation of phenol solution. At the experimental conditions of initial phenol solution at 10 mg/L, initial pH of the phenol solution at 6.0, UV lamp at 20 W, catalysts concentration at 0.5 g/L, the COD removal of 99 % could be achieved after 240 min of photodegradation reaction.

Introduction

The expansion in industrial processes has led to an increase in water pollution due to industrial discharges. Phenol is a basic raw material for various products such as herbicides, drugs, paints, cosmetics, and lubricants. Its largest use (35%) is as an intermediate in the production of phenolic resins like phenol-formaldehyde resins[1–3]. Also, its conversion to a precursor of plastics, such as condensation with acetone to give bisphenol-A (BPA) for the production of polycarbonates and epoxide resins, is from its other major uses which together with the phenolic resins includes about two thirds of its general use. It is well known that phenol and its derivatives (phenols) are the most common organic pollutants in wastewaters. Such pollutants could pollute the environment and endanger the creatures. 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. Micro-organisms, e.g. bacteria, fungi, and yeasts, which are able to metabolize phenol can be considered as one of the cheapest and safer alternative approach for the removal of phenol from wastewater [10].

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, TiO₂ 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[11–13].

Among the existing processes to decompose the organic compounds, photocatalytic oxidation process coupled with TiO₂ 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 TiO₂ for solar energy conversion, such as solar cells or photocatalytic systems have been developed for the past four decades[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 TiO₂ (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 TiO₂ 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, Fe doping TiO₂ particles were synthesized by sol-gel method. Then the structure and photocatalytic activity of the Fe/TiO₂ catalyst were studied.

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 TiO₂ 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 TiO₂ precursor gel was obtained. Then the gel was dried at 70 °C of 2 hours and afterwards was calcined at 450 °C during 4 h.

For the doped particles, the same procedure was followed. In the case of Fe-TiO₂ particles, the precursor reagent for Fe doping was iron(III) nitrate (Fe₂(NO₃)₃ · 9H₂O) that was added directly to the initial n-Butyl titanate solution with the hydrolysis water. Two samples with calculated concentration of 0.3% 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 N₂ 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 catalysts, TiO₂ and Fe-doped TiO₂ were recorded by Lampda 850 (PE, American). And the particles size distribution of TiO₂ and Fe-doped TiO₂ were analysed by Mastersizers v2000 (Malvern, English)

Evaluation of UV-light catalytic activity

Moreover, the different catalysts were evaluated for the photodegradation of phenol under the irradiation of UV light. A monochromatic 365 nm UV light with a power of 20 W in a dark chamber was used. A solution of phenol with an initial concentration of 10 mg/L was used in order to evaluate the efficiency in the decomposition of the phenol 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. The pH of the phenol solution was adjusted to 6. Once the adsorption-desorption equilibrium was reached, the solution was subjected to the UV and the concentration of the phenol at different times was determined by COD value. The COD value was determined using the dichromate titrimetric standard method[22].

Results and discussion

Characterization of TiO₂ 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. The typical TGA thermograms of amorphous powder are presented in Fig. 1.

The two curves all shows two decomposition steps, 30–200 °C and 200–420 °C. During the first step, about 4%(TiO₂) of weight loss and 6%(0.3% Fe/TiO₂) of weight loss were showed. These losing were due to the physically absorbed moisture present in the sample. The weight losing rating of two samples were slow during the first period.

During the second step, about 15%(TiO₂) of total weight loss and 25%(0.3%Fe/TiO₂) of total weight loss occurred. The weight losing rating of two samples were fast during this period. And just because the Fe/TiO₂ power sample added Fe₂(NO₃)₃ solution as doping agent, so the weigh loss of the sample was larger than the weigh loss of TiO₂ power

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 TiO₂.

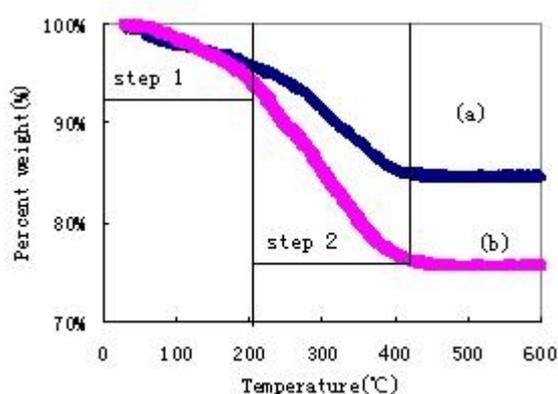


Fig.1. TGA thermogram for (a) TiO₂ , (b) 0.3% Fe doping TiO₂.

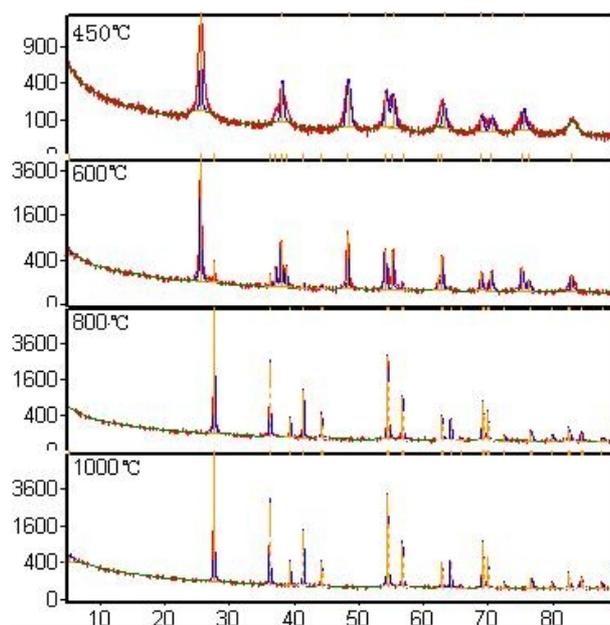


Fig.2. XRD patterns of 0.3% Fe/TiO₂ prepared at different calcination temperature.

X-ray diffraction studies

Fig. 2 represents the XRD patterns of 0.3% Fe/TiO₂ catalyst calcined at different temperatures ranging from 450 °C to 1000 °C. As the calcination temperature was 450 °C, the peaks at $2\theta=25.4, 37.9, 48.1, 53.9, 55.2,$ and 62.9° are attributed to the diffractions of the anatase phase (PDF NO 841286). As the calcination temperature was 800 °C and 1000 °C, the peaks at $2\theta=27.5, 36.0,$ and 41.2° are attributed to rutile phase (PDF NO 860147). As the calcination temperature was 600 °C, the peaks of the anatase phase still exist, but the peaks of rutile phase display ,and these peaks intensity is weaken.

With the increase of the calcination temperature, crystal structure of Fe/TiO₂ catalyst gradually from anatase phase into rutile phase. Just because TiO₂ 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 450 °C for 4 h was used in the follow experiments.

UV-vis DRS analysis

The UV-vis diffuse reflectance spectra of the TiO_2 and 0.3% Fe/ TiO_2 is shown in Fig. 3. The pure TiO_2 can only absorb UV light ($\lambda \leq 410$ nm). The light absorption edges of 0.3% Fe/ TiO_2 move remarkably to the visible range, the absorption intensity of visible light ($\lambda > 400$ nm) is obviously stronger than that of pure TiO_2 . It can be inferred from the spectra that Fe-doped TiO_2 exhibits a higher light absorption both in the visible and ultraviolet ranges than TiO_2 . Similar types of results were reported [23].

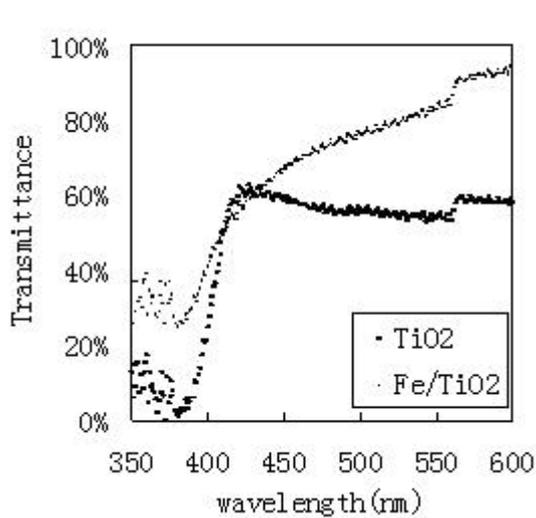


Fig. 3 UV-visible diffuse reflectance spectra of different samples

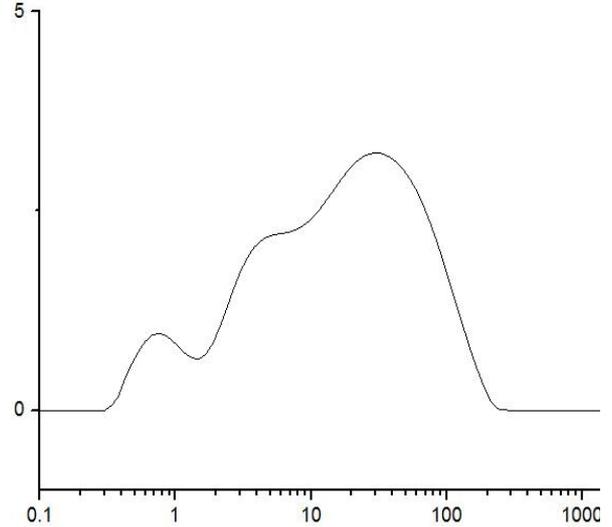


Fig. 4. particle size distribution curves of 0.3% Fe/ TiO_2

The particle size distribution of catalyst

The particle size distribution curves of 0.3% Fe/ TiO_2 is presented in Fig. 4. The particle size was mainly from 2 nm to 110 nm) and an average particle size of 59.5 nm was observed.

Evaluation of photocatalytic activity

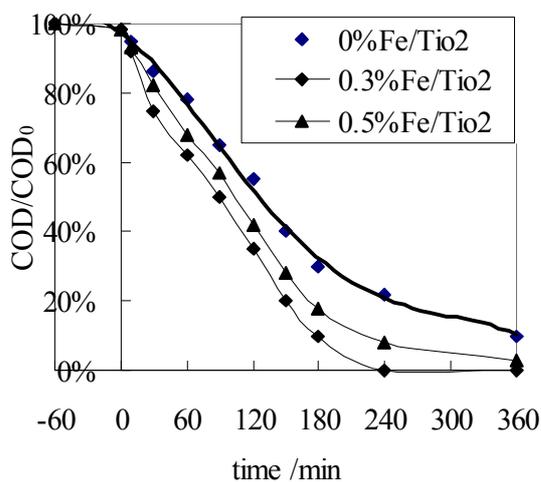


Fig 5. Photocatalytic performance of the samples for removal of phenol in the aquare solution

The photocatalytic activity of the Fe/ TiO_2 was investigated for phenol removal reactions under UV-light irradiation. It was confirmed that only a small extent of phenol adsorption (ca. 2%) was observed after 2 h in the dark condition. For 10 h-UV light irradiation, both TiO_2 and Fe/ TiO_2 showed catalytic activity, as shown in Fig.5. Under UV lamp irradiation, it is worth noting that 0.3% Fe/ TiO_2 shows the photocatalytic activity for the degradation of phenol aqueous solution with a degradation

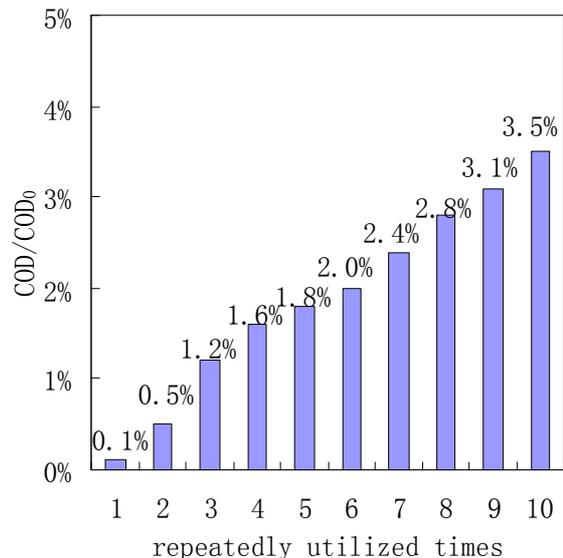


Fig. 6. Reusability of 0.3% Fe/ TiO_2 for photodegradation of phenol during ten cycles.

rate of 99.3% within 240 min. It is significantly higher than that of 0.5% Fe/TiO₂ (95.2%), and TiO₂ (77.7%).

In order to investigate the long-term stability of Fe/TiO₂, the photocatalysts were recycled after each 4h photocatalytic degradation experiment, and then were reused in the next run without regenerating the catalyst. As shown in Fig.6, the 0.3% Fe/TiO₂ photocatalysts can efficiently degrade phenol under uv light without significant deactivation after 10 cycles (degradation efficiency remains about 95%).

Conclusion

Fe doped TiO₂ particles were synthesized by sol-gel method. The structure and photocatalytic activity of the Fe/TiO₂ were study. Under calcinations at 450 °C (4 h), catalyst particles with an average diameter around 59 nm and monophasic anatase structure were obtained. The 0.3 wt% Fe/TiO₂ 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, initial pH of the phenol solution to 6 and a COD removal of 99 % could be achieved after 240 min of reaction.

References

- [1] M.M. Matlock, B.S. Howerton, D.A. Atwood, *Water Res.* 36 (2002) 4757–4764.
- [2] F.J. Alguacil, M. Alonso, F. Lopez, A. Lopez-Delgado, *Chemosphere* 72 (2008) 684–689.
- [3] C.H. Ko, P.J. Chen, S.H. Chen, F.C. Chang, F.C. Lin, K.K. Chen, *Bioresour. Technol.* 101 (2010) 1528–1531.
- [4] Z. Rappoport, *The Chemistry of Phenols*, John Wiley & Sons, West Sussex, 2003.
- [5] S. Ahmed, M.G. Rasul, W.N. Martens, R. Brown, M.A. Hashib, *Desalination* 261 (2010) 3–18.
- [6] G.S. Veeresh, P. Kumar, I. Mehrotra, *Water Res.* 39 (2005) 154–170.
- [7] T.C. Zhang, R.Y. Surampalli, S. Vigneswaran, R.D. Tyagi, S.L. Ong, C.M. Kao, *Membrane technology and environmental applications*, sponsored by membrane technology task committee of the environmental council, Environmental and Water Resources Institute (EWRI) of the American Society of Civil Engineers (ASCE), Reston, Virginia (2012) 169–216.
- [8] M. Takht Ravanchi, T. Kaghazchi, A. Kargari, *Desalination* 235 (2009) 199–244.
- [9] R. Chandra, S. Yadav, R.N. Bharagava, V. Rai, *World J. Microbiol. Biotechnol.* 27 (2011) 2939–2947.
- [10] S.Y. Yuan, S.H. Wei, B.V. Chang, *Chemosphere* 41 (2000) 1463–1468.
- [11] Vinodgopal K. and Kamat PV, *Environ. Sci. Technol.*, 1995, 29: 841.
- [12] Yu J.G., *Rare Met.*, 2004, 23: 289.
- [13] Xie Y.B. and Yuan C.W., *Rare Met.*, 2004, 23: 20.
- [14] X. Zhang, F. Wu, Z. Wang, Y. Guo, N. Deng, *J. Mol. Catal. A: Chem.* 2009, 301, 134–139.
- [15] G. Wang, F. Wu, X. Zhang, M. Luo, N. Deng, *J. Hazard. Mater.* 2006, 133, 85–91.
- [16] A. B. Zaki, M. Y. El-Sheikh, J. Evans, S. A. El-Safty, *Polyhedron* 2000, 19, 1317–1328.
- [17] E. M. Rodríguez, B. Núñez, G. Fernández, F. J. Beltrán, *Appl. Catal., B* 2009, 89, 214–222.
- [18] C. S. Lu, C. C. Chen, F. D. Mai, H. K. Li, *J. Hazard. Mater.* 2009, 165, 306–316.
- [19] M. Li, H. Y. Lin, C. P. Huang, *Nanostructured catalysts TiO₂ nanoparticles for water purification*, in *Nanotechnologies for Water Environment Applications* (Eds.: T. C. Zhang, Z. Hu, R. Y. Surampalli, R. D. Tyagi, K. C. K. Lai, I. M. C. Lo), American Society of Civil Engineers, Reston, VA 2009, pp 43–78.
- [20] P. Bansal, D. Sud, *Desalination* 2011, 267, 244–249.
- [21] M. Asiltürk, F. Sayilkan, E. Arpaç, *J. Photochem. Photobiol., A* 2009, 203, 64–71.
- [22] B.H. Jin, Y. He, J.C. Shen, etc. *Engineering Management Journal*, 1999, 5: 673-678.
- [23] G. Kumaravel Dinesh, S. Anandan, T. Sivasankar. *RSC Adv.*, 2015, 5: 10440-10451.