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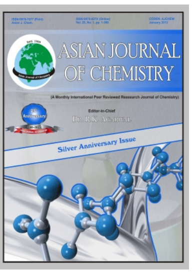

Effection of Chlorine-Doped TiO_2 Photocatalysts for Photocatalytic Activity

XINLIN LIU[1], PENG LV[1], GUANXIN YAO[1], YAN YAN[2], PENGWEI HUO[2] and YONGSHENG YAN[2,*]

[1]College of Material Science and Engineering, Jiangsu University, Zhenjiang 212013, P.R. China
[2]College of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, P.R. China

*Corresponding author: Fax: +86 511 88791108; Tel: +86 511 88790187; E-mail: xiaoliu1117@126.com

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The photocatalyst Cl-TiO_2 is prepared using the sol-gel method. The light absorption of the Cl-TiO_2 red shifts and extended the absorption spectrum ($\lambda > 400$ nm). The photocatalyst of Cl-TiO_2 is characterized by the UV-visible diffuse reflection spectroscopy, scanning electron microscopy, X-ray powder diffraction and X-ray photoelectron spectroscopy. The photocatalytic activity of as-prepared samples was evaluated by degradation of ciprofloxacin under visible light irradiation, with degradation rate of 50.69 % in 1 h. The results show that the photocatalytic activity of the Cl-TiO_2 photocatalyst is lower than that of pure TiO_2. Our work highlights the simple way to modify TiO_2 photocatalyst for practical use.

Key Words: TiO_2, Chlorine-doped, Photocatalysis, Ciprofloxacin.

INTRODUCTION

In the past decades, semiconductor mediated photocatalytic oxidation and reduction offers a potentially facile and economical method for removing inorganic and organic pollutants from wastewaters, air and soil[1-3]. TiO_2 is frequently used as photocatalyst to degrade a great deal of pollutants resulting from industrial and agricultural wastes because of its excellent properties. However, the large band gap of TiO_2-based photocatalyst makes it difficult to achieve a high photocatalytic efficiency unless the ultraviolet irradiation ($\lambda < 388$ nm) which only accounts for the energy of *ca.* 4 % in solar radiation was performed. In order to overcome these defects, many studies have been performed several works reported that doping of TiO_2 with nonmetallic elements, such as nitrogen[4-7], sulphur[8], carbon[9] and halogen element[10] to shift the optical absorption edge of TiO_2 towards longer wavelength for the enhancement of the photocatalytic activity under visible-light irradiation.

In the present work, the chlorine doped titania photocatalyst with high photocatalytic performance under visible light was prepared using the sol-gel method. The prepared samples were characterized by X-ray powder diffraction, X-ray photoelectron spectroscopy, UV-visible diffuse reflection spectroscopy, scanning electron microscopy. The photocatalytic performance was evaluated by means of the degradation for ciprofloxacin (CIP) under visible light illumination.

EXPERIMENTAL

In this study, titanium isopropoxide was chemically pure and others were analytically pure. All chemicals were used without any further purification. Water used was deionized water.

In a typical synthesis, 10 mL titanium butoxide was added dropwise into 100 mL absolute ethanol (99.9 %, Merck) under magnetic stirring for 0.5 h at ambient temperature. Then 100 mL of 1 mol/L HCl was added dropwise into the above solution, followed by stirring for 6 h and aging 2 h to obtain the gel. The gel was dried at 70 ºC for about 10 h in an oven, ground into fine powder and calcinated at 200, 300, 400, 500, 600 and 700 ºC for 4 h in a muffle furnace under air atmosphere to obtain the final products. The final samples were used as the photocatalysts for the evaluation of photocatalytic activity and characterization.

General procedure: The photodegradative reaction of ciprofloxacin (CIP) was carried out at 308 K in a homemade photochemical reactor under visible light. The photochemical reactor contains 0.1 g catalyst and 10 mg/L of 100 mL ciprofloxacin solution. To determine the initial absorbency of samples, kept the reactor into darkness for 0.5 h to reach absorption equilibrium. Then turned on the lamps and open the magnetic stirring apparatus. The photochemical reactor was irradiated with two 150 W tungsten halogen lamps (wavelength range 360-760 nm) which were located with a distance of 8 cm at one side of the containing solution. UV lights with wavelengths less than 420 nm were removed by a glass filter. The sampling analysis was conducted in 10 min interval. The photocatalytic degradation ratio was calculated by the following fomula:

$$\text{Degradation ratio (DR)} = \left[\left(\frac{1-A_i}{A_0}\right)\right]\times 100\,\% \qquad (1)$$

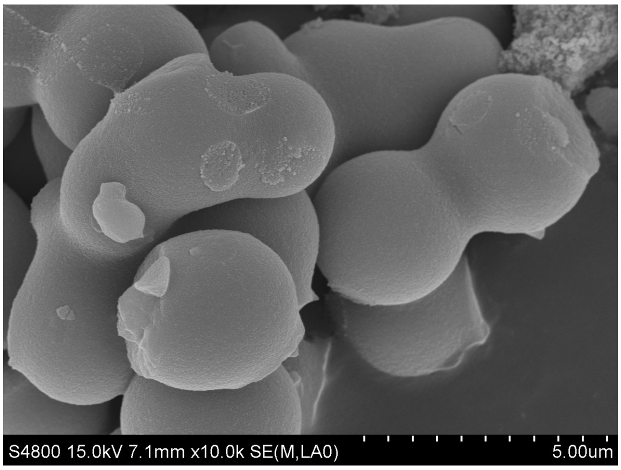
A_0 is the initial absorbency of ciprofloxacin that reached absorption equilibrium, while A_i is the absorbency after the sampling analysis.

Detection method: The SEM images were examined with S-4800 scanning electron microscopy with EDS (HITACHI, Japan). X-Ray diffraction (XRD) technique was used to characterize the crystal structure. In this work, XRD patterns were obtained with a D8 ADVANCE X-ray diffractometer (Bruker AXS Company, Germany) equipped with Ni-filtrated CuK_α radiation (40 kV, 30 mA). The 2θ scanning angle range was 10-90º with a step of 0.04º/0.4 s. X-Ray photoelectron spectroscopy (XPS) data was recorded with a PHI5300 spectrometer using AlK_α (12.5 kV) X-ray source. UV-VIS diffuse reflectance spectra (UV-VIS DRS) of the photocatalyst powder was obtained for the dry-pressed disk samples using spectrometer Specord 2450 (Shimadzu, Japan) equipped with the integrated sphere accessory for diffuse reflectance spectra, using $BaSO_4$ as the reflectance sample.

RESULTS AND DISCUSSION

SEM Measurement: Fig. 1 shows a typical scanning electron microscopy (SEM) image of Cl-TiO_2 at 500 ºC. The crystallites are spherical particles with a particle size of *ca.* 20-30 μm, they flock together, but the spheric feature is obvious. We may conclude that Cl doping made no obvous change in the morphology of P25 TiO_2.

XRD Measurements: The structure characterizations of the as-prepared samples were performed using X-ray diffraction. As shown in Fig. 2, (Cl-TiO_2) samples with low calcination temperatures have no obvious peak, with the increasing calcined temperature, the rate of rutile phase increases and after 700 ºC calcinations, rutile phase is predominant over the anatase phase. The phase change of crystal structure by calcination greatly destroyed the p-n bond between anatase and rutile phases and this may impact the catalytic action of Cl-TiO_2. Fig. 3 shows the powder X-ray diffraction (XRD) patterns of the undoped TiO_2 and as synthesized Cl-TiO_2 powders at 500 ºC. There no new peaks were observed, suggesting the doping amount is too little to be observed.



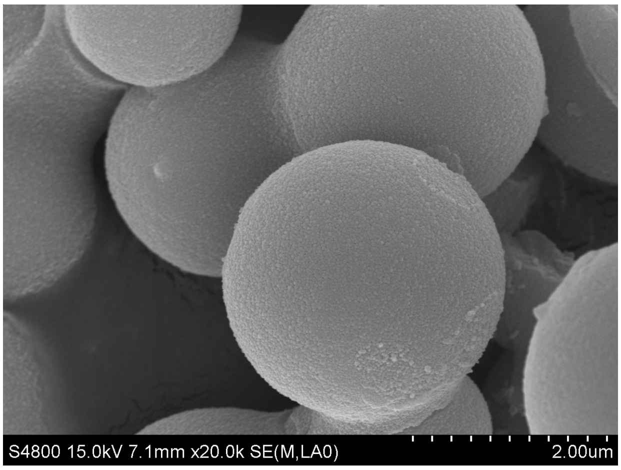


Fig.1. SEM images of Cl-TiO_2 at 500 ºC

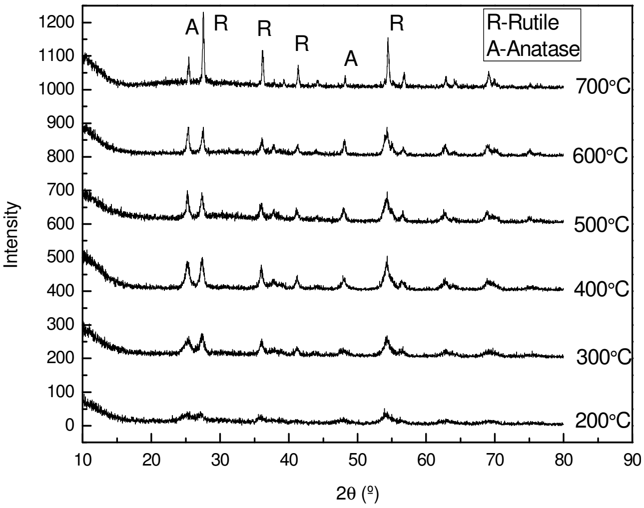


Fig. 2. XRD patterns of Cl doped samples with different calcination temperature

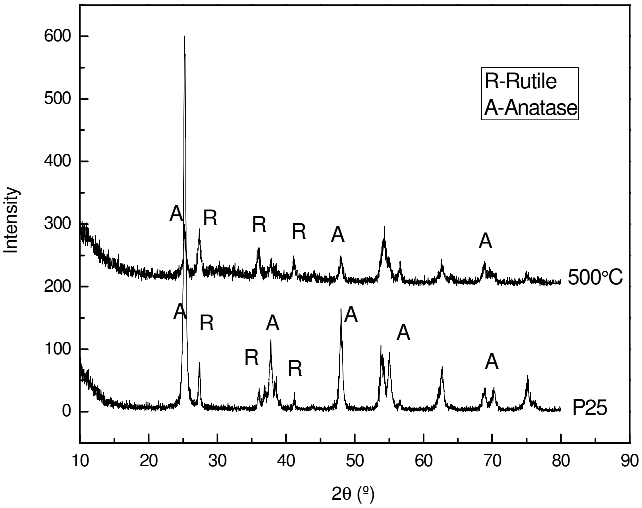


Fig. 3. XRD patterns of Cl doped sample at 500 ºC and P25

UV-visible diffuse reflectance spectrum of Cl-TiO_2: The energy band structure played a key role in determine the photocatalytic activity of semiconductor, the UV-visible diffusion reflection spectra studies were performed. Fig. 4 shows the UV-visible diffuse reflection spectroscopy of the Degussa P-25 and the chlorine-doped TiO_2, respectively. From which we can clearly see that the doping greatly increased the absorption of visible light of samples compared with P25 TiO_2 and made a red shift to the absorption edge. All that means Cl doped made a great improvement on the absorption of visible light and decrease the band gap energy.

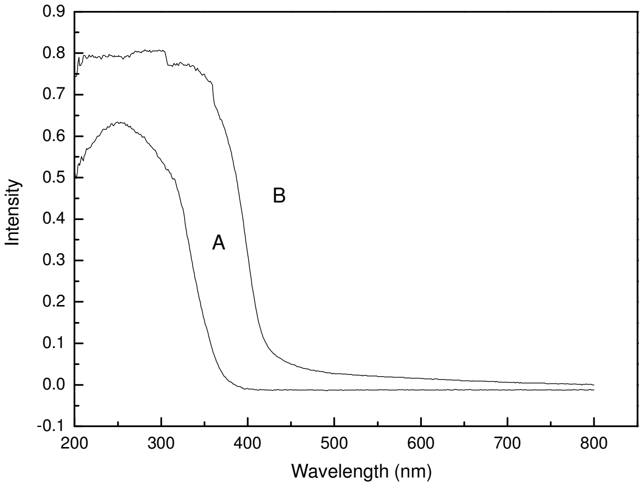
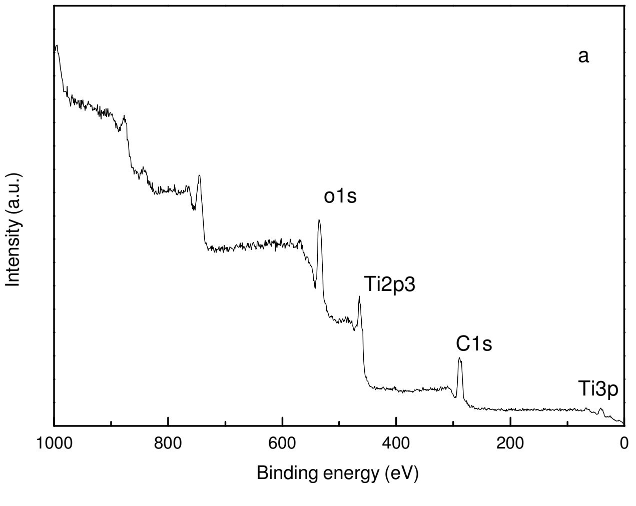


Fig. 4. UV-VIS diffuse reflection spectra of photocatalysts A-Degussa P-25; B-chlorine-doped TiO_2 at 500 °C

XPS of Cl-TiO_2: Fig. 5a shows the XPS survey spectrum of the Cl-TiO_2. The peaks related to Ti, O, C elements. Fig. 5b give the high-resolution XPS spectrum of Cl 2p region around 199 eV. The peak around 199 eV is corresponding to the Cl 2p3, which reveals the existence of Cl ion[11]. Under the calcination temperature both HCl and $TiCl_4$ cannot exist in the sample, so chlorine must enter into the crystal lattice and replace oxygen and exist as anion species.

Photocatalytic activity of chlorine-doped TiO_2 under visible light irradiation: The photocatalytic activity of Cl doped TiO_2 were evaluated by the photodegradation of 10 mg L^{-1} aqueous solution of ciprofloxacin. Fig. 6 shows the photocatalytic degradation curves of of Cl-TiO_2 calcined by different temperatures. It can be find that calcined sample at 500 °C possess the highest activity with the degradation rate of 50.69 % in 1 h, but which is lower than undoped TiO_2 (Fig. 7). This may results from destroy of p-n bonds between anatase and rutile phases of P25 TiO_2 by the calcination, which was confirmed by the XRD study. The heterojunction between p-type and n-type semiconducters can act as seperaters of photogenerated electron-hole pairs by p-n bonds. The Cl doped TiO_2, on the one hand, generates oxygen vacancies that are the recombination centres of electron-hole pairs and destroy the heterojunction equilibrium from anatase and rutile phases of TiO_2. Therefore, this sample shows the low photocatalytic activity.



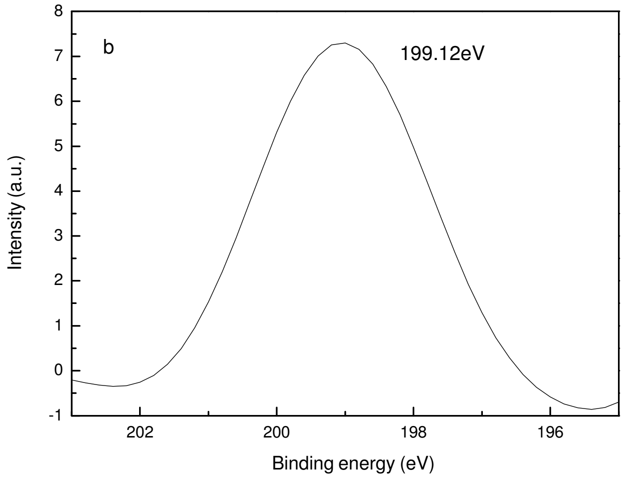


Fig. 5. (a) XPS spectra of Cl-TiO_2 at 500 °C and high resolution scanning XPS spectra of (b) Cl2p

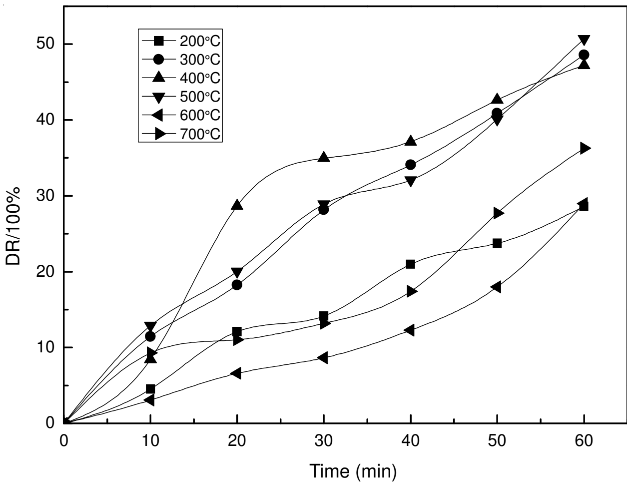


Fig. 6. Degradation rate of Cl-TiO_2 calcined by different temperatures

Conclusion

A novel chlorine-doped titanium dioxide photocatalyst with visible light response was prepared by sol-gel method. Our photocatalysts show apparent differences of photocatalytic activities in the degradation of ciprofloxacin, the highest degradation rate is 50.69 % of Cl-TiO_2 at 500 °C and which is still lower than 38 % of P25 TiO_2. This is supposed to because of the decrease in specific area and the destruction of p-n bond between the rutile and anatase phases, but the absorption of light already has been enhanced by Cl-doped.

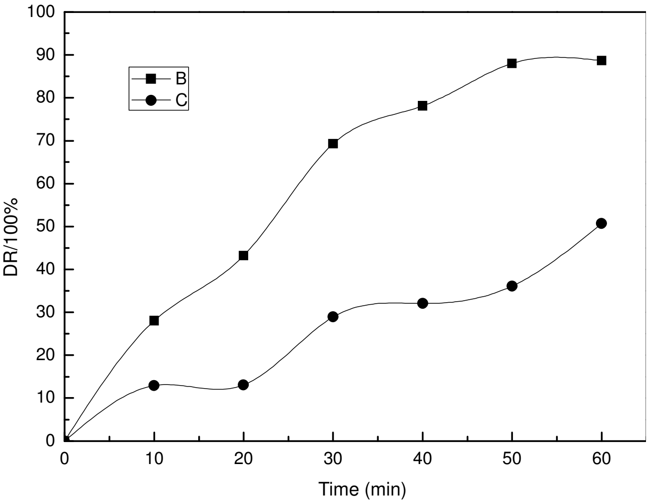


Fig. 7. Degradation rate of undoped TiO_2, Cl-TiO_2 at 500 ºC

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