Preparation and Visible-light Photocatalytic Activity of $Pt/TiO_{2-x}N_y$

Rui Liu[1, a *], Wein-Duo Yang [2,b] and Hui-Yi Tsai[3,c]

[1] Institute of Petrolem and Commodity, Harbin University of Commerce, Harbin;150076, China

[2] Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 807, Taiwan

[a]57776806@qq.com, [b]ywd@cc.kuas.edu.tw, [c]liurui19992007@163.com

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Abstract. $Pt/TiO_{2-x}N_y$ film has been synthesized successfully through the sol-gel method and spin coating method. The roughness and absorption wavelength were analyzed by atomic force microscopy (AFM) and ultraviolet and visible spectrophotometer(UV-vis). X-ray photoelectron spectroscopy(XPS) showed that the elements contain Pt, N, Ti and O. Moreover, the photocatalytic degradation of methylene blue demonstrate that $Pt/TiO_{2-x}N_y$ film is much higher than $TiO_{2-x}N_y$.

Introduction

TiO2 is an important functional inorganic material due to good stability, strong oxidizing power, low cost and non-toxicity [1]. TiO2 as a semiconductor has excellent photo-catalytical properties, which can be excited by ultraviolet light [2, 3]. Most scholars [4-8] have found that N-doping is the most promising path towards photo-catalytical applications. Nitrogen ions substituted oxygen atoms in the TiO2 lattice and thus the band-gap energy are narrower compared with TiO2, as a result, higher photo-electrochemical efficiencies can be obtained. In addition, deposition of noble metals also become of current importance for maximizing the photocatalytic efficiency. The noble metals such as Pt deposited or doped on the TiO2 surface act as electron traps and thus promote the separation of electron–hole pairs. Despite the positive attributes, there are also a few defects for TiO2nanotubes in photocatalysis, which are similar to those of TiO2 films. So it is necessary to follow the proven methods to enhance its photocatalytic activity. In this paper, we report sol-gel method and spin coating method to synthesize Pt/TiO2-xNy film. The performance of photocatalytic degradation are improved greatly.

Experimental section

Synthesis of $Pt/TiO_{2-x}N_y$ films. Titanium isopropoxide [Ti(O-i-$C_3H_7)_4$, density 0.995 g cm^{-1}, purity 98%] was reacted with acetylacetone to obtain a Ti-acetylacetonate precursor. Iso-propyl alcohol was applied for solvent, and Hexadecyltrimethylammonium bromide (CTAB) of surfactant used as template. In the reaction, water and hydrochloric acid were added to the mixture, and stirred vigorously. To determine crystal phase, the samples were heated at 300℃-800℃ at normal atmospherical condition to produce a yellowish powders. To obtain $Pt/TiO_{2-x}N_y$ film, the $TiO_{2-x}N_y$ coating was formed on the glass substrate in the K_2PtCl_6 solution by a dip-coating method, and then the samples were calcinated at 500℃-550℃ for 3 h.

Characterization analysis. The surface roughness was analyzed by atomic force microscopy (BASO-AFM). X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD) patterns were obtained using a monochromatic Al-anode X-ray gun. The UV–vis DRS spectra (Perkin Elmer; Lambda 35) measurements of the samples were collected as the optical absorption spectra using an UV–vis spectrophotometer.

Photo-catalytic measurements. A reactor, irradiated by the light source placed above the methylene blue solution at a certain position, was utilized to perform the photo-catalytic experiments.

The volume of the reactor was 250 ml. A369 nmUV lamp was used as the light source and 1×1 mm^2 of $TiO_{2-x}N_y$ film was putted into 50 ml of 9 ppm methylene blue solution to measure the photodegradation activity of as-prepared photo-catalyst. The photodegradation runs lasted several hours and samples were taken for examination during the interval of degradation. The concentration of methylene blue was measured at the maximum absorption wavelength of 664 nm by a HITACHIU-2800 UV–vis spectrophotometer.

Results and discussions

Figure 1 shows the AFM images of $TiO_{2-x}N_y$ and $Pt/TiO_{2-x}N_y$ films. The average roughness are 28 and 39 for $TiO_{2-x}N_y$ and $Pt/TiO_{2-x}N_y$ films, respectively. The higher roughness factor indicates that the $Pt/TiO_{2-x}N_y$ films exhibited a higher specific surface area.

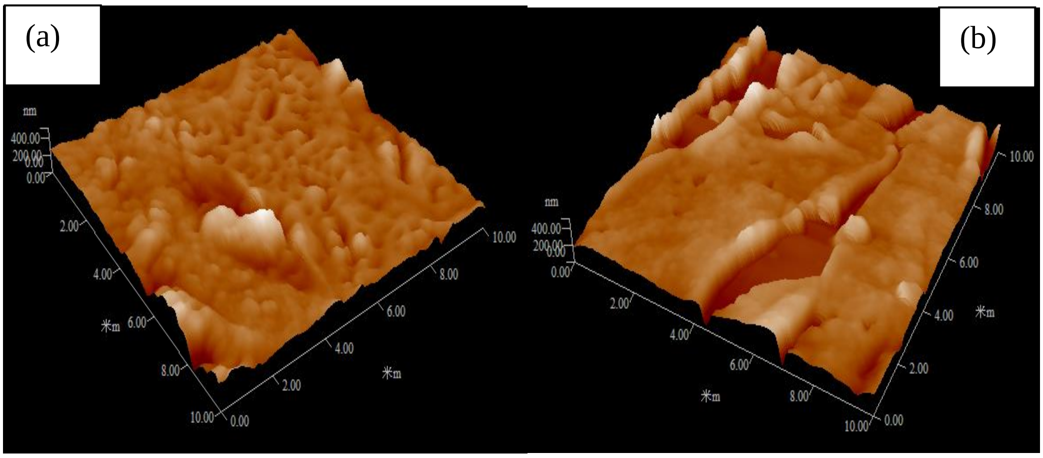
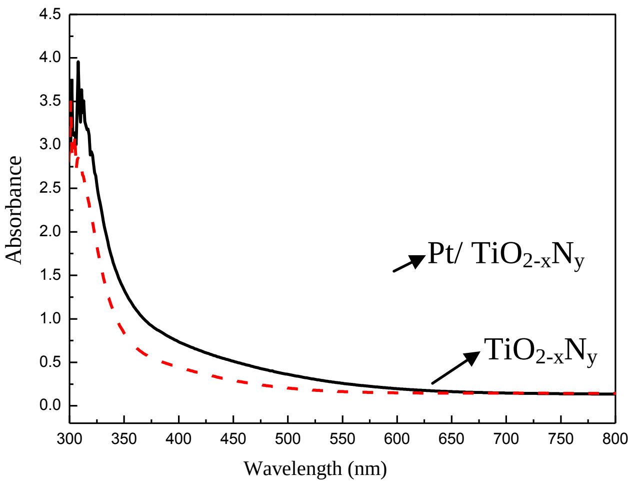


Figure. 1 AFM analysis of (a) $TiO_{2-x}N_y$ and (b) $Pt/TiO_{2-x}N_y$ films.

Figure. 2 shows diffuse reflectance UV-vis spectroscopy of $TiO_{2-x}N_y$ and $Pt/TiO_{2-x}N_y$ films with a wavelength range of 300-800 nm. An obvious red-shifts comparing with $TiO_{2-x}N_y$ film may be owing to differences in the surface state. It is because that existence Pt can modify the optical properties, to extend the range of excited spectrum and favor the absorption light in visible region.



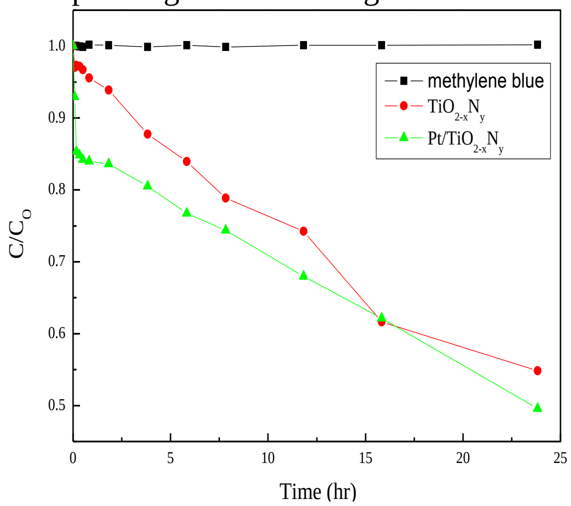


Figure.2 UV-vis RDS spectra of $TiO_{2-x}N_y$ and $Pt/TiO_{2-x}N_y$ films.

Figure. 4 The photodegradation reaction of methylene blue by $Pt/TiO_{2-x}N_y$ and $TiO_{2-x}N_y$ films

The chemical components of $Pt/TiO_{2-x}N_y$ films were examined by XPS, as shown in Figure 3. Figure 3 (A) shows the spectra of $Pt/TiO_{2-x}N_y$ films over the wide scan range. The elements of $Pt/TiO_{2-x}N_y$ films contain Pt, N, Ti and O. High resolution XPS spectra of the Pt for the surface of $Pt/TiO_{2-x}N_y$ films were shown in Figure 3 (B). The XPS peak of Pt 4f around 70.9 eV, was clearly observed.

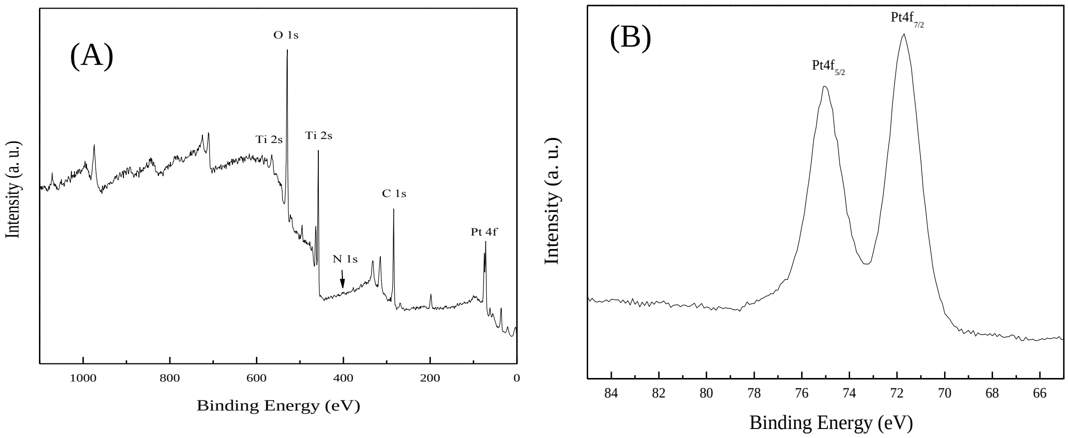


Figure. 3 XPS of $Pt/TiO_{2-x}N_y$ films in (A) the wide scan range, (B) the Pt 4f level peak.

The concentration of methylene blue was determined by a UV-vis spectrophotometer. The photo-catalytic decolorization of methylene blue is first-order reaction and its kinetics can be expressed as followed [Eq. (1)] [9,10]:

$$\ln\frac{C}{C_0} = -kt \qquad \text{Eq. (1)}$$

Where k is the apparent reaction rate constant, C_0 and C are the initial concentration and the reaction concentration of methylene blue, respectively.

The photodegradation reaction of methylene blue by $Pt/TiO_{2-x}N_y$ film were measured as shown in Figure 4. Clearly, the photocatalytic degradation of methylene blue demonstrate that $Pt/TiO_{2-x}N_y$ film is much higher than $TiO_{2-x}N_y$.

Conclusions

$Pt/TiO_{2-x}N_y$ film has been synthesized successfully through the sol-gel method and spin coating method. The roughness of $Pt/TiO_{2-x}N_y$ film is much higher than $TiO_{2-x}N_y$ film. XPS showed that the elements contain Pt, N, Ti and O.The photocatalytic degradation experiments were examined and they demonstrated that methylene blue remarkably enhanced the degradation for $Pt/TiO_{2-x}N_y$ film compared with $TiO_{2-x}N_y$ film.

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