



Preparation of W, N Codoped TiO₂ with Enhanced Visible Light Response

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The W, N co-doped TiO₂ nanoparticles have been synthesized by sol-gel method. The prepared photocatalysts were characterized by X-ray diffraction, field emission scanning electron microscopy, Fourier transform infrared spectroscopy and diffuse reflectance spectra. The results showed that the codoped photocatalyst with a spherical shape exhibited a smaller size than the undoped titania. Compared to un-doped TiO₂, N-TiO₂ and P-25, the absorption edge of the W, N co-doped TiO₂ shifted to longer wavelength and its photocatalytic activity for degradation of methyl orange under Xe-lamp (350 W) was higher.

Key Words: TiO₂, Co-doped, Visible light, Photocatalytic activity.

INTRODUCTION

TiO₂ has been widely used as an efficient photocatalyst for the decomposing organic pollutants in aqueous systems and in air owing to its inexpensiveness, strong oxidizing power, non-toxicity and long-term photostability¹⁻⁴. Upon irradiation with light energy greater than or equal to the band gap, the electrons and holes are generated and trapped on the surface of the photocatalyst, producing reactive oxygen species such as •OH to degrade organic pollutions. However, it can be activated only under UV light irradiation because of its large energy band gap (3.2 eV for anatase TiO₂)⁵. For further improvement of effective utilization of the solar energy, considerable efforts have been made to shift its photocatalytic activity to the visible-light region. To increase the visible-light absorption of TiO₂ materials, the doping of a third element such as nonmetal ions (C⁶, S⁷, N^{8,9}, F¹⁰) to reduce the energy band gap, or a transition metal Cr¹¹, V¹², Fe¹³, W^{14,15} to enable the separation of photogenerated electron-hole pairs and increase the light absorption.

One of the most promising ideas to extend the light-absorbing property of TiO₂ and to enhance its photocatalytic efficiency is the codoping of TiO₂ with metal and nonmetal elements. This method has several advantages, including narrowing the energy band gap, the improvement of charge separation, the increase in the lifetime of the charge carrier. Xu *et al.*¹⁶ had prepared Eu, N-co-doped TiO₂ and the as-prepared TiO₂ had a stable photocatalytic activity for reactive brilliant red X-3B under visible-light irradiation ($\lambda > 400$ nm). Among nonmetal elements, N-doped TiO₂ is considered to be

one of the most effective photocatalysts and it has been investigated widely¹⁷. Among transition metal elements, W⁶⁺ ion can substantially reduce the recombination process between dopant cation and TiO₂ matrixes¹⁴. It seems to be an interesting dopant in order to extend the absorption threshold towards visible range.

Furthermore, to our best of knowledge, the preparation of tungsten and nitrogen-codoped titania has never been reported. In the present research, a novel tungsten and nitrogen-codoped titania photocatalyst was synthesized through a sol-gel method. The phase compositions and crystalline structure were analyzed.

EXPERIMENTAL

Preparation of photocatalyst samples: All of the chemicals were analytical grade and used without further purification. In a typical process of preparing W and N-codoped titania by sol-gel method at room temperature with the following procedure: tetrabutyl titanate (10 mL) was dissolved into ethanol (30 mL) followed by stirring for 0.5 h (solution A). Then, acetylacetone (0.5 mL) was dropped into solution A, after 3 h solution B that contains ethanol (10 mL), appropriate amount ammonium tungsten, ammonium nitrate and distilled water (10 mL) was added drop-wise into solution A. After adjusting the pH value with nitride acid to 2-3, the mixture solution was stirred for an additional 3 h. The resulting transparent aged 24 h, then baked at 353 K to gradually form a precursor gel, then grounded into powder. The powders were calcined at 823 K for 3h, then grounded in agate and screeded to obtain W,N-codoped titania powders finally. For comparison,

W-doped sample, N-doped sample and pure titania were prepared through the same method, without adding the corresponding dopants.

Characterization: The morphology of the prepared TiO₂ powder was characterized by the field emission scanning electron microscopy (FE-SEM; SUPRA35, Holland). The crystalline structure of samples was measured by X-ray diffraction (XRD, D8 ADVANCE, Germany) using Cu-K_α radiation with rotating anode at 40 kV, over the range of 20-80° (wave length at 0.15406 nm and K was 0.89). IR spectra of the prepared TiO₂ were measured on FT-IR spectrometer (NEXUS 470) by the transmission method using the KBr pellet technique. A UV-VIS spectrophotometer (Tianmei UV-2600) was used to record the diffuse reflectance spectra (DRS) of samples.

Photocatalytic experiments: The photocatalytic activities of W, N, co-doped TiO₂ were evaluated by methyl orange decomposition under Xe-lamp (350 W, the light is close to the natural light). Catalyst powder (100 mg) was dispersed in methyl orange solution (25 mg/L, 100 mL). The photocatalytic activity of catalyst was tested after stirring the aerated suspension for 1 h in darkness to achieve adsorption-desorption equilibrium. At the defined time interval, 5 mL of suspension was removed and centrifuged, the concentration of aqueous methyl orange can be instead of absorbance of aqueous methyl orange, which was determined with a UV-VIS (UV9600) spectrophotometer by measuring the absorbance at 464 nm (λ_{\max} for methyl orange). The degradation rate of aqueous methyl orange is calculated by followed formula: $X = (A - A_0) \cdot 100\% / A_0$ (X : the degradation rate; A_0 : the absorbance of initial aqueous methyl orange; A : the absorbance of final aqueous methyl orange).

RESULTS AND DISCUSSION

Crystalline structure analysis: The crystal structure of titanium dioxide greatly affects its photocatalytic activity. Amorphous titania seldom displays photoactivity due to some nonbridging oxygen in bulk titania. Additionally, different crystal phases show different photocatalytic activity. Generally, the anatase phase is reported to have the highest photocatalytic activity. Therefore, the phase characterization of W, N-codoped titania, N-doped titania and pure TiO₂ was investigated by XRD (Fig. 1). It can be seen that all the samples have an anatase structure. No hint of tungsten-containing phase could be detected by the XRD. It may be attributed to the resemblance in ionic radius between tungsten and titanium ions ($r(\text{Ti}^{4+}) = 0.061$ nm, $r(\text{W}^{6+}) = 0.062$ nm). With calcination treatment at high enough temperature, the W⁶⁺ ion would likely enter into the titania crystal lattice structure. Therefore, W atoms could replace the Ti atoms inside the lattice. Generally, the crystallite size is calculated by the Scherrer formula

$$D = K\lambda / (\beta \cos \theta) \quad (1)$$

where D is the crystalline size, λ the wavelength of X-ray radiation (0.1541 nm), K the constant usually taken as 0.89 and β is the peak width at half-maximum height after subtraction of equipment broadening, $2\theta = 25.4^\circ$ for anatase phase titania. Using eqn. 1, it is estimated that the average particle sizes were 22.58, 27.31 and 26.95 for W, N-codoped titania, N-doped titania and pure titanium dioxide, respectively.

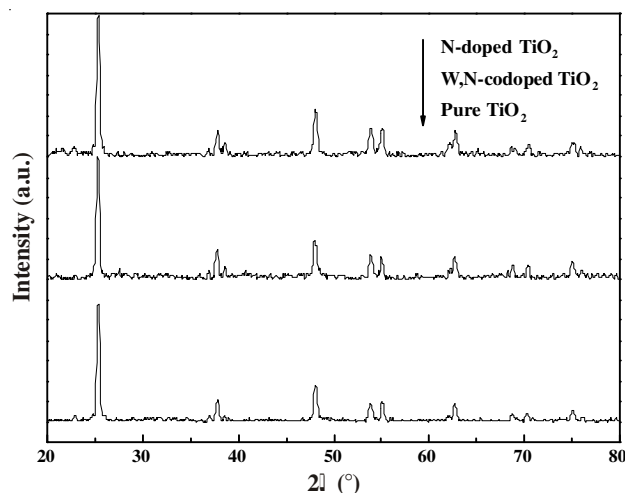


Fig. 1. XRD patterns of the as-prepared powders

Morphology analysis: The morphology of the W, N-codoped titania particles characterized by FE-SEM is given in Fig. 2. It is noteworthy that the particles with a homogeneously spheroidal shape distributed on the support and the size is about 24.55 nm. It is similar to the result calculated by XRD analysis. Picture also showed agglomeration existed in the powders. Mainly due to the synthetic process of ultrafine TiO₂, the particles formed hydrogen bonds between the water molecules of surface with hydroxyl radical and the dewatering process may result in the formation of chemical bonds. Moreover, the reunion of ultra-fine powders may be caused by the interaction of a variety of results, such as capillary adsorption, crystal bridge, etc. Therefore, there will be some agglomeration.

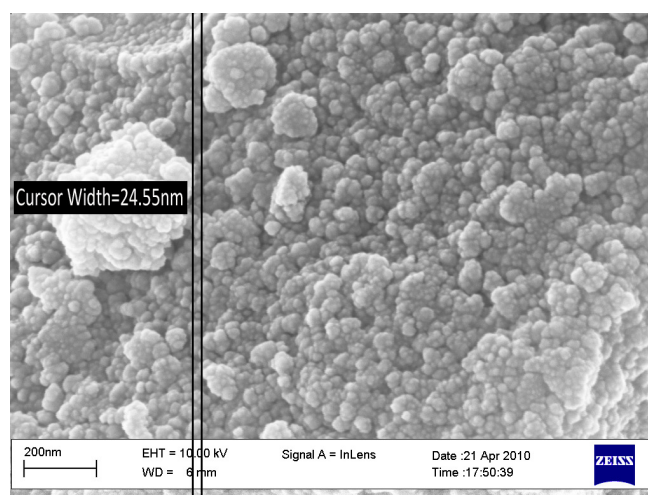


Fig. 2. FE-SEM image of W, N-codoped titania

Diffuse reflectance spectra analysis: It is well known that the photocatalytic activity of a semiconductor is related to its band-gap structure. The UV-VIS spectra of the TiO₂ samples are shown in Fig. 3. The onset of the absorption spectrum of pure TiO₂ appears at about 380 nm which matches well with the intrinsic band gap of anatase (3.2 eV). Furthermore, it can be seen that there is a significant shift in the onset absorption toward the higher wavelength for the W,N-codoped sample (470 nm) and N-doped titania (448 nm). Specially, the

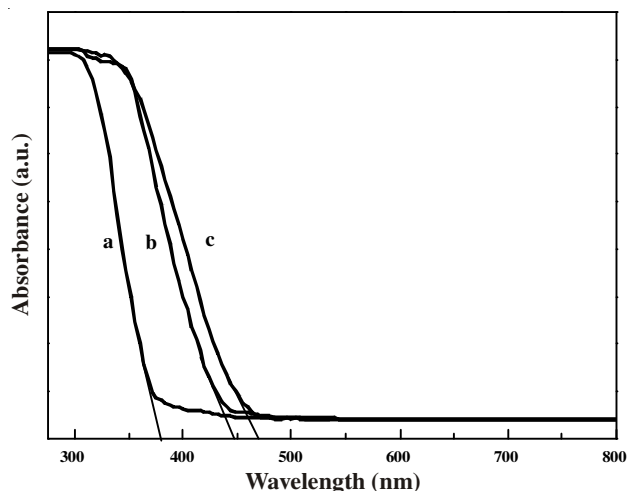


Fig. 3. DRS spectra of (a) pure titania; (b) N-doped titania; (c) W,N-codoped titania

codoped sample exhibits a greater red shift than the N-doped sample. It is demonstrated that W,N-codoped titania could greatly improve the absorption of visible light. The reason may be due to the N and W dopant. As known, the band gap could be narrowed by the N dopant¹⁷. At the same time, N dopant could induce oxygen vacancy on the surface of TiO₂, which is beneficial to strengthen the absorption of visible light. Moreover, WO₃ possessed the lower levels than TiO₂. W dopant was introduced could change the levels of the transition of electron, which could cause the absorption region red shift.

FT-IR spectrum analysis: The IR spectra of the TiO₂ samples are shown in Fig. 4. The peaks were assigned to the OH binding and stretching of water at 1630 and 3430 cm⁻¹, respectively. There is no peak at 1125-1035 cm⁻¹ defining for Ti-O-C vibrations showed that the tetrabutyl titanate hydrolysed completely. There are also no peaks at 2920 and 2858 cm⁻¹, which was assigned to -CH₃ and -CH₂ stretching vibration, implied that the organic completely decomposed. In the spectrum a band is visible at 520 cm⁻¹ that is assigned to Ti-O vibration. Both doped samples exhibited wide peaks compared to pure titania at 900-400 cm⁻¹, which could be attributed to Ti-N (532-565 cm⁻¹) coincided with Ti-O broad band absorption. There was little difference between W, N-codoped titania and N-doped titania at 400-900 cm⁻¹. It could be attributed to the W-O-Ti (750 cm⁻¹) vibration. However, it is not observed, which might be ascribed to its low doping content and high dispersion.

Photocatalytic activity: Fig. 5 shows the photocatalytic decomposition of methyl orange under the irradiation of Xe lamp for the powders prepared using sol-gel method. As shown in Fig. 5, it is obvious that the photocatalytic activity of W,N-codoped titania outclasses that of N-doped titania, P25 and pure titania (at the same conditions, it is shown in the Fig. 5 that little decomposition was detected for no catalyst). Approximately 92.3 % methyl orange were degraded in 2 h. The reason might be ascribed as follows: (1) the N dopant may induce the oxygen vacancy, which might generate Ti³⁺ or Ti²⁺ that plays an important role in the surface absorption process. Further, the lattice defects could be active centres of catalyst, which is beneficial to photocatalytic reaction. (2) The radius

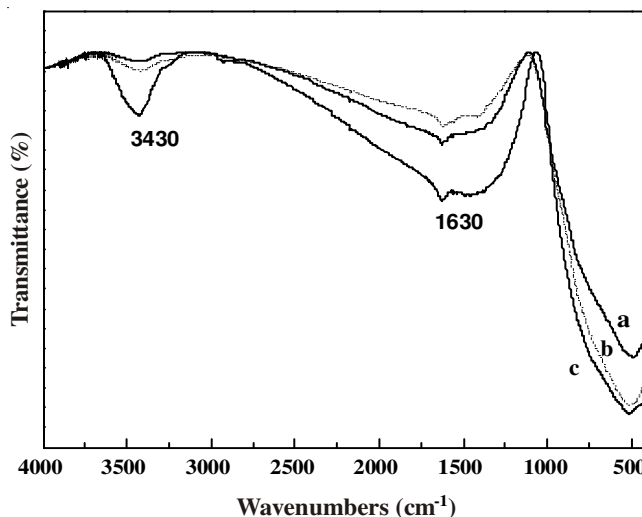


Fig. 4. FT-IR spectra of (a) pure titania; (b) N-doped titania; (c) W,N-codoped titania

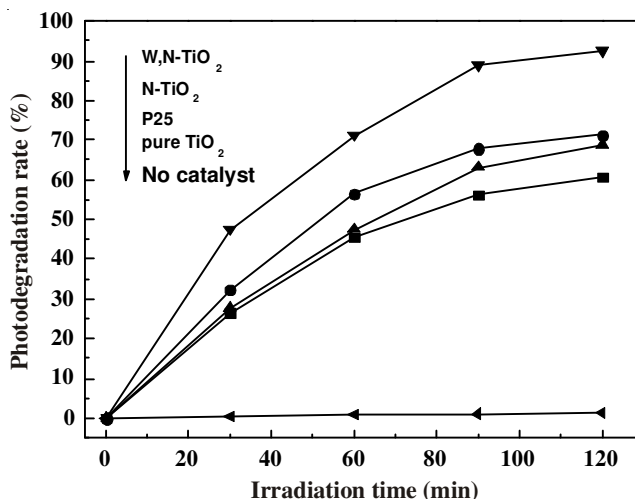


Fig. 5. Degradation rate curves of various samples under natural light irradiation

of W ion is close to Ti ion, therefore, Ti⁴⁺ could be replaced with W⁶⁺. W⁶⁺ can capture the electron and inhibit the electron-hole pair recombination effectively.

Conclusion

A novel W, N-codoped TiO₂ material was synthesized by sol-gel method. For comparison, N-doped TiO₂ and pure TiO₂ were also prepared by the same method. It can be seen that all the samples have an anatase structure. During doping with W and N atoms, the transformation from anatase to rutile was suppressed. It was found that the codoped photocatalysts exhibited smaller spheroidal shape particles about 22.6 nm. Furthermore, the absorbance spectra of W, N-codoped TiO₂ exhibited a significant red shift to the visible region. The photocatalytic activity of W, N-codoped TiO₂ under natural light was highly improved compared to N-doped TiO₂, P25 and pure TiO₂. The degradation rate for methyl orange was over 92.3 % within 2 h.

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