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# Tungsten and nitrogen co-doped $TiO_2$ nano-powders with strong visible light response

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## Abstract

A two-step method, combining with sol–gel and mechanical alloying (MA) method, was used to fabricate the tungsten and nitrogen co-doped $TiO_2$ nano-powders ((W, N) co-doped $TiO_2$ NPs). The (W, N) co-doped $TiO_2$ NPs showed strong absorbance in visible range, as long as 650 nm. Enhanced photocatalytic activities under visible light irradiation were also observed from the results of photodegradation experiments and chemical oxygen demand (COD) analysis. Physical, chemical, and optical properties of the samples were investigated. Possible reasons for the enhanced photocatalytic activities were analyzed based on the experimental results. Oxygen vacancies detected by electron spin response (ESR) spectra, acting as trapping agencies for electrons ($e^-$) to produce active oxygen species ($^\bullet O^{2-}$), were proved to be the main cause for the improved photocatalytic performances.

*Keywords:* $TiO_2$; Co-doped; Two-step method; COD

## 1. Introduction

Titanium dioxide ($TiO_2$) has been studied extensively as a kind of efficient photocatalyst for its excellent properties, such as non-toxicity, high thermal-stability and low cost [1–3]. However, $TiO_2$ photocatalysts can be excited only by expensive ultraviolet (UV) light, because of the large band gap of 3.0–3.2 eV [4]. In order to conserve energy and make full use of the solar energy, visible light is considered as an ideal exciting light source for $TiO_2$ photocatalysts. Thus, currently a hot research field on $TiO_2$ photocatalysts is to make the threshold of the absorption spectra red-shifted and enlarged, so that a high ratio of the usage of visible light can be conducted.

Visible light sensitive $TiO_2$ photocatalysts have been investigated by many researchers and several approaches have been proved to be effective to some extent. Modification of $TiO_2$ photocatalysts with metal ions was extensively studied [5–8]. A systematic study of metal ion doping in $TiO_2$ colloids was carried out by Choi et al. [9]. It was found out that the photoreactivity of $TiO_2$ colloids for both oxidation and reduction can be enhanced by doping with $Fe^{3+}$, $Mo^{5+}$, $Ru^{3+}$, $Os^{3+}$, $Re^{5+}$, $V^{4+}$ and $Rh^{3+}$ at 0.1–0.5 at%, while reduced photoreactivities were observed in $Co^{3+}$ and $Al^{3+}$ doped $TiO_2$ colloids.

Besides metal ions, some non-metal ions, such as C [10,11], N [12–14], S [15,16], F [17] and P [18] were also used as dopants in the modification of $TiO_2$ photocatalysts. Asahi et al. [12] prepared films and powders of $TiO_{2-x}N_x$ by sputtering the $TiO_2$ target in an $N_2$ (40%)/Ar gas mixture and annealing anatase $TiO_2$ powders in the $NH_3$ (67%)/Ar atmosphere, respectively. It was reported that the $TiO_{2-x}N_x$ samples were superior to its $TiO_2$ counterpart under visible light irradiation although both the samples showed similar UV activities, when methylene blue (MB) and gaseous acetaldehyde were chosen as photodegradation targets. First-principle calculations were also carried out to approximate the possibilities of non-metal doping.

Though there are a lot of literatures about the metal ions doped $TiO_2$ and the non-metal ions doped $TiO_2$, reports on the metal ions and non-metal ions co-doped $TiO_2$ photocatalysts are seldom. Sakatani et al. [19] prepared the metal ions and nitrogen co-doped $TiO_2$ powders by a polymerized complex

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method. Several metal ions were studied, including $K^+$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$, $Nb^{5+}$, $Fe^{3+}$, $Zn^{2+}$, and $Al^{3+}$. Of them all, the photocatalysts of $Sr^{2+}$ and nitrogen co-doped $TiO_2$ exhibited the highest activities in the decomposition of acetaldehyde under visible light illumination. It was suggested that the formation of paramagnetic N species at interstitial positions in the $TiO_2$ lattice was responsible for the visible light response of the catalyst.

In the present report, tungsten and nitrogen co-doped $TiO_2$ NPs were prepared. And the behavior of the (W, N) co-doped $TiO_2$ NPs in the photodegradation of methylene blue (MB) and sulfosalicylic acid (SSA) using visible light excitation was investigated. The study is intended to give a picture of physical and chemical properties of this kind of photocatalyst and the influence of the amounts of W and N on the photocatalytic reactions, which is a reference when synthesis of other metal and non-metal co-doped $TiO_2$ by this method.

## 2. Experimental

### 2.1. Preparation of (W, N) co-doped $TiO_2$

The (W, N) co-doped $TiO_2$ NPs were prepared by a two-step method. In the first step, tungsten doped $TiO_2$ nano-powders (W-doped $TiO_2$ NPs) were prepared by the sol–gel technique as follows. Tetrabutyl titanate (TTOB, 34 ml) and ethanol (EtOH, 88 ml) were mixed together with strong stirring for 30 min, and then 1.4 ml of nitrate ($HNO_3$, 70 wt%) was added. Consequently different amount of $Na_2WO_4$ aqueous solution was added drop-wise. The amount of W added varied from 0.5 to 10 wt%. After 2-day gelation at room temperature, the obtained gel was dried at 60 °C. The dried gel was then calcined at 600 °C to obtain the W-doped $TiO_2$ NPs.

In the second step, urea and the obtained W-doped $TiO_2$ powders were ball-milled together in a 50-ml agate vessel. The procedures were described firstly by Yin and co-workers [20]. Considering that the process parameters play an important role in the nature and kinetics of the product phase obtained by mechanical alloying (MA), most of the parameters, such as the milling temperatures, milling time, grinding ball diameter, ball-to-powder weight ratio and relative proportion of the reactants, were kept constant in the present work. Besides, no other process control agencies (PCA) were used. In the work, the weight ratio of W-doped $TiO_2$ and urea was 10:1, and the milling time was 5 h. After MA, the milled powders were calcined in the flowing $N_2$ atmosphere at 400 °C for 1 h to remove the residual urea.

### 2.2. Characterization

The purity and crystallinity of the prepared samples were examined by powder X-ray diffraction (XRD) using an X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The average crystallite size was calculated using the Scherre's equation [21].

Raman spectrum analysis was conducted on a Labram HR800 Laser Raman Spectroscopy made by Jobin Yvon, France, using the 632.8-nm He–Ne ion laser as an excitation source. The laser power on the sample was 10 mW.

Morphologies of the samples were investigated on a JEOL 2010 Field Emission Electron Microscope. The samples were dispersed in ethanol solution using ultrasonic, and then dropped on carbon-coated copper collars.

$N_2$ adsorption–desorption analysis was conducted on an ASAP 2010 Surface Area and Porosity Analyser made by Micrometritics Instrument Corporation, USA, to get the Brunauer–Emmett–Teller (BET) surface area, mesopore volume and size distribution by Barrett–Joyner–Halenda (BJH) method.

X-ray photoelectron spectra (XPS) of the samples were measured using a PHI5300 photoelectron spectrometer system with an Al Kα source (1486.6 eV). The shift of binding energy due to relative surface charging was corrected using the C 1s level at 284.6 eV as an internal standard of the surface adventitious carbon.

FTIR spectra on pellets of the samples mixed with KBr were recorded on a MATNA-IR 560 (made by Nicolet, USA) spectrometer.

The electron spin response (ESR) spectra were recorded at room temperature using a JEOL JES-FE3AX ESR spectrometer.

UV–vis spectrum analysis was measured using a Jasco V-550 spectrophotometer.

### 2.3. Photocatalytic reactions

The photocatalytic activities of the received samples were evaluated by measuring both the photodiscoloration of MB and the photodegradation of SSA under visible light. A 13-W fluorescent lamp was used as the visible light source. About 95% of the radiant energy in the electromagnetic spectrum of the fluorescent lamp is in visible light region, and the other 5% in the ultraviolet light region. A light filter was employed to exclude the disturbance of ultraviolet light. The distance between the strip lamp and fluid level was kept as 10 cm. The initial concentrations of the solutions of MB and SSA were 20 and 40 mg/l, respectively. And the amounts of the samples added into the MB solution and SSA solution were 0.5 and 1 g/l, respectively. Before the light was on, the target solution was stirred for 30 min in the dark until adsorption-desorption balance was reached on the sample. Degussa P25 was used as a reference.

To evaluate the mineralization degree of the (W, N) co-doped $TiO_2$ samples in MB discoloration, COD analysis was conducted just after the photodiscoloration experiments. After the experiments, a proper amount of the remained solution was adopted and filtered by macromolecular films. Then, the clarified MB solution was analyzed according to the potassium dichromate method [22], and denoted as $COD_{Cr}$.

### 2.4. Labels of the prepared samples

The (W, N) co-doped $TiO_2$ samples were named as *n*-NWT series, and the W-doped $TiO_2$ were named as *n*-WT series,