



# Well-dispersed ultrafine nitrogen-doped TiO<sub>2</sub> with polyvinylpyrrolidone (PVP) acted as N-source and stabilizer for water splitting<sup>☆</sup>

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## ABSTRACT

In this paper, ultrafine nitrogen-doped TiO<sub>2</sub> photocatalyst with enhanced photocatalytic water-splitting properties was successfully fabricated via a solvothermal method. Herein, polyvinylpyrrolidone (PVP) was used as both nitrogen source and stabilizer. The enhancement in water-splitting process can be attributed to the doping of element nitrogen, which could supply an intermediate energy level and promote the separation of photo-excited holes and electrons. Moreover, this paper provides a new application of high-molecular polymer to synthesize solar-driven water-splitting photocatalysts.

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## 1. Introduction

As a common *n*-type semiconductor which has been investigated for more than 40 years, TiO<sub>2</sub> has attracted much attention because of its unique properties such as chemically stable, non-toxic, low-cost, high light conversion efficiency, favorable band edge positions, and biocompatibility. Since Fujishima and Honda first found TiO<sub>2</sub> to be an electrode to water splitting in 1972 [1], to date, many researchers have been broaden its application fields in diverse aspects like dye-sensitized solar cells (DSSC), water-splitting, organic pollutant photocatalysts and antibacterial materials [2–9]. As we all know, the band gap of TiO<sub>2</sub> (3.2 eV for anatase, 3.0 eV for rutile and 3.3 eV for brookite, respectively) is suitable for the absorbance of UV light, which only takes up 3%–5% of solar light [10,11]. That is a small proportion and makes the UV light-photocatalyst used with limitations under visible portion of solar spectrum. The ultimate goal of utilizing solar light as an abundant energy in the photocatalytic processes is still a hot topic. Otherwise, hydrogen is considered as a clean, renewable and attractive energy source to substitute for fossil fuels. In recent years, water splitting for hydrogen-evolution using semiconductors and light is one of the potential ways to support the future energy industry. Presently, the solar-to-hydrogen energy conversion efficiency is still too low. The main challenges are the rapid recombination of photo-generated electron-hole pairs and the poor response to the solar light.

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To pursue the better photocatalytic performance and a higher use of solar energy, doping TiO<sub>2</sub> with nonmetal elements such as carbon, nitrogen and sulfur can noticeably improve the photocatalytic activity of TiO<sub>2</sub> under visible light, which may contribute to the absorption edge of TiO<sub>2</sub> shift to the visible region and broaden the use of TiO<sub>2</sub> [12]. According to the report of Asahi [13], nitrogen doping is one of feasible ways which can enhance the photocatalytic activity of TiO<sub>2</sub> under visible light irradiation. Nitrogen atoms were considered to substitute for the lattice oxygen sites and were responsible for the visible-light activity. Furthermore, based on Tsetseris' density functional theory (DFT) calculations [14], N-doped TiO<sub>2</sub> can be easily formed at lower temperatures (100 °C–300 °C). During the past few decades, the synthesis of N-doped TiO<sub>2</sub> nanomaterials were achieved using aliphatic amines [15,16], NH<sub>4</sub>Cl [17,18], N<sub>2</sub>H<sub>4</sub> [19], NH<sub>4</sub>NO<sub>3</sub> [20], HNO<sub>3</sub> [21], ammonia [22,23] or urea [24,25] as nitrogen sources. In addition, polyvinylpyrrolidone (PVP), as a mild and non-toxic non-ionic high-molecular nitrogen containing polymer, was extensively used in synthesis of noble metal nanostructures such as gold [26], silver [27–29], palladium [30], platinum and rhodium [31]. To the best of our knowledge, no reports about PVP as nitrogen source to synthesize nano-semiconductors have been seen before.

In this work, we proposed a solvothermal strategy to synthesize N-doped ultrafine TiO<sub>2</sub> nanoparticles using polyvinylpyrrolidone (PVP), which act as both dopant and stabilizer. A form of Ti–O–N in the lattice of N-doped TiO<sub>2</sub> in XPS spectrum certified the role of dopant, and the well dispersion and ultrafine size of samples in TEM images showed the role of PVP as stabilizer. The photo-generated electrons and holes have been proved to separate efficiently after

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doping according to PL measurement. The N-doped TiO<sub>2</sub> nanocrystals exhibit a high H<sub>2</sub>-evolution rate from photocatalytic water splitting under simulated solar-light irradiation.

## 2. Experimental

### 2.1. Sample synthesis

TiCl<sub>4</sub> and PVP were purchased from Sinopharm Chemical Reagent Co. Ltd. (A.R.). And other normal reagents were used without any further purification. TiCl<sub>4</sub> was inhaled by a disposable dropper and kept in refrigerator before use (–18 °C). In a typical synthesis, different amounts of PVP were dissolved in 20 mL ethylene glycol (EG) with magnetic stirring. After the PVP was dissolved, the solution was stirred in an ice bath (about 4 °C) for another 2 h. Then 2 mL TiCl<sub>4</sub> was squeezed into the above solution quickly. The magnetic stirring was lasted for another 2 h. During this time the turbid mixture was gradually changed into transparent and light yellow. Finally, the above solution was transferred into a Teflon-lined stainless steel autoclave with a capacity of 80 mL. The autoclave was sealed and heated at 180 °C for 12 h. After the reaction the autoclave was cooled to room temperature naturally, and the resulting brownish mixture was washed and centrifuged with absolute ethanol for several times. After drying at 60 °C for 12 h, the light-grey powders were grinded by agate mortar and then kept for further use and characterization. In this work the amount of PVP was changed and the other experimental parameters were kept constant. For simplicity, we denote N-doped TiO<sub>2</sub> samples with 0, 0.2, 0.4, 0.6, 0.8 and 1.0 g PVP dopant as T0, T2, T4, T6, T8 and T10.

### 2.2. Characterization

The power X-ray diffraction patterns (XRD) was obtained on a D8 Bruker advanced X-ray diffractometer (40 kV, 40 mA) with Cu K<sub>α</sub> radiation ( $\lambda = 0.15402$  nm) to identify the crystalline phases and estimate the crystallite size from the full width at half-maximum of the diffraction peaks of the dried products using Scherrer's formula. Raman spectra were carried out using a Renishaw Invia Raman microscope excited by an argon ion laser beam (514.5 nm, 20 mV). The morphology, size distribution and the crystallographic features of the samples were observed by a JEM-2100 (JEOL) transmission electron microscope (TEM) with an accelerating voltage of 200 kV and allocated with a Gatan 794 charge-coupled device (CCD) camera and an EDAX energy dispersive X-ray spectroscopy. The FTIR spectrum in the range from 4000 cm<sup>-1</sup> to 500 cm<sup>-1</sup> was obtained from a ThermoFisher Nicolet iS 10 Fourier transform infrared spectrometer. The elemental compositions and chemical states of the as-prepared samples were analyzed by X-ray photoelectron spectrum (XPS) on a Phi Quantera II SXM X-ray photoelectron spectrometer with a monochromatic Al K<sub>α</sub> radiation ( $\lambda = 8.4$  Å) as the exciting source. N<sub>2</sub> adsorption–desorption isotherms were conducted on a Micromeritics ASAP 2020 apparatus at 77 K. The samples were degassed at 180 °C for 12 h before measuring. Specific surface areas were calculated using the BET model. UV–vis diffuse reflectance spectra of the as-prepared samples were measured by a UV–vis spectrophotometer equipped with an integrating sphere (Shimadzu UV-2500) from 200 nm to 800 nm at room temperature and BaSO<sub>4</sub> was used as a reference. Solid-state photoluminescence (PL) measurements ( $\lambda_{\text{ex}} = 325$  nm) were recorded on an FL3-TCSPC fluorescence spectrophotometer using 1 nm slit width in the range from 350 nm to 600 nm.

### 2.3. Photoelectrochemical performance measurements

The photoelectrochemical properties were performed in a three-electrode system connected with the CHI 760E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd, China). The

as-prepared samples were used as working electrode while Pt foil and Ag/AgCl were used as the counter and reference electrodes, respectively. The working electrode was prepared as follows: The N-doped TiO<sub>2</sub> samples were dispersed in absolute ethanol with a concentration of 1.0 g/L. After the mixture was ultrasonically dispersed, five drops of the suspension were put onto a piece of transparent ITO conducting glass (1 × 1 cm<sup>2</sup>) and then dried in room temperature slowly until a layer of film formed on the surface. 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as electrolyte to keep the stability of the working electrode. A 300 W Xe lamp was utilized as the simulated sun light source. The photocurrent responses of the working electrodes were recorded by sudden light on and off under the light illumination at the bias voltage of 0 V. The illuminated area of the working electrode was 1 cm<sup>2</sup>.

### 2.4. Photocatalytic performance for water splitting

The photocatalytic hydrogen evolution from water splitting was also evaluated. In a typical run, 0.1 g as-prepared photocatalyst was added into a solution containing 100 mL methanol as sacrificial reagent and 100 mL deionized water in the Pyrex reactor. Then the suspension was sonicated for several minutes, and the whole reaction system was irradiated by a 300 W Xe lamp as the simulated sun light source. Before the photocatalytic H<sub>2</sub> generation, the system was evacuated and refilled with ultrahigh purity Ar gas for several times. Circulating cooling water was used to reflux the steam of methanol and water. The evolved H<sub>2</sub> was analyzed by an online gas chromatograph (GC-1690, Jiedao, TCD equipped with molecular sieve 5 Å column, Ar carrier with flow rate 15 mL/min). Reference experiments were performed without either light or photocatalyst. In both cases, no H<sub>2</sub> production was observed.

## 3. Results and discussion

### 3.1. XRD and Raman analysis

The ultrafine N-doped TiO<sub>2</sub> nanoparticles were successfully synthesized by PVP assisted EG solvothermal method. The XRD patterns of the as-prepared samples were shown in Fig. 1. Obviously, all the diffraction peaks between 20° and 80° can be assigned to tetragonal anatase TiO<sub>2</sub> (JPCDS No.21-1272) with a space group of I4<sub>1</sub>/amd. Among them, the diffraction peaks with  $2\theta = 25.3^\circ$ ,  $37.8^\circ$  and  $48.0^\circ$  can be indexed to (101), (004) and (200) crystal planes of anatase TiO<sub>2</sub>, respectively. The average crystallite sizes of the as-prepared nanoparticles calculated using Scherrer's equation ( $D = K\lambda/\beta\cos\theta$ )

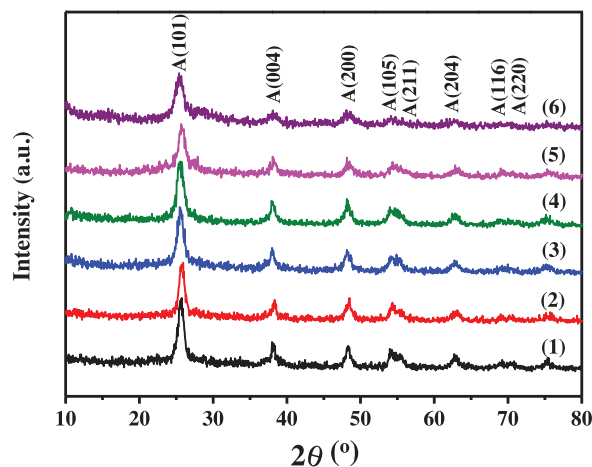


Fig. 1. XRD patterns of the as-prepared N-doped TiO<sub>2</sub> nanoparticles with different amounts of PVP: (1) T0, (2) T2, (3) T4, (4) T6, (5) T8 and (6) T10.

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