



# Product selectivity of visible-light photocatalytic reduction of carbon dioxide using titanium dioxide doped by different nitrogen-sources

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## ABSTRACT

The influence of nitrogen-source on the photocatalytic properties of nitrogen-doped titanium dioxide is herein first investigated from the perspective of the chemical bond form of the nitrogen element in the nitrogen-source. The definitive role of groups such as N–N from the nitrogen-source on the surface of as-prepared samples in the selectivity of the dominant product of photocatalytic reduction is demonstrated. Well-crystallized one-dimensional N–TiO<sub>2</sub> nanorod arrays with a preferred orientation of the rutile (3 1 0) facet are manufactured via a hydrothermal treatment using hydrazine and ammonia variously as the source of nitrogen. Significant selectivity of the dominant reduced products has been exhibited for N–TiO<sub>2</sub> prepared from different nitrogen-sources in carbon dioxide photocatalytic reduction under visible light illumination. CH<sub>4</sub> is the main product with N<sub>2</sub>H<sub>4</sub>-doped N–TiO<sub>2</sub>, while CO is the main product with NH<sub>3</sub>-doped N–TiO<sub>2</sub>, which can be attributed to the existence of the reducing N–N groups in the N<sub>2</sub>H<sub>4</sub>-doped N–TiO<sub>2</sub> surfaces after the hydrothermal treatment. Compared with the approaches previously reported, the facile one-step route utilized here accomplishes the fabrication of N–TiO<sub>2</sub> possessing visible-light activity and attainment of selectivity of dominant photocatalytic reduction product simultaneously by choosing a nitrogen-source with appropriate chemical bond form, which provides a completely new approach to understanding the effects of doping treatment on photocatalytic properties.

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## 1. Introduction

In 1972, Fujishima and Honda achieved the milestone of water splitting using titanium dioxide (TiO<sub>2</sub>) under UV irradiation [1]; shortly thereafter, Inoue et al. discovered the photoelectrocatalytic reduction of carbon dioxide (CO<sub>2</sub>) into organic compounds in the presence of a photosensitive semiconductor [2]. Since then, TiO<sub>2</sub>, as one of the most promising photocatalysts due to its high photoactivity, inertness, durability and low cost, has attracted extensive attention for its potential application for converting CO<sub>2</sub> into energy-containing fuels such as methane and carbon monoxide [2–4], which can function as an alternate to conventional fossil fuels and alleviate the notorious greenhouse effect. However, the inherent bandgap of TiO<sub>2</sub> forms, 3.2 eV and 3.0 eV for anatase and rutile, respectively, has limited it to generate a photo response only in a spectrum with a wavelength of less than 387 nm, thus failing

to utilize visible light which comprises the majority of the solar energy spectrum.

It has been proven that doping with elements such as nitrogen [5,6] can effectively narrow the bandgap of TiO<sub>2</sub> and thus extend the visible-light photocatalytic property to TiO<sub>2</sub>. Presently, the synthesis of N–TiO<sub>2</sub> with various morphologies and topologies is mainly classified in two ways in terms of the manner of introduction of the nitrogen element; namely process-treatment and post-treatment [3–8]. Asahi et al. reported the synthesis of TiO<sub>2-x</sub>N<sub>x</sub> film by sputtering the TiO<sub>2</sub> target in a N<sub>2</sub>(40%)/Ar gas mixture followed by annealing treatment [9]. The resulting film showed photocatalytic activity under visible light irradiation for the photodegradation of methylene blue. They studied the nitrogen in doped TiO<sub>2</sub> via X-ray photoelectron spectra, and determined that it was not the interstitial nitrogen whose binding energy peak is located at about 400 eV, but the substitutional nitrogen with peak at approximately 396 eV that played a key role in narrowing the TiO<sub>2</sub> bandgap.

Efforts have been made to achieve selective photocatalysts to obtain certain reduced products in the photocatalytic reduction of CO<sub>2</sub> [10–13]. Liao et al. prepared amine-functionalized TiO<sub>2</sub> improve CO<sub>2</sub> adsorption through a solvothermal method using

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monoethanolamine [14]. Their results showed enhanced photocatalytic activity for CO<sub>2</sub> reduction, with the major reduced product of CO under UV irradiation, which was explained as being due to as the existence of amine groups on the TiO<sub>2</sub> surfaces. Woolerton and Verykios obtained TiO<sub>2</sub> nanoparticles decorated with attached carbon monoxide dehydrogenase (CODH) and ruthenium (Ru) photosensitizer through aqueous dispersion which produced CO under visible light illumination [15,16]. The observations were attributed to the mediates which could bypass the one-electron radical pathway and adopt a two-electron pathway to selectively produce CO. Liu et al. synthesized 1D CdS@TiO<sub>2</sub> core-shell nanocomposites by a two-step solvothermal method, and this CdS@TiO<sub>2</sub> NPs showed efficiently selective reduction of heavy-metal ions under visible light irradiation. They assumed that it was the special core-shell structure which could allow the photo-generated electrons from CdS core to transfer to its conduction band while restrain the tunneling of the photo-generated holes from the CdS core to the surface of the TiO<sub>2</sub> shell that led to the selectivity in photocatalytic reaction [17].

To our knowledge, studies on nitrogen-doped titanium dioxide (N-TiO<sub>2</sub>) to date have mainly concentrated on fabrication with a certain nitrogen-source and investigating the corresponding photocatalytic performance. There are few reports that consider either the influence of different chemical bond forms of the nitrogen element in each particular nitrogen-source on the photocatalytic performance of N-TiO<sub>2</sub>, or the selectivity of the dominant reduced product of CO<sub>2</sub> photocatalytic reduction.

Herein, hydrazine (N<sub>2</sub>H<sub>4</sub>) and ammonia (NH<sub>3</sub>) were selected as nitrogen-sources, as they have different chemical bond forms of the nitrogen element (N-N for N<sub>2</sub>H<sub>4</sub>, and N-H for NH<sub>3</sub>), and both consist simply of the same elements, namely nitrogen and hydrogen. Hence, when different nitrogen-sources are used containing the same moles of nitrogen atoms, the chemical bond form of the nitrogen element in the nitrogen-source is fixed as the unique variable, permitting examination of its effects. Well-crystallized one-dimensional N-TiO<sub>2</sub> nanorod arrays were synthesized using a hydrothermal treatment with the aforementioned nitrogen-sources. The resulting samples were examined, especially through measurements of their corresponding photocatalytic activity via conducting the photocatalytic reduction of CO<sub>2</sub> under visible light illumination and identifying the resulting products by gas chromatographic analysis. By such a comparison, the relationship between nitrogen-source and photocatalytic reduction performance of N-TiO<sub>2</sub> can be revealed. Both types of photocatalyst exhibited good abilities to convert CO<sub>2</sub> into carbon-containing fuels, but there was a significant distinction in the dominant reduced product, with CH<sub>4</sub> for N<sub>2</sub>H<sub>4</sub>-doped N-TiO<sub>2</sub>, while CO was the main product with NH<sub>3</sub>-doped N-TiO<sub>2</sub>. It should be clarified that the main objective herein is not to achieve a higher photocatalytic reduction yield, rather, to survey the difference between photocatalytic properties with the different N-moieties in the photocatalysts. A mechanism leading to this observed difference in photocatalytic properties is proposed.

## 2. Experimental

### 2.1. Fabrication of samples

The Ti-precursor was a mixture consisting of deionized water, hydrochloric acid (HCl, AR, Sinopharm Chemical Reagent Co., Ltd.), tetrabutyl titanate (TBT, AR, Sinopharm Chemical Reagent Co., Ltd.), in which the volume ratio of the above three components was 30:30:1 sequentially. After half an hour of vigorous stirring, different nitrogen-sources (NH<sub>3</sub> and N<sub>2</sub>H<sub>4</sub>, AR, Sinopharm Chemical Reagent Co., Ltd.) containing the same moles of nitrogen

atoms were added to prepare the N-containing hydrothermal treatment solution, followed by an hour of stirring. Thoroughly purged fluorine-doped tin oxide (FTO, HEPTACHROMA) slides were then placed into a stainless steel autoclave containing the hydrothermal treatment solution. The hydrothermal treatment proceeded for 24 h at 120 °C. When the treatment ended, the resulting samples were consecutively rinsed with deionized water and dried in air.

### 2.2. Characterization

Morphologies of the as-prepared samples were observed via field emission scanning electron microscopy (FESEM, Hitachi S4800). Specific surface area of the resultant samples was analyzed by nitrogen adsorption at 77 K with the Brunauer-Emmett-Teller (BET) method on a gas adsorption apparatus (AUTOSORB-1-C, Quantachrome Instruments). X-ray diffraction (XRD) patterns of the samples were recorded using a PANalytical X'Pert PRO X-ray diffractometer with Cu K $\alpha$  radiation, in which the 2 $\theta$  rate was 4°/min in the range from 20 to 80°. X-ray photoelectron spectroscopy (XPS) measurements were performed utilizing a VG ESCALAB MARK II spectrometer with an Mg K $\alpha$  (1253.6 eV) X-ray source, with spectra calibrated by the C 1s peak at 284.6 eV. Fourier transform infrared (FTIR) spectra were obtained on a Bruker Tensor 27 infrared spectrometer using pressed KBr discs. UV-vis absorption spectra of resulting samples were obtained on a UV-3600 UV-vis spectrophotometer (Shimadzu Corporation) using a 350 nm excitation wavelength at room temperature.

### 2.3. Photocatalytic reduction of CO<sub>2</sub>

Photocatalytic reduction of CO<sub>2</sub> was carried out under the illumination of two 300 watt visible light sources (UV < 5%) at room temperature in a quartz photoreactor. A specific amount of the N-TiO<sub>2</sub> or the pristine TiO<sub>2</sub> samples was situated in the bottom of the reactor. In this study, the reacting gas was comprised of CO<sub>2</sub> and water with a flow rate of 50 ml/min during the whole process. In order to purge any residuals from the reactor, the reacting gas was pumped for 30 min in advance. After the purging step, the light sources were turned on, and the test commenced to run for 12 h. Data were collected once per hour to record the variation of reduced products constituents and their concentrations in the effluent gas with illumination time using a gas chromatograph equipped with N 2000 dual-channel chromatography data workstation (GC, Zheda Zhida).

## 3. Results and discussion

The FESEM images in Fig. 1 display the typical TiO<sub>2</sub> nanorod array morphology of the resulting samples. Generally, the nanorod arrays have a uniform distribution on the support, while an obvious change occurs to the nitrogen-doped TiO<sub>2</sub> nanorod in the shape and length. Compared with other one-dimensional structure such as the disordered nanofiber which tends to agglomerate, the as-prepared samples possess homogenous nanorod arrays in a perpendicular orientation with support, which promotes the utilization of incident light [4,7]. The pristine TiO<sub>2</sub> nanorod is cubic column with a quasi-square top and smooth side surface (Fig. 1a), being in agreement with the growth rule of tetragonal crystal structures [18], and the average length of the pristine TiO<sub>2</sub> nanorods is 0.9  $\mu$ m. When N was introduced, the former architecture is replaced by a cone-like structure with sharp top (Fig. 1b and c), which can be ascribed to the anisotropic growth of TiO<sub>2</sub> derived from the presence of the N dopant. Furthermore, the mean length of the N-TiO<sub>2</sub> nanorods varies depending on the nitrogen-sources, 1.2  $\mu$ m and 1.5  $\mu$ m for NH<sub>3</sub>-doped and N<sub>2</sub>H<sub>4</sub>-doped N-TiO<sub>2</sub>, respectively. In addition, the BET surface areas of the resultant samples were analyzed (Fig. 1d).

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