



Iron-titanium dioxide composite nanoparticles prepared with an energy effective method for efficient visible-light-driven photocatalytic nitrogen reduction to ammonia

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ABSTRACT

Photocatalytic nitrogen (N₂) reduction with iron-titanium dioxide composites (Fe-TiO₂) for ammonium (NH₃) production is of energy effective and environmental friendly. However, the most common used Fe-TiO₂ preparation method is problematic due to the intensive energy. Therefore, development of improved methods for Fe-TiO₂ preparation is desirable. The objective of this research was to develop an energy-effective approach for the synthesis of highly active and stable Fe-TiO₂ catalysts for photocatalytic reduction of N₂ to ammonium (NH₃). Here, TiCl₄ low-temperature hydrolysis method is used to prepare Fe-TiO₂ instead of the conventional high-temperature calcination method. The Fe-TiO₂ catalysts prepared by the new method achieved 52.6% higher activity than the one prepared by the conventional method. The improved activity mainly resulted from better absorption of visible light, more efficient electron-hole splitting and the increase of N₂ and H₂O adsorption. Therefore, the new Fe-TiO₂ catalyst preparation method appears most promising.

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1. Introduction

Nitrogen is an important element for the life growth and survival [1,2]. However, most organisms can only take up nitrogen in the form of ammonia ion (NH₄⁺) and nitrate ion (NO₃⁻) rather than the molecular nitrogen due to the strong N≡N triple bond [3,4]. So far, the Harber-Bosch process provides most of the required nitrogen for the human beings, but it consumes 1–2% of the world's energy supply and generates more than 300 million tons of carbon dioxide annually [5,6]. Photocatalytic reduction of molecular nitrogen to ammonia provides a green and sustainable ammonia synthesis route [7]. In 1977, Schrauzer and Guth firstly reported the photocatalytic molecular nitrogen reduction to ammonia over iron-titanium dioxide composites under UV light irradiation [8]. Afterwards, Radford and Francis investigated photocatalytic molecular nitrogen fixation on iron-anatase and rutile composites under visible light [9].

Most of the Fe-TiO₂ catalysts are prepared by the high-temperature calcination method, which includes mixing of nitrate iron with titanium dioxide (TiO₂), boiling of the suspension until drying and calcination of the precipitates at 1000 °C [7,8]. Although

these Fe-TiO₂ catalysts can converse a certain amount of molecular nitrogen to ammonia under visible or UV light, the conversions are as low as 0 μM h⁻¹ to 9 μM h⁻¹ and the catalyst preparation is of energy intensive. These disadvantages limit the development and practical use of photocatalytic N₂ fixation. Therefore, development of an energy effective preparation method of Fe-TiO₂ for highly photocatalytic reduction of molecular nitrogen to ammonia is not only necessary but also a challenge in the promotion of the development of photocatalytic molecular nitrogen to ammonia.

Herein, a new method for the preparation of Fe-TiO₂ was developed. Compared with the conventional high-temperature calcination method, the new one is more energy effective, whose calcination temperature is as low as 300 °C. More importantly, the catalytic activity of the new catalyst is 52.6% higher than that of the conventional one. In this study, the catalytic processes involving Fe-TiO₂ prepared by the new and conventional methods were systematically investigated to analyze the above phenomenon.

2. Experimental

2.1. Catalyst preparations

The TiO₂ was prepared by two methods as shown in Fig. 1a and b. One was the TiCl₄ low-temperature hydrolysis method (TiCl₄

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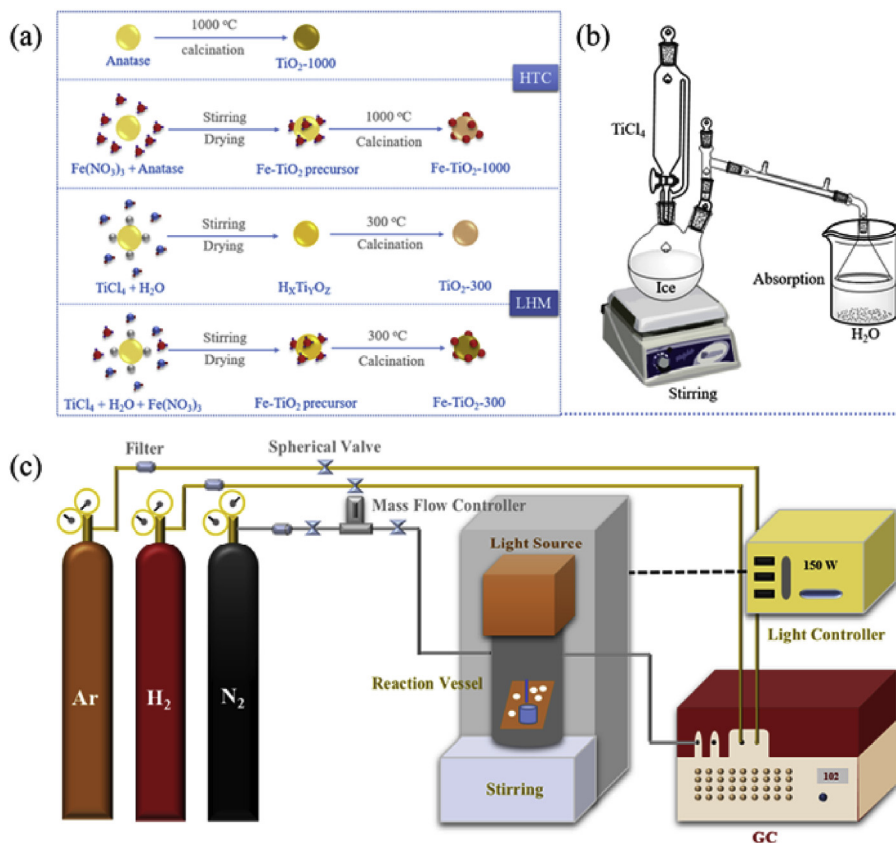


Fig. 1. (a) Catalysts prepared by high-temperature calcination method (HTC) and low-temperature hydrolysis method (LHM); (b) Equipment for the catalyst preparations; (c) Experimental set-up for photocatalytic N₂ reduction.

LHM). Typically, 5 mL titanium tetrachloride (TiCl₄, Sigma Aldrich) was dropwise added into 30 mL ice under stirring to prepare a transparent TiCl₄ aqueous solution. After stirring for 10 min, the TiCl₄ aqueous solution was rapidly heated to 100 °C to remove the water and hydrogen chloride (HCl). The HCl was absorbed by the water to form HCl solutions. The obtained white solid was dried in air at 80 °C for 12 h and calcination in a muffle furnace at the temperature of 300 °C for 2 h. The product was denoted as TiO₂-300. The other method was the high-temperature calcination (HTC) of anatase TiO₂ (Sigma Aldrich) at 1000 °C for 2 h. The resulting catalyst was designated as TiO₂-1000.

The Fe-TiO₂ was also prepared by the similar methods. Typically, 5 mL titanium tetrachloride (TiCl₄, Sigma Aldrich) was dropwise added into 30 mL ice containing 0.0315 g Fe(NO₃)₃·9H₂O under stirring. After stirring for 10 min, the above mixed solution was rapidly heated to 100 °C to remove the water and hydrogen chloride. The obtained solid was dried in air at 80 °C for 12 h and calcination in a muffle furnace at temperatures of 300 °C for 2 h. The product was denoted as Fe-TiO₂-300.

The other procedure was the impregnation method according to the literature with modifications [10]. Briefly, the solution containing 0.0290 g Fe(NO₃)₃·9H₂O was dropwise added into the suspension with 1 g anatase. After stirring for 24 h, the above mixed solution was rapidly heated to 100 °C to remove the water. The obtained solid was dried in air at 80 °C for 12 h and calcination in a muffle furnace at the temperature of 1000 °C for 2 h. The resulting catalyst was denoted as Fe-TiO₂-1000.

2.2. Characterization of catalysts

The BET surface areas were tested by a volumetric system

Autosorb IQ ASIQC0100-4 Quantachrome Instruments. X-ray diffraction (XRD) patterns were collected at the scanning speed of 8°/min from 10° to 90° with 0.02° on a Rigaku Smartlab XRD system. The thermogravimetric analyses (TGA) were carried out on a SDT Q600 thermogravimetric analyzer at the rate of 10 °C/min from 50 to 1000 °C under nitrogen (100 mL/min). The infrared (IR) spectra were recorded on a Nicolet 6700 spectrometer with a spectral resolution of 4 cm⁻¹. X-ray photoelectron spectroscopy (XPS) were conducted using a Kratos Axis Ultra DLD X-ray photoelectron spectrometer with monochromated Al K-alpha source running at 150 W. The morphology of the catalysts was studied by transmission electron microscopy (TEM) using FEI-Tecna G2 S-Twin 200 kV equipment. The in-situ IR spectra were recorded on a Nicolet 6700 spectrometer with a resolution of 4 cm⁻¹. The cell was evacuated for 30 min to remove the physisorbed nitrogen and oxygen species. Afterwards, the H₂O vapor together with N₂ (UHP, US Welding) was introduced into in-situ cell. The exhaust gas was analyzed by the mass spectrometer (MS). Nitrogen temperature-programmed desorption (N₂-TPD) tests were performed on an Autosorb IQ ASIQC0100-4, quantachrome instrument, equipped with thermal conductivity detector (TCD). The adsorption was conducted at room temperature with 100 vol% N₂, and finally the desorption was programmed at 10 °C/min to 900 °C in flowing Ar. The UV–vis diffuse reflectance spectra (DRS) were performed on a Shimadzu UV-2550 UV–vis spectrophotometer using BaSO₄ as the reference sample. Raman analysis was carried out on a Renishaw InVia Raman spectrometer and the spectra were obtained with the green line of an Ar-ion laser (514.53 nm) in micro-Raman configuration. The electrochemical analysis was carried out in a conventional three electrode cell, using two Pt plates as counter and reference electrodes, respectively. The working electrode was

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