Applied Catalysis B: Environmental 201 (2017) 58–69

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Fe^{3+} doping promoted N_2 photofixation ability of honeycombed graphitic carbon nitride: The experimental and density functional theory simulation analysis

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ARTICLE INFO

Article history:
Received 9 May 2016
Received in revised form 25 July 2016
Accepted 1 August 2016
Available online 2 August 2016

Keywords:
Graphitic carbon nitride
Honeycomb structure
Nitrogen photofixation
Fe^{3+} doping
DFT simulation

ABSTRACT

Honeycombed iron doped graphitic carbon nitride with outstanding N_2 photofixation ability is synthesized in this work. Characterization results indicate that Fe^{3+} inserts at the interstitial position and is stabilized in the electron-rich g-C_3N_4 through the coordinative Fe-N bonds. Fe^{3+} sites can chemisorb and activate N_2 molecules, then transfer the photogenerated electrons from the g-C_3N_4 to adsorbed N_2 molecules. Fe0.05-CN displays the highest NH_4^+ generation rate, which is approximately 13.5-fold higher than that of neat g-C_3N_4. Density functional theory simulations prove the N_2 activation effect of Fe^{3+} sites due to the high adsorption energy and prolonged N≡N bond. Charge density difference result confirms the electrons transfer process from the Fe^{3+} doping sites to N_2 molecule. DOS results indicate that the electrons of σ_g2p orbital (HOMO) in nitrogen atom is delocalized significantly when N_2 adsorbed on Fe^{3+} doping sites, leading to its orbital energy almost connects to that of π_g^*2p orbital (LUMO), which confirming that Fe^{3+} doping sites can activate the N_2 molecule effectively. The Mulliken charge of nitrogen is −3.1 when the N_2 adsorbed on Fe^{3+} doping sites, indicating that N_2 molecule is enriched by large number of electrons, which is beneficial to the H$^+$ attack to form NH_4^+.

1. Introduction

Nitrogen is a necessary element of human, animal and plant growth. Although ∼78% of the atmosphere is nitrogen, it is unusable directly to most organisms because of its strong nonpolar N≡N covalent triple bond. Thus, artificial nitrogen fixation is carried out through the Haber-Bosch process, in which hydrogen gas reacts with nitrogen gas to yield ammonia in the presence of catalysts under high pressure and temperature. Both the raw material costs and energy consumption are high for this process. Therefore, artificial nitrogen fixation under milder conditions is of great significance because of the reduction of input energy and no use of hydrogen. This significance has directed many chemists to find chemical [1,2], electrochemical [3,4] and photochemical routes [5,6] to fix nitrogen under mild conditions.

Nitrogen photofixation technology is considered to be a promising method to replace the traditional Haber-Bosch process. In 1977, the process of N_2 reduction to NH_3 over Fe doped TiO_2 was discovered by Schrauzer et al. [5]. Since then, many Ti-based semiconductor catalysts were reported [7–11]. However, because of the poor visible light absorption caused by the wide band gap energy, the nitrogen fixation abilities of these Ti-based semiconductor catalysts are still low under visible light. Moreover, the interfacial charge transfer efficiency of these semiconductor photocatalysts is far from satisfactory because of the poor interaction between catalyst and N_2 molecule [12–14]. Besides that, compared with the photocatalytic H_2 evolution and CO_2 reduction, photocatalytic N_2 fixation is more challenging because the N_2 fixation is seriously hampered by the high-energy N_2 intermediates in the reduced or protonated form (N_2^- or N_2H) [15] Thus, designing a new photocatalyst is not only important but also a challenge to develop the photocatalytic N_2 fixation technology. Against this background, in recent years, many novel nitrogen-fixation systems are reported successively [15–19]. Zhu et al. synthesized hydrogen-terminated diamond which can yield facile electron emission into

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http://dx.doi.org/10.1016/j.apcatb.2016.08.002

water, thus inducing photofixation of N_2 to NH_3 at ambient temperature and pressure [15]. Hu et al. prepared a novel ternary metal sulfide photocatalyst $Zn_{0.1}Sn_{0.1}Cd_{0.8}S$ with outstanding nitrogen photofixation ability under visible light [16]. Kitano et al. synthesized Ru-loaded $[Ca_{24}Al_{28}O_{64}]^{4+}(e^-)_4$(Ru/C12A7:$e^-$). It has high electron-donating power, chemical stability and efficient ammonia synthesis performance [17]. Banerjee et al. prepared chalcogels containing FeMoS inorganic clusters, which are capable of photochemically reducing N_2 to NH_3 under white light irradiation [18]. Li et al. synthesized BiOCl nanosheet. DFT theoretical calculation results show that the fixation of terminal end-on bound N_2 on the oxygen vacancies of BiOCl {001} facets follows an asymmetric distal mode by selectively generating NH_3 [19].

Graphitic carbon nitride (g-C_3N_4), a novel metal-free semiconductor material, has been widely applied in many fields, including photocatalysis [20,21], fuel cells [22,23], organic synthesis [24] and gas storage [25,26]. The versatile application of g-C_3N_4 is largely due to its unique physicochemical properties, such as moderate band gap energy, energy-storage capacity, gas-adsorption capacity and special optical properties. However, the disadvantage of g-C_3N_4 is as prominent as its shortcomings. First of all, the high recombination rate of electrons and holes causes the low quantum efficiency. Secondly, a low surface area of g-C_3N_4 ($\sim$10 $m^2\,g^{-1}$) leads to the poor adsorption capacity of reactant and less active chemical sites.

Recently, Li et al. [27] reported oxygen vacancies introduced BiOBr nanosheet and Dong et al. [28] synthesized nitrogen vacancies doped g-C_3N_4. They suggested that, as the surface defects, oxygen vacancies and nitrogen vacancies could activate N_2 and promote interfacial electron transfer, leading to the improved N_2 photofixation ability. We hypothesize that, as another surface defects, the doping ions could have a similar effect on nitrogen photofixation. Owing to that Fe^{3+} doping can improve the nitrogen photofixation ability of TiO_2 based catalysts, in this work, honeycombed Fe^{3+} doped graphitic carbon nitride with outstanding nitrogen photofixation performance under visible light was prepared. On the one hand, Fe^{3+} doping can effectively trap the photogenerated electrons to improve the separation rate [29–31]. On the other hand, by controlling the Fe^{3+} concentration, honeycomb structure was obtained which significantly improved the surface area of as-prepared catalysts. The experimental and DFT calculation results indicate that Fe^{3+} doping sites can not only chemisorb and activate the N_2 molecule, but also promote interfacial electron transfer from catalysts to N_2 molecules, thus significantly improving the nitrogen photofixation ability.

2. Experimental

2.1. Preparation and characterization

All the chemicals used in this experiment were reagent grade and without further treatment. 4 g of melamine was dissolved into 60 mL of methanol at 60 °C and stirred for 10 min. Then, 100 mL of HNO_3 (0.2 M) was added dropwise into above solution and the white precipitation was separated out. After cooling to room temperature, the white precipitate was collected, washed by methanol for three times and dried at 60 °C for 12 h. Desired amount of $Fe(NO_3)_3\cdot 9H_2O$ and the obtained white precipitate were added into 30 mL of methanol under stirring. The obtained suspension was heated to 50 °C for evaporating methanol. The solid was dried at 60 °C for 12 h, ground and calcined at 550 °C for 2 h under flowing high purity argon gas at the rate of 5 °C min^{-1}. The obtained sample was denoted as Fex-CN, where x stands for the mass ratio of $Fe(NO_3)_3\cdot 9H_2O$ to melamine. For comparison, neat g-C_3N_4 was prepared following the same procedure mentioned above in the absence of $Fe(NO_3)_3\cdot 9H_2O$ and denoted as Fe0-CN.

The XRD patterns of the prepared samples were recorded on a Rigaku D/max-2400 instrument using Cu-Kα radiation (λ = 1.54 Å). The scan rate, step size, voltage and current were 0.05°/min, 0.01°, 40 kV and 30 mA, respectively. UV–vis spectroscopy was carried out on a JASCO V-550 model UV–vis spectrophotometer using $BaSO_4$ as the reflectance sample. The morphologies of prepared catalyst were observed by using a scanning electron microscope (SEM, JSM 5600LV, JEOL Ltd.). Nitrogen adsorption was measured at −196 °C on a Micromeritics 2010 analyser. All the samples were degassed at 393 K prior to the measurement. The BET surface area (S_{BET}) was calculated based on the adsorption isotherm. Thermogravimetric analysis (TGA) was performed using a TGA-DSC 2 (Mettler-Toledo) instrument. ICP was performed on a Perkin-Elmer Optima 3300DV apparatus. The XPS measurements were performed on a Thermo Escalab 250 XPS system with Al Kα radiation as the excitation source. The binding energies were calibrated by referencing the C 1 s peak (284.6 eV) to reduce the sample charge effect. Temperature Programmed Desorption (TPD) studies were performed using a CHEMBET-3000 (Quantachrome, U.S.A.) instrument in the temperature range of 313–1073 K. The photoluminescence (PL) spectra were measured at room temperature with a fluorospectrophotometer (FP-6300) using a Xe lamp as the excitation source. The photocurrents were measured using an electrochemical analyzer (CHI 618C Instruments) equipped with a rectangular-shaped quartz reactor (20 × 40 × 50 mm) using a standard three-electrode system. The prepared sample film was used as the working electrode, a Pt flake was used as the counter electrode, and Ag/AgCl was used as the reference electrode. A 500 W Xe lamp was used to irradiate the working electrode from the back side. The light intensity on the working electrode was 120 mW cm^{-2}. In addition, a mechanical shutter was used to minimize the exposure of the sample to light. A 1.0 M Na_2SO_4 solution was used as the electrolyte. The applied potential was 0.00 V vs. Ag/AgCl. All the measurements were performed at room temperature (298 K).

Isotopic labeling experiments are carried out as follow. Labeled $^{15}N_2$ gas was purchased from Sigma-Aldrich Chemical Company. In the experimental process, Ar was used to eliminate air and the possible adsorbed ammonia in the reaction system. Then, $^{15}N_2$ was passed through the reaction mixture for 30 min. After that, the reactor was sealed. Other experiment conditions were the same as those for $^{14}N_2$ photofixation. Indophenol method was used to examine the produced $^{15}NH_4^+$, owing to the low mass of $^{15}NH_4^+$ for LC–MS studies. The sample for LC–MS analysis was prepared as follows. 0.5 mL of the reaction reacted with 0.1 mL of 1% phenolic solution in 95% ethanol. Then, 0.375 mL of 1% NaClO solution and 0.5 mL of 0.5% sodium nitroprusside solution were added into above solution. MS studies were carried on an Ultimate 3000-TSQ (LCMS-ESI).

The DFT simulations were performed using the program package Dmol3. The substrate is modelled by one layer of g-C_3N_4 separated by a vacuum layer of 12 Å. All the atoms in the layer and the N_2 molecule are allowed to relax. The Brillouin zones of the supercells were sampled by the Gamma points. Based on the structures of g-C_3N_4, the g-C_3N_4 surface with nitrogen atom vacancy was modelled to study the N_2 adsorption properties.

2.2. Photocatalytic reaction

The nitrogen photofixation property was evaluated according to previous literature [11]. The nitrogen photofixation experiments were performed in a double-walled quartz reactor in air. For these experiments, 0.2 g of photocatalyst was added to a 500 mL 0.789 g/L ethanol as a hole scavenger [11]. The suspension was dispersed using an ultrasonicator for 10 min. During the photoreaction under visible light irradiation, the suspension was exposed to a 250 W high-pressure sodium lamp with main emission in the range of 400–800 nm, and N_2 was bubbled at 100 mL/min through the solu-