Applied Catalysis B: Environmental 218 (2017) 515–524

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Carbon vacancy regulated photoreduction of NO to N_2 over ultrathin g-C_3N_4 nanosheets

Guohui Dong[a,*], Daniel L. Jacobs[b], Ling Zang[b,*], Chuanyi Wang[a,*]

[a] School of Environmental Science and Engineering, Shaanxi University of Science and Technology, Xi'an 710021, China
[b] Nano Institute of Utah and Department of Materials Science and Engineering, University of Utah, Salt Lake City, UT 84112, United States

ARTICLE INFO

Article history:
Received 22 May 2017
Received in revised form 19 June 2017
Accepted 4 July 2017
Available online 5 July 2017

Keywords:
Graphitic carbon nitride
NO removal
Photoreduction
Carbon vacancy

ABSTRACT

Photocatalytic oxidation has recently been recognized as an attractive technology for NO removal, in which the main products are NO_2 or HNO_3. However, these products may cause secondary pollution and deactivation of the involved photocatalysts. In this study, we demonstrate that carbon vacancy-modified nanosheet structure g-C_3N_4 (Ns-g-C_3N_4) can efficiently and selectively reduce NO to N_2 under visible light. Since N_2 is a green gas and can easily desorb from the active sites, the problems such as secondary pollution and catalyst deactivation are largely avoided. It was found that two structural characters of Ns-g-C_3N_4, ultrathin nanostructure and abundant surface defect sites, could promote its visible light absorption, and favor the separation and transfer of photogenerated charge carriers as well as strong chemisorption of NO, leading to high photoreactivity. Meanwhile, the surface defects of Ns-g-C_3N_4 shift the adsorption structure of NO from C—N—O for the bulk counterpart to Cv—O—N (adsorbed at the carbon vacancy site, Cv), eventually resulting in its high selectivity of converting NO to N_2. The present study underlines the impetus of utilizing surface defect structure to regulate photocatalytic reaction pathway.

1. Introduction

Nitric oxide (NO) is one of the most common and dangerous gaseous pollutants which can cause environmental problems, such as haze, photochemical smog, and acid rain [1–3]. A major source of NO is through combustion, and since the increase of automobiles and industrial activities, the concentration of NO in the atmosphere has greatly increased over the past few decades [4,5]. Therefore, it is necessary to develop efficient, low cost and green technologies to remove NO from the atmosphere. Conventional NO removal methods include chemical adsorption, physical adsorption and thermal catalytic reduction [6–9]. However, most of these methods suffer from the problems of low efficiency, deactivation of catalyst, and secondary pollution. Semiconductor photocatalysis has recently been recognized as an attractive alternative technology for NO removal due to its high catalytic performance at moderate conditions and the abundant solar energy available [10]. In photocatalysis, light irradiation causes the bandgap excitation, producing electrons (e^-) and holes (h^+) located at valence and conduction band, respectively, which can then migrate to the surface and trigger subsequent redox reactions [11]. Through the redox reaction, NO can be eliminated effectively. It was reported that TiO_2, ZnO_2, and Fe_2O_3 could act as efficient photocatalysts for removing NO under UV light irradiation [12–14]. However, their intrinsic wide band gap nature makes these photocatalysts only active in UV region, which occupies only ~5% of sunlight. Therefore, it is essential to develop photocatalysts that are responsive to visible light (accounting for about 43% of sunlight). Many visible light-driven photocatalysts including $(BiO)_2CO_3$, BiOBr, Bi_2MoO_6, $InVO_4$ and graphitic carbon nitride (g-C_3N_4) have been developed and utilized for NO removal [15–20]. Among these materials, g-C_3N_4 has attracted increasing attention because of its stability, low cost, suitable band gap of 2.7 eV and surface flexibility for chemical modification [21]. We found that g-C_3N_4 could oxidize NO to NO_2 under visible light irradiation in our previous work [22]. However, NO_2 is an undesired product as it is more toxic than NO. Very recently, we demonstrated that the photooxidation product NO_2 could be further oxidized to NO_3^- by modifying g-C_3N_4 with Pd nanoparticles. Unfortunately, NO_3^- will occupy the active sites and cause the catalytic deactivation of g-C_3N_4 [23]. Therefore, it is of the utmost urgency but a challenge to design a route to remove NO without secondary pollution and catalytic deactivation.

Aside from NO_2 and NO_3^-, N_2 is also a possible product in the photocatalytic removal of NO. Since N_2 is a clean gas and can easily desorb from the active sites, the problems of deactivation

---

* Corresponding authors.
E-mail addresses: dongguohui@sust.edu.cn (G. Dong), lzang@eng.utah.edu (L. Zang), cywang@ms.xjb.ac.cn (C. Wang).

http://dx.doi.org/10.1016/j.apcatb.2017.07.010
0926-3373/© 2017 Elsevier B.V. All rights reserved.

and secondary pollution can be largely avoided [24]. However, the conversion from NO to N_2 is very difficult because of high dissociation energy of N≡O triple bond (632 KJ/mol). Although it has been reported that TiO_2 can reduce NO to N_2 under UV light irradiation, the conversion efficiency is only 2% [24]. According to previous reports, chemical adsorption is critical to the reduction of gas molecules, such as O_2, CO_2 and N_2 [25–27]. It has been shown that the chemisorption mode of the gas molecules on the surface of catalyst can control either reaction path or the reaction products [25–28]. In general, chemisorption mode of gas molecules on a catalytic material depends on its surface structure [25–28]. This is due to the fact that different surface structures may have different atom terminations and surface energies. Thus, to alter the products of photocatalytic NO removal, the catalyst's surface structure would be an important factor to control.

Recent experimental studies have shown that two dimensional nanosheet materials possess unique surface structure, giving rise to enhanced photocatalytic performance compared to their bulk counterparts [29,30]. It is reasonable to consider that nanosheet structure of g-C_3N_4 may exhibit different behavior in photocatalytic NO conversion process than the bulk structured one. However, to the best of our knowledge, there lacks systematic study on the photocatalytic NO removal by nanosheet structured g-C_3N_4 under visible light. In this study, we report on a simple method of synthesizing ultrathin nanosheets of g-C_3N_4 and the application as photocatalyst for converting NO to N_2, for which the detailed structure of g-C_3N_4 nanosheet and photocatalytic mechanism were extensively investigated.

2. Experimental section

2.1. Preparation of catalysts

All chemicals used in this study were analytical-grade reagents without further purification. Nanosheet structure graphitic carbon nitride (Ns-g-C_3N_4) was synthesized by mixing melamine (1 g) with cyanuric acis (2 g) in 20 mL of ethanol with stirring at 333 K to remove the ethanol. The resultant mixture was put into an alumina crucible with a cover and then heated to 550 °C for 4 h in air to obtain the final samples. The bulk graphitic carbon nitride (g-C_3N_4) was prepared by heating melamine (3 g) in 20 mL of ethanol using the same heating procedures as just described.

2.2. Sample characterization

The crystal structures of the final samples were analyzed by Bruker D8 Advance X-ray diffractometer (XRD) with Cu Kα radiation at 40 KV and 40 mA. The morphology of the final samples was analyzed by transmission electron microscopy (TEM, JEOL JSM-2010). Surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C, Al KR). All of the XPS spectra were calibrated to the C 1s peak at 284.6 eV of the surface adventitious carbon. Electron paramagnetic resonance (EPR) signals were recorded at room temperature (298 K) with a Bruker ESR A300 spectrometer. The UV–vis diffuse reflectance spectra (DRS) were obtained using a UV–vis spectrometer (Shimadzu UV-2550) by using $BaSO_4$ as a reference and were converted from reflection to absorbance by the Kubelka-Munk method. Photoluminescence spectra (PL) of the final samples were obtained using a fluorescence spectrometer (Hitachi F-4500) at 293 K. The nitrogen adsorption and desorption isotherms at 77 K were measured using Micrometrics ASAP2020 system after samples were vacuum dried at 180 °C overnight. Fourier transform infra red spectroscopy (FT-IR) spectra were obtained using a FT-IR spectrophotometer (Nicolet iS50, Thermo) with KBr as the reference sample.

2.3. Photocatalytic activity measurement

The experiments of photocatalytic NO removal on g-C_3N_4 and Ns-g-C_3N_4 were carried out in a continuous flow reactor. In the experiment, 50 mg of g-C_3N_4 or Ns-g-C_3N_4 was added to 10 mL of H_2O and ultrasonicated for 15 min. The aqueous suspension was then cast onto the glass dish (R = 3 cm), followed by drying at 60 °C until the water was completely removed. The glass dish was placed in the middle of the reactor. A 300 W Xe lamp with a 420 nm cutoff filter was vertically placed above the quartz window, so that the incident light can irradiate directly on the sample dish. Compressed NO (10 ppm, balance with Ar) was used as the NO source. NO concentration was diluted to about 600 ppb by air stream. The flow rate was controlled at 1 L/min by a mass flow controller. The change in NO concentration was continuously measured by using a chemiluminescence NO analyzer (Thermo Scientific, 42i).

NO removal efficiency (η) was calculated as follows:

$$\eta(\%) = (1-[NO]_f/[NO]_i) \times 100\%$$

where $[NO]_f$ and $[NO]_i$ are the concentrations of NO in the outlet stream and feeding stream, respectively.

2.4. Anaerobic photocatalytic NO removal

In the anaerobic photocatalytic NO removal, a 0.1 g amount of photocatalyst was uniformly dispersed on a glass reactor with an area of 4.2 cm^2. The volume of the reaction system was about 230 mL. The reaction setup was vacuum-treated several times, and then 1500 ppb NO (Banlance with Ar) was introduced into the reaction to achieve ambient pressure. During the irradiation, about 1 mL of gas was taken from the reaction cell at given intervals for subsequent N_2 concentration analysis with a gas chromatograph (GC-14B, Shimadzu Corp., Japan).

The selectivity of N_2 (S_{N2}) was calculated as follows:

$$S_{N2} = ([N_2]/[N_2] + [NO_2]) \times 100\%$$

2.5. Electrochemical and photoelectrochemical experiments

Electrochemical and photoelectrochemical measurements were performed in a three-electrode cell with a platinum plate (1 × 1 cm^2) as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode on a CHI 660C workstation. The working electrode (photoelectrode) was immersed in a 0.1 M KCl aqueous solution. Time dependent photocurrent curves were measured with amperometric i–t curve method. A 300 W Xe lamp with a 420 nm cutoff filter was chosen as a visible light source. Nyquist plots were obtained by using the AC impedance method.

The photoelectrodes were prepared as described in our previous report [31]. Typically, the aqueous slurries of g-C_3N_4 and Ns-g-C_3N_4 were spin-coated on ITO glass substrate at a spin rate of 3000 rpm for 30 s under low vacuum. The films on ITO glass substrate were dried in air and annealed at 200 °C for 1 h as the final photoelectrodes.

3. Results and discussion

3.1. Structure characterization for samples

The microstructures of the result samples were investigated by transmission electron microscopy (TEM). Fig. 1a shows that the bulk g-C_3N_4 sample synthesized with only melamine is of a multilayer structure. Alternatively, when the mixture of melamine and cyanuric acid was used as precursor, the resulting Ns-g-C_3N_4 sample was composed of ultrathin nanosheets with a thickness of 10 nm