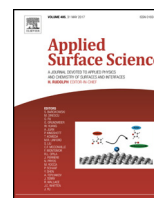




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Carbon vacancy-induced enhancement of the visible light-driven photocatalytic oxidation of NO over g-C₃N₄ nanosheets

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ABSTRACT

g-C₃N₄ (gCN) with carbon vacancy has been extensively investigated and applied in (photo)catalysis. Engineering the carbon vacancy in gCN is of great importance, but it remains a challenging task. In this work, we report for the first time the fabrication of gCN with carbon vacancy (C_v-gCN) via thermal treatment of pristine gCN in CO₂ atmosphere. The photocatalytic performance of C_v-gCN is evaluated on the basis of NO oxidization under visible light irradiation ($\lambda > 400$ nm) in a continual reactor. The successful formation of carbon vacancy in gCN is confirmed through electron paramagnetic resonance (EPR) and X-ray photoelectron spectroscopy (XPS). The photocatalytic oxidation removal rate of NO over C_v-gCN is 59.0%, which is two times higher than that over pristine gCN (24.2%). The results of the quenching experiment show that superoxide radicals (O₂^{•-}) act as the main reactive oxygen species, which is responsible for the oxidation of NO. The enlarged BET surface areas and negatively shifted conduction band (CB) potential enhance the photocatalytic activity of C_v-gCN, which facilitates the efficient electron transfer from the CB of C_v-gCN to the surface adsorbed oxygen, resulting in the formation of O₂^{•-} that can oxidize NO.

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1. Introduction

Extensive use of fossil fuels remarkably contributes to environmental contamination, which results in air quality deterioration and atmospheric pollution problems, such as greenhouse effect, ozone layer depletion, and acid rain [1]. Thus, efforts have been devoted for the development of sustainable and efficient air purification methods. One such method is semiconductor photocatalysis, which has been considered as a promising strategy and has achieved progress in recent years [2–6]. Among semiconductor photocatalysts [7–15], g-C₃N₄ (gCN) is an intriguing photocatalyst stimulated by visible light because of its appropriate band position, which can satisfy the thermodynamic requirements for various potential photocatalytic applications, such as hydrogen evolution [16], organic pollutant degradation [17–20], air purification [21], and CO₂ reduction [22,23]. However, the photocatalytic performance of pristine gCN fails to meet the expected results

because of its low specific surface area and rapid photo-generated electron–hole pair recombination. In practical applications, strategies with high-efficiency must be developed to increase the surface area of gCN and improve the separation/transport of photogenerated carriers.

Although vacancies are common defects in photocatalysts, they function as mediators that provide new mechanisms that promote the separation efficiency of carriers and engineer the electronic structure of photocatalysts. Vacancies have also been found to enhance photocatalytic efficiencies. As their name implies, vacancies can be introduced when the atoms escape from a lattice and subsequently expose on the surface of materials. In general, these vacancies can be further divided into two types, namely, anionic and cationic vacancies. The following anionic vacancies are of great importance: O-vacancies in oxide photocatalysts, such as TiO₂ [24], In₂O₃ [25], SrTiO₃ [26], CeO₂ [27], BiPO₄ [28], γ -Bi₂O₃ [29], La(OH)₃ [30], NiCo₂O₄ [31], BiOI [32], HfO₂ [33], ZnO [34], SnO₂ [35], WO₃ [36], and Fe₂O₃ [37], S-vacancies in sulfide photocatalysts, such as CdS [38] and ZnS [39], and N-vacancies in nitride photocatalysts, including gCN [40,41]. These anionic vacancies provide an optimum platform for high light-harvesting capacity, rapid photo-induced

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charge carrier separation or transport, and evident photocatalytic performance. Meanwhile, cationic vacancies have been extensively investigated because of their positive effects on photocatalytic reactivity, which are comparable to or even better than those of anionic vacancies. Ti vacancies in anatase have been achieved via a sol-gel method [42]. Since then, the cationic vacancies of photocatalysts have been widely explored. Enamul et al. [43] synthesized ZnO single crystal with Zn vacancy through UV radiation. Guan et al. [44] then developed Bi vacancies in ultrathin BiOCl nanosheets to promote the photodegradation of rhodamine B under simulated solar light irradiation. Wang et al. [45] investigated the surface Bi vacancies of Bi₆S₂O₁₅ core/shell nanowires with enhanced photocatalytic decomposition of methylene blue. Meanwhile, Savariraj et al. [46] demonstrated that knit-coir-mat-like CuS thin films with Cu vacancies exhibit comparable electrochemical and photovoltaic performances. In addition to the widely investigated monovacancies, Bi/Cu dual vacancies of BiCuSeO have been developed, and their electrical conductivity has been significantly increased [47].

On the basis of the strong influence of the characteristics of vacancies, such as electronic structure, charge carrier separation/transport, and superior performance, researchers suggested that the photocatalytic performances of gCN can also be tuned by introducing carbon vacancies into gCN. By etching gCN in NH₃ atmosphere, Liang et al. [48] successfully fabricated gCN nanosheets with surface carbon vacancies (C_v-gCNs); in their work, the photocatalytic hydrogen production rate of C_v-gCN increased nearly 20 times in comparison with that of bulk gCN. Li et al. [49] prepared C_v-gCN by thermally treating gCN under high purity argon gas flow and found that the presence of carbon vacancies not only enhances photocatalytic H₂O₂ production, but also changes the H₂O₂ generation pathway from a two-step single-electron indirect reduction to a one-step two-electron direct reduction. Therefore, searching novel methods for synthesizing gCN with carbon vacancies and applying such methods to address environmental issues is of great importance.

In the present work, gCN nanosheets with surface carbon vacancies (C_v-gCN) were fabricated through a double thermal etching method performed under CO₂ gas flow. As expected, the introduction of carbon vacancies effectively enhanced the photocatalytic activity of gCN in photocatalytic oxidation of NO. The structure and photocatalytic performance of C_v-gCN were then systematically studied.

2. Experimental

2.1. Synthesis

All chemicals were of analytical grade and used without further purification. Samples were synthesized through simple thermal pyrolysis in a muffle furnace. Pristine g-C₃N₄ (gCN) was obtained by heating four crucibles (each containing 10 g of thiourea) at 550 °C for 2 h with a heating rate of 15 °C min⁻¹. The obtained fulvous solid product was mixed and ground into powder in an agate mortar. C_v-gCN was also synthesized at 550 °C for 2 h by calcining six crucibles, of which four contained 0.5 g of the as-prepared gCN powder each and two contained 10.0 g of sodium bicarbonate each to produce CO₂ gas atmosphere. The gas produced during calcination was absorbed by 0.05 M dilute alkaline solution before emission.

2.2. Characterization

The phase structures of the samples were investigated with an X-ray diffractometer (XRD; D/max RA, Japan). The morphological characteristics and microstructures of the samples were characterized through scanning electron microscopy (SEM; JEOL

JSM-6490, Japan) and transmission electron microscopy (TEM; JEM-2010, Japan). Nitrogen adsorption-desorption isotherms were obtained in a nitrogen adsorption apparatus (ASAP 2020, USA). All the samples were degassed at 150 °C prior to the measurements to investigate the surface areas and pore size distributions of the samples. The samples embedded in the KBr pellets were subjected to Fourier transform infrared (FT-IR) spectroscopy in a Nicolet Nexus spectrometer to detect the functional groups on the sample surface. The surface chemical composition was investigated, and valence band (VB) was probed through X-ray photoelectron spectroscopy (XPS; Thermo ESCALAB 250, USA) with Al K_α X-ray ($h\nu = 1486.6$ eV) operated at 150 W. The shift of the binding energy attributed to relative surface charging was corrected with the C 1s level at 284.8 eV as an internal standard. The optical properties of the samples were obtained in a scan UV-vis spectrophotometer (UV-vis diffuse reflectance spectra [DRS]; UV-2450, Shimadzu, Japan) equipped with an integrating sphere assembly, and BaSO₄ was used as the reflectance sample.

2.3. Photocatalytic activity evaluation

The photocatalytic activity of the photocatalyst was evaluated in terms of the oxidation of NO and NO₂ at ppb levels in a continuous flow reactor at ambient temperature. Composed of stainless steel and covered with quartz glass, the rectangular reactor had a volume of 4.5 L (30 cm × 15 cm × 10 cm; L × W × H). A visible LED lamp (150 W) with a cut-off filter ($\lambda > 400$ nm) was used as the light source. Approximately 0.2 g of the as-prepared photocatalyst was added to 30 mL of H₂O. The resulting mixture was ultrasonicated for 30 min, which was then coated onto a dish in diameter of 11.5 cm. The coated dish was heated at 70 °C to ensure the complete evaporation of water and then cooled to room temperature prior to photocatalytic testing. NO and NO₂ gases were acquired from a compressed gas cylinder containing 50 ppm of NO and NO₂ (N₂ balance) in accordance with the traceable standards recommended by the National Institute of Standards and Technology. The initial NO and NO₂ concentrations were diluted to approximately 600 ppb with an air stream supplied by a zero-air generator (Advanced Pollution Instrumentation, A Teledyne Technologies Company, Model 701). The gas streams were completely premixed in a gas blender, and the flow rate was controlled with a mass flow controller at 1.0 L min⁻¹. After the adsorption-desorption equilibrium was achieved, the lamp was turned on. The NO and NO₂ concentrations were continuously measured with a chemiluminescence NO_x analyzer (Advanced Pollution Instrumentation, A Teledyne Technologies Company, Model T200), which monitors the concentration of NO, NO₂, and NO_x (NO_x represents NO + NO₂) with a sampling rate of 1.0 L min⁻¹.

The removal ratio (η) of NO or NO₂ was calculated according to Eq. (1):

$$\eta(\%) = (1 - C/C_0) \times 100\% \quad (1)$$

where C and C_0 are NO or NO₂ concentration in the outlet steam and feeding stream, respectively.

3.1. Active species trapping

Active species trapping experiments were performed to investigate the photocatalytic oxidation mechanism of NO. Potassium iodide (KI), potassium dichromate (K₂Cr₂O₇), and *tert*-butyl alcohol (TBA) were selected as scavengers of the photo-generated holes, electrons, and hydroxide radicals (\cdot OH), respectively. Specifically, 0.2 g of photocatalyst containing 0.002 g of KI, 0.002 g of K₂Cr₂O₇, or 1 mL of TBA was dispersed in 30 mL of H₂O to obtain different

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