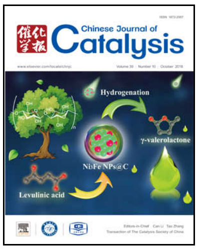
Chinese Journal of Catalysis 39 (2018) 1695–1703

available at www.sciencedirect.com

ScienceDirect

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



Article

Generation and transformation of ROS on g-C_3N_4 for efficient photocatalytic NO removal: A combined *in situ* DRIFTS and DFT investigation

Jieyuan Li [a], Ping Yan [b], Kanglu Li [a], Wanglai Cen [b], Xiaowei Yu [d,*], Shandong Yuan [b,#], Yinghao Chu [a,$], Zhengming Wang [c]

[a] *College of Architecture and Environment, Sichuan University, Chengdu 610065, Sichuan, China*
[b] *Institute of New Energy and Low Carbon Technology, Sichuan University, Chengdu 610065, Sichuan, China*
[c] *Environmental Management Research Institute, National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba, Ibaraki, 305-8569, Japan*
[d] *South China Institute of Environmental Sciences, the Ministry of Environmental Protection of PRC, Guangzhou 510655, Guangdong, China*

ARTICLE INFO

Article history:
Received 21 April 2018
Accepted 7 May 2018
Published 5 October 2018

Keywords:
Photocatalysis
Reactive oxygen species
g-C_3N_4
NO removal
Reaction mechanism

ABSTRACT

Understanding the performance of reactive oxygen species (ROS) in photocatalysis is pivotal for advancing their application in environmental remediation. However, techniques for investigating the generation and transformation mechanism of ROS have been largely overlooked. In this study, considering g-C_3N_4 to be a model photocatalyst, we have focused on the ROS generation and transformation for efficient photocatalytic NO removal. It was found that the key to improving the photocatalysis performance was to enhance the ROS transformation from $\bullet O_2^-$ to $\bullet OH$, elevating the production of $\bullet OH$. The ROS directly participate in the photocatalytic NO removal and tailor the rate-determining step, which is required to overcome the high activation energy of the intermediate conversion. Using a closely combined experimental and theoretical method, this work provides a new protocol to investigate the ROS behavior on g-C_3N_4 for effective NO removal and clarifies the reaction mechanism at the atomic level, which enriches the understanding of ROS in photocatalytic environmental remediation.

1. Introduction

Reactive radicals are of key importance in many fields of degradation of environmental pollutants, such as heterogeneous catalysis for the NO_x/VOCs removal [1,2], advanced oxidation for the organic pollutants treatment of wastewater [3,4] and photocatalytic environmental remediation [5–7]. Thus, the generation and transformation of active radicals gives rise to a general concern in the environmental and catalysis fields. As in photocatalysis, the redox reactivity is brought about by photoexcited electrons (e^-) and holes (h^+) produced in the photocatalysts [8–10]. Several active radicals, which are the major

---

* Corresponding author. E-mail: yuxiaowei@scies.org
# Corresponding author. E-mail: sdyuan@scu.edu.cn
$ Corresponding author. E-mail: chuyinghao@scu.edu.cn

This work was supported by the National Natural Science Foundation of China (51508356), Science and Technology Support Program of Sichuan Province (2014GZ0213, 2016GZ0045), and Youth Project in Science and Technology Innovation Program of Sichuan Province (17-YCG053). The authors also acknowledge the AM-HPC in Suzhou of China for computational support.

DOI: 10.1016/S1872-2067(18)63097-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 10, October 2018

source of oxidation capacity, are subsequently generated through the redox reaction with e^- and h^+. As photocatalysis normally takes place involving oxygen and water as the reactants, the reactive radicals converted by oxygen and water are thus called reactive oxygen species (ROS) [11].

Since ROS are the primary oxidants in photocatalytic environmental remediation, the generation and transformation of ROS is important to understand the photocatalysis mechanism, which improves the photocatalytic efficiency and facilitates practical applications. Four major ROS are commonly recognized, which include superoxide radical ($\bullet O_2^-$), singlet oxygen ($^1O_2$), hydrogen peroxide (H_2O_2) and hydroxyl radical ($\bullet OH$) [12–14]. In a typical photocatalysis reaction, since both reduction and oxidation occur simultaneously, ROS could be generated through the h^+ induced stepwise oxidation path of H_2O, alongwith the production of $\bullet OH$, H_2O_2, $\bullet O_2^-$ and $^1O_2$ [15,16]. On the other hand, the stepwise reduction of O_2 generates $\bullet O_2^-$, H_2O_2 and $\bullet OH$ [17]. Among these, $\bullet OH$ and $\bullet O_2^-$ are recognized as the most stable radicals during the reaction, which can be effectively detected and are regarded as important reactants in the photocatalytic oxidation process.

In typical photocatalysts, their band structures, which possess wide bandgaps and suitable band edges to align the redox potential of $O_2/\bullet O_2^-$ and $OH^-/\bullet OH$ [18], normally provide a tolerated band range to produce both $\bullet O_2^-$ and $\bullet OH$ [19,20]. Hence, the generation mechanism of ROS can be directly summarized as: $O_2 + e^- \rightarrow \bullet O_2^-$ and $OH^- + h^+ \rightarrow \bullet OH$ [21]. However, in some new types of two-dimensional photocatalysts such as graphite carbon nitride (g-C_3N_4) [22–26] and MoS_2 [27–29], their valence band (VB) edge is not low enough to directly oxidize H_2O to generate $\bullet OH$ [30,31]. Thus, $\bullet OH$ are generated through the O_2 reduction at the conduction band (CB), along the paths: $O_2 + e^- \rightarrow \bullet O_2^-$, $\bullet O_2^- + 2H^+ + e^- \rightarrow H_2O_2$ and $H_2O_2 \rightarrow 2\bullet OH$ [32–34]. However, the rate-determining step in the reaction pathways has not been clarified yet. As a major ROS with high oxidation capacity, $\bullet OH$ manifests much more importance in photocatalytic remediation than $\bullet O_2^-$ [11,35]. The generation mechanism of $\bullet OH$ is thus required to be further investigated. Moreover, understanding the conversion of ROS driven pollutants is highly desirable, in order to direct the design of photocatalysts toward more efficient environmental and energy applications.

In this study, we have synthesized g-C_3N_4 with a facile method based on the property that it exhibits photocatalytic activity toward NO removal. By a combined *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and density functional theory (DFT) method, it is determined that the H_2O_2 dissociation is the rate-determining step of $\bullet OH$ generation in g-$C_3N_4$and the reaction coordinates of ROS driven NO removal are presented. It is found that the oxidation capacity of g-C_3N_4 largely depends on the production and oxidation capacity of $\bullet OH$, rather than $\bullet O_2^-$. This article presents a research protocol to investigate the photocatalytic ROS generation and transformation, and clarifies the reaction mechanism of ROS driven NO removal. This approach could be extended to many environmental and catalytic applications.

2. Experimental

2.1. Photocatalyst fabrication

All chemicals used in this study were analytical grade and no further treatment was required. The CN product was fabricated with a reported method [36]. In a typical synthesis procedure, 10 g thiourea was added to a crucible with 20 mL deionized water. The mixed solution was dried at 80 °C for recrystallization. Then, the precursor was placed in a semi-closed alumina crucible with a cover and roasted at 550 °C for 2 h with a heating rate of 15 °C/min in static air. After the calcining treatment, the crucible was cooled to room temperature.

2.2. Characterization

X-ray diffraction (XRD) was used to investigate the crystal phases with Cu K_α radiation (model D/max RA, Rigaku Co. Japan). Scanning electron microscopy (SEM, model JSM-6490, JEOL, Japan) and transmission electron microscopy (TEM, JEM-2010, Japan) were used to investigate the morphology. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Nexus spectrometer (IRPrestige-21, SHIMADAZU, Japan) using samples embedded in KBr pellets. A scanning UV-vis spectrophotometer (TU-1901, China) was used to characterize the UV-vis diffuse reflectance spectrometry. The photoluminescence (PL) spectra were investigated using a fluorescence spectrophotometer (Edinburgh Instruments, FLSP-920) equipped with a Xe lamp with an excitation wavelength of 420 nm. Electron spin resonance (ESR) spectra of chemical radicals were obtained on a JES FA200 spectrometer to determine the involvement of the ROS in methanol dispersion for DMPO-$\bullet O_2^-$ and aqueous dispersion for DMPO-$\bullet OH$, respectively.

2.3. Photocatalytic efficiency evaluation

The photocatalytic activity was investigated via the NO removal at 500 ppb in a self-designed continuous-flow reactor (Scheme S1 in the Supplementary Information). The rectangular reactor (30 cm × 15 cm × 10 cm) is made of polymeric glass and covered with Saint-Glass. The as-prepared sample (0.20 g) was dispersed onto two glass dishes for testing. A 150 W tungsten halogen lamp (0.16 W/cm^2) was vertically placed above the reactor. After the adsorption-desorption equilibrium was achieved, the lamp was turned on. The NO gas was acquired from a compressed gas cylinder at a concentration of 100 ppm of NO (N_2 balance). The initial concentration of NO was diluted to about 550 ppb by a zero air generator and the relative humidity (RH) level of the NO flow was controlled at 50% by passing zero air stream through a humidification chamber. The flow rates of the air stream and NO were controlled at 2.4 L/min and 24 mL/min, respectively. The NO removal ratio (η) was calculated as

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

where C and C_0 refer to the NO concentration in the outlet stream and feeding stream, respectively. The resulting final product (nitrate) was removed by washing the dilute NaOH