



# Photocatalytic oxidation of NO over TiO<sub>2</sub>-Graphene catalyst by UV/H<sub>2</sub>O<sub>2</sub> process and enhanced mechanism analysis



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## ABSTRACT

This study aimed at investigating the photocatalytic oxidation (PCO) of NO under the UV/H<sub>2</sub>O<sub>2</sub> system over a series of TiO<sub>2</sub>-Graphene (TiO<sub>2</sub>-GR) catalysts, which was able to dramatically improve the PCO efficiency of NO compared with pure TiO<sub>2</sub>, and the NO oxidative product was the stable nitrate. The electronic interfacial interaction between GR and TiO<sub>2</sub> resulted in a negative shift of the CB of TiO<sub>2</sub> evidenced by MS. The excellent conductivity of GR suppressed e<sup>-</sup>/h<sup>+</sup> pairs recombination effectively, and GR as a kind of dispersant reduced the size of TiO<sub>2</sub>, increased the active sites. These advantages offered e<sup>-</sup> and h<sup>+</sup> more opportunities to participate in PCO of NO, resulting in significant improvement of the PCO efficiency. The effects of the active species involved in the photocatalytic process were also examined. Moreover, different tests were designed to further confirm the improved mechanism. Further investigations showed that the h<sup>+</sup> could oxidize NO directly.

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## 1. Introduction

Nitrogen oxides (NO<sub>x</sub>) can cause ozone depletion, photochemical smog and the acid rain [1,2]. Over the past few decades, atmospheric NO<sub>x</sub> concentrations have greatly increased with the development of society and industry [3]. The SCR of NO<sub>x</sub> is considered as the most effective method for the removal of NO<sub>x</sub> from stationary sources [4]. However, this reaction must be controlled at a certain temperature (320–400 °C) [5]. That indicates SCR devices must be placed before the air pre-heater, where the high concentration of ash (e.g. K<sub>2</sub>O, CaO and As<sub>2</sub>O<sub>3</sub>) in the flue gas would reduce the performance and longevity of catalysts. Moreover, this technique using NH<sub>3</sub> to reduce NO to N<sub>2</sub> is not economical in terms of atoms. Therefore, development of a method, by which NO<sub>x</sub> is oxidized to nitrate species dissolved in water at a low temperature, overcoming the bottlenecks of the SCR technique, is important [6].

Advanced oxidation processes (AOPs) can produce free radicals with strong oxidation, such as •OH, •O<sub>2</sub><sup>-</sup> and HO<sub>2</sub>•, which can simultaneously oxidize and remove multiple pollutants, such as NO<sub>x</sub>, H<sub>2</sub>S, trace elements, and volatile organic compounds in recent years [7]. The UV/H<sub>2</sub>O<sub>2</sub> process, as a representative of the AOPs, has been widely studied for the water remediation. Since the process

can produce more •OH and •O<sub>2</sub><sup>-</sup> by photolysis of H<sub>2</sub>O<sub>2</sub>. Cooper et al. [8] first used •OH produced by UV decomposition of H<sub>2</sub>O<sub>2</sub> to oxidize NO from simulated flue gas. Liu et al. [9] developed a more applicable wet UV/H<sub>2</sub>O<sub>2</sub> to remove NO from simulated flue gas. The process is a promising way to take place of SCR. The low utilization ration of H<sub>2</sub>O<sub>2</sub> limited its wide application.

Titanium dioxide (TiO<sub>2</sub>) reported first by Frank and Bard [10], has attracted enormous attention because of its high-efficiency, nontoxicity, low cost, and photochemical stability [11]. However, the PCO of TiO<sub>2</sub> is low due to the rapid recombining of photo-generated e<sup>-</sup>/h<sup>+</sup> pairs. Graphene discovered first in 2004 [12] has been a rising star on the horizon of materials science because of its superior electron conductivity, unique 2D structure with a high surface area, structural flexibility and chemical stability [13]. These unusual properties make it a suitable candidate to couple with TiO<sub>2</sub> to improve the photocatalytic performance. In 2008, Williams et al. firstly reported the fabrication of TiO<sub>2</sub>-GR nanocatalyst through in situ induced photocatalytic reduction of GO [14]. TiO<sub>2</sub>-GR photocatalysts have attracted a lot of attention for diverse applications, such as H<sub>2</sub> production from water splitting [15], hydrocarbon production from CO<sub>2</sub> reduction [16], organic photosynthesis [17]. Accordingly, TiO<sub>2</sub>-GR photocatalysts have the potential to be applied in photocatalytic oxidation (PCO) of NO in flue gas under the UV/H<sub>2</sub>O<sub>2</sub> system. However, few reviews focusing on applications and mechanism analysis of TiO<sub>2</sub>-GR catalysts to the PCO of NO under UV/H<sub>2</sub>O<sub>2</sub> are reported.

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In this study, we investigated the PCO of NO over a series of TiO<sub>2</sub>-GR catalysts under the UV/H<sub>2</sub>O<sub>2</sub> system. Compared with TiO<sub>2</sub>, the TiO<sub>2</sub>-GR catalysts exhibited higher PCO efficiency of NO under the UV/H<sub>2</sub>O<sub>2</sub> system. The reasons contributing to the high PCO of NO were discussed and corresponding mechanism was further analyzed. Moreover, a trapping experiment was conducted to examine the effects of the active species involved in the PCO of NO. This study could provide a new insight into the interaction between TiO<sub>2</sub> and GR, as well as the mechanism on PCO of NO under UV/H<sub>2</sub>O<sub>2</sub>.

## 2. Experimental

### 2.1. Preparation of materials

#### 2.1.1. Synthesis of TiO<sub>2</sub>

A sol-gel method was used to prepare TiO<sub>2</sub> support. 0.064 mol of TBOT was added to 0.128 mol of acetylacetone under continuous stirring. Then the solution was diluted with 50 mL ethanol. After being stirred for 2 h at room temperature, the solution was heated at 60 °C for 4 h in a water bath and dried at 120 °C for 6 h. Then it was calcined at 450 °C for 3 h.

#### 2.1.2. Synthesis of TiO<sub>2</sub>-GR

The graphite oxide (GO) used to prepare the TiO<sub>2</sub>-GR catalyst was synthesized using the improved GO synthesis method [18]. GO was ultrasonicated in deionized water and anhydrous ethanol solution. Then the TiO<sub>2</sub> was added to the GO solution to prepare 2.5, 5, and 7.5 wt% TiO<sub>2</sub>-GR catalysts (2.5, 5, and 7.5 wt% represent the mass fraction of GO). Then, a Teflon-sealed autoclave was filled with the homogeneous suspension up to 80% of the total volume, maintained at 150 °C for 24 h, and cooled down to room temperature naturally. The resulting catalysts were washed by water, dried at 60 °C in oven to get the final TiO<sub>2</sub>-GR catalyst with different weight addition ratios of GR. These catalysts of TiO<sub>2</sub> and GR are denoted as TiO<sub>2</sub>-xGR (x = 2.5, 5, 7.5).

### 2.2. Characterizations

The structural and chemical information for prepared samples were measured by X-ray diffraction (XRD, Cu K, Purkinjie XD-3), Raman spectroscopy (DRX, Thermo Fisher, USA), Transmission electron microscope (a Philips CM-10 at 80 kV and a CM-12 at 120 kV), UV-vis diffuse reflectance spectra (DRS, Shimadzu UV-2550), X-ray photoelectron spectroscopy (PHI-5000C ESCA system), Photoluminescence spectra (PL, He-Cd laser, Labram-HR800), Electron paramagnetic resonance (EPR, Bruker EMX-10/12-type spectrometer in the X-band). Produced ions in the solution were analyzed by Ion Chromatography (IC, Dionex ICS90). The temporal absorption spectra change of RhB was characterized by UV-vis Spectrophotometer (T6 New Century, Beijing Persee Co, Ltd.).

All photoelectrochemical tests were performed on a CHI660D electrochemical workstation (Chenhua Instrument, Shanghai, China) with a conventional three-electrode cell. Platinum wire and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The working electrode was prepared by dip-coating powders onto fluorine-doped tin oxide (FTO) substrate with a size of 1 cm × 1 cm; 2 mg of catalyst was suspended in 5 mL ethanol to produce a slurry by ultrasonic dispersion for 30 min, which was then coated on a FTO glass electrode. After the films were dried under ambient conditions, and subsequently treated at 180 °C for 2 h. The electrochemical impedance spectra (EIS) were carried out in the frequency ranging from 10<sup>5</sup> to 0.1 Hz in an aqueous solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub>. The Mott-Schottky analysis was measured at potential ranging from -0.8 to 0.6 V, an amplitude of 5 × 10<sup>-3</sup> V, and frequency of 1 × 10<sup>3</sup> Hz. Prior to and during all measurements,

the electrolyte (0.1 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>] in 1 M KCl) was purged with nitrogen.

### 2.3. Photocatalytic activity

The PCO of TiO<sub>2</sub>-GR was evaluated by removing NO in simulated flue gas. These samples were performed in a quartz tubular vessel (*d* = 1 cm, *h* = 15 cm) in a fixed-bed with continuous flow reactor at room temperature and atmospheric pressure. A 500 W Hg-lamp equipped with a visible cut off filter to provide ultraviolet was chosen as the ultraviolet light source. The catalyst (0.2 g) was loaded in the reactor paralleled with the Hg-lamp. The reactant gases included 400 ppm NO, 5% O<sub>2</sub> and balanced N<sub>2</sub> with a total flow rate of 100 mL min<sup>-1</sup>. Prior to the light irradiation, adsorption-desorption equilibrium between NO and photocatalysts had been reached. Meanwhile, 30% H<sub>2</sub>O<sub>2</sub> solution was injected into the reactor with a flow rate of 0.02 mL min<sup>-1</sup>. The gas products (every 12 min reaction) were analyzed by an Ecom-JZKN flue gas analyzer (Germany). The NO conversion was defined as Eq. (1):

$$\text{NO Conversion} = \frac{\text{NO}_{\text{inlet}} - \text{NO}_{\text{outlet}}}{\text{NO}_{\text{inlet}}} \times 100\% \quad (1)$$

## 3. Results and discussion

### 3.1. Photocatalytic activities

The photocatalysts with different GR mass ratios were applied on the PCO of NO under ultraviolet light illumination to basically evaluate the potential ability for air purification (Fig. 1a). In the absence of UV radiation, the no-catalyst system showed low NO removal efficiency. In such a case, NO could only be removed by single oxidation of H<sub>2</sub>O<sub>2</sub>, which could be represented by the reaction Eq. (2) [19,20]:

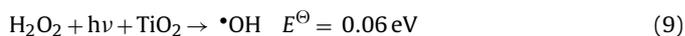
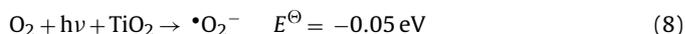


When the UV light was introduced, the NO removal efficiency improved significantly. It could be attributed to the •OH free radicals produced by photolysis of H<sub>2</sub>O<sub>2</sub>, and NO could be removed by the oxidation of •OH free radical (3)–(7) [21]:

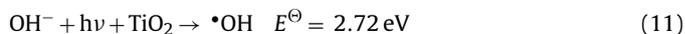
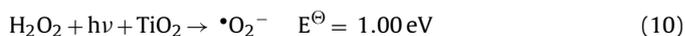


Under UV light, for the TiO<sub>2</sub> catalyst, the NO removal efficiency was higher. It is well known that TiO<sub>2</sub> can promote the formation rate of •OH and •O<sub>2</sub><sup>-</sup> from O<sub>2</sub>, H<sub>2</sub>O (surface hydroxyl groups) and H<sub>2</sub>O<sub>2</sub> under the H<sub>2</sub>O<sub>2</sub>/UV system. This could be represented by reaction Eqs. (8)–(11) [22,23].

The reaction of conduction band is represented by reaction Eqs. (8)–(9).



The reaction of valence band is given by reaction Eqs. (10)–(11).



It is well known that •O<sub>2</sub><sup>-</sup> could oxidize NO according to reaction Eqs. (12)–(14) [21]. Therefore, •OH and •O<sub>2</sub><sup>-</sup> improved the NO

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