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NO removal efficiency of high-yield carbon nitride irradiated under various light sources

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ABSTRACT

Graphitic carbon nitride (g-C_3N_4) is a well-known photocatalyst. In this work, the NO removal efficiency of g-C_3N_4 irradiated under various light sources is explored. For achieving high productivity and activity photocatalyst, the pyrolysis temperature is adjusted from 450 °C to 600 °C. All prepared g-C_3N_4 are put into a transparent reaction box one by one to remove the NO with the initial concentration of 1000 ppb level in air flow under real indoor illumination of three light resources: metal halide lamp, LED lamp and high pressure sodium lamp. According to the photocatalytic reaction results, the NO removal ratio of g-C_3N_4 synthesized under 500 °C can reach to 29.26% under the irradiation of metal halide lamp, overwhelming that of g-C_3N_4 irradiated under other light sources. Several characterization methods were adopt to analyze the photocatalytic reaction mechanism and the micro structures of g-C_3N_4 prepared from melamine. Because of the conduction band potential difference between g-C_3N_4 and melem, heterojunction of melem and g-C_3N_4 can form the convention-type charge transfer, which greatly reduce the combination ratio of photogenerated electrons and holes, thus enhance the photocatalytic activity of g-C_3N_4 under the irradiation of metal halide lamp indicating why the g-C_3N_4 synthesized under 500 °C possesses the best NO removal efficiency among these samples. In addition, compared with other lamps, metal halide lamp is proved to be the most suitable light resource to motivate g-C_3N_4 because of its relatively concentrated light intensity. The present work provide us new perspectives for selecting suitable light resources and proper synthesis conditions for the generation of g-C_3N_4 to achieve better air purification performance in tunnels and indoors.

1. Introduction

NO_x (including NO and NO_2) and SO_2, are indoor and outdoor air pollutants, both of which are the major contributors to acid rain and smog outdoors [1]. NO is a kind of colorless gas, it could be oxidized by O_2 to produce NO_2 in specific condition. It is known that NO could trigger serious air pollution and water pollution, which further cause serious diseases, such as pulmonaryedema, lung cancer and even premature death [1]. At present, the purification of NO in air has been attracting increasing concerns of humans. There are a great number of conventional approaches developed for NO removal, such as wet scrubbing, adsorption, catalytic decomposition, TiO_2 and so on [2–4]. However, these approaches are hard to be applied in large scale due to several reasons like that these approaches are not economically feasible for NO removal or they are not stable enough when operating or they can not work efficiently irradiated under usual light resources [5].

The g-C_3N_4 can be motivated by visible light resources, which are mainly natural sunlight or artificial indoor light, to remove NO to a low concentration level. Melamine can be thermally decomposed at the temperature of 500 °C to 600 °C in a muffle furnace to produce g-C_3N_4 [5–8]. Other raw materials rich in C and N elements, such as urea, thiourea and dicyandiamine, can also be served as sources to prepare g-C_3N_4, however, the yields of them are more or less lower than that of the former which is an important limitation for industrialized application.

At present, big exhaust fans are equipped at the entrance and the exit of tunnels to solve the problem of air pollutants. However, the efficiency of purifying air pollutants triggered by vehicles is quite low, especially in long tunnels. Furthermore, these air pollutants are just transferred to exterior instead of being eliminated which could lead to second pollution to environment. TiO_2 is a traditional photocatalyst which is commonly applied for practical NO removal in several researches [9–14]. However, its band gap limited its application in the environment without sunlight or ultraviolet rays even many methods to extend its absorption range with high cost [15–17]. While g-C_3N_4 could remove the major air pollutant contributor (NO) under

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visible light due to its band gap characteristic.

As we know that g-C_3N_4 is a promising photocatalyst to be applied in various fields, such as hydrogen evolution from splitting water [18], pollutants removal [19], solar energy utilization [20], and so on. However, induced by its disadvantages, such as high recombination rate of photogenerated electron-hole pairs and small surface area, g-C_3N_4 still needs to be reformed by various approaches to obtain higher photocatalitic performance. It is an usual method to dope other materials with g-C_3N_4 for increasing the photocatalitic activity of g-C_3N_4. For instance, Santosh Kumar et al. [21] reported that the photocatalitic activity of g-C_3N_4 could be improved by doping Fe_3O_4 with it, and Fe_3O_4 could not only increase the separating efficiency of photogenerated electron-hole pairs in g-C_3N_4, but also endue the photocatalyst magnetic, which is good for recycling use in practical applications. Satyabadi Martha et al. [22] disclosed that g-C_3N_4, which was synthesized from mixed precursors of melamine and urea, could be coupled with Pt (1.0 wt%) to exhibit higher separating efficiency and lower recombination rate of photogenerated electron-hole pairs, which triggered better photocatalitic performance when comparing with pristine g-C_3N_4. Liu Yong et al. [23] sensitized the g-C_3N_4 with CdS quantum dots, they found that after being sensitized by the Cds quantum dots, the absorption of g-C_3N_4 in the visible region was enhanced and the photoelectrochemical activity was higher than that of the pristine g-C_3N_4 and CdS quantum dots. Xiang et al. [24] reported that g-C_3N_4 could exhibit much higher hydrogen evolution rate than that of pure g-C_3N_4 after being coupled with graphene (1.0 wt%), and this phenomenon could be induced by the heterojunction of graphene and g-C_3N_4. In addition, the surface area is another key factor to influence the photocatalitic performance of g-C_3N_4, to obtain larger surface area of g-C_3N_4, templates are applied in many researches. For example, Cui Y et al. [25] pyrolyzed cyanamide/ammonium thiocyanate, which was templated by silica firstly, to produce g-C_3N_4 with the surface area as large as 239 m^2/g. Lee SC et al. [26] increased the surface area of g-C_3N_4, which was synthesized from urea, to 224 m^2/g in templating approach. Different nanoscale morphological structures also have intensive impact on the activity of g-C_3N_4. Wang SP et al. [27] prepared the g-C_3N_4 with nanotube-type morphological structure, they disclosed that the prepared sample could be motivated under the irradiation of visible light and it possessed fluorescent properties. Through the application of chemical exfoliation, Xu J et al. [28] produced the g-C_3N_4 which could trigger heterojunction effect to enhance the separation efficiency of photogenerated electron-hole pairs and thus improve its photocatalitic performance. However, almost all of the approaches which are aimed at enhancing the photocatalitic performance of g-C_3N_4 require incorporating other materials, which may cause the chemical instability of photocatalysis and the high cost of it. Thus, the utilization of facile precursors with simple synthesis method can be a good selection to prepare g-C_3N_4.

The usual light resources which are applied in tunnels are LED lamps, metal halid lamps and high pressure sodium lamps(HPSL). To select the most suitable light resource among them for motivating g-C_3N_4 to degrade the NO, the conditions of photocatalytic reaction in tunnels are simulated in laboratories. Three lamps were used to inspire g-C_3N_4 to purify NO in the premixed flow. LED lamp is a semiconductor device that can emit light, which belongs to cold light illuminators, and its spectra cover almost all visible light except ultraviolet and infrared light [29], and the light wavelength of LED lamp is from 360 nm to 630 nm. High pressure sodium lamp is a high-intensity gas discharge lamp with a light wavelength of about 589 nm, it could produce golden-white light with high efficiency. It is widely used in tunnels due to its capacities of penetrating fog. The characteristics of its light are related to its inner sodium vapor pressure [30]. Metal halide lamp is also called HID lamp, its main spectra range cover from 350 nm to 450 nm with a concentrated intensity of light with a relatively shorter wavelength, it can be lighted up soon and its life is also long [31]. These three kinds of lamps are widely applied in tunnels to emit light at present. To investigate the difference of NO removal activity under the three usual lamps in tunnels, we measured the NO removal speed and efficiency of g-C_3N_4 irradiated under these three lamps to uncover which is beneficial for practical application of g-C_3N_4 in the future.

2. Experimental section

2.1. Preparation of g-C_3N_4

In a typical experiment, 10 g melamine is put into an alumina crucible, which is then packaged firmly with aluminum foil to avoid the melamine be cast by the gas generated in the producing process of g-C_3N_4. After the alumina crucible is packaged, it is heated in the muffle furnace and kept for 2 h under 500 °C, the temperature is increased from indoor temperature 25 °C to 500 °C in 40 min. Furthermore, in order to achieve the best air purification performance sample, we prepared the g-C_3N_4 with different reaction temperature 450 °C, 500 °C, 550 °C and 600 °C, while the other producing conditions are identical completely. For convenient recognition, we take CN 450, CN 500, CN 550, and CN 600 to represent the g-C_3N_4 prepared under 450 °C, 500 °C, 550 °C and 600 °C.

2.2. Analysis of g-C_3N_4

Several characteristic devices are adopt to analyze the prepared g-C_3N_4. The X-ray diffraction (XRD, model D/max RA, Holland) with Cu Kα radiation at a scan rate of 0.013° 2θ/s scanned from 10° to 80°, is applied to analyze the crystal phase of g-C_3N_4. The UV–vis DRS is applied to analyze the absorption range of g-C_3N_4 towards various light with different wavelength and band gap analysis. Transmission electron microscope (TEM JEM-1200EX, Japan(120 kV)), is used to reveal the morphology of g-C_3N_4. BET-BJH analysis (Micromeritic ASAP 2020) is used to reveal the size and the specific surface area of g-C_3N_4 nanoparticles. Elemental analysis of CHN was measured by a CHNS/O analyzer (Euro EA Elemental Analyzer-Flash 2000).

2.3. NO removal efficiency

The photocatalytic reaction is operated in a transparent reactor with volume of 4.5 L (30 × 15 × 10 cm). One side of the reactor is linked to the feeding stream of premixed gas which is composed of NO and air, the other side of the reactor is linked to a NO_x analyzer (Thermo Environment Instruments, Inc, 42i-HL), which monitors NO and NO_2 continuously with a sampling interval time of 60 s. The initial concentration of NO is 100 ppm and then the NO concentration is diluted to 1000 ppb with premixed wet-dry air. Thus, thanks to the premixed gas, the humidity of the feeding stream is controlled strictly at 50% while the volume fraction of wet air, dry air and NO is controlled at 1:1:0.25. All the lamps are placed about 10 cm above the reactor alternately to irradiate each sample. The transparent reactor is sheltered firmly with a piece of black fabric to avoid the disturbance resulted from outer light resources, and in the process of each reaction, this fabric will not be removed and lamp will not be turned on until the imports-exports equilibrium of stream achieved, which can be identified on the screen of NO_x analyzer. The examining time of each sample is identically 30 min, the NO_x outlet steam is released to outdoors. The removal efficiency of NO is calculated as $\eta(\%) = (1\text{-}C/C_0) \times 100\%$ (C stands for the final concentration of NO, C_0 stands for the concentration of NO in the feeding stream, both of them are continuously measured by NO_x analyzer) [32].

3. Results and discussion

3.1. Yields of g-C_3N_4

The yields of g-C_3N_4 from different raw materials (including urea,