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Enhanced photocatalytic activity of rGO/TiO_2 for the decomposition of formaldehyde under visible light irradiation

Lian Yu[1,*], *Long Wang*[1], *Xibo Sun*[1], *Daiqi Ye*[1,2,3]

1. *College of Environment and Energy, South China University of Technology, Guangzhou 510006, China*
2. *Guangdong Provincial Key Laboratory of Atmospheric Environment and Pollution Control, Guangzhou 510006, China*
3. *National Engineering Laboratory for VOCs Pollution Control Technology and Equipment, South China University of Technology, Guangzhou 510006, China*

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ABSTRACT

Due to the low concentration of indoor air contaminants, photocatalytic technology shows low efficiency for indoor air purification. The application of TiO_2 for photocatalytic removal of formaldehyde is limited, because TiO_2 can only absorb ultraviolet (UV) light. Immobilization of TiO_2 nanoparticles on the surface of graphene can improve the visible light photocatalytic activity and the adsorption capacity. In this study, rGO (reduced graphene oxide)/TiO_2 was synthesized through a hydrothermal method using titanium tetrabutoxide and graphene oxide as precursors, and was used for the degradation of low concentration formaldehyde in indoor air under visible light illumination. Characterization of the crystalline structure and morphology of rGO/TiO_2 revealed that most GO was reduced to rGO during the hydrothermal treatment, and anatase TiO_2 nanoparticles (with particle size of 15–30 nm) were dispersed well on the surface of the rGO sheets. rGO/TiO_2 exhibited excellent photocatalytic activity for degradation of formaldehyde in indoor air and this can be attributed to the role of rGO, which can act as the electron sink and transporter for separating photo-generated electron–hole pairs through interfacial charge transfer. Furthermore, rGO could adsorb formaldehyde molecules from air to produce a high concentration of formaldehyde on the surface of rGO/TiO_2. Under visible light irradiation for 240 min, the concentration of formaldehyde could be reduced to 58.5 ppbV. rGO/TiO_2 showed excellent moisture-resistance behavior, and after five cycles, rGO/TiO_2 maintained high photocatalytic activity for the removal of formaldehyde (84.6%). This work suggests that the synthesized rGO/TiO_2 is a promising photocatalyst for indoor formaldehyde removal.

Introduction

People usually spend more than 80% of their time in houses, cars and offices, so indoor air quality is very important for humans. Volatile organic compounds (VOCs) are the main indoor air pollutants. Formaldehyde (HCHO) is a major pollutant among VOCs, and long-term exposure to HCHO can cause health problems, such as skin irritation and nasal tumors (Nie et al., 2013). The indoor HCHO concentration is usually at ppbV to ppmV levels, which is much higher than the WHO (World Health

* *Corresponding author. E-mail:* esyulian@scut.edu.cn (Lian Yu).

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Organization) guideline (80 ppbV) (Rong et al., 2017). Therefore, it is very important to develop cost-effective and simple technologies for removing indoor HCHO.

A number of techniques, such as adsorption (Ye et al., 2017), photocatalysis (Huang et al., 2016; Ma et al., 2016; Wang et al., 2017a), catalytic oxidation (Wang et al., 2017b; Li et al., 2014) and plasma technology (Zhu et al., 2015b), have been applied for the removal of indoor HCHO. Adsorption is widely used for indoor HCHO removal. The indoor HCHO concentration can be successfully reduced to very low levels by some absorbents (Ye et al., 2017); however, the application of adsorption technology is limited by the adsorption capacities and the possibility of secondary pollution during regeneration. Photocatalytic oxidation (PCO) has been generally applied for indoor HCHO purification (Rong et al., 2017; Bourgeois et al., 2012), by which HCHO can be degraded into innocuous products (such as H_2O and CO_2) without the input of significant energy.

In general, the indoor HCHO concentration is usually very low, and the diffusional resistance for HCHO molecules in the neighborhood of the photocatalyst is very strong (Shiraishi et al., 2009), so the photocatalytic decomposition efficiency is very low. In addition, some severe problems often occur in PCO of indoor HCHO, such as inhibition by H_2O (Shang et al., 2017), low visible light photocatalytic activity (Portela et al., 2017), low degradation rate (Fu et al., 2011) and catalyst deactivation (Zhu et al., 2015a). Some methods have been used to enhance the photocatalytic purification efficiency, mainly as follows (Leary and Westwood, 2011): (1) inhibiting the recombination of photo-generated electron–hole pairs, (2) narrowing the band gap of photocatalysts and (3) enhancing the adsorption performance of photocatalysts.

Tong et al. (2011) prepared N, Fe^{3+} doped and WO_3 compounded TiO_2 particles, which showed excellent activity for HCHO photocatalytic oxidation under visible light. In order to adsorb trace levels of HCHO, TiO_2 has been widely studied and is often immobilized on inorganic materials, with the catalysts showing higher photocatalytic activity (Liu et al., 2005). Portela et al. (2017) and Lu et al. (2010) prepared silicate-TiO_2 hybrids and activated carbon-TiO_2 for photocatalytic oxidation of HCHO, and because of the improvement of the adsorption ability toward HCHO, the photocatalytic activity of the photocatalysts was significantly improved.

Due to its excellent properties, such as high electron mobility, high adsorption capacity for organic pollutants and chemical stability, graphene has been extensively used as an electron cocatalyst and support in photocatalysis (Adamu et al., 2016). Based on its excellent electron mobility, graphene can efficiently separate and transfer photo-induced electrons, thus inhibiting their recombination (Zhang et al., 2010). Wang et al. (2017a) reported that photo-generated electrons in TiO_2 could be transferred into graphene, with the holes remaining on TiO_2, thus suppressing the recombination of holes and electrons (Babu et al., 2015). Recently, graphene has been used in photocatalysis, and it has been demonstrated that graphene can improve the photocatalytic activity of TiO_2 by extending the light absorption range and providing excellent adsorption performance (Chen et al., 2016; Adamu et al., 2016; Xu et al., 2016). Many graphene-based photocatalysts have been developed, and the most widely used semiconductors are CdS, TiO_2 and ZnO (Jiang et al., 2014). Among the widely used graphene-based photocatalysts, TiO_2-graphene is considered to be viable and effective for photocatalytic degradation of organic pollutants (Wang et al., 2017a). Among graphene materials, reduced graphene oxide (rGO) shows excellent adsorption properties toward organic pollutants due to its high surface area, low oxygen content and high hydrophobicity. Several studies reported that the improved photocatalytic activity of TiO_2-graphene can be ascribed to the significant improvement of interfacial electron transfer, which is very important for photocatalytic reactions (Razzaq et al., 2016).

In this study, rGO/TiO_2 with excellent visible light photocatalytic activity was synthesized by a hydrothermal method. The synthesized photocatalyst combines the advantages of rGO and TiO_2, and was used for indoor HCHO removal. In the hydrothermal process, TiO_2 nanoparticles were immobilized effectively on the surface of GO, which possesses surface oxygen functional groups (such as COOH and OH). Then GO was reduced to form rGO, and the surface functional groups were removed (Chen et al., 2016). The synergistic interaction between photocatalysis and adsorption improved the photocatalytic oxidation efficiency toward HCHO, and the synergetic mechanism was discussed. Regeneration of rGO/TiO_2 was also studied to assess its potential for practical applications.

1. Experimental

1.1. Chemicals and reagents

Graphite powder with an average particle diameter of 20 μm (99.9 wt.% purity) was purchased from Yingshida graphite Co. Ltd., Qingdao, China. Sulfuric acid (H_2SO_4, 98.0 wt.%), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 30.0 wt.%), hydrochloric acid (HCl), sodium nitrate ($NaNO_3$), titanium tetrabutoxide (TBOT) and formaldehyde (HCHO) were of analytical grade, and were purchased from Sinopharm Chemical Reagent Co., Ltd. A Millipore-Elix water purification system was used to produce ultrapure water (18.0 MΩ·cm) for use in the experiments.

1.2. Characterization methods

X-ray diffraction (XRD) patterns were measured using a Philips X'Pert PRO X-ray diffraction instrument (X'Pert PRO, Panalytical, Netherlands), operating at 40 kV and 30 mA, scanned with a step size of 0.02° in the range of 2θ = 10–80°. The morphologies were analyzed by transmission electron microscopy (TEM), using a Tecnai G^2 20 S-TWIN microscope (Tecnai G^2 F20 S-TWIN, FEI, USA). A Micromeritics TriStar II 3020 surface area and porosity analyzer (TriStar II 3020, Micromeritics Instrument Corporation, USA) was used to record N_2 sorption isotherms. X-ray photoelectron spectroscopy (XPS) was performed using a Perkin-Elmer PHI 5000C ESCA system (PHI 5000C ESCA, Perkin-EImer, USA). Raman spectra were measured by a Via Reflex Raman spectrometer (INVIA, Renishaw plc, UK) at room temperature with the excitation wavelength of 514 nm. The ultraviolet–visible (UV–vis) diffuse reflectance spectra (DRS) were obtained using a Lambda 750S UV/Vis spectrometer (Lambda 750S, Perkin-EImer, USA), equipped with an integrating sphere assembly.

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