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2D reduced graphene oxide–titania nanocomposites synthesized under different hydrothermal conditions for treatment of hazardous organic pollutants

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ABSTRACT

Two-dimensional reduced graphene oxide–titania (RGO–TiO_2) composites were prepared using a single-step hydrothermal method under various hydrothermal reaction conditions. The morphological and surface characteristics of the RGO–TiO_2 composites and reference materials were determined. The RGO–TiO_2 composites showed photocatalytic activity for the decomposition of two target pollutants that was superior to both pure TiO_2 and RGO under fluorescent daylight lamp illumination. The photocatalytic activity of the RGO–TiO_2 composite increased as the hydrothermal treatment time increased from 1 to 24 h, but then it decreased as the time increased to 36 h, which indicated the presence of an optimal treatment time. RGO–TiO_2 composites activated by violet light-emitting diodes (LEDs) displayed lower decomposition efficiency than those activated by a daylight lamp, likely because of the lower light intensity of violet LEDs (0.2 mW/cm^2) when compared with that of the daylight lamp (1.4 mW/cm^2). However, the photocatalytic decomposition of the target pollutants using the RGO–TiO_2 composite was more energy-efficient using the violet LEDs. The photocatalytic reaction rates increased as the residence time decreased, whereas the reverse was true for the decomposition efficiency.

Introduction

Adsorption processes using sorbents such as activated carbon have traditionally been used for the removal of a broad spectrum of water and air pollutants (Nabatilan, Harhad, Wolenski, & Moe, 2010; Zermane & Meniai, 2012). However, this approach has the significant drawback that the pollutants are not eliminated, only transferred from water or air to the solid phase, and the consumed adsorbents become a hazardous waste. A photocatalytic process using UV-irradiated TiO_2 is a promising alternative for the purification of water and air because it can eliminate most organic pollutants by decomposing them into innocuous species such as carbon dioxide and water vapor (Ayati et al., 2014; Ochiai & Fujishima, 2012). Nevertheless, practical application of TiO_2 for pollution treatment is restricted by low photocatalytic performance owing to the high recombination rate of the photo-induced charge carriers, low adsorptivity, and wide band gaps (Di Paola, García-lópez, Marcì, & Palmisano, 2012). Consequently, a range of strategies, such as the incorporation of foreign species and morphological transformation, have been used to enhance the photocatalytic activity of TiO_2.

The incorporation of two-dimensional graphene materials into TiO_2 is an approach that has been investigated for the improvement of the photocatalytic performance of TiO_2. Graphene oxide (GO) is a two-dimensional catalyst support, in which basal planes contain oxygenated functional groups, such as carboxylic acids, hydroxides, and epoxides (Lightcap, Kosel, & Kamat, 2010). These functional groups facilitate the anchoring of TiO_2 nanoparticles onto the basal planes of GO to form GO-based TiO_2 (GO–TiO_2) composite materials (Yadav & Kim, 2016). The enhanced performance of GO–TiO_2 composites was ascribed to synergistic functions between electron transfer at the interface of the two substrates and the high adsorption capacity of graphene materials (Yadav & Kim, 2016; Zhang et al., 2017). Additionally, GO acts as a photosensitizer, which extends the light absorption range of GO–TiO_2 composites (Nguyen-Phan et al., 2011). Consequently, several researchers (Jiang et al., 2011; Jo, 2014; Nguyen-Phan et al., 2011) have examined the feasibility of using GO–TiO_2 composites for environmental

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applications, and they observed elevated photocatalytic activities for GO–TiO_2 photocatalysts when compared with pure TiO_2 in the photocatalytic decomposition of aqueous chemical species under UV or visible illumination. However, GO is significantly less conductive than pure graphene, owing to its ability to store and shuttle electrons (Lightcap et al., 2010). This drawback can be addressed by reducing the GO, which restores the sp^2 hybrid carbon network and thus enhances its conductivity (Kamat, 2010). Reduced GO (RGO) sheets, suspended in an aqueous phase, can be used to anchor TiO_2 nanoparticles to produce RGO-based TiO_2 (RGO–TiO_2) composites (Hamandi, Berhault, Guillard, & Kochkar, 2017; Kamat, 2010; Liu et al., 2017; Sohail et al., 2017).

Previous studies (Pastrana-Martínez et al., 2012; Zhang, Lv, Li, Wang, & Li, 2010; Zhang, Tang, Fu, & Xu, 2010) investigated the applicability of two-dimensional RGO–TiO_2 composites for the decomposition of various environmental pollutants. Pastrana-Martínez et al. (2012) observed that RGO–TiO_2 composites, synthesized using an aqueous deposition process and post-thermal reduction treatment, showed a significant improvement in the efficiency of the photocatalytic decomposition of diphenhydramine and methyl orange in the aqueous phase when compared with pureTiO_2. Zhang, Lv, et al. (2010) reported that an RGO–TiO_2 composite, produced using a simple hydrothermal method, exhibited higher activity in the photocatalytic reaction of aqueous methylene blue when compared with P25 TiO_2. Another study (Zhang, Tang et al., 2010) found that RGO–TiO_2 composites prepared using a similar hydrothermal treatment had higher photocatalytic activity toward the decomposition of gaseous benzene than P25 TiO_2. However, although the previous studies found that longer hydrothermal processes resulted in improved photocatalytic performance, they did not report optimized hydrothermal treatment times. Therefore, the issue of optimal hydration time for the production of hydrothermally synthesized RGO–TiO_2 composites with a maximum efficiency in degradation of environmental pollutants remains unaddressed.

Here, two-dimensional RGO–TiO_2 composites were prepared using a single-step hydrothermal method under various hydrothermal treatment conditions. Their photocatalytic activities for the decomposition of gaseous hexane and toluene were investigated using a continuous-flow reactor. The model gas-phase pollutants were chosen on the basis of their frequent detection within buildings, and their hazardous health effects (IARC, 2013; Shin & Jo, 2013). In addition, toluene is a commonly investigated model gas-phase pollutant in photocatalysis research (AFNOR, 2009). A sub-ppm concentration of the target compounds was used to approximate typical indoor air concentration levels. When continuous-flow photocatalytic reactors are used, the residence time influences the efficiency of the decomposition of the target compounds (Destaillats et al., 2012); therefore, various residence times were tested. For comparison, the photocatalytic activities of the same weight of neat graphene and neat TiO_2 were also tested.

Experimental

Preparation of RGO–TiO_2 composites

RGO–TiO_2 composites were synthesized using a hydrothermal process over six different hydrothermal processing times (1, 3, 12, 24, 30, and 36 h). Purified graphite powder (5 g, <20 μm, Sigma–Aldrich) was added to sulfuric acid (110 mL, H_2SO_4, ACS grade, Sigma–Aldrich) in a box containing ice (<5 °C). Potassium permanganate (15 g, $KMnO_4$, ACS grade, Sigma–Aldrich) was then added to the mixture. This mixture was heated to 40 °C and held for 100 min, and then 250 mL of distilled water was added. After 30 min, this solution was mixed with a solution of 70 mL of distilled water and hydrogen peroxide (15 mL, H_2O_2, 30%, Fluka) to yield a yellowish mixture. The suspended mixture was centrifuged to isolate the final solid, which was then cleaned using hydrochloric acid (HCl, 30%, Fluka) and dimethyl ketone ($(CH_3)_2CO$, ACS grade, Sigma–Aldrich). The washed solid was conditioned at 80 °C for 12 h to yield oxidized graphite powder, which was then resuspended in distilled water using ultrasonication for 100 min to yield GO suspension.

To synthesize the RGO–TiO_2 photocatalysts, 10 mg of GO was added to a solution of ethanol (50 mL, C_2H_5OH, ACS grade, Sigma–Aldrich) in 100 mL of distilled water, which was then was sonicated for 1 h. Subsequently, 1.0 g of P25 TiO_2 powder was added and the mixture was stirred for 2 h at ambient temperature to yield a homogeneous suspension. The suspended solution was transferred into a 200 mL Teflon-sealed autoclave and heated to 120 °C for the specified reaction time. The suspension was subsequently filtered, washed with distilled water, and conditioned under vacuum at 50 °C for 4 h to yield an RGO–TiO_2 composite powder. The RGO–TiO_2 composites prepared using the hydrothermal reaction times of 1, 3, 12, 24, 30, and 36 h were denoted RGO–TiO_2-1, RGO–TiO_2-3, RGO–TiO_2-12, RGO–TiO_2-24, RGO–TiO_2-30, and RGO–TiO_2-36, respectively. Blank RGO and TiO_2 were prepared using the same procedure without the addition of TiO_2 and GO, respectively. The materials were characterized using scanning electron microscopy (SEM, S-4300, Hitachi, Japan)/energy-dispersive X-ray (EDX, EDX-350, Hitachi), transmission electron microscopy (TEM, H-7600, Hitachi), Fourier transform infrared spectroscopy (FTIR, Spectrum GX, PerkinElmer, USA), X-ray diffraction (XRD, 2500, Rigaku, Japan), ultraviolet (UV)-visible spectroscopy (CARY 5G, Varian, USA), and N_2 adsorption–desorption isotherms (ASAP 2020, Micromeritics, USA).

Photocatalytic activity test

The photocatalytic activity of the RGO–TiO_2 composites, along with the two reference materials (neat graphene and neat TiO_2), for the photocatalytic decomposition of two model gas-phase pollutants (toluene and hexane) under illumination by a daylight lamp or violet light emitting diodes (LEDs) was evaluated using a continuous-flow Pyrex tube reactor (3.9 cm inner diameter and 26.0 cm length). Each of the prepared photocatalysts was coated onto an aluminum sheet (11 cm × 21 cm) using a dip-coating method (Natarajan, Natarajan, Bajaj, & Tayade, 2011). The inside surface of the Pyrex tube was covered with the coated aluminum foil, and a second Pyrex tube (2.7 cm outer diameter) was placed inside the larger reactor tube. A cylindrical fluorescent daylight lamp (8 W), or a tetrahedral tube with 32 LEDs (0.06 W, 400–430 nm, 20 mA, and 3.0 V), was then inserted into the inner, smaller-diameter, Pyrex tube. Air flowing into the reactor was passed through the void between the inner Pyrex tube and the photocatalyst-coated aluminum foil. The relative humidity (50%) of the air stream was adjusted by mixing pure dried air with humidified air at a specified ratio. The humidified air was prepared by passing a portion of dried air through a vial containing water. A standard air stream, which contained 0.1 ppm of each target compound, was synthesized by mixing the target compounds, which were injected into a Pyrex chamber (0.5 L) using a syringe pump, with the humidified air at a specified ratio. This standard air stream was then directed into a buffering chamber (1 L) to stabilize the gas flow, and then finally transferred into the Pyrex reactor. The residence times were adjusted by varying the airflow rate to 1.0, 1.9, 3.8, or 7.6 s.

Samples of the gas streams were taken at the upstream and downstream ports of the reactor before and after activating the light source. New light sources were used each day to reduce any confounding effect on the photocatalytic outputs. The pho-

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