Preparation of LaMnO₃/graphene thin films and their photocatalytic activity

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Abstract: A novel photocatalyst of LaMnO₃/graphene thin films with the perovskite-type was synthesized by sol-gel process assisted with spin-coating methods on glass substrates. The prepared samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Brumauer-Emmett-Teller (BET) surface area analyzer, X-ray photoelectron spectroscopy (XPS) and UV-vis diffuse reflectance spectroscopy. Results showed that after the introduction of graphene, the perovskite structure was unchanged and the size of LaMnO₃ particles was about 22 nm, which uniformed growth in graphene sheet. Determination of contact angle indicated that the contact angle of glass substrate decreased and the hydrophilicity improved after treating with H_2SO_4 and APTES. The UV-Vis photocatalytic activity of the photocatalysts was evaluated by the degradation of diamine green B. LaMnO₃/graphene thin films had better photocatalytic ability than LaMnO₃ and TiO₂ films. The obtained k was 0.5627 and 0.3441 h⁻¹ corresponding to LaMnO₃/graphene films and TiO₂ films, respectively.

Keywords: perovskite; graphene; film; photocatalysts; rare earths

Organic dyes are one of the major groups of pollutants in waste water produced from textile and other industrial processes and over 15% of the textile dyes are lost in waste water stream during dyeing operation[1–3]. A large number of studies have shown that the photocatalytic oxidation play a good role in the removal of dyes from waste water containing direct dyes, reactive dyes, acid dyes, sulfur dyes, and so on. TiO₂ is the most widely used semiconducting photocatalyst resulting from its prominent characteristics and common employment as a nanoparticle powder[4–5]. However, its practical application has not run up to a satisfying extent, it only can absorb the ultraviolet (UV) light occupying a small fraction (<6%) of the solar energy due to its wide band gap (3.2 eV) and high recombination of electron-hole pairs[6–8].

In recent years, the photocatalyst perovskite-type oxides have attracted considerable attention because of its high catalytic activity, low cost, and environmental friendliness[9,10]. The perovskite structure as the photocatalyst has limitation in practical applications, such as the problem of easily composited photo-generated electrons and holes that may reduce catalytic efficiency. In order to improve its photocatalytic performance and efficiency of electron-hole separation, graphene was introduced to modify perovskite-type oxides. Low et al. obtained Ag and graphene co-modified Bi₂WO₆ photocatalysts and photocatalytic activities were observed. The

results showed that the photocatalytic activity of Bi₂WO₆ was significantly enhanced by the loading of Ag and graphene[11].

Graphene, a two-dimensional nanocarbon with a flat monolayer, has attracted a great deal of interest due to its variety of excellent functions, such as high chemical stability, and large specific surface area[12]. In the semiconductor material composite, graphene can play the role of electron transfer channel, which makes the thansfer of electron hole become easier[13,14]. Xiang Quanjun and Yu Jiaguo reported graphene-based semiconductor photocatalysts and graphene-based photocatalysts for hydrogen generation[15,16]. They summarized the recent progress in the design and fabrication of graphene-based semiconductor photocatalysts and the applications of the new materials in photocatalytic hydrogen evolution. As a typical ABO₃-type perovskite structure material, LaMnO₃ has received considerable attention because of its strong catalytic activity. In order to enhance the photocatalytic activity of LaMnO₃, graphene as supporter was introduced to modify LaMnO₃, and it is rarely reported in recent years. Studies on perovskite particles have been carried out[17–19], but the number of reports about perovskite films is limited. Compared with powder catalysts, catalytic membranes are easy to recover and reuse.

In this study, one-step synthesis of LaMnO₃/graphene thin film was carried out through a sol-gel and spin-

coating methods on glass substrates. We used graphene as supporter that was successfully deposited with $LaMnO_3$ nanoparticles and investigated the photocatalytic activity by decomposition of diamine green B. It was demonstrated that the prepared $LaMnO_3$/graphene films exhibited excellent visible-light photocatalytic activity.

1 Experimental

1.1 Preparation of graphene

Graphene was synthesized from natural graphite (Qingdao Graphite Company) using a modified Hummers method[20]. We mixed 45 mL of sulfuric acid (98%), 23 mL of nitric acid (68%), and 2.5 g of natural graphite under an ice-water bath. Then, 7 g of $KMnO_4$ was gradually added with stirring and cooled to control the temperature of the mixture to ≤10 °C. The mixture was stirred at 35 ºC for 30 min. Then, 250 mL of distilled water was added slowly, and the mixture was stirred for 40 min. Finally, 500 mL of distilled water and 50 mL of 30% H_2O_2 solution were added. After the reaction, the solution was held at room temperature for 24 h. The solid product was washed with distilled water until neutralization to obtain graphene oxide. After drying under vacuum at 60 °C, the dried graphene oxide was added into hydrazine hydrate solution (adding 2 mL of hydrazine hydrate per 100 mg of graphene oxide) by gentle water bath (70 ºC) ultrasonication for 12 h. The reaction product was dried under vacuum at 60 °C, and graphene was obtained.

1.2 Pre-treatment of the substrate

The glass of the size 25 mm×38 mm was soaked in the H_2O_2 and H_2SO_4 mixture with 3:7 (*v/v*) for 3 h at 60 ºC. It was washed with distilled water and blown dry with a stream of filtered nitrogen after soaking. Then the glass was dipped in the 120 mmol/L 3-aminopropyltriethoxysilane (APTES) ethanol solution for 10 min. Washing with anhydrous ethanol, gently dried under nitrogen stream, then cured in a muffle burner at 120 ºC for 2 h to allow the APTES molecules to fully condense onto the substrate surface.

1.3 Preparation of thin films

The samples of $LaMnO_3$/graphene thin films were prepared from $La(NO_3)_3$, and $Mn(NO_3)_2$ on glass substrates by sol-gel and spin-coating methods. In brief, 2 mmol/L $La(NO_3)_3$ solution were mixed with 2 mmol/L $Mn(NO_3)_2$ solution. Citric acid as the chelating agent (at a molar ratio of 1:1 with respect to the cations), alkylphenol polyoxyethylene (OP-10) as the dispersing agent (at a molar ratio of 1:9 with respect to the cations), polyvinyl alcohol as the agglomerant (at a molar ratio of 1:8 with respect to the cations), and polyethylene glycol as the plasticizer (at a molar ratio of 1:8 with respect to the cations) were added to the solution. Then, the solution was mixed with 100 mL of 0.1 g/L graphene water suspension, which was subjected to ultrasonic vibration for 0.5 h. The mixed solution was adjusted to pH 10 using aqueous ammonia. After aging for 48 h by spin-coating method, the solution was coated on the pre-treated glass, and dried at 50 ºC for 30 min to form the gel films. The dried gel films were heated at 1 ºC/min in air until reaching 350 ºC. This course was repeated five times, and the last time was maintained for 30 min at 350 ºC. Finally, the films were calcined at 600 ºC for 30 min in vacuum to produce the samples. The mass of five layers $LaMnO_3$/graphene thin film was about 2.3 mg. For comparison, $LaMnO_3$ thin films and Degussa P25 TiO_2 films were also prepared by the same method (Beijing Chemical Reagent Ltd.).

1.4 Characterizations

The surface morphology and structure of the samples were characterized by field emission scanning electron microscopy (FESEM, Hitachi S-4800), transmission electron microscopy (TEM, JEOL-2010), X-ray diffraction (Neo-3014 X-ray diffractometer) with Cu Kα radiation (V=35 kV). The contact angle was measured by a Contact Angle Meter (HARKE-SPCA). The surface zeta potential of $LaMnO_3$/graphene nanocomposite was measured in distilled water utilizing Zetasizer Nano ZS. The Brunauer-Emmett-Teller (BET) specific surface areas were evaluated on the basis of nitrogen adsorption isotherms at −196 ºC on a NOVE 4000e analyzer. The analysis of element chemical status was measured at room temperature by X-ray photoelectron spectroscopy (XPS, ESCALAB250).

1.5 Photocatalytic experiments

The photocatalytic activities of the as-prepared samples were investigated by the degradation of diamine green B under irradiation of a 300 W xenon lamp (CHF-XM-300W, Beijing Trusttech Co. Ltd.). Two pieces of glass with thin films were placed in 50 mL of 10 mg/L diamine green B solution. For comparison, Degussa P25 TiO_2 films were placed in the same solution. The distance between the light source and the liquid surface was about 20 cm. Before illumination, the solution was mechanically stirred for 30 min in the dark to ensure the adsorption/desorption equilibrium between the photocatalyst and dye. Every 1 h, 4 mL of suspension was continually taken from the reaction beaker and measured in the range of 200–800 nm using the UV-vis spectrophotometer (Shimadzu UV-2550). The degradation percentage of the dye is defined as

$$D=(A_0−A)/A_0×100\% \tag{1}$$

where A_0 and A are the dye absorbance before and after irradiation, respectively.