Preliminary Study of Hydrothermal Synthesis of TiO₂–GO Composites as a High Performance Photocatalyst

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Abstract. In this study, the addition of graphene oxide (GO) into TiO₂ was investigated. GO was prepared by modified Hummer method before it was added into TiO₂ via hydrothermal method. The graphite and GO was characterized by Raman spectra, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscope (SEM) along with the TiO₂-GO composites also have been characterized. The morphology of TiO₂ deposited on the surface of the GO sheet was observed by SEM, the phase formation of anisotropic anatase (TiO₂) of the TiO₂-GO was detected in XRD. The photocatalytic activity was determined by calculating the photodegradation efficiency of methylene blue (MB) under UV light irradiation. The photodegradation of MB were increased with time for TiO₂-GO compared to pure TiO₂. The results indicated that TiO₂-GO composites was successfully produced using hydrothermal method for the photocatalytic application.

1 Introduction

Titanium dioxide (TiO₂) is viewed as one of the most promising catalyst materials due to its small band gap, superior photocatalytic performance, easy availability, long-term stability, and nontoxicity. Photocatalysis has become a method that can effectively degraded and mineralize a variety of pesticide contaminants in the presence of TiO₂ and TiO₂ based nanocomposite [1]. However, it is well known that the size and morphology of TiO₂ particles play crucial roles in its properties and applications [2]. There a number of ways to improve the rate of photocatalytic activity and producing a TiO₂ photocatalyst that utilises both UV and visible light. One solution to these problems is the use of a TiO₂ heterojunction photocatalyst. While anatase is commonly considered the most photocatalytically active phase of TiO₂. Previous studies used two phases (anatase and brookite or anatase and rutile) as a heterojunction had improved the photocatalytic activity when compared with the use of anatase alone [2].

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Graphene is ideally suited for the implementation in electrochemical applications due to its reported large electrical conductivity, vast surface area, unique heterogeneous electron transfer and charge carrier rates, widely applicable electrocatalytic activity and low production cost [3]. The TiO2-C composites can be generally categorized into three kinds: TiO2-mounted activated carbon, carbon-doped TiO2, and carbon coated TiO2, and each of them exhibits good photocatalytic activity [4]. However, several problems still hinder further promotion of efficiency of the present TiO2-C composites, such as the marked decrease of the absorptivity during photodegradation, the weakening of the light intensity arriving at catalysts' surface, and the lack of reproducibility due to the preparation and treatment variation. Sohail, M et. al reported the photocatalytic activities of TiO2@rGO nanocomposites are higher than pure TiO2. The TiO2@rGO nanocomposite with 84wt% of TiO2 is well responsible for enhancement in photocatalytic [5]. Therefore, it is a great significance to obtain a TiO2-C composite possessing photocatalytic activity well beyond pure TiO2 with reproducibility and controllability, which could be potent in environmental remediation.

Different methods including chemical vapor deposition, sol-gel, spray pyrolysis and sputtering have been reported for the synthesis of TiO2 in literature to date. Despite all the astonishing properties of TiO2, it suffers from the band gap of 3.2 eV, which occupies only about 4% of the sunlight and the low separation probability of photo-induced electron-hole pairs in photocatalysts [2]. Various modification methods have been proposed via either doping or compositing to narrow its band gap and to enhance the photocatalytic activity in the range of under the visible light radiation. In the present paper, a simple hydrothermal synthesis is reported which TiO2 structures were attached to the GO sheet under hydrothermal treatment.

2 Experimental

The TiO2-GO composites were prepared using hydrothermal method. Graphene oxide (GO) was prepared using modified Hummers method by using graphite powder as a precursor.

2.1 Synthesis of GO

The first stage of synthesis involving oxidation of graphite where H2SO4:H3PO4 (180:20 ml), graphite powder (1.5 g), and KMnO4 (9.0 g) were mixed using magnetic stirrer. The mixture was stirred for 6 h, at a constant speed before it was poured into ice water (~200 ml) and then added with H2O2 to stop the oxidation process. The GO formed after the resultant mixture solution was centrifuged (5000 rpm) for 7 minutes for one time with HCl and the supernatant was decanted away. Then, washing process was repeatedly done with distilled water until a pH of 4–5 was achieved. Next, it was dried at 80 °C in an oven overnight.

2.2 Synthesis of TiO2

The TiO2-GO composites were prepared using titanium (IV) sulfate (Ti(SO4)2) and GO aqueous suspension as the starting materials. In a typical preparation process, 0.12 ml Ti(SO4)2 was added into 5 ml of ethanol and then a certain amount of GO suspension was gradually dropped into the solution. Subsequently, deionized water was added to get a total volume of 10 ml. After stirring for 1 h, the obtained solution was transferred into a 5 ml Teflon-sealed autoclave and maintained at 180°C for 9 h in a furnace. Finally, the resulting products were isolated by centrifugation at 6000 rpm for 10 min, washed with deionized water and ethanol several times and dropped on the silica substrates. The composites dried in an oven at 70°C for 12 h.
2.3 Characterizations

Raman spectra analysis that was conducted to ensure that graphite was transform to graphene oxide using this method. Raman spectra were carried out by Renishaw invia Raman Microscope using a 100× objective lens with a 532 nm laser excitation (WITEC, Germany). The phase structure of the samples as characterized by X-ray diffraction (XRD) on a Bruker D8 diffractometer using Cu Kα (k = 1.5406 Å) radiation at 40 kV and 40 mA. Scanning electron microscopy (SEM) images were taken on a Hitachi S-4800 field emission scanning electron microscope at a voltage of 10 kV.

2.4 Photocatalytic Activity Measurement

The photocatalytic activity was determined by calculating the photodegradation efficiencies of methylene blue (MB) under UV light irradiation. In this experiment, the TiO$_2$-GO composites were placed in aqueous of MB.

3 Results and discussion

GO samples were synthesis using modified Hummer method. The Raman spectra of graphite and graphene oxide (GO) shows in Fig. 1. Highly ordered graphite has three of Raman-active bands visible in the spectra, the in-phase vibration of the graphite lattice (G band) at 1551 cm$^{-1}$ as well as the (weak) disorder band caused by the graphite edges (D band) at approximately 1330 cm$^{-1}$ and 2655 cm$^{-1}$. The GO showed a G-band at 1599 cm$^{-1}$ and a D-band at 1350 cm$^{-1}$, the findings value was similar to result obtained by Chen et. Al [6]. The G-band is associated with graphitic carbons and the D-band is related to the structural defects or partially disordered graphitic domains [7]. The D-bands in both spectra were strong, confirming the lattice distortions of graphene basal planes. While the lattice vibration with the frequency of the D band is, in fact, present in the infinite graphene sheet, it remains Raman-inactive until the edges “light” it up due to the symmetry breaking and the corresponding change in the selection rules. Both the G and the D bands undergo significant changes upon amorphization of graphite as amorphous carbon contains a certain fraction of sp$^3$ carbons. The higher disordered in graphite led to a broader G band, as well as to a broad D band of higher relative intensity compared to that of the G band was observed.
Furthermore, XRD patterns of the raw graphite, synthesis GO and TiO$_2$-GO composite were shown in Fig. 2. It was obviously that the graphite has a peak at $2\Theta = 27^\circ$ meanwhile the GO has peak at $2\Theta = 11.9^\circ$. GO peak corresponding to the [001] interlayer spacing of 7.43 Å. The XRD pattern of TiO$_2$–GO show clearly diffraction peak of anisotropic anatase TiO$_2$. However, the [001] reflections of GO are not observed in the XRD pattern of TiO$_2$–GO composite because the regular stack of GO was destroyed by the intercalation of TiO$_2$ [8].
Fig. 2. XRD patterns of the raw graphite, synthesis GO and TiO$_2$-GO composite.

Figure 3 shows the morphology of graphite powder and graphene oxide which observed under SEM. There were differences between graphite and graphene oxide where for the graphite the sheets were stalked together. But for graphene oxide it was clearly seen the sheets were exfoliated. These was proved by Paulchamy et al. where the graphite was clearly seen exfoliated after oxidation process [9].

Fig. 3. SEM for (a) graphite as starting material and (b) GO after synthesis using modified Hummer method
The morphology of TiO$_2$-GO composite using hydrothermal method was further observed by SEM. It was easy to find many platelets of TiO$_2$-GO composites, along with large aggregated TiO$_2$ particles. (Fig 4). The as-prepared GO was composed of several sheets and maintained a layered structure with micrometres-long wrinkles on the surface [10]. The TiO$_2$ were well distributed on the both sides of the GO, due to self-assembling of the TiO$_2$ on the GO during hydrothermal proses.

![Fig. 4. SEM for TiO$_2$-GO composite](image)

The Raman spectra, XRD and SEM analysis confirmed the effective self-assembly of TiO$_2$ at GO sheet grow as a composite on the silica substrate using hydrothermal method. The prerequisite of successful self-assembly was good dispersion of both TiO$_2$ and GO. As reported by Liu, J et. al, GO and Degussa P25 are used to fabricate Go-P25 composites because of P25 was not dispersed in DI water well, only some of the P25 nanoparticles are anchored to the GO sheet [8]. Moreover, the hydrothermal method was easy to control the TiO$_2$/GO ratio by decreasing the TiO$_2$ quantity.

Fig. 5 shows the photodegradation efficiencies vs irradiation time of MB under UV light for TiO$_2$-GO composite, where T degradation% decreased when the times increased. During the photodegradation process, MB molecules were absorbed on the surface of GO and then reacted with photocarrier transferred from TiO$_2$. Therefore, GO was taken as a carrier of photocatalysis which effectively accelerated the photocatalytic reaction rate as reported by Zhang & Pan [11]. It was obvious that GO could enhanced the photocatalytic activity of TiO$_2$ under UV light irradiation due to a synergy effects including the formation of π-π conjugations between dye molecules and aromatic rings and retarding the charge recombination. From the result, no degradation of methylene blue was observed over a long period. Such behavior was probably due to the low crystallinity present in these materials, and to surfactant residue impurities in their pore walls [12].
In this study, the graphene oxide worked as adsorbent, electron acceptor, photosensitizer and enhanced the photodecomposition efficiently. Since GO has the similar structure to TNT, we speculated that the electron can transport along the GO sheet and then reacted with absorbed O$_2$ to form •OH for the further photocatalytic degradation of MB. It was well known that the carbonaceous materials had extraordinary adsorption properties which were used in various environmental applications. Most industrial dyes and related pollutants were usually aromatic in nature and had the ability to create stacking interactions with graphene aromatic domains reported by Wang et al. [2012].

4 Conclusion

In conclusion, we have successfully grown TiO$_2$ on GO using one step method hydrothermal method. This method produced a TiO$_2$-GO composites with strong interactions between the two components. The resulting composite material shows superior photocatalytic activity to other forms of TiO$_2$. Our method could be further extended to grow other functional materials on GO for photocatalytic [13].

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