Preparation of graphene and TiO$_2$ layer by layer composite with highly photocatalytic efficiency

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Abstract: A process for fabricating graphene and TiO$_2$ layer by layer composite was introduced to improve the photocatalytic activity by controlling the layers, thickness and the mass ratio between graphene and TiO$_2$. The graphene oxide (GO) was synthesized from natural graphite powder by the modified Hummers method. Large-area uniform GO and TiO$_2$ thin films were made by a spin-coating process in turn. After exposure of the TiO$_2$/GO multilayer film to UV light irradiation which allows the reduction of GO to graphene, a novel photocatalytic structure as graphene and TiO$_2$ layer by layer composite was synthesized. The cross-sectional SEM image showed that a clear layer by layer microstructure with a single layer thickness of graphene or TiO$_2$ was in the range of about 50 nm. The total thickness of the film was around 5 $\mu$m which was varied according to the layer number of spin coating process. Raman spectra revealed that significant structural changes occurred through UV light irradiation. Photodegradation for methylene blue (MB) exhibited that the layer by layer composite is of higher photocatalytic activity than the pure TiO$_2$ layer.

Key words: graphene; TiO$_2$; photocatalysis; layer by layer; composite

1 Introduction

Resulting from its good chemical stability, favourable photooxidation power, nontoxicity, and low price, TiO$_2$ has been expected to play more and more important role in solving many serious environmental and pollution challenges [1, 2]. However, there are two bottlenecks to hinder its practical applications. One is that the band gap of TiO$_2$ is 3.2 eV, hence it can absorb only the ultraviolet light ($\lambda<400$ nm), which occupies about 4% of the sunlight. The other drawback comes from the low separation probability of photo-induced electron-hole pairs in photocatalysts. Up to now, various processes have been proposed via either doping or compound modification to narrow its band gap and enhance the photocatalytic activity in the range of under the visible light radiation [3–6].

Graphene is another allotrope of carbon besides fullerenes and CNTs, which can be considered a two-dimensional (2D) single atomic layer of graphite. It has been widely investigated due to the unique physical, chemical and mechanical properties. It processes high charge carrier mobility (15000 cm$^2$/V·s) at room temperature, high specific surface area up to 2630 m$^2$/g, complex band structure with conduction and valence bands overlapping for a multi-layer graphene and so on [7]. Among the applications of graphene, integrating graphene with other inorganic materials to fabricate composites or hybrids is the focus. Particularly, the composite of TiO$_2$ and graphene has been considered a potential photocatalyst in the purification of air and water [8, 9]. In our previous work, we have prepared the TiO$_2$/graphene composite from reduction of graphene oxide (GO) by heat treatment, and it has been found that graphene exhibits an ideal carrier for photocatalyst and plays a key role in adsorption of MB molecules, separation of electron-hole pairs and improvement of the visible light absorption due to C doping at the TiO$_2$ surface [10].

Based on spontaneous ionic adsorption of oppositely charged materials from aqueous solution, the layer by layer self assembling method can be a promising technique to fabricate thin films containing nanoparticles. It is a versatile bottom-up method offering superior structural control for preparation of multilayer films and has been successfully applied in various devices [11, 12]. In this work, a process for fabricating graphene and TiO$_2$
layer by layer composite is introduced to improve the photocatalytic activity by controlling the layers, thickness and the mass ratio between graphene and TiO$_2$.

## 2 Experimental

### 2.1 Materials

Graphite powder and other chemical reagent were purchased from Sinopharm Chemical Reagent Co., Ltd. P25 was purchased from Degussa. All chemicals were of analytical grade and used as-received.

### 2.2 Preparation of graphene oxide

The graphene oxide (GO) was synthesized from natural graphite powder (99.95%, 32 μm) by the modified Hummers method [13, 14]. 1) The graphite powder (0.3 g) was put into the solution containing 2–4 mL concentrated H$_2$SO$_4$, 0.5 g K$_2$S$_2$O$_7$ and 0.5 g P$_2$O$_5$. The resultant dark blue mixture was kept stirring for 4 h at 80 °C, and was carefully diluted with distilled water, then the initial product was obtained by filtering and drying at ambient temperature. 2) The initial product was re-dispersed into 12 mL concentrated H$_2$SO$_4$, and 1.5 g KMnO$_4$ was added laggardly. During the processing, an ice bath should be used in order to avoid the temperature increasing over 20 °C. 3) The mixture was stirred at 35 °C for 2 h, and 25 mL distilled water was added. 4) 70 mL distilled water and 2 mL 30% H$_2$O$_2$ solution were added and the reaction was terminated in 15 min. Then the color of the mixture was changed from snuff color to bright yellow. 5) At last, the mixture was washed with HCl solution and distilled water in turn until the pH value of rinse water became neutral, and the GO was obtained after drying.

### 2.3 Preparation of TiO$_2$/graphene layer by layer composites

Large-area uniform GO and TiO$_2$ thin films were made by a spin-coating process in turn. Ethanol suspensions of GO and TiO$_2$ were prepared at concentration of 0, 10%, 20%, 30% and 50%, respectively, and spin coating was performed in air by flooding the substrate surface (Si substrate) with the two ethanol suspensions in turn and spinning at 3500 r/min for 30 s. After exposure of the TiO$_2$/GO multilayer film to UV light irradiation which allows the reduction of GO to graphene [15], a novel photocatalytic structure as graphene and TiO$_2$ layer by layer composite was synthesized.

### 2.4 Characterization

Phase identification of the samples was processed by using X-ray diffractometer (XRD) (AXS D8 Advanced XRD, Germany) with Cu K$_α$ radiation. The cross-sectional morphology of the layer by layer composite was observed by using a scanning electron microscope (Sirion SEM, FEI, Netherlands), and the observation of microstructure was carried out using a transmission electron microscope (TEM, JEM–2010, JEOL, Japan). Raman measurement was carried out by using a Raman spectroscopy (HORIBA Jobin Yvon LabRAM HR, France) with parameters including 10 mW power of laser, 488 nm of laser excitation, extended scan range of 100–2000 cm$^{-1}$ and 2 s of exposure time. UV-vis diffuse reflectance spectra (DRS) and visible absorption spectra of methylene blue (MB) were obtained by using an UV-vis spectrophotometer (Shimadzu UV-2550, Japan), and BaSO$_4$ was used as a reflectance standard in UV-vis diffuse reflectance experiment.

Photocatalytic properties of the samples were examined by measuring the decomposition rate of methylene blue in the presence of the photocatalyst. In the experiment, a 250 W high pressure mercury lamp which generates light in the range of 350–450 nm with a maximum intensity at 365 nm was used as a light source. The lamp was placed 10 cm above the liquid surface. Each sample was placed in a quartz cuvette filled with 4 mL MB aqueous (1.0×10$^{-5}$ mol/L), and after every 30 min, the variation of the MB concentration was evaluated by the absorbance of the solution at 665 nm.

## 3 Results and discussion

The graphene and TiO$_2$ layer-by-layer composite with variable graphene contents was obtained using the spin coating technique. Figure 1 shows the XRD patterns of the samples. It was confirmed that the GO layers reduced to graphene layers after UV irradiation because of the reappearance of peak at 26.3°, which was corresponded to {002} planes of graphene. The cross-sectional SEM image of spin coated graphene and TiO$_2$ layer by layer composite are captured as shown in Fig. 2(a). It can be concluded that large-area uniform graphene and TiO$_2$ films were successfully obtained with a clear layer by layer microstructure, and a single layer thickness of graphene or TiO$_2$ is in the range of about 50 nm. The total thickness is around 5 μm which was varied according to the layer number of spin coating process. Meanwhile, more microscopic structural information of graphene and TiO$_2$ composite was revealed by using systematic TEM analysis. Figure 2(b) shows a typical low magnification TEM image. As can be seen, the TiO$_2$ nanoparticles are evenly distributed on the graphene surface, which means that the graphene-TiO$_2$ with a firm and effective contact has been fabricated.

Figure 3 shows the Raman spectra of TiO$_2$/GO and TiO$_2$/graphene layer by layer composite. According to
The symmetry group analysis, modes $A_{1g}$ (519 cm$^{-1}$), $B_{1g}$ (399 and 519 cm$^{-1}$), and $E_g$ (144, 197, and 639 cm$^{-1}$) are Raman-active modes of anatase. Significant structural changes occurring during the process of UV-assisted photocatalytic reduction of graphene oxide can be characterized from the spectra. The Raman spectrum of graphene oxide displays D band at 1350 cm$^{-1}$ and G band at 1580 cm$^{-1}$, and for reduced graphene oxide, the spectrum also contains both D and G bands. However, the D/G intensity ratio ($I_D/I_G=0.85$) is larger than that of graphene oxide ($I_D/I_G=0.8$), which suggests a decrease in the average size of the sp$^2$ domains upon reduction of graphene oxide, as well as an increase of edge planes and the degree of disorder in the prepared graphene sheets [16, 17].

FTIR spectra (as shown in Figure 4) reveals that GO presents the peaks of $C-O$ ($\nu_{C-O}$, 1045 cm$^{-1}$), $C-O-C$ ($\nu_{C-O-C}$, 1250 cm$^{-1}$), $C-OH$ ($\nu_{C-OH}$, 1365 cm$^{-1}$), $C=O$ ($\nu_{C=O}$, 1720 cm$^{-1}$) in carboxylic acid, and a broad peak in the range of 3000–3500 cm$^{-1}$ which is attributed to the O–H stretching vibrations of the C–OH groups and water [18, 19]. However, after exposure of the TiO$_2$/GO multilayer film to UV light irradiation, in the spectrum of TiO$_2$/graphene layer by layer composite, these peaks almost totally disappear, which demonstrates that all oxygen-containing functional groups are removed through the UV irradiation.

Figure 5(a) shows the UV-vis diffusion reflectance spectroscopy of the pure TiO$_2$ films and TiO$_2$/graphene layer by layer composite. It is quite obvious that the pure TiO$_2$ films can not absorb any visible light due to the fact that its absorption edge is located at about 400 nm.
However, the TiO$_2$/graphene layer by layer composite exhibited not only a red shift about 30 nm in the absorption edge, but also a strong absorption in the visible light range, which implies the possibility of high photocatalytic activity under UV-vis irradiation.

According to the Kubelka-Munk equation [20]:

$$\alpha h\nu = \text{const}(h\nu - E_g)^2$$

where $\alpha = (1 - R)^2 / 2R$, $R = 10^{-4}$, and $A$ is an optical absorption. Band gap of photocatalyst can be calculated from the equation. Figure 5(b) plots the relationship of $(\alpha h\nu)^{1/2}$ versus photon energy, showing that the band gap of pure P25 is 3.10 eV, and whereas the band gap of layer by layer composite has been slightly reduced to 2.9 eV. This result indicates that the narrowing of the band gap of P25 occurred with the graphene introduction, which should be attributed to the chemical bonding between P25 and graphene sheets [6]. This phenomenon can be explained as follows: graphene oxide, with its extended epoxy and carboxylate groups, readily interacts with TiO$_2$ particles and undergoes reduction under UV irradiation, upon this situation, the $\pi$ electrons of the carbon atom do not entirely bond with others to form the delocalized large $\pi$ bond, and some unpaired $\pi$ electrons could bond with the free electrons on the surface TiO$_2$ to form a Ti—O—C structure. Figure 5(c) shows the efficiencies of the photocatalytic degradation under UV-vis irradiation, $c$ is the concentration of MB at the irradiation time $t$ and $c_0$ is the concentration in the absorption equilibrium of photocatalysts before irradiation. Blank test (MB without any photocatalysts) indicates that the photolysis is neglectable. As shown in this figure, about 55% of MB solutions were degraded after 3 h irradiation for TiO$_2$ and graphene layer by layer composite (TiO$_2$/10% graphene, mass fraction), whereas 30% for pure TiO$_2$ film made by spin-coating, which reveals that the photocatalytic activity has been extremely improved due to the layer by layer structure. Figure 5(d) shows the relationship of time versus ln($c/c_0$) for all photocatalysts. According to the results, it is of great importance to note that the photocatalytic efficiency of TiO$_2$ and graphene layer by layer composite (TiO$_2$/10% graphene) is two times that of pure TiO$_2$ film.

As illustrated in Figure 6, the photocatalytic modified mechanism is discussed as follows: 1) Graphene processes remarkable electrical transport...
property. Thereby in the present system, the graphene layer plays a key role in collecting photocarriers and then improves the photocatalytic efficiency. 2) Graphene is of great specific surface area and strong capacity of absorption. During the photodegradation, a mass of MB molecules are absorbed on the graphene layer surface, and then react with the photocarriers transferred from TiO₂. Thus, the graphene layers can be regarded as a carrier of photocatalysis. 3) It has been known that a multi-layer graphene becomes a semimetal with a complex band structure and the conduction and valence bands overlapping. This indicates that graphene can also absorb the visible light and the excited state electrons are subsequently injected into the conduction band of TiO₂, and then transferred to the surface where they react with oxygen to yield superoxide radicals, which later oxidize the MB directly [21].

Fig. 6 Schematic of transfer and separation of photogenerated electrons and hole between TiO₂ and graphene

4 Conclusions

A series of novel graphene and TiO₂ layer by layer composites with different graphene contents were successfully fabricated by spin coating process. The results suggest that the optimized photocatalyst possesses extended photosensitizing range and enhanced charge separation and transportation properties simultaneously. It is expected that the graphene and TiO₂ layer by layer composite with high photocatalytic activity will play important roles in elimination of pollutants in wastewater and atmosphere.

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