

Graphene/TiO₂ nano-composite for photocatalytic removal of pharmaceuticals from water

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Introduction

The use of pharmaceuticals is on a global increase and Ireland is no exception to this trend. Many pharmaceutical compounds pass through sewage treatment plants to end up in fresh water sources [1,2] Over the past decades TiO₂-based photocatalytic systems have attracted much attention because of their properties for purification of wastewater polluted with dilute organic compounds. One of the newest methods is combining titanium dioxide and an adsorbent material to create integrated photocatalytic adsorbents (IPCAs) which overcome some of the limitations of TiO₂ nano-particles such as low photocatalytic efficiency at low pollutant concentrations and complicated separation after purification [3-5]. Recently, nanostructured carbon materials, such as carbon nanotubes and graphene sheets, offer an exciting research area owing to their structurally interesting and unusual properties. In the carbon materials and TiO₂ composite systems, carbon exhibited the multifunctional properties, for example, the important roles for efficient adsorption of substances as well as preventing the recombination of photo-formed electron-hole pairs [6-9].

In this project a room temperature sol-gel preparation of TiO₂-graphene

nanocomposite was developed and its ability to purify water and wastewater was evaluated. In this reaction, titanium isopropoxide was used as precursor, and TiO₂ was crystallized and immobilized in situ onto graphene substrate to form the TiO₂-graphene nanocomposite.

Methods

Expandable flaked graphite was used as graphene source and Titanium (IV) isopropoxide, as a TiO₂ precursor. Nitric acid, Sulfuric acid and Hydrochloric acid were used to oxidize graphite. In this work, two simple strategies have been proposed to synthesize TiO₂ nano-particles on the surfaces of reduced graphene oxide (RGO): direct mixing of graphene oxide (GO) with TiO₂ powder and in-situ sol-gel synthesis of TiO₂ nano-particles on the surface of graphene oxide sheets. Graphene sheets have been synthesized by thermal induced exfoliation of graphite at 1050 °C for 15 seconds followed by chemical exfoliation using sulfuric and nitric acids at room temperature stirring overnight. Finally chemical reduction has been done using hydrazine solution after making GO/TiO₂ composite to turn it to RGO/ TiO₂ followed by washing and drying three times.

The photodegradation experiments were carried out using a 1 liter cylindrical reactor

and an immersion well as shown in Fig.1. The UV irradiation source was a 125 W medium pressure mercury lamp. Before the illumination, the suspension was stirred in the dark for 120 min to establish the adsorption-desorption equilibrium and study adsorption properties. HPLC with the same method published in previous work [10] was used to measure famotidine concentration.

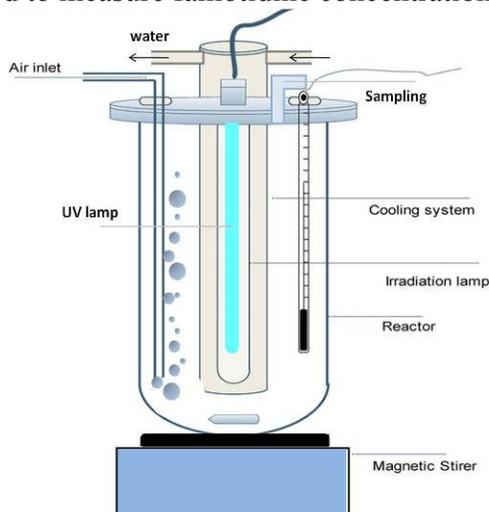


Fig.1. Photocatalytic reactor with UV lamp

Results

As shown in SEM image of Fig 2(a), TiO₂ dispersed uniformly between graphene sheets to form a sandwich-like structure. TiO₂ nanoparticles deposited on graphene sheets had a diameter of 20-50 nm. The dimensions of the composite sheets were about 3-5 micrometer scale both in length and width, which allows an easy separation of the composite with conventional filtration. Graphene oxide consists of epoxy and hydroxyl groups attached to the basal planes and carboxylic on the edge planes. Those oxygen-containing groups can interact with titanium isopropoxide complex which favours the nucleation of fine TiO₂ nanoparticles during the hydrolysis. While as shown in Fig(b) in the absence of graphene oxide, TiO₂ particles has agglomerated to

form coarse particles with the average size of 1-2 micrometer which resulting in lower photocatalytic activity.

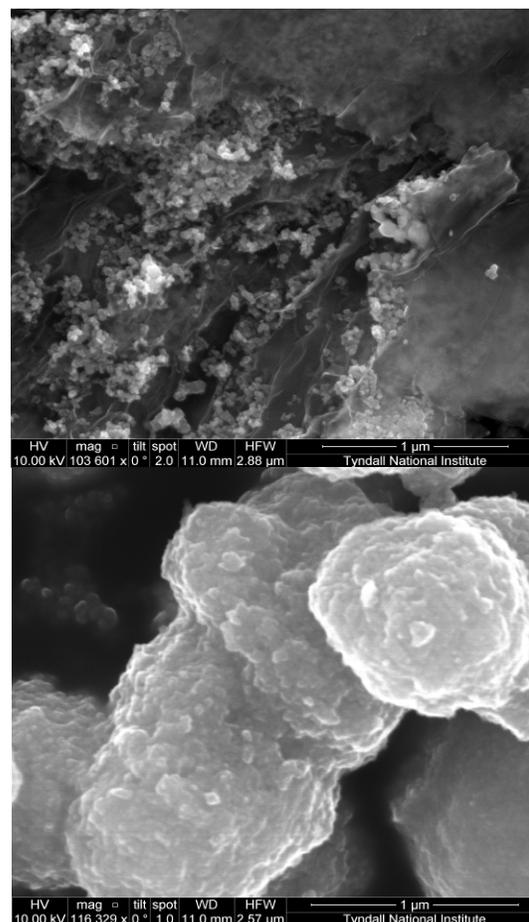


Fig. 2. SEM images of in-situ synthesized RGO/TiO₂ (a), neat TiO₂ powder (b)

Photodegradation of famotidine as a pollutant model is shown in Fig.3. Before the photocatalytic experiment, the suspension of 1 liter solution with the famotidine concentration of 100 mg/l and 0.5 g/l catalyst was magnetically stirred for 2 h in dark to discount the adsorption on the catalyst. The rapid degradation of famotidine over the in-situ synthesized graphene/TiO₂ was clearly shown in Fig.3. About 90% of the famotidine was degraded within 45 min

which is a significant photodegradation in comparison with graphene-TiO₂ mixed together and neat TiO₂ powder that respectively exhibited less than 50% and 30% degradation respectively.

In the case of adsorption, both composites show the same adsorption trend which is higher than neat TiO₂ because of adsorption by functional groups attached to the graphene basal plane.

After photodegradation, the catalyst can be removed easily by filtration or settling in the reactor which is another advantage of using composite over neat TiO₂.

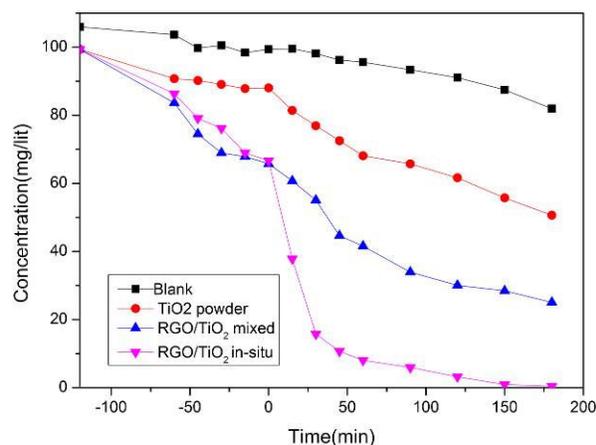


Fig.3. Photocatalytic degradation of 100 mg/L famotidine by (●) neat TiO₂, (▲) mixture of neat TiO₂ and graphene, (▼) in-situ synthesized graphene/TiO₂ composite, (■) photolysis without catalyst

Discussion and Conclusions

Using graphene sheets as a support, a simple method to prepare graphene/TiO₂ composite by in situ sol-gel synthesis of TiO₂ nanoparticles on graphene sheets was developed. The novel composite exhibited excellent photocatalytic activity for degradation of pharmaceuticals which is attributed to a thin two-dimensional sheet support, a large surface area and much increased adsorption capacity, and a good electron acceptor favoring the transfer of

photo-generated electrons from the conduction band of TiO₂ to the graphene sheet [11, 12]. The higher degradation rates over in-situ synthesized RGO/TiO₂ to RGO/TiO₂ mixture can be attributed to attachment of TiO₂ on graphene basal plane which facilitate electron transfer to produce radicals. In summary adsorption, transparency, conductivity and very large planar structure of graphene are the key enhancing factors of photodegradation of the pollutants over reduced graphene/TiO₂ composites. This new composite shows promising applications in the field of environmental photocatalysis specially water purification.

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