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One-step hydrothermal synthesis of surface fluorinated TiO_2/reduced graphene oxide nanocomposites for photocatalytic degradation of estrogens

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ABSTRACT

The surface fluorinated TiO_2/reduced graphene oxide (RGO) nanocomposites (denoted as FTG) were synthesized by a facile one-step hydrothermal method. The prepared photocatalysts were characterized by Transmission electron microscopy, X-ray diffraction, Raman spectroscopy and X-ray photoelectron spectroscopy. The results showed that, the anatase TiO_2 nanoparticles were well dispersed on RGO sheets, and there was a C–Ti bond in FTG. Moreover, the F^- was adsorbed on the surface of TiO_2, and generated the stable F–Ti bonds. The adsorption ability and photocatalytic activity of the nanocomposites was evaluated by degradation of 17β-estradiol (E2) and 17α-ethynyl-estradiol (EE2) under UV light illumination. The removal ratio was strongly affected by the mass ratio of RGO in FTG, and the optimal mass ratio of RGO for both E2 and EE2 was 4.0 wt% (FTG-4). Further more, the presence of F^- enhanced the photocatalytic activity effectively. Under the optimal degradation conditions, the total removal ratios of E2 over FTG-4, TiO_2/4 wt% RGO (denoted as TG, without adding hydrofluoric acid) and P25 (Commercial TiO_2) were 99.8%, 83.3% and 74.4%, respectively. And the total removal ratios of EE2 over the same catalysts were 99.7%, 82.6% and 75.6%, respectively. The results indicated that FTG exhibited much higher efficient removal ability for estrogens compared to TG and P25. The introduction of GO in the TiO_2 can enhance the adsorption ability for estrogens, meanwhile, GO and the F^- can both improve the photocatalytic activity of TiO_2 for degradation of estrogens greatly. Further more, the prepared catalyst was found to be reusable.

1. Introduction

The bad effects of endocrine disrupting compounds (EDCs) have become a critical environmental issue and attracted more attention [1,2], since they can endanger human and animal health via influencing the endocrine systems [3]. EDCs consist of a great variety of chemicals, among them, steroid hormones are the most potent ones, including natural estrogen 17β-estradiol (E2) and synthetic estrogen 17α-ethynyl-estradiol (EE2) [4,5]. Even in low concentration (ng/L), estrogens can lead to a number of huaman diseases, such as developmental abnormalities, endocrine disorders, reproductive dysfunction, and so on [4,6]. According to field investigations, estrogens are related to a number of reproductive and sexual abnormalities seen in wildlife [7,8]. Previous studies showed that

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E2 and EE2 are frequently detected in surface waters and sewages at trace levels [9], which may influence the habitat sanctuaries or drinking water district. As a result, there is an urgent need to find a sustainable, effective and economical method to remove E2 and EE2 from water environment.

A variety of sewage treatment techniques have been proposed and examined to improve the removal efficiency of estrogens. Due to the long removal period of physical methods [10,11], and low removal efficiency of biodegradation methods [12,13], semiconductor-mediated heterogeneous photocatalysis, which operates under solar irradiation without generating harmful by-products, is considered an important alternative for the elimination of estrogens. TiO_2 is currently the most extensively used semiconductor photocatalyst [14,15], since it is nontoxic, chemically stable, and relatively inexpensive. However, the rapid recombination of photogenerated electron-hole pairs and low adsorption capacity for organic contaminants restricted the applications of TiO_2 in wastewater treatment.

In order to improve the photocatalytic performance of TiO_2, many methods have been employed, such as noble metal deposition, surface modification and combining with other semiconductors [16–23]. Recently, graphene for improving photocatalytic properties has emerged as a high potential material due to its unique physical and electronical properties, such as a very large surface area ($\sim$2600 m^2/g), the high mobility of charge carriers and good mechanical properties [24–26]. Graphene is an ideal nanomaterial for pairing with TiO_2 for photocatalysis because its effective adsorption of pollutants deduced by π–π interactions between pollutants and graphene. Moreover, electrons are easily transported to the graphene nanosheets and the recombination of conduction band electrons (e^-) and valence band holes (h^+) is significantly reduced [27,28]. Reducing electron-hole recombination rates and improving the adsorption capacity of the organic contaminants by graphene on the surface of TiO_2 can play a synergetic role in the removal of pollutants. In recent years, the combination of TiO_2 and graphene had been proved to be an effective pathway to degrade organic dye and split water for hydrogen [29–32].

Meanwhile, surface fluorination of TiO_2 has been intensively studied as a new method of surface modification in recent years [33–35]. Surface fluorination can be done by a simple ligand exchange between surface hydroxyl groups on TiO_2 and fluoride ions (Eqs (1)). The F^- on the surface of TiO_2 can enhance the crystallization of the TiO_2 anatase phase [36,37]. Further more, it has been reported that the •OH radical-mediated photocatalytic degradation reactions are greatly accelerated on surface fluorinated TiO_2 [38–40]. Therefore, it can be inferred that the introduction of fluorine can enhance the photocatalytic activity of TiO_2.

$$\equiv Ti-OH+F^- \leftrightarrow \equiv Ti-F+OH^- \quad (1)$$

Up to now, investigations on photocatalytic degradation of estrogens mainly focused commercial TiO_2 (P25) as catalysts [41–43]. To the best of our knowledge, the surface fluorinated TiO_2/reduced graphene oxide nanocomposites have not been used to degrade estrogens. In this paper, we presented a one-step hydrothermal method to synthesize surface fluorinated TiO_2 graphene based nanocomposites. The structure, phase composition, and morphology of the prepared nanocomposites were studied and their adsorption capacity and photocatalytic activity on the E2 and EE2 were determined. Commercial TiO_2 (P25) was used as a reference photocatalyst.

2. Experimental

2.1. Materials and reagents

E2 (purity 98%) and EE2 (purity 98%) were purchased from Sigma-Aldrich Corporation. Pristine graphite (325 mesh) was purchased from Qingdao Golden Days Graphite Co., Ltd. Tetrabutyl titanate (TBT) and hydrofluoric acid (HF 40 wt%) were supplied by Chengdu Kelong Chemical Instrument Factory. P25 (commercial TiO_2) was purchased from Evonik. Methanol (HPLC grade) was purchased from Tedia. All the reagents were at analytical grade and used without further purification.

2.2. Preparation of surface fluorinated TiO_2/RGO nanocomposites

Graphene oxide (GO) was prepared from natural flake graphite powder (325 mesh) using a modified Hummers' method [44,45]. GO aqueous solution was obtained by sonication of graphite oxide in distilled water for 2 h. Surface fluorinated TiO_2/reduced grapheme oxide (RGO) nanocomposites (denoted as FTG) were prepared using tetrabutyl titanate (TBT), 1 mg/mL GO aqueous suspension and hydrofluoric acid (HF 40 wt%) as the starting materials. The FTG with different contents of RGO (2, 4, 6, and 8 wt%) were prepared by adjusting the mass ratio of RGO in the composites and were denoted as FTG-2, FTG-4, FTG-6 and FTG-8. In a typical preparation process of FTG-4, 10 mL of 1 mg/mL GO solution and 20 mL of distilled water were mixed and sonicated for 30 min, and then 0.2 mL of HF was added dropwise into the suspension. Then 1 mL of TBT was added dropwise to the above mixed solution with stirring. After continuously stirring for 1 h, the resulting solution was transferred to a Teflon lined stainless-steel autoclave and then kept at 160 °C for 12 h. Finally, the resulting products were obtained by centrifugation at 4000 rpm for 10 min, and then washed with distilled water several times and dried at 60 °C overnight in vacuum. For comparison, surface fluorinated TiO_2 nanocomposites (denoted as FT) and RGO were also synthesized under the same conditions in the absence of GO and TBT, respectively. To investigate the effect of F^- on the photocatalytic activity of graphene-TiO_2 nanocomposites, TiO_2/4 wt% RGO nanocomposites (denoted as TG) and bare TiO_2 were synthesized under the same conditions in the absence of HF. The detailed reaction conditions were listed in Table 1.

2.3. Photocatalysts characterization

The particle size and morphology of the nanocomposites were observed on a JEM-2100 transmission electron