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Immobilized TiO_2-reduced graphene oxide nanocomposites on optical fibers as high performance photocatalysts for degradation of pharmaceuticals

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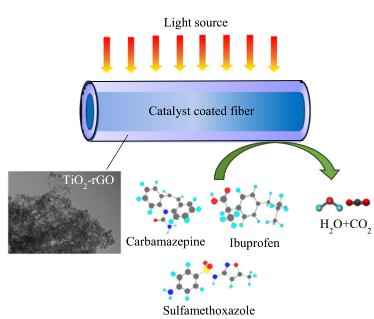
HIGHLIGHTS

- PAHD was successful to reduce GO and synthesize TiO_2-rGO nanocomposites on SOFs.
- TiO_2-rGO coated SOFs were effective for photocatalytic oxidation of pharmaceuticals.
- Pharmaceuticals had different decomposition rate but similar mineralization rate.
- TiO_2-2.7% rGO had the highest photocatalytic activity for pharmaceuticals oxidation.
- Degradation rate constants were strongly correlated to light quantum flux.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of TiO_2-reduced graphene oxide (rGO) coated side-glowing optical fibers (SOFs) were synthesized by polymer assisted hydrothermal deposition method (PAHD), and characterized by crystallographic and spectroscopic methods. Fourier transform infrared spectroscopy showed that the mixed graphene dioxide (GO) was reduced during PAHD coating of TiO_2-GO nanocomposites. X-ray diffraction patterns revealed TiO_2 presented as a mixture phase of anatase, rutile and brookite in the TiO_2-rGO nanocomposites. UV–vis absorption spectra of TiO_2-rGO nanocomposites indicated that mixing rGO into TiO_2 particles could reduce band gap energy, thereby enhancing utilization efficiency of visible light. Photocatalytic performance of the synthesized nanocomposites was measured by the degradation of three pharmaceuticals under UV and visible light irradiation, including carbamazepine, ibuprofen, and sulfamethoxazole. TiO_2-rGO nanocomposites exhibited significantly higher photocatalytic activities as compared to pure TiO_2, and were strongly affected by the amount of rGO in the catalysts. While photocatalysis with 2.7% rGO achieved 54% degradation of carbamazepine, 81% of ibuprofen, and 92% of sulfamethoxazole after 180 min UV irradiation, the mineralization rates of the pharmaceuticals were similar between 52% and 59%. The photocatalytic oxidation of pharmaceuticals by the prepared nanocomposites followed the Langmuir–Hinshelwood kinetic model. There was an obvious positive correlation between degradation rate constant and quantum flux for both UV and visible light, with correlation coefficient of 0.991. In addition, long-term photoactivity testing of TiO_2-rGO coated SOFs demonstrated the durability of the immobilized TiO_2-rGO nanocomposites on optical fibers for water treatment.

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1. Introduction

In recent decades, pharmaceuticals have been detected in wastewater, surface water, and even in drinking water due to their extensive uses [1]. One of the major pathways of pharmaceuticals in surface water is the discharge of urban wastewater effluent because conventional wastewater treatment is not capable of removing pharmaceuticals effectively. Although pharmaceuticals present in surface water are usually at low concentrations, their adverse effects on terrestrial and aquatic organisms have been a prevailing environmental concern [2]. Recently, advanced oxidation processes (AOPs) using O_3, H_2O_2, and ultraviolet (UV) irradiation have been employed for removal of pharmaceuticals in water and wastewater [3,4]. However, AOPs have the shortcomings of high chemical usage, intense energy consumption, and considerable cost.

Photocatalysis is an attractive technology because it can use solar energy to degrade organics and inactivate pathogens. In comparison to traditional oxidation processes, photocatalytic oxidation has the advantages of energy-neutral, chemical-free, and operation-simple. Many refractory organic contaminants could be destroyed by photocatalytic reactions [5]. However, low solar energy utilization efficiency and slow photocatalytic degradation rate must be improved before practical applications [6].

Among various photocatalysts, TiO_2 is the most widely studied in water treatment due to its strong oxidizing ability, excellent chemical stability, long durability, water insolubility, superhydrophilicity, and low cost [6–8]. TiO_2 has three main crystalline structures: anatase, brookite, and rutile. Both anatase and rutile phases are commonly used in photocatalysis, with anatase generally demonstrating greater photocatalytic performance [9]. However, anatase TiO_2 is not an ideal sunlight-driven photocatalyst due to its large band gap (band-gap energy 3.2 eV) and low quantum yield, because anatase TiO_2 absorbs UV light with a wavelength less than 387 nm (only 5% of solar light) and an energy higher than 3.2 eV [9].

Substantial efforts have been devoted to improve the light utilization efficiency of TiO_2, such as doping with metal ions, nonmetal ions, and creation of heterojunctions with other semiconductors [10–13]. Due to the unique electron-transferring property, incorporation of the emerging graphene and TiO_2 is considered a promising nanocomposite to expand the light absorption region [14–17]. Graphene could transform wide-band-gap semiconductors (including TiO_2) into visible light photocatalysts [18]. Considerably higher photoactivity was attained than the commonly used Degussa P25 TiO_2 powder [19]. As a result, TiO_2–graphene particles can absorb wider light region for both UV and visible light, as well as have faster photocatalytic kinetics [20–27]. Additionally, graphene can work as an electron acceptor/transporter for TiO_2 particles; graphene is therefore anticipated to significantly enhance the lifetime of electron-hole pairs [28]. Higher activity of the coupled adsorption and photocatalytic oxidation can be achieved due to the large specific surface area of graphene along with its high adsorption capacity [29]. Because of the high production costs of graphene, one of the most popular approaches to graphene-based nanomaterials is to reduce graphene oxide (GO). GO can be produced at low cost by chemical oxidation of graphite [30].

Most researches used TiO_2-GO or reduced GO (rGO) as suspended photocatalysts in the solution of traditional heterogeneous slurry photoreactors to remove contaminants in water [19,22,23,31,25,32]. The model contaminants studied were predominantly dyes (e.g., rhodamine B, methylene blue, and methyl orange) although other compounds such as 2,4-dichlorophenoxyacetic acid [33], butane [34], diphenhydramine [35,36], and 4-nitrophenol [37] were also studied to evaluate the photocatalytic performance of TiO_2-GO/rGO composites. Such suspended particles contact well with contaminants in water, thereby achieving the highest possible catalytic efficiency. These reactors however, are mostly limited to laboratory study due to low light utilization, loss of photocatalysts, and difficulty and high cost for separation of suspended photocatalyst particles from aqueous solutions. Hence an ideal photoreactor should be able to recover catalysts from treated water easily, and reduce the light loss from liquid absorption and catalyst particles scattering.

So far the use of immobilized TiO_2–graphene/GO/rGO for water treatment is still in its inception. There are only a limited number of studies on this new area. For example, coating TiO_2–graphene nanocomposite on glass surface degraded butane in a gas phase under UV and visible light [38,39]. Incorporation of TiO_2-GO in filtration membranes improved water flux and achieved higher removal of methylene blue, organic dyes, and diphenhydramine in water [36,40,41].

An immobilized photoreactor with catalyst-coated side-glowing optical fibers (SOFs) was developed during our previous study to treat organic contaminants in water [42] and desalination concentrate [43]. SOF is an innovative fiber with nude quartz glass fiber as the core and coated with silicone rubber, light irradiance distribution for SOFs is more uniform along the fiber length as compared to conventional optical fibers (i.e., end-emitting optical fibers) [42]. Bundles of SOFs were incorporated in batch or continuous-flow photoreactors, which provide both light transmission and catalyst support. In comparison to a conventional photoreactor, the SOFs allow the light to transmit directly through the inner fiber cores to reach the photocatalysts coated on the surface, as well as on the exterior surface of the photocatalysts, thus significantly improving the light utilization efficiency. This is an economical way to deliver photons efficiently and uniformly in a large-scale reactor while avoiding the separation step of photocatalysts from water.

In this study, TiO_2-rGO nanocomposite thin films were synthesized on SOFs using polymer assisted hydrothermal deposition (PAHD) method. PAHD is a relatively simple and inexpensive process that enables the formation of a range of high quality materials by precise control of the stoichiometric ratio of precursor solutions, polymers, and dopants, for multi-phase materials. Polymers used in the PAHD can enhance the durability and stability of SOFs coated with photocatalysts in air and water. In addition, hydrothermal method requires lower deposition temperature (e.g., 180–200 °C), which allows the deposition of catalysts on SOF because the silicone rubber coating of SOFs can only endure 250 °C.

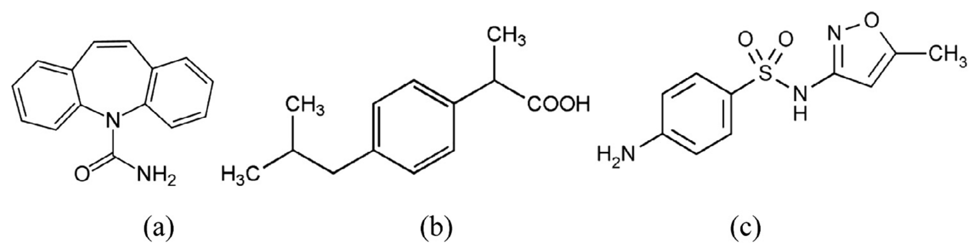

Fig. 1. Structures of the pharmaceuticals: (a) carbamazepine, (b) ibuprofen, and (c) sulfamethoxazole.