Immobilized TiO₂-reduced GrapheneOxide Nanocomposites on Optical Fibers as High Performance Photocatalysts for Degradation of Pharmaceuticals

Lu Lin, Huiyao Wang^{*}, Pei Xu^{*}

Department of Civil Engineering, New Mexico State University, 3035 S Espina Street, Las Cruces, NM 88003, USA

^{*}Corresponding author: Huiyao Wang, Email: huiyao@nmsu.edu

^{*}Corresponding author: Pei Xu, Email: pxu@nmsu.edu

Abstract

A series of TiO₂-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 TiO₂-GO nanocomposites. X-ray diffraction patterns revealed TiO₂ presented as a mixture phase of anatase, rutile and brookite in the TiO₂-rGO nanocomposites. UV-vis adsorption spectra of TiO₂-rGO nanocomposites indicated that mixing rGO into TiO₂ 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. TiO₂-rGO nanocomposites exhibited significantly higher photocatalytic activities as compared to pure TiO₂, 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 TiO₂-rGO coated SOFs demonstrated the durability of the immobilized TiO₂-rGO nanocomposites on optical fibers for water treatment.

Keywords: photocatalysis; pharmaceuticals; titanium dioxide; graphene oxide; water purification; side-glowing optical fibers

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, the 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]. Due to 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, 31-33]. 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[34], butane[35], diphenhydramine[36, 37], and 4-nitrophenol[38] were also studied to evaluate the photocatalytic performance of TiO₂-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 TiO₂-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 TiO₂-graphene nanocomposite on glass surface degraded butane in a gas phase under UV and visible light [39, 40]. Incorporation of TiO₂-GO infiltration membranes improved water flux and achieved higher removal of methylene blue, organic dyes, and diphenhydramine in water[37, 41, 42].

An immobilized photoreactor with catalyst-coated side-glowing optical fibers (SOFs) was developed during our previous study to treat organic contaminants in water [43] and desalination concentrate [44]. 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)[43]. 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.

The designed photoreactor with immobilized TiO_2 -rGO SOFs was investigated to degrade pharmaceuticals including ibuprofen, carbamazepine, and sulfamethoxazole using different light sources. These pharmaceuticals are commonly used anti-inflammatory drug, anticonvulsant and mood stabilizer, and antibiotic used for bacterial infections (Figure 1). The objective of this study was to characterize and optimize the photocatalytic efficiency of TiO_2 -rGO nanocomposites, and to investigate the photodegradation and mineralization of pharmaceutical compounds under different light irradiations in immobilized photoreactors.

The durability of the synthesized TiO_2 -rGO nanocomposites as photocatalyst was evaluated during multiple treatment cycles. The overall goal of the present work was to develop highly efficient SOFs photocatalytic reactors with immobilized catalysts to degrade contaminants of emerging concern (e.g., pharmaceuticals) in water and wastewater using natural sunlight.

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

2. Materials and Methods

2.1 Synthesis of graphene oxide (GO) nanosheets

GO nanosheets were synthesized from graphite using modified Hummer's method [30]. Three grams of graphite (ACS reagent grade, Sigma-Aldrich, St Louis, MO) and 1.5 gram of sodium nitrate (ACS reagent grade, Fisher Scientific, Fair Lawn, NY) were added into 75 mL of 98% sulfuric acid (ACS reagent grade, Sigma-Aldrich, St Louis, MO). The mixture was cooled down to 4°C in an ice-bath and stirred for 2 hours. Nine grams of potassium permanganate (ACS reagent grade, Sigma-Aldrich, St Louis, MO) were added to the suspension and continuously stirred at 4°C for 12 hours. The addition rate was controlled carefully to prevent the temperature of the suspension from exceeding 20°C . The ice-bath was

then removed and 100 mL of deionized water was added slowly to the suspension. The temperature of the mixture was brought to 90°C and continuously stirred for 2 hours. Then 300 mL of deionized water was added and continuously stirred at 90°C for 12 hours. In order to end the reaction, 30 mL of 30wt% hydrogen peroxide (Fisher Scientific, Fair Lawn, NY) and 3L of hot water were added and diluted the mixture. The mixture was then rinsed with deionized water to pH 7. After filtration, the mixture was dispersed in deionized water by sonication for 2 hours, then the mixture was centrifuged to remove unoxidized graphite and unexfoliated graphite oxide. Finally, the supernatant was filtrated through a 0.22μm membrane (EMD Millipore, Billerica, MA) and dried at 40°C to retrieve GO nanoflakes.

2.2 Preparation of TiO₂-rGO coating on SOFs

SOFs are unique optical fibers designed specifically to make the light irradiance distributed uniformly along the fiber length (M200-1; Nanjing Chunhui Science & Technology Industrial Co, China). TiO₂-rGO nanocomposite thin films were coated onto SOFs using PAHD method[43]. The titanium solution was prepared by adding 0.5mL titanium tetrachloride (99.9%, Acros Organics, NJ) dropwise into 3mL of 30wt% hydrogen peroxide. The titanium solution was then added to a solution containing 2 grams of 50wt% polyethylenimine (Fluka, Sigma-Aldrich, St Louis, MO), 1gram of ethylenediaminetetraacetic acid (ACS reagent grade, Acros Organics, NJ), and 40mL of deionized water to form a bright orange solution. To coat TiO₂-rGO film on the SOFs surface, 0.1%, 0.3%, 0.5%, 0.8%, 1.4%, 2.1%, 2.7%, 4.0%, 5.0%, and 10% solutions were prepared based on the corresponding weight ratio of GO and TiO₂. The solutions were added to the bright orange solution before

transferring $\text{TiO}_2\text{-rGO}$ precursor solution into a Teflon-lined acid digester vessel (Parr Instrument Company, Moline, IL). Then the SOFs were placed in the Teflon holder in a stainless steel autoclave with precursor solution. After an 8-hour hydrothermal process at 200°C , the coated SOFs were rinsed with deionized water and dried at 40°C for subsequent degradation experiments. Low temperature hydrothermal treatment used in this method can lessen the decomposition or aggregation of the product nanocomposite particles, and avoid temperature damage to the SOFs.

To compare photocatalytic activity of the prepared $\text{TiO}_2\text{-rGO}$ nanocomposites with the standard TiO_2 Degussa P25 photocatalyst, Aeroxide[®] P25 titania nanoparticles ($\geq 99.5\%$ trace metals basis, Sigma-Aldrich Chemie GmbH, Germany) were used in the SOFs coating using the PAHD method. P25 is a mixture of anatase and rutile phases and the primary particle size is 21 nm.

2.3 Characterization of the catalysts and coated SOFs

The structure and morphology of the catalyst-coated SOFs was characterized by an H-7650 transmission electron microscope (TEM; Hitachi High-Technologies Corp., Pleasanton, CA). X-ray diffraction (XRD; MiniFlex II, Rigaku, Japan) was used to analyze the crystal phase of the catalysts. Fourier transform infrared spectroscopy (FTIR) measurements (Nicolet iS10 FT-IR Spectrometer, Thermo Fisher Scientific Inc., MA, USA) were performed in the transmittance mode in the spectral range of $600\text{-}4000\text{ cm}^{-1}$. UV-visible light absorption spectra were collected using the UV-vis spectrophotometer (DR6000; Hach Company, Loveland, Colorado, USA).

2.4 Photocatalysis experiments

The experimental assembly included a photocatalytic reactor with UV light or visible light source. A bundle of thirty 10cm photocatalyst-coated SOFs were placed in a glass petri dish with 25mL deionized water solution spiked individually with 5mg/L pharmaceuticals (ibuprofen, carbamazepine, and sulfamethoxazole; Acros Organics Co, NJ, USA) (Figure 2). The photocatalytic experiments were conducted at pH 6 and room temperature 23°C.

Three light sources were compared in this study: a high-pressure UV Mercury Vapor lamp (160W PUV-10, Zoo Med Laboratories, San Luis Obispo, CA), a low-pressure UV lamp (39W T5 HO, Zoo Med Laboratories, San Luis Obispo, CA), and a visible light source provided by a fluorescent lamp (40W F40T12/DX, Philips, USA). The irradiance of high-pressure UV lamp concentrates on both UV (minor peaks at 290, 315, 335 nm, and a dominant peak at 365 nm) and visible light (405, 435, and 545 nm) wavelength ranges. The irradiance of low-pressure UV lamp is primarily at 253.7 nm. The fluorescent lamp simulates natural sunlight emitting a small amount of UV light (primary peak at 365 nm, and a minor peak at 378 nm), and broad spectrum range of visible light from 400 to 700 nm with distinct peaks at 405, 436, 488, 546, 577-593, 611, 621, 650, 663 nm. The photon flux density of the light sources was measured using a quantum sensor (MQ-200, Apogee Instruments, Inc., UT, USA).

The durability test was conducted by repeating the above experiment with new pharmaceutical solutions after every 3-hour UV irradiation.

Figure 2. Photoreactor with catalyst-coated SOFs

The concentrations of pharmaceuticals were analyzed by highperformance liquid chromatography (HPLC; PerkinElmer Series 200, CT, USA) equipped with a reverse phase column (Discovery C-18, Supelco). An isocratic method set at a flow rate of 1 mL/min was used with the eluents consisting of a water phase and an acetonitrile phase. The mobile water phase was 25 mM KH_2PO_4 buffer solution (pH 2.5) to control the pH of mobile phase. Acetonitrile/water ratio of 75:25 was chosen to quantify the single-spiked ibuprofen and carbamazepine solutions and 55:45 ratio to detect single-spiked sulfamethoxazole samples. Mineralization of the pharmaceuticals was measured by total organic carbon (TOC) quantified using a carbon analyzer (Shimadzu TOC-L, Kyoto, Japan). The absorbance of pharmaceutical solutions at 254 nm was analyzed by a spectrophotometer (DR6000; Hach Company, Loveland, CO, USA).

3. Results and Discussion

3.1. Characterization of TiO_2 -rGOnanocomposites

Figure 3a shows FTIR spectra of the synthesized GO and TiO_2 -2.7% rGOnanocomposite. GO presented different types of functionalities as confirmed at 3400 cm^{-1} (O-H

stretching vibration), 2900 cm^{-1} (C-H stretching vibration), 1720 cm^{-1} (C=O stretching vibration), 1600 cm^{-1} (skeletal vibration from unoxidized graphite), 1355 cm^{-1} (C-N stretching vibration), 1220 cm^{-1} (C-OH stretching vibration), and 1040 cm^{-1} (C-O stretching vibration). The FTIR spectrum of TiO_2 -2.7% rGO presented significant peak reduction of oxygen functionalities as compared to those of GO. O-H stretching vibration observed at 3400 cm^{-1} was considerably reduced in TiO_2 -2.7% rGO due to deoxygenation during PAHD coating process. The stretching vibrations from C=O at 1720 cm^{-1} , C-OH at 1220 cm^{-1} , and C-O at 1040 cm^{-1} completely disappeared. However, C-O stretching vibration at 1380 cm^{-1} was observed. The FTIR spectrum of TiO_2 -2.7% rGO displayed the absorption band at 1622 cm^{-1} , which is attributed to the stretching vibration of aromatic C=C. The high intensity of C=C band and absence or reduction of oxygen functionalities in TiO_2 -2.7% rGO indicates that GO was nearly completely reduced to rGO. Hence, the synthesized catalysts were TiO_2 -rGO nanocomposites.

The XRD spectra illustrate the feature diffraction peak of GO at 11.02° , which refers to an interlayer distance of $8.03\text{ \AA}$. Besides, there was no obvious peak around 26° (graphite peak), indicating that graphite was fully exfoliated after oxidation. As shown in Figure 3b, XRD patterns demonstrated that all peaks in the spectra were related to anatase, rutile, and brookite TiO_2 phase in the TiO_2 and TiO_2 -rGO nanocomposites. Anatase TiO_2 was the major phase in the synthesized thin films with peaks at 2θ angles of 25.3° , 37.9° , 48.0° , 54.4° , 55.4° , and 62.6° , which can be indexed to (101), (004), (200), (105), (211), and (204) crystal faces, respectively [19]. On the other hand, the characteristic diffraction peaks at 2θ angles of 27.0° and 31.8° are assigned to (110) plane of rutile TiO_2 and (121) plane of brookite TiO_2 [39]. Hence, the

synthesized nanocomposites had TiO_2 in the anatase, rutile, and brookite phases, which was unique to our synthesized materials.

Figure 3.(a) FTIR characterization of GO and TiO_2 -2.7% rGO nanocomposites. (b) X-ray diffractograms of TiO_2 , TiO_2 -0.3%rGO, TiO_2 -1.4%rGO, and TiO_2 -2.7%rGO.

a: anatase, r: rutile, and b: brookite.

Photocatalytic reactions have been reported to be affected by the catalyst crystallite structure [45]. Mixtures of different phases usually exhibited higher photocatalytic activity

than each phase alone [46-48]. The formation of surface-phase combinations improved the transfer of photogenerated electrons from the conduction band of one phase to the trapping sites of another phase [48]. As a result, the combination of GO and TiO₂ demonstrated better photocatalytic performance than pure TiO₂ and photolysis for pharmaceuticals (as discussed later). Anatase was the major phase for all photocatalysts, which had been proved to be more active in photocatalysis than brookite and rutile phases [9]. The peaks of brookite (121) and rutile (110) occurred with the introduction of GO, but they disappeared when GO concentration increased to 2.7% (Figure 3b). This may be attributed to the high surface area of GO, which suppressed the phase transformation from anatase to other phases [19].

The grain sizes of the TiO₂ dominating phase crystals were calculated to be 11.3, 11.6, 10.2, and 10.2 nm for TiO₂, TiO₂-0.3% rGO, TiO₂-1.4% rGO, and TiO₂-2.7% rGO, respectively, based on Scherrer equation described below:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Where D is the crystallite size (nm), λ is the wavelength of the Cu K α radiation applied ($\lambda=1.5418\text{\AA}$), θ is the Bragg's angle of diffraction, and β is the full-width at half maximum intensity of the peak observed (converted to radian).

An optical microscopy photo of SOF coated with TiO₂-0.8% rGO is shown in Figure 4, and the morphological and structural features of the synthesized materials were examined by TEM. TiO₂-rGO nanoparticles were nearly round in shape with irregular dimensions (Figure 4). It has been found that direct interaction between TiO₂ nanoparticles and GO nanosheets prevents the re-aggregation of the GO nanosheets [40]. Additionally, the particle sizes measured by TEM were consistent with the calculated values using Scherrer equation that the

grain sizes decreased from 12 nm in TiO_2 -0.3%rGO to 10 nm in TiO_2 -1.4%rGO and TiO_2 -2.7%rGO nanocomposites.

Figure 4. TEM micrographs of (a) GO nanosheets, (b) TiO_2 -0.3%rGO, (c) TiO_2 -1.4%rGO, and (d) TiO_2 -2.7%rGO nanocomposites; (e) picture of SOF coated with TiO_2 -0.8% rGO.

To investigate the band gap alteration of TiO_2 -rGO nanocomposites, the UV-visible

absorption spectra of TiO_2 , TiO_2 -1.4% rGO, and TiO_2 -2.7% rGO were measured. The optical band gaps of TiO_2 and TiO_2 -rGO were determined using a Tauc plot of the modified Kubelka-Munk (KM) function with a linear extrapolation[49]. The band gaps of TiO_2 , TiO_2 -1.4% rGO, and TiO_2 -2.7% rGO were computed to be 3.20, 3.05, and 2.85 eV, respectively. The increased absorption intensity of light and narrowed band gap indicated the introduction of rGO resulted in an enhanced light utilization efficiency under visible light irradiation, which was further evidenced by the degradation of pharmaceuticals using TiO_2 -rGO nanocomposites.

3.2. Photocatalytic performance of different catalysts

To evaluate the photocatalytic activity of synthesized TiO_2 -rGO nanocomposites, three pharmaceuticals (ibuprofen, carbamazepine, and sulfamethoxazole) were employed for photodegradation experiments.

One of the interesting findings was to compare the effectiveness of photocatalysis and photolysis in the degradation of pharmaceuticals in water (Figure 5). The degradation efficiency of direct photolysis (no catalyst) was measured under the same conditions for photocatalysis (with catalyst). After 180 min of high-pressure UV light exposure, the concentrations of ibuprofen and carbamazepine were observed a slight change (0.1-0.3%), while there was 28% degradation of sulfamethoxazole (Figure 5). It suggests sulfamethoxazole molecules absorb UV light in the region of the lamp emission, but this effect was less important on the reaction intermediates because no TOC degradation was detected in the absence of catalyst.

Figure 5. Photodegradation of carbamazepine (CBZ), ibuprofen (IBP), and sulfamethoxazole (SMZ) after 180 min high-pressure UV irradiation without catalyst and with the catalysts of commercial TiO₂ (P25), TiO₂, TiO₂-0.1% rGO, TiO₂-0.3% rGO, TiO₂-0.5% rGO, TiO₂-0.8% rGO, TiO₂-1.4% rGO, TiO₂-2.1% rGO, TiO₂-2.7% rGO, TiO₂-4.0% rGO, TiO₂-5.0% rGO, and TiO₂-10% rGO

In the presence of catalysts, photodegradation was remarkably increased due to the enhancing effect of the catalyst under the UV irradiation (Figure 5). After 180 min of high-pressure UV light exposure, the sulfamethoxazole removal was 10-35% higher than ibuprofen and carbamazepine probably due to direct photolysis. The photocatalytic efficiency increased with increasing rGO content (in the range of 0-2.7%) in the catalyst for all three pharmaceuticals, but the photocatalytic activity was inhibited as the rGO content increased continuously. Although TiO_2 -4.0% rGO had the highest degradation efficiency of ibuprofen (83%), the catalyst of TiO_2 -2.7% rGO showed the best overall photocatalytic activity, achieving removal of 81% for ibuprofen, 54% carbamazepine, and 92% sulfamethoxazole. For comparison, the photocatalytic activity of SOFs coated with Degussa TiO_2 P25 was measured under the same reaction conditions. P25 was photocatalytically more active than the synthesized TiO_2 and the nanocomposite photocatalysts with low rGO content (TiO_2 -0.1% rGO, TiO_2 -0.3% rGO, and TiO_2 -0.5% rGO) for the degradation of pharmaceuticals, but only degraded 38% ibuprofen, 38% and 64% sulfamethoxazole.

This photocatalytic enhancement might be ascribed to three aspects. In the photocatalysts, pharmaceutical molecules adsorb onto both TiO_2 and rGO. Due to large specific surface area of rGO, the surface area of catalysts could increase due to mixing of rGO, thereby promoting the adsorption of organic molecules. However, the adsorption of pharmaceuticals was not the major mechanism responsible for the degradation enhancement because less than 4% pharmaceuticals adsorbed onto the catalysts during 3-hour dark experiment. The second enhancement involves mixing rGO into TiO_2 nanoparticles that reduces band gap energy and absorb broader spectrum range of both UV and visible light [20-27], thus improving light

absorption in longer wavelength spectrum of the visible light and resulting in higher photoactivity. The third enhancement may be due to the formation of a heterojunction interface in the TiO₂-rGO nanocomposites, where there is a space-charge separation region. After the photoactivation of TiO₂, the electrons can easily transfer to the rGO nanosheets and photoinduced holes migrate into TiO₂; recombination of e⁻ and h⁺ is strongly reduced, which increases the photon yield. However, there is also an optimal rGO ratio for photocatalytic efficiency, since some active sites of TiO₂ could be disadvantageously occupied by rGO, the number of the active sites of the catalyst may decrease [19]. As a result, the nanocomposite of TiO₂-2.7% rGO demonstrated the best photocatalytic activity while further increase in rGO content was detrimental to photocatalysis.

3.3. Heterogeneous photocatalytic degradation of pharmaceuticals

As the TiO₂-2.7%rGO coated SOFs exhibited the best photocatalytic activity, it was selected to study the photocatalytic degradation mechanism of pharmaceuticals. The photodegradation of pharmaceuticals was analyzed in terms of HPLC, TOC, and UV absorbance measurements. As shown in Figure 6, the concentrations of pharmaceuticals measured by HPLC decreased remarkably with the increase of reaction time. After 180 min, the TiO₂-2.7%rGO coated SOFs achieved 54% removal for carbamazepine, 81% for ibuprofen, and 92% for sulfamethoxazole. The TOC measures the organic carbon concentrations of all compounds, including parent compounds and their degradation intermediates, thus providing the evaluation of the mineralization degree. The TOC increased at first probably due to the polymer residuals (derived from coating process) leaching from the catalysts. The reduction of

TOC with TiO_2 -2.7%rGO achieved 54%, 52%, and 59% for carbamazepine, ibuprofen, and sulfamethoxazole, respectively. Interestingly, although the decomposition of the three pharmaceuticals during the 180 min high-pressure UV irradiation varied from 54% to 92%, their mineralization rates were similar. Hence, photocatalysis oxidizes sulfamethoxazole faster compared to carbamazepine and ibuprofen, however the organic intermediates from the sulfamethoxazole oxidation need similar amount of time to be mineralized as carbamazepine and ibuprofen. The intermediates of carbamazepine were more degradable than parent compound by comparing decomposition and mineralization rates, likely due to the complex structure of carbamazepine (Figure 1). Therefore, the decomposition from parent compounds to intermediates is the control step of carbamazepine photocatalysis. On the contrary, the degradation of the intermediates is the control step for the photocatalytic mineralization of ibuprofen and sulfamethoxazole.

Specific UV absorbance (SUVA) is the absorbance of a solution at 254 nm normalized for dissolved organic carbon (DOC), which is determined by dividing the UV absorbance by the corresponding DOC concentration. It has been found that the SUVA value is strongly correlated to aromatic percentage of organic compounds[2]. Interestingly, the aromatic percentage of three pharmaceuticals increased during the 180 min irradiation, only sulfamethoxazole started to decrease at 60 min of reaction. The increase of SUVA implies, after an incomplete oxidation, the intermediates become more aromatic than the parent compounds, probably during the early stages of oxidation reaction. In this way, pharmaceuticals could undergo reactions of dimerization or the bonding of a new ring by the loss of -OH and -H, or $-\text{C}_x\text{H}_y$. So far, a great number of identified degradation products of pharmaceuticals have been

detected during AOPs or photochemical reactions. It indicates the complexity of the photocatalysis process and the existence of various reductive and oxidative degradation routes resulting in multi-step and interconnected pathways. For instance, the possible degradation pathway of ibuprofen studied by Madhavan *et al.* included the formation of a number of products such as substituted phenols, aromatic carboxylic acids, etc.[50]. Various intermediates of carbamazepine photodegradation had been detected and identified by Chiron *et al.*, and the byproducts included 10-hydroxycarbamazepine, hydroxyacridine-9-carboxaldehyde, etc.[51]. As for sulfamethoxazole, SUVA began to reduce after 60-min irradiation, this decrease demonstrated the gradual cleavage of the aromatic rings along the photocatalytic reaction, decomposed into smaller molecules.

Figure 6. TOC reduction and SUVA values as a function of reaction time with the TiO_2 -2.7%rGO coated SOFs under high-pressure UV irradiation. (a) carbamazepine (CBZ), (b) ibuprofen (IBP), and (c) sulfamethoxazole (SMZ)

3.4 Photocatalytic performance under different light sources

Based on the previous results, ibuprofen was selected to investigate the effect of different light sources on photocatalysis to minimize the impact of direct photolysis. The degradation of ibuprofen under the irradiation of high-pressure and low-pressure UV, as well as visible light is illustrated in Figure 7. The degradation efficiencies followed the order of high-pressure UV > low-pressure UV > visible light, with the same order of quantum flux which was 903, 212, 112 $\mu\text{mol}/(\text{m}^2 \cdot \text{s})$, respectively. Even though the photodegradation efficiency of TiO_2 -2.7%rGO under visible light (18%) was only half to one-fourth of UV light (41% for low-pressure UV; 81% for high-pressure UV), it was slightly higher than that of pure TiO_2 under high-pressure UV irradiation (15%, Figure 7). Since TiO_2 can only utilize UV light, this observation confirms that combination of TiO_2 and rGO reduced the band-gap energy. Although the enhancement in the light-response range of these semiconductors from UV to visible light is not significant due to limited photons from the fluorescent lamp in this study, the improvement could be remarkable when using natural solar energy because of its higher irradiation intensity than the fluorescent lamp.

Figure 7. Photodegradation of ibuprofen with TiO_2 -2.7%rGO coated SOFs under different light sources

As calculated in Section 3.5, the degradation rates under high-pressure UV, low-pressure UV, and visible light were 0.539h^{-1} , 0.199h^{-1} , and 0.080h^{-1} , respectively (Table 1). Interestingly, there was an obvious positive correlation between degradation rate constant and quantum flux for both UV and visible light, of which correlation coefficient was 0.991. Therefore, even though the photodegradation rate under visible light was 2-4 times lower than UV light, the photocatalytic would be significantly enhanced due to over tens or hundreds of times quantum flux for solar light. Further study will focus on the application of TiO_2 -2.7%rGO coated SOFs to develop an effective continuous-flow photoreactor with the utilization of solar light.

3.5 Kinetic study

Although there is a limited understanding on photocatalytic oxidation pathways, Langmuir–Hinshelwood kinetic model is typically used to characterize the behavior of organic contaminants under TiO_2 photocatalytic oxidation [52-58]. In the present work, the kinetics of pharmaceuticals photodegradation was fitted by Langmuir–Hinshelwood kinetics model as expressed in Equation 2:

$$r = \frac{dC}{dt} = \frac{kKC}{1+KC} \quad (2)$$

Where r is the degradation rate ($\text{mg}/(\text{L}\cdot\text{h})$); C is the concentration of the pharmaceuticals (mg/L); t is the illumination time (h); k is the reaction rate constant ($\text{mg}/(\text{L}\cdot\text{h})$); and K is the adsorption coefficient of pharmaceuticals (L/mg).

When the initial concentration of pharmaceuticals is low enough (millimolar), the equation (2) can be simplified to an apparent first-order equation [55, 59]:

$$\ln\left(\frac{C_0}{C}\right) = kKt = k_{app}t \quad (3)$$

Where k_{app} is the apparent first-order rate constant (h^{-1}) and is affected by pharmaceuticals concentration.

The photocatalytic degradation of pharmaceuticals was fitted by curves of the Langmuir–Hinshelwood kinetic model and the corresponding rate constants were given in Table 1. The kinetic equation fitted well with the experimental data and most correlation coefficients (R^2) obtained were greater than 0.9. The TOC and UV absorbance kinetic parameters strongly depended on the target contaminant and the light source. Langmuir-Hinshelwood kinetics model is based on the assumption that only the adsorbed molecules can be degraded by catalyst. Hence, the adsorption of the pharmaceutical is an important step in determining photocatalytic degradation rate. Adsorption could be due to the formation of both π - π conjugations and the interactions between organic molecules and oxygenated surface groups at the edges or on the surfaces of rGO[15], high removal efficiency of sulfamethoxazole probably contributes to more interactions between the nanocomposites and the organic compound. On the other hand, the apparent first-order rate constants of pharmaceutical and TOC concentration under UV light decrease with the order of sulfamethoxazole, ibuprofen, and carbamazepine, but the variation among pharmaceutical degradation rates is more significant than TOC. Thus, as discussed in Section 3.3, although photocatalysis could oxidize sulfamethoxazole and ibuprofen two to three times faster than carbamazepine, the degradation rates of organic intermediates from these pharmaceuticals do not have large difference.

Table 1. Apparent first-order rate constant (k_{app}) and correlation coefficients (R^2) of photodegradation for different pharmaceuticals and light sources

Pharmaceuticals	Light source	Measurement	$k_{app}(h^{-1})$	R^2
Carbamazepine	High-pressure UV	HPLC	0.258	0.994
		TOC	0.249	0.835
Sulfamethoxazole	High-pressure UV	HPLC	0.757	0.966
		TOC	0.338	0.917
Ibuprofen	High-pressure UV	HPLC	0.539	0.989
		TOC	0.264	0.944
Ibuprofen	Low-pressure UV	HPLC	0.199	0.927
Ibuprofen	Visible light	HPLC	0.080	0.805

3.6 Durability of photocatalyst films

It is crucial to evaluate durability of the catalysts for practical applications of photocatalysis in real water treatment. Therefore, TiO_2 -2.7%rGO coated SOFs were operated for 15 cycles to test the durability of the catalyst (Figure 8). The removal efficiency of ibuprofen under high-pressure UV irradiation varied slightly during 45-hour operation (over 80% most of time), and the efficiency was slightly higher than that of first 20 hours. It is probably ascribed to the polymers residuals in the catalysts released from the catalysts, which derived from coating process, resulting in slightly increased surface area and adsorption sites. Nevertheless, the prepared TiO_2 -2.7%rGO nanocomposites exhibited excellent degradation

capacity and durability, demonstrating the promising technology for pharmaceuticals as well as micropollutants treatment.

Figure 8. Durability testing of photocatalytic degradation of ibuprofen with TiO_2 -2.7%rGO coated SOFs under 3-hour high-pressure UV irradiation

4. Conclusions

This study investigated the photocatalytic efficiency of treating pharmaceuticals using an immobilized optical fiber photoreactor with a series of TiO_2 -rGOnanocomposites under UV and visible light irradiation. TiO_2 was present in the mixture phases in the TiO_2 -rGO nanocomposite. The photocatalytic activity increased with increasing concentrations of rGO (0-2.7%) in composites, but the degradation was inhibited when the rGO concentration was larger than 2.7%. The highest catalytic activity was observed with 2.7%rGO, resulting in the degradation of 54% for carbamazepine, 81% for ibuprofen, and 92% for sulfamethoxazole after 180 minhigh-pressure UV irradiation. The TiO_2 -rGOthin films coated on SOFs exhibited high durability and maintained consistent photocatalytic efficiency.The Langmuir-Hinshelwood kinetic model expressed well the heterogeneous photocatalysis

degrading pharmaceuticals. Interestingly, there was an obvious positive correlation between degradation rate constant and quantum flux regardless of UV or visible light. This work made it possible to develop TiO₂-rGO coated SOFs into a continuous-flow photoreactor for degrading pharmaceuticals or other environmental contaminants in aqueous solutions under natural solar light.

Acknowledgments

Support for this study was provided by the United States National Science Foundation (NSF) Engineering Research Center Program under Cooperative Agreement EEC-1028968 (ReNUWIt), New Mexico State University (NMSU), and NMSU College of Engineering Research Center.

Reference

- [1] E. Hapeshi, A. Achilleos, M.I. Vasquez, C. Michael, N.P. Xekoukoulotakis, D. Mantzavinos, D. Kassinos, Drugs degrading photocatalytically: Kinetics and mechanisms of ofloxacin and atenolol removal on titania suspensions, *Water Res.* 44 (2010) 1737-1746.
- [2] M.N. Abellán, J. Giménez, S. Esplugas, Photocatalytic degradation of antibiotics: The case of sulfamethoxazole and trimethoprim, *Catal. Today* 144 (2009) 131-136.
- [3] X. Van Doorslaer, J. Dewulf, J. De Maerschalk, H. Van Langenhove, K. Demeestere, Heterogeneous photocatalysis of moxifloxacin in hospital effluent: Effect of selected matrix constituents, *Chem.Eng. J.* 261 (2015) 9-16.
- [4] S. Carbonaro, M.N. Sugihara, T.J. Strathmann, Continuous-flow photocatalytic treatment of pharmaceutical micropollutants: Activity, inhibition, and deactivation of TiO₂ photocatalysts in wastewater effluent, *Appl.Catal. B* 129 (2013) 1-12.

- [5] P. Gogate Parag R , Aniruddha B, A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions, *Adv. Environ. Res.* 8 (2004) 501-551.
- [6] K. Nakata, A. Fujishima, TiO_2 photocatalysis: Design and applications, *J. Photochem. Photobio. C* 13 (2012) 169-189.
- [7] S.G. Kumar, L.G. Devi, Review on modified TiO_2 photocatalysis under UV/visible light: selected results and related mechanisms on interfacial charge carrier transfer dynamics, *J. Phys. Chem. A* 115 (2011) 13211-13241.
- [8] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, *J. Photochem. Photobio. C* 1 (2000) 1-21.
- [9] Q. Xu, *Nanoporous Materials: Synthesis and Applications*, CRC Press 2013.
- [10] H. Labiadh, T.B. Chaabane, L. Balan, N. Becheik, S. Corbel, G. Medjahdi, R. Schneider, Preparation of Cu-doped ZnS QDs/TiO_2 nanocomposites with high photocatalytic activity, *Appl. Catal. B* 144 (2014) 29-35.
- [11] S. Zhang, L. Chen, H. Liu, W. Guo, Y. Yang, Y. Guo, M. Huo, Design of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ and $\text{Ag/H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ film-coated optical fiber photoreactor for the degradation of aqueous rhodamine B and 4-nitrophenol under simulated sunlight irradiation, *Chem. Eng. J.* 200-202 (2012) 300-309.
- [12] P.Y. Ayekoe, D. Robert, D.L. Goné, $\text{TiO}_2/\text{Bi}_2\text{O}_3$ photocatalysts for elimination of water contaminants. Part 1: synthesis of α - and β - Bi_2O_3 nanoparticles, *Environ. Chem. Lett.* 13 (2015) 327-332.
- [13] J. Fei, J. Li, Controlled Preparation of Porous TiO_2 -Ag Nanostructures through Supramolecular Assembly for Plasmon-Enhanced Photocatalysis, *Adv. Mater.* 27 (2015) 314-319.
- [14] R. Leary, A. Westwood, Carbonaceous nanomaterials for the enhancement of TiO_2 photocatalysis, *Carbon* 49 (2011) 741-772.
- [15] S. Morales-Torres, L. Pastrana-Martínez, J. Figueiredo, J. Faria, A.T. Silva, Design of graphene-based TiO_2 photocatalysts—a review, *Environ. Sci. Pollut. Res.* 19 (2012) 3676-3687.

- [16] D.R. Dreyer, S. Park, C.W. Bielawski, R.S. Ruoff, The chemistry of graphene oxide, *Chem. Soc. rev.* 39 (2010) 228-240.
- [17] Y.H. Ng, A. Iwase, N.J. Bell, A. Kudo, R. Amal, Semiconductor/reduced graphene oxide nanocomposites derived from photocatalytic reactions, *Catal. Today* 164 (2011) 353-357.
- [18] Y. Zhang, N. Zhang, Z.-R. Tang, Y.-J. Xu, Graphene Transforms Wide Band Gap ZnS to a Visible Light Photocatalyst. The New Role of Graphene as a Macromolecular Photosensitizer, *ACS Nano* 6 (2012) 9777-9789.
- [19] M.S.A. Sher Shah, A.R. Park, K. Zhang, J.H. Park, P.J. Yoo, Green Synthesis of Biphasic TiO₂-Reduced Graphene Oxide Nanocomposites with Highly Enhanced Photocatalytic Activity, *ACS Appl. Mater. Interfaces* 4 (2012) 3893-3901.
- [20] D. Zhao, G. Sheng, C. Chen, X. Wang, Enhanced photocatalytic degradation of methylene blue under visible irradiation on graphene@TiO₂ dyade structure, *Appl. Catal. B* 111-112 (2012) 303-308.
- [21] M. Shi, J. Shen, H. Ma, Z. Li, X. Lu, N. Li, M. Ye, Preparation of graphene-TiO₂ composite by hydrothermal method from peroxotitanium acid and its photocatalytic properties, *Colloids Surf. A* 405 (2012) 30-37.
- [22] Y. Min, K. Zhang, W. Zhao, F. Zheng, Y. Chen, Y. Zhang, Enhanced chemical interaction between TiO₂ and graphene oxide for photocatalytic decolorization of methylene blue, *Chem. Eng. J.* 193-194 (2012) 203-210.
- [23] Y. Zhang, C. Pan, TiO₂/graphene composite from thermal reaction of graphene oxide and its photocatalytic activity in visible light, *J. Mater. Sci.* 46 (2011) 2622-2626.
- [24] X. Liu, L. Pan, T. Lv, G. Zhu, T. Lu, Z. Sun, C. Sun, Microwave-assisted synthesis of TiO₂-reduced graphene oxide composites for the photocatalytic reduction of Cr(vi), *RSC Adv.* 1 (2011) 1245-1249.
- [25] J. Liu, H. Bai, Y. Wang, Z. Liu, X. Zhang, D.D. Sun, Self-Assembling TiO₂ Nanorods on Large Graphene Oxide Sheets at a Two-Phase Interface and Their Anti-Recombination in Photocatalytic Applications, *Adv. Funct. Mater.* 20 (2010) 4175-4181.
- [26] G. Jiang, Z. Lin, C. Chen, L. Zhu, Q. Chang, N. Wang, W. Wei, H. Tang, TiO₂nanoparticles assembled on graphene oxide nanosheets with high photocatalytic activity for removal of pollutants, *Carbon* 49 (2011) 2693-2701.

- [27] D.-H. Yoo, T.V. Cuong, V.H. Pham, J.S. Chung, N.T. Khoa, E.J. Kim, S.H. Hahn, Enhanced photocatalytic activity of graphene oxide decorated on TiO₂ films under UV and visible irradiation, *Curr. Appl. Phys.* 11 (2011) 805-808.
- [28] Y. Zhang, N. Zhang, Z.-R. Tang, Y.-J. Xu, Improving the photocatalytic performance of graphene-TiO₂ nanocomposites via a combined strategy of decreasing defects of graphene and increasing interfacial contact, *Phys. Chem. Chem. Phys.* 14 (2012) 9167-9175.
- [29] T.N. Lambert, C.A. Chavez, B. Hernandez-Sanchez, P. Lu, N.S. Bell, A. Ambrosini, T. Friedman, T.J. Boyle, D.R. Wheeler, D.L. Huber, Synthesis and Characterization of Titania–Graphene Nanocomposites, *J. Phys. Chem. C* 113 (2009) 19812-19823.
- [30] W.S. Hummers Jr, R.E. Offeman, Preparation of graphitic oxide, *J. Am. Chem. Soc.* 80 (1958) 1339-1339.
- [31] Y. Liang, H. Wang, H. Sanchez Casalongue, Z. Chen, H. Dai, TiO₂ nanocrystals grown on graphene as advanced photocatalytic hybrid materials, *Nano Res.* 3 (2010) 701-705.
- [32] J. Liu, H. Bai, Y. Wang, Z. Liu, X. Zhang, D.D. Sun, Self-Assembling TiO₂ Nanorods on Large Graphene Oxide Sheets at a Two-Phase Interface and Their Anti-Recombination in Photocatalytic Applications, *Adv. Funct. Mater.* 20 (2010) 4175-4181.
- [33] H. Li, W. Zhang, L. Zou, L. Pan, Z. Sun, Synthesis of TiO₂–graphene composites via visible-light photocatalytic reduction of graphene oxide, *J. Mater. Res.* 26 (2011) 970-973.
- [34] Y.H. Ng, I.V. Lightcap, K. Goodwin, M. Matsumura, P.V. Kamat, To What Extent Do Graphene Scaffolds Improve the Photovoltaic and Photocatalytic Response of TiO₂ Nanostructured Films?, *J. Phys. Chem. Lett.* 1 (2010) 2222-2227.
- [35] V.c. Štengl, D. Popelková, P. Vlácil, TiO₂–graphene nanocomposite as high performance photocatalysts, *J. Phys. Chem. C* 115 (2011) 25209-25218.
- [36] L.M. Pastrana-Martínez, S. Morales-Torres, V. Likodimos, J.L. Figueiredo, J.L. Faria, P. Falaras, A.M. Silva, Advanced nanostructured photocatalysts based on reduced graphene oxide–TiO₂ composites for degradation of diphenhydramine pharmaceutical and methyl orange dye, *Appl. Catal. B* 123 (2012) 241-256.
- [37] L.M. Pastrana-Martinez, S. Morales-Torres, J.L. Figueiredo, J.L. Faria, A.M. Silva, Graphene oxide based ultrafiltration membranes for photocatalytic degradation of organic

pollutants in salty water, *Water Res.* 77 (2015) 179-190.

[38] R.S. Ribeiro, A.M. Silva, L.M. Pastrana-Martínez, J.L. Figueiredo, J.L. Faria, H.T. Gomes, Graphene-based materials for the catalytic wet peroxide oxidation of highly concentrated 4-nitrophenol solutions, *Catal. Today* 249 (2015) 204-212.

[39] V. Štengl, D. Popelková, P. Vlášil, TiO₂–Graphene Nanocomposite as High Performance Photocatalysts, *J. Phys Chem. C* 115 (2011) 25209-25218.

[40] V. Stengl, S. Bakardjieva, T.M. Grygar, J. Bludská, M. Kormunda, TiO₂-graphene oxide nanocomposite as advanced photocatalytic materials, *Chem. Cent. J.* 7 (2013) 41.

[41] Y. Gao, M. Hu, B. Mi, Membrane surface modification with TiO₂–graphene oxide for enhanced photocatalytic performance, *J. Membr. Sci.* 455 (2014) 349-356.

[42] P. Gao, Z. Liu, M. Tai, D.D. Sun, W. Ng, Multifunctional graphene oxide–TiO₂ microsphere hierarchical membrane for clean water production, *Appl. Catal. B* 138 (2013) 17-25.

[43] L. Lin, H. Wang, H. Luo, P. Xu, Enhanced photocatalysis using side-glowing optical fibers coated with Fe-doped TiO₂ nanocomposite thin films, *J. Photochem. Photobio. A* 307-308 (2015) 88-98.

[44] L. Lin, H. Wang, H. Luo, P. Xu, Photocatalytic Treatment of Desalination Concentrate Using Optical Fibers Coated With Nanostructured Thin Films: Impact of Water Chemistry and Seasonal Climate Variations, *Photochem. Photobio.* (2016).

[45] D.D. Dionysiou, M.T. Suidan, E. Bekou, I. Baudin, J.-M. Laîné, Effect of ionic strength and hydrogen peroxide on the photocatalytic degradation of 4-chlorobenzoic acid in water, *Appl. Catal. B* 26 (2000) 153-171.

[46] D.C. Hurum, A.G. Agrios, K.A. Gray, T. Rajh, M.C. Thurnauer, Explaining the Enhanced Photocatalytic Activity of Degussa P25 Mixed-Phase TiO₂ Using EPR, *J. Phys. Chem. B* 107 (2003) 4545-4549.

[47] Z. Ding, G.Q. Lu, P.F. Greenfield, Role of the Crystallite Phase of TiO₂ in Heterogeneous Photocatalysis for Phenol Oxidation in Water, *J. Phys. Chem. B* 104 (2000) 4815-4820.

[48] J. Zhang, Q. Xu, Z. Feng, M. Li, C. Li, Importance of the relationship between surface phases and photocatalytic activity of TiO₂, *Angew. Chem.* 47 (2008) 1766-1769.

[49] L.-L. Tan, W.-J. Ong, S.-P. Chai, A.R. Mohamed, Reduced graphene oxide-TiO₂

nanocomposite as a promising visible-light-active photocatalyst for the conversion of carbon dioxide, *Nanoscale Res. Lett.* 8 (2013) 465-474.

[50] J. Madhavan, F. Grieser, M. Ashokkumar, Combined advanced oxidation processes for the synergistic degradation of ibuprofen in aqueous environments, *J.hazard. mater.* 178 (2010) 202-208.

[51] S. Chiron, C. Minero, D. Vione, Photodegradation Processes of the Antiepileptic Drug Carbamazepine, Relevant To Estuarine Waters, *Environ. Sci.Technol.* 40 (2006) 5977-5983.

[52] S.G. Kumar, L.G. Devi, Review on modified TiO₂ photocatalysis under UV/visible light: selected results and related mechanisms on interfacial charge carrier transfer dynamics, *J. Photochem. Photobiol. A* 115 (2011) 13211-13241.

[53] C.S. Turchi, D.F. Ollis, Photocatalytic degradation of organic water contaminants: Mechanisms involving hydroxyl radical attack, *J. Catal.* 122 (1990) 178-192.

[54] H.M. Coleman, B.R. Eggins, J.A. Byrne, F.L. Palmer, E. King, Photocatalytic degradation of 17- β -oestradiol on immobilised TiO₂, *Appl. Catal. B* 24 (2000) L1-L5.

[55] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.-M. Herrmann, Photocatalytic degradation pathway of methylene blue in water, *Appl. Catal. B* 31 (2001) 145-157.

[56] K. Tanaka, K. Padermpole, T. Hisanaga, Photocatalytic degradation of commercial azo dyes, *Water Res.* 34 (2000) 327-333.

[57] D.F. Ollis, E. Pelizzetti, N. Serpone, Photocatalyzed destruction of water contaminants, *Environ. Sci. Technol.* 25 (1991) 1522-1529.

[58] Y. Li, X. Li, J. Li, J. Yin, Photocatalytic degradation of methyl orange by TiO₂-coated activated carbon and kinetic study, *Water Res.* 40 (2006) 1119-1126.

[59] I.K. Konstantinou, T.A. Albanis, TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations, *Appl. Catal. B* 49 (2004) 1-14.

[60] T.-G. Nanocomposites, UV-Assisted Photocatalytic Reduction of Graphene Oxide Williams, Graeme; Seger, Brian; Kamat, Prashant V, *ACS Nano* 2 (2008) 1487-1491.

[61] I.V. Lightcap, T.H. Kosel, P.V. Kamat, Anchoring semiconductor and metal nanoparticles on a two-dimensional catalyst mat. Storing and shuttling electrons with reduced graphene oxide, *Nano lett.* 10 (2010) 577-583.

Graphic abstract