

Enhanced photoactivity of graphene/titanium dioxide nanotubes for removal of Acetaminophen



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ABSTRACT

Acetaminophen is commonly used as an antipyretic or analgesics agent and poses threat to human health. In this research, TiO₂ and graphite oxide were used as precursors of titanium dioxide nanotubes and graphene respectively. Titanium dioxide nanotube and graphene (GR-TNT) nanocomposites were synthesized through a hydrothermal method. FT-IR, UV-Vis, XRD, and TGA were used to characterize the catalysts. The acetaminophen degradation rate can reach up to 96% under UV light irradiation for 3 h and with the 5% GR-TNT dosage of 0.1 g L⁻¹. Further experiments were done to probe the mechanism for the photocatalytic reaction catalyzed by the GR-TNT composite. EDTA (hole scavengers) and t-BuOH (radical scavengers) were used to detect the main active oxidative species in the system. The results showed that the holes are the main oxidation species in the photocatalytic process. This study provides a new prospect for acetaminophen degradation by using high efficiency catalysts.

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1. Introduction

Pharmaceuticals and Personal Care Products (PPCPs) is a category of pollutants causing global concern in recent years. The current study of PPCPs needs further research to determine its environmental migration behavior. Aromatic and heterocyclic rings are always contained in the structure of PPCPs, therefore, photocatalytic degradation could be a promising method to decompose it. Although PPCPs generally have a low concentration in water bodies, many kinds of pharmaceuticals have been found in the natural environment, including domestic and sewage treatment plant wastewaters [1], surface water [2], and ground water [3].

Acetaminophen is a widely used substance that is extensively employed in medical treatments. It is commonly used as an antipyretic or analgesics agent [4] and is considered a “Persistent Organic Pollutant” [5] which can be found in human excrement and in natural water bodies generally have a concentration from ng/L to μg/L. Acetaminophen is a common cause of drug-induced liver injury [6].

Recently, the treatment of acetaminophen is focused on the methods of spectrophotometry [7], high-performance liquid

chromatography (HPLC) [8], ion chromatographic separation [9], titrimetry [10], High Performance Capillary electrophoresis ampere law [11], electrochemistry [12], biodegradation, and advanced oxidation processing [13]. Most of the above methods require pre-treatment of acetaminophen before reaction [14], and further, those processes may be time consuming and cause sample pollution. Spectrophotometry as an effective method can be used to solve the pollution problem of acetaminophen due to its main characteristics such as high sensitivity, good selectivity, suitable concentration range, low cost analysis, low dependence of chemical use, and easy and speed of operation [15].

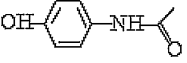
To achieve low cost, chemical stability, non-toxicity, and no harm to the human body, TiO₂ is the most widely used semiconductor in many fields such as cosmetics, paper, and coating. They have been found having photocatalytic activities by Fujishima in 1972 for splitting water into hydrogen and oxygen [16]. Regarding TiO₂ powder, many researches have focused on the higher photocatalytic performance via larger surface areas. Efforts have been made to turn TiO₂ powder into titanium nanotubes (TNTs), which possess both higher inner and outer surface area. TNTs were first synthesized by Tomoko Kasuga in 1998, with Ti(Oi-C₃H₇)₄ and Si(OEt)₄ as precursors, though an alkaline hydrothermal method [17].

Even though TNTs have such unique properties, they also have a disadvantage in the rapid recombination of electrons and holes, which limits their photocatalytic activity. Therefore, other composites should be combined with TNTs to increase photocatalysis.

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Table 1
Characteristics of acetaminophen.

Name	Molar mass (g mol ⁻¹)	λ_{max} (nm)	Molecular formula	Structure
Acetaminophen	151.16	243	C ₈ H ₉ NO ₂	

Graphene as a new allotrope of carbon element was found by British scientist Novoselov [18] by adopting mechanical stripping in 2004, cause a worldwide attention. Graphene is made up of six carbon atoms, is formed by sp² hybridization, has a single atomic layer thickness, and has a two-dimensional planar structure of honeycomb. It has many unique properties such as very high surface area (theoretical value of 2630 m² g⁻¹), good electrical properties, mechanical strength and stability [19,20]. Combining graphene and TNTs is a promising way to enhance the composite's photocatalytic activity and many research efforts exist [21–24].

In order to prepare GR-TNT hybrids, generally two methods are used: using Ti and graphene precursors [25,26] and direct compounding [27]. Compared to the former method, direct compounding is easy and time-saving. In this study, we synthesize GR-TNT nanocomposites using TiO₂ and graphite oxide (GO) as precursors through a hydrothermal method. Different weight ratios of GR-TNT nanocomposites were used to decompose acetaminophen.

2. Materials and methods

2.1. Reagents

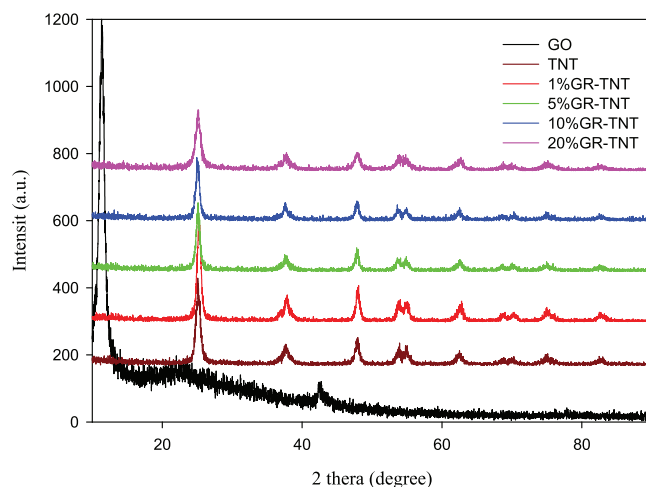
Natural graphite powder (325 mesh) and commercial TiO₂ (P25, 80% anatase and 20% rutile) were purchased from ACROS. Acetaminophen was purchased from Acros. The properties of acetaminophen are illustrated in Table 1. All other reagents were analytical grade and used without any further purification. The experiments were carried out at room temperature.

2.2. Preparation of GR-TNT nanocomposites

Graphite oxide (GO) was prepared by the modified Hummers' method [28]. A specific amount of natural graphite was mixed with H₂SO₄, NaNO₃, and KMnO₄. The reaction undergoes low, medium and high temperature respectively. At the end of the high temperature phase, additional H₂O₂ was added to the solution. Finally, the GO solution was centrifuged and washed with 5% HCl and DI water several times, then dried at 80 °C.

TNTs were synthesized through an alkaline hydrothermal method using commercial TiO₂ powder as the Ti source. The specific steps are as noted as follows. 5 g TiO₂ was added into 10 M NaOH solution, and magnetically stirred for 1 h, to get a uniform solution. Then the solution was transferred to a Teflon-lined stainless steel autoclave and heated at 135 °C for 72 h. The product was washed with water and 0.1 M HNO₃ several times, dried at 100 °C, then the product calcinated at 400 °C for 2 h. The product was grinded and sieved (200 mesh). TNTs were obtained.

GR-TNT nanocomposites with different weight ratios of GO were prepared through a hydrothermal treatment. First, the obtained GO with different weight ratios of 1%, 5%, 10%, and 20% was added into water and underwent sonication for 30 min. Next, TNTs were added into the GO solution and underwent sonication for 45 min to obtain a uniform solution. Then, the solution was transferred to a Teflon-lined stainless steel autoclave and heated at 120 °C for 4 h. The product was filtered and dried for use.

**Fig. 1.** XRD of different GR-TNT nanocomposites.

2.3. Characterization of the GR-TNT nanocomposites

Specific surface areas of the GR-TNT composites were measured and calculated by the Brunauer–Emmett–Teller (BET) method from nitrogen adsorption–desorption data with an automated adsorption apparatus (Micromeritics, ASAP 2020). The degas temperature was 150 °C. UV–vis spectra of composites were obtained using a UV–vis spectrophotometer (Hitachi, U-3900) equipped with a diffusion reflectance accessory. The specific chemical bond vibration of the compounds was examined by Fourier Transform Infrared Spectroscopy (FT-IR). The crystal phases of the GR-TNT composite were measured using an X-ray diffractometer (XRD, Rigaku Ultima IV) with Cu K α radiation, $k = 1.1514$ nm.

2.4. Photocatalytic Measurements

The photocatalytic activity of the GR-TNT nanocomposites was evaluated by the photodegradation of acetaminophen. The initial concentration was 5 mg L⁻¹. Then 0.05 g of GR-TNT composites were mixed with a 500 mL acetaminophen solution and stirred in the dark for 30 min to attain adsorption equilibrium. Then, we turned on the UV lamp (14 W, 254 nm), using a 0.2 μ m syringe filter to get a 3 mL aliquot at a certain time interval. The solution concentration was determined by a UV–vis spectrophotometer at $\lambda = 243$ nm.

3. Results and discussion

3.1. Characterization of the GR-TNT composites

3.1.1. XRD

Fig. 1 shows XRD of different GR-TNT composites. All of the catalysts have similar diffraction peaks; the anatase phase of TiO₂ (JCPDS21-1272) is the main structure in all the catalysts, which means the crystallinity of TNTs did not change by the hydrothermal process. Compared with pure TNTs, they are all anatase structure, which confirms that through the hydrothermal process, the crystallinity of the TNTs did not change. The different GO content that the GR-TNT composites exhibit several diffraction peaks at 25.1° (1 0 1), 37.8° (0 0 4), 48.0° (2 0 0), 53.9° (1 0 5), 55.1° (2 1 1), and 62.7° (2 0 4) which corresponds to the anatase phase. The characteristic peak of graphene is located near 26° [29], which is not obviously due to overlapping by the peak of TNTs at 25°. After hydrothermal treatment, the strong peak at near 10° [30] of GO is absent in all of the

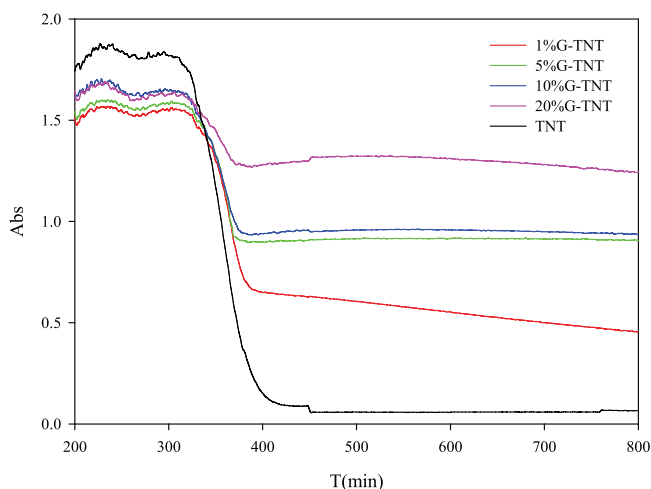


Fig. 2. UV-vis diffuse reflectance spectra of TNT and GR-TNT.

GR-TNT nanocomposites, which confirms the successful reduction of GO into graphene.

3.1.2. UV-vis

The Ultraviolet-visible (UV-vis) diffuse reflectance spectroscopy of TNT and different GR-TNT nanocomposites is shown in Fig. 2. As can be seen, the composites of GR-TNT show enhanced adsorption in the visible range compared to pure TNTs. The absorbance in the 400–800 nm range increased when the graphene content increased. The adsorption edge expands to a longer wavelength which confirms a red shift of the nanocomposites, which can be assigned to the forming of the chemical bonds of Ti–O–C and facilitates the efficient use of light for the photodegradation [31]. The band gap energy of the composites is calculated by the transformed Kubelka–Munk function, as is shown below, the band gap energy of TiO₂ and TNT are similar while the band gap of the GR-TNT narrowed with the addition of graphene (Table 2). The band gap decreased with graphene loading increased. This phenomenon should be ascribed to the formation of Ti–O–C bond.

$$E_g = 1240/\lambda_g \quad (1)$$

3.1.3. TEM

The morphology of GR-TNT composite is analyzed by TEM. Fig. 3 shows the TEM image of the nanocomposites. TEM analysis shows that the graphene is layered morphology and the sheet is thin,

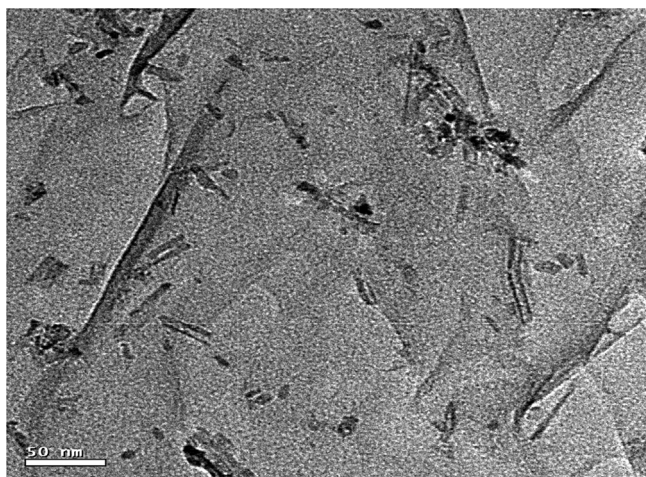


Fig. 3. TEM of 5% GR-TNT.

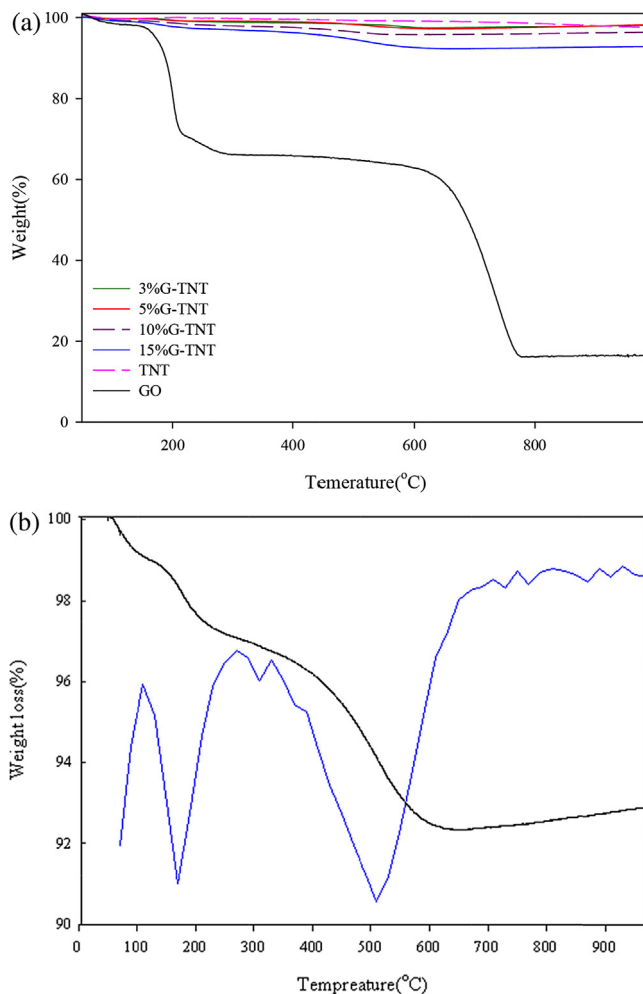


Fig. 4. (a). The thermal gravimetric curves of GR-TNT, TNT, and GO. Fig. 4 (b). TGA-DTA of 15% GR-TNT nanocomposites.

transparent and wrinkled, while the TNTs are still tubular formation through the hydrothermal process. Graphene is a supporting for the TNTs and TNTs are well dispersed on the sheet.

3.1.4. N₂ adsorption/desorption measurements

N₂ adsorption/desorption measurements and Brunauer–Emmett–Teller (BET) analysis were used to investigate the specific surface areas of the composite nanomaterial. The surface areas and the band gap of the composites are given in Table 2. As can be seen in Table 2, the BET surface areas of GR-TNT nanocomposites are all larger than pure TiO₂. The surface area increased and with the increasing amount of GO weight. Larger surface area can provide more active sites and provide good contact between the photocatalyst and pollutant; in addition, graphene also facilitates the transport of charge carriers, thereby enhancing the photocatalytic activity the loading of graphene is critical for photo reaction [32].

3.1.5. TGA analysis

TGA studies can confirm the thermal stability of the nanocomposites. Fig. 4(a) shows the TGA of GO, TNT, and GR-TNT nanocomposites. As shown in the Fig. 4, the TGA curve of GO demonstrates an obvious weight loss at about 200 and 700 °C, which is ascribed to the combustion of oxygen-containing functional groups of GO [33]. Fig. 4(b) shows the TGA-DTA curves of 15%GR-TNT. As shown in Fig. 4(b), below 100 °C, the weight is assigned to the removal of the physically absorbed water on the catalyst surface, with the temperature increasing to 180 °C, another

Table 2

The band gap and surface area of different GR-TNT composites.

Catalysts	TiO ₂	TNT	1%GR-TNT	5% GR-TNT	10% GR-TNT	20% GR-TNT
Band gap (eV)	3.12	3.18	3.03	2.98	2.86	2.34
Surface area (m ² g ⁻¹)	49.9	118.3	101.9	123.5	156.4	131.0

obvious weight loss appeared, which belongs to the decomposition oxygen-containing groups into carbon dioxide (CO₂) and water. When the temperature heated up to about 510 °C, an obvious mass loss appeared, which is due to the destruction of the double carbon bond of graphene [34]. The relative thermal stability of the GR-TNT nanocomposites may be ascribed to the chemical bond between TNT and graphene [35].

3.1.6. FT-IR

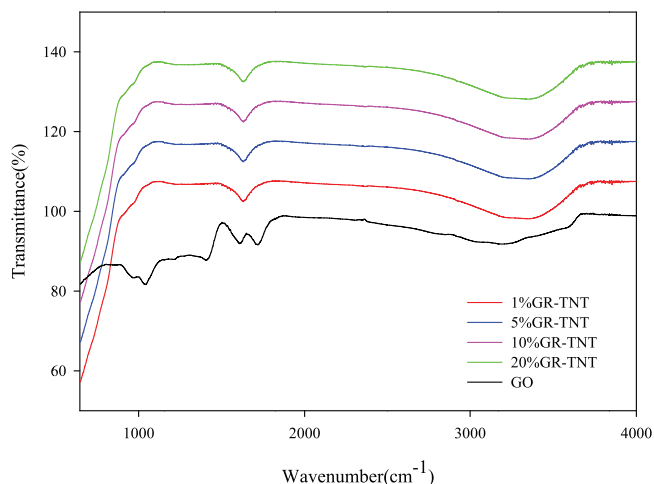
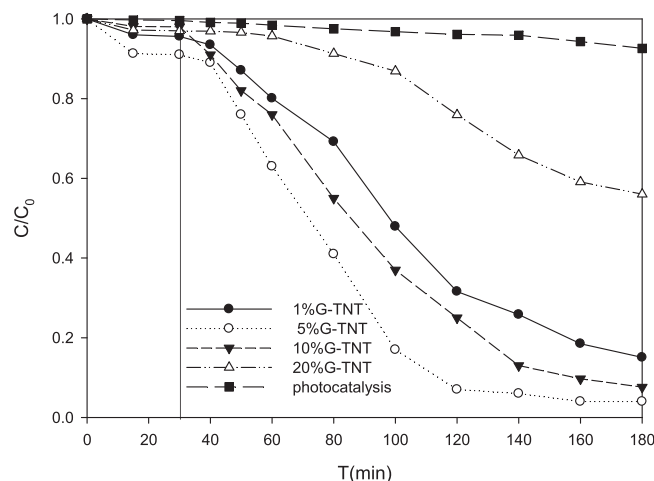
FT-IR shows the functional groups of the nanocomposites. As shown in Fig. 5, the broad vibration at 3400 cm⁻¹ is assigned to the O–H band of water. The vibration between 400 and 690 cm⁻¹ is ascribed to the signal of the Ti–O–Ti bond (Ge et al., 2006). In the case of synthesized GR-TNT, the absorption below 1000 cm⁻¹ is the vibration of Ti–O–C and Ti–O–Ti. The carbonyl and epoxy groups of GO were at 1723 and 1228 cm⁻¹ respectively [36]. Compared to GO, the oxygen containing groups almost disappeared, which confirmed the successful reduction of GO to graphene through hydrothermal treatment.

3.2. Photocatalytic measurement of acetaminophen

As shown in Fig. 6, under UV light (254 nm), using GR-TNT composites to degrade acetaminophen, we test the photocatalytic activities of the composites. Before photoreaction the samples were placed in the dark for 30 min to reach the adsorption–desorption equilibrium. At certain time intervals, four milliliter aliquots were withdrawn, then syringe filtered to remove the catalyst. The withdrawn solution was measured by UV-Vis spectroscopy and the dye concentration was measured by testing the absorbance at $\lambda_{\text{max}} = 243$ nm. The photodegradation efficiency (%) can be calculated by the following equation:

$$\text{Efficiency} = ((C_0 - C)/C_0) \times 100 \quad (1)$$

Where C_0 is the initial concentration of the acetaminophen solution and C is the concentration of solution at different times after light irradiation.

**Fig. 5.** FT-IR of GO and different GR-TNT nanocomposites.**Fig. 6.** Effect of different GO content of GR-TNT nanocomposites on photodegradation for acetaminophen (5 ppm acetaminophen, 0.1 g L⁻¹).

3.2.1. Effect of different loading catalysts

The loading of graphene in nanocomposites is an important factor for the acetaminophen solution degradation effect, as shown in Fig. 6. Without any photocatalysts, the degradation of acetaminophen is negligible. The photocatalytic activity of different graphene loading was measured under the same conditions. After we turned on the light, the reaction started. All of the GR-TNT nanocomposites show a similar tendency for acetaminophen decomposition. When the GO content increases, the degradation efficiency increases correspondingly, however, too much GO in the composite leads to a reduction in degradation efficiency, due to the obstruction of light. There, the content of GO has an optimum in our experiment, where the best efficiency can be attained with 5% GO loading. Too low or too high graphene loading underperforms for the reaction.

To calculate the kinetic k , the following pseudo first-order kinetics equation was used:

$$r = -dC/dt = kKC/(1 + KC) = kk_{\text{app}}C \quad (2)$$

Integrating Eq. (2) gives

$$-\ln C/(C_0) = k_1 t \quad (3)$$

Where C_0 is the original concentration of dye solution and C_t is the concentration of acetaminophen solution at $t = t$, and $k_1 = kk_{\text{app}}$ (min⁻¹) is the kinetic efficiency, which can be obtained by the slope of the relationship between reaction time and the concentration of solution concentration. All the results fit the pseudo first-order rate model with high correlation coefficients ($R^2 > 0.9$), as shown in Table 3.

Table 3

The kinetic parameters of GR-TNT nanocomposites.

Catalyst	R^2	K (min ⁻¹)
1%GR-TNT	0.9817	0.0133
5%GR-TNT	0.9592	0.0248
10%GR-TNT	0.9826	0.0184
20%GR-TNT	0.9382	0.004

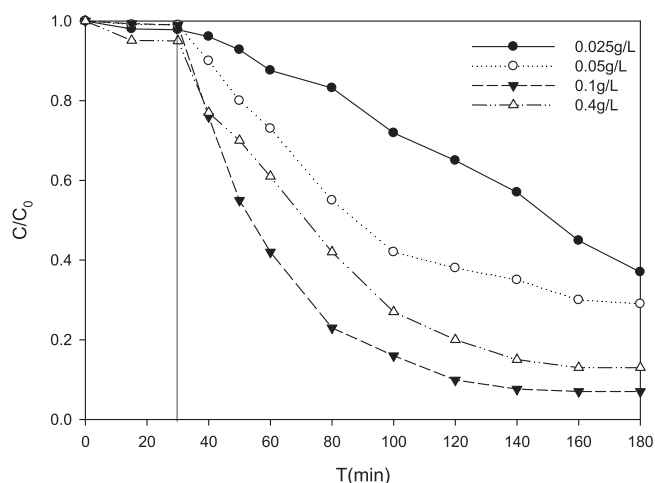


Fig. 7. Effect of dosage on the degradation efficiency (5 ppm acetaminophen).

3.2.2. Effect of dosage of the catalyst

The dosage of the photocatalyst plays an important role in the acetaminophen treatment. The results have been depicted in Fig. 7. By increasing the dosage of photocatalysts, the adsorption increased accordingly and the degradation efficiency of acetaminophen correspondingly increased. However, when the dosage reached 0.4 g L^{-1} , the degradation efficiency decreased. This phenomenon can be attributed to the shield of light generated by the dark color of the catalysts. Therefore, both high and low dosages of catalyst are problematic. These results are similar to the reports of Wiszniewski et al. (2003), where photocatalytic capacity had an optimum dosage of TiO_2 [37].

3.2.3. Effect of initial pH

PH has a great effect on the photocatalytic degradation of acetaminophen. The effect of pH was studied by adjusting pH values from 3.0 to 11.0 at 5 ppm acetaminophen and the dosage of photocatalyst was 0.1 g L^{-1} 5%GR-TNT. As shown in Fig. 8, with the photocatalysis process in effect, the degradation efficiencies increased. After 180 min, the degradation efficiency was about 95% for pH 9. All of the pH results show that the degradation efficiency of acetaminophen is not obviously affected by pH. When the pH changes from 3 to 7, the degradation efficiency decreases from 80.8 to 70.6%, respectively. While the degradation efficiency dramatically dropped to 37.8% for pH 11. The reaction rate constants

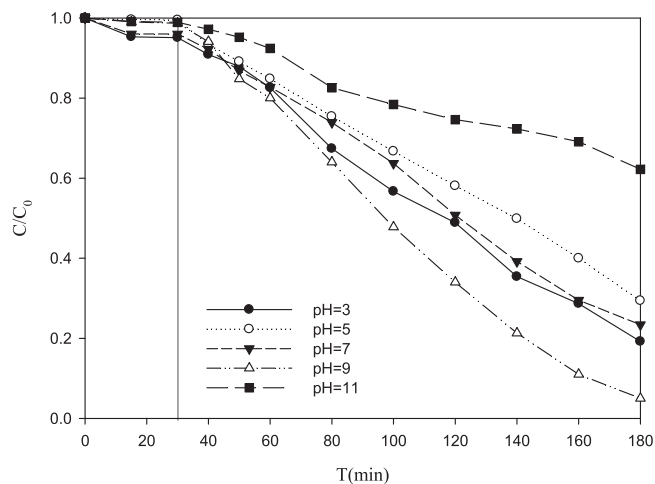


Fig. 8. Effect of pH on the photodegradation of acetaminophen (5 ppm acetaminophen, 0.1 g L^{-1}).

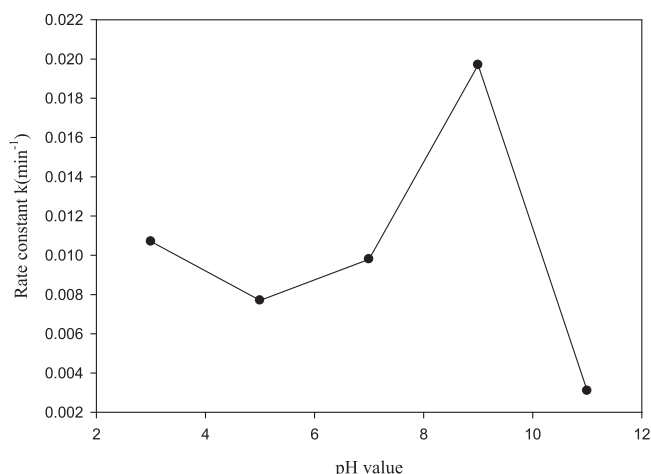


Fig. 9. The relationship between pH and rate constants.

were also studied. As is shown in Fig. 9, the reaction constant rate decreased from 0.0107 min^{-1} for pH 3 to 0.0071 min^{-1} for pH 5, and to 0.0098 min^{-1} for pH 7, but increased to 0.0197 min^{-1} for pH 9, however, decreased to 0.0031 min^{-1} at pH 11.

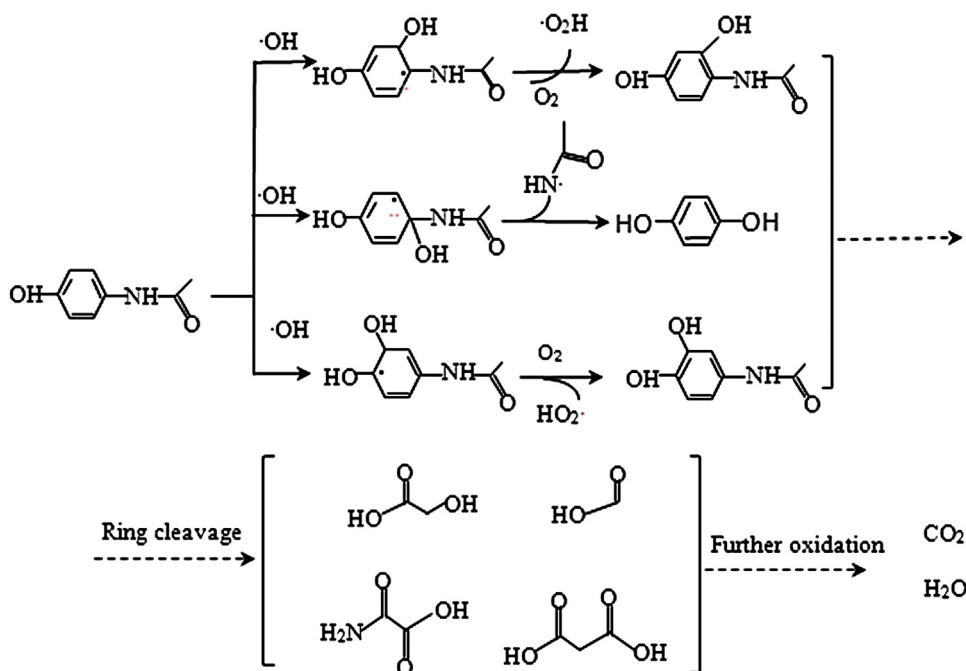
The photocatalyst reaction always occurred at the TNTs surface; after light irradiation, photocatalytic degradation happened on the surface of photocatalysts, then generated holes or $\bullet\text{OH}$ radicals [38]. The TiO_2 surface isoelectric point pH is about 6.8. The catalyst surface is positively charged when the $\text{pH} < 6.8$; the pK_a value of acetaminophen was 9.5. When pH value is lower than 9.5, acetaminophen mainly is positive; when pH value is higher than 9.5, it maintains as neutral [39]. When the pH value is low, both the photocatalysts and the acetaminophen molecules are positive. The repelling effect plays a dominant role in the reaction, so the degradation efficiency is relatively low. With increased pH value, the less positive surface of TiO_2 and more neutral acetaminophen exist.

So the absorption on positive TiO_2 particles acetaminophen increased slowly. When the pH range is between 6.3 and 9.5, TiO_2 becomes negative, while acetaminophen exists as positive molecules, where the photocatalyst process is enhanced by electrostatic attraction. These results are similar with the research of Taicheng An et al. in 2011, using TiO_2 in the photocatalysis of the antiviral drug-lamivudine [39].

3.2.4. Effect of holes and radicals in photocatalytic experiments by scavenger agents (EDTA/t-BuOH)

In the photocatalyst process, the photogenerated holes and electrons always act as the main oxidant. In order to further understand the mechanism during the photocatalytic process, the hole and radical scavengers were added (with 10 mM of EDTA or t-BuOH, respectively) into the reaction for the degradation of acetaminophen with GR-TNT nanocomposites [40].

Fig. 10 shows the results of GR-TNT without of any scavengers and the presence of t-BuOH and EDTA. Adding t-BuOH to the solution, the degradation efficiency decreased. These results indicate that holes are the major active oxidations in the photocatalyst process for which EDTA was used as hole scavengers. On the other hand, adding t-BuOH to the solution also caused the reaction rate to decrease. These results show that the reactive species, such as hydroxyl ($\text{HO}\bullet$) and hydroperoxyl ($\text{HOO}\bullet$) radicals [40], also have some function in photocatalysis, but they are not the major oxidation species in the process.



Scheme 1. Possible pathway for photocatalytic oxidation of acetaminophen using GR-TNT nanocomposite.

3.2.5. Possible reaction mechanism

The intermediates of photocatalytic degradation of acetaminophen were investigated by GC-MS. The obtained intermediates and break products were concluded and the possible pathway for oxidation of acetaminophen was presented in Scheme 1. $\cdot\text{OH}$ radicals attack the aromatic ring of acetaminophen with hydroxylation at ortho-, meta- or para- to OH group. However, early studies of NMR found that meta- position hydroxylation is minor [41]. The identified intermediates are classified into different categories, such as aromatic compounds, carboxylic acids and inorganics. Among the intermediates, N- (3,4-dihydroxyphenyl) acetamide, N- (2,4-dihydroxyphenyl)acetamide, and hydroquinone are the main aromatic compounds, as they are the basic structure of acetaminophen. These results indicates that at early stage of photocatalytic degradation of acetaminophen, $\cdot\text{OH}$ attack onto the aromatic ring at ortho and para positions, as is shown in Scheme 1. The three aromatic compounds undergo the cleavage of aromatic rings by successive $\cdot\text{OH}$ oxidation and were then

degraded into other carboxylic acids. In this paper the reaction route for acetaminophen photocatalytic degradation was similar to other recent study [42].

3.2.6. Cycle experiment

The recycling and the stability of photocatalysts are very important for high photocatalytic degradation and practical applications. To evaluate the reusability of the GR-TNT nanoparticles, repeatability experiments were conducted by the following method. After each photocatalytic process, the photocatalyst was irradiated with UV light for 2 h and washed with a large amount of water, then filtered several times and dried at 100°C . The obtained product was then used for photocatalysis again. The degradation efficiency with 5% GR-TNT after 180 min irradiation of the successive five times is shown in Fig. 11. It could be seen that the photocatalytic efficiency of the catalyst was still maintained above 90% after five cycles (Fig. 11). The slight decrease of degradation efficiency is

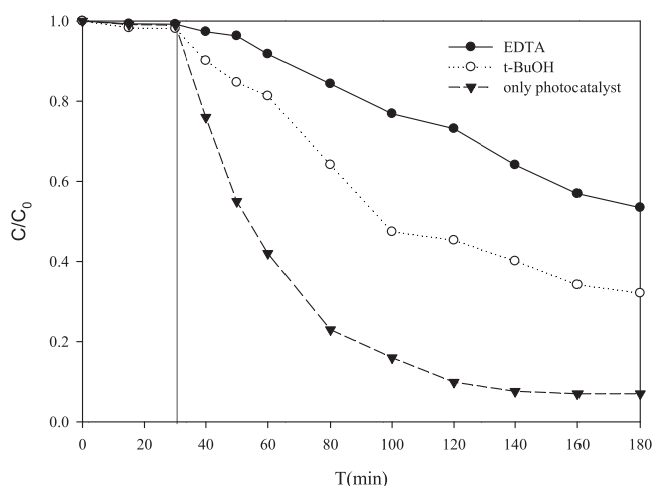


Fig. 10. Effect of EDTA and t-BuOH on the photocatalytic degradation of acetaminophen (5 ppm acetaminophen, 0.1 g L^{-1}).

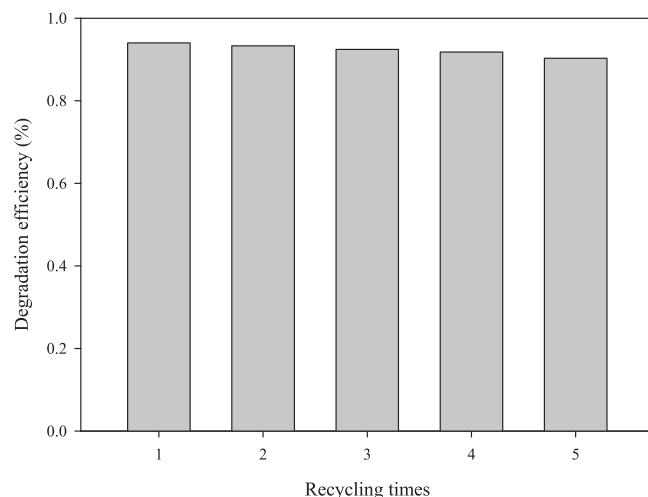


Fig. 11. Recycling experiment of 5%GR-TNT (0.1 g L^{-1}) nanocomposites on degradation Acetaminophen (5 ppm).

due to the absorbed intermediates on the surface of the catalyst and to a few GR-TNT nanoparticles that are leached into the solution during the photodegradation or cleaning process. These results indicate that GR-TNT nanocomposites are relatively stable during the photodegradation process.

4. Conclusions

In this study, the catalysts with different GO content were successfully prepared through a simple hydrothermal treatment, by using GO and TNTs as precursors. The composites with graphene loading show similar XRD with pure TNTs and larger BET surface area. With GO loading increased, the photocatalytic degradation efficiency increased correspondingly. The best photocatalytic degradation efficiency is attained with a 5% GR-TNT. To understand the mechanism of the reaction, the EDTA and t-BuOH were used as hole and electron scavengers, respectively. The result confirmed that the holes are the main active species in the photocatalytic progress. The intermediates of photocatalytic degradation of acetaminophen were investigated by GC-MS and the possible pathway was studied in the paper.

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