Applied Surface Science 324 (2015) 258–264

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

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

Hong Tao [a], Xiao Liang [a], Qian Zhang [b], Chang-Tang Chang [c,*]

[a] School of Environment and Architecture, University of Shanghai for Science and Technology, Shanghai 200093, PR China
[b] Graduate Institute of Environmental Engineering, National Taiwan University, 10617, Taiwan
[c] Department of Environmental Engineering, National I-Lan University, 26047, Taiwan

ARTICLE INFO

Article history:
Received 2 July 2014
Received in revised form 9 October 2014
Accepted 24 October 2014
Available online 1 November 2014

Keywords:
Graphene
Titanium nanotubes
Acetaminophen
Photocatalysis

ABSTRACT

Acetaminophen is commonly used as an antipyretic or analgesics agent and poses threat to human health. In this research, TiO_2 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 of 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.

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].

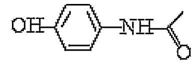
To achieve low cost, chemical stability, non-toxicity, and no harm to the human body, TiO_2 is the most widely used semiconductor in many fields such as cosmetics, paper, and coating. They have been found having photocatalytic activities by Fujishima in 1972 for splitting water into hydrogen and oxygen [16]. Regarding TiO_2 powder, many researches have focused on the higher photocatalytic performance via larger surface areas. Efforts have been made to turn TiO_2 powder into titanium nanotubes (TNTs), which possess both higher inner and outer surface area. TNTs were first synthesized by Tomoko Kasuga in 1998, with $Ti(Oi\text{-}C_3H_7)_4$ 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.

* Corresponding author at: No.1, Sec.1, Shen-Lung Road, I-Lan City, Taiwan, 26047, Republic of China; Tel.:+886 3 9357400x741; fax: +886 3 9359674.
E-mail addresses: ctchang@niu.edu.tw, ctchang73222@gmail.com (C.-T. Chang).

http://dx.doi.org/10.1016/j.apsusc.2014.10.129
0169-4332/

Table 1
Characteristics of acetaminophen.

Name	Molar mass ($g\,mol^{-1}$)	λmax (nm)	Molecular formula	Structure
Acetaminophen	151.16	243	$C_8H_9NO_2$	

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 sp^2 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 $2630\,m^2\,g^{-1}$), 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 TiO_2 and graphite oxide (GO) as precursors though 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 TiO_2 (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 H_2SO_4, $NaNO_3$, and $KMnO_4$. The reaction undergoes low, medium and high temperature respectively. At the end of the high temperature phase, additional H_2O_2 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 TiO_2 powder as the Ti source. The specific steps are as noted as follows. 5 g TiO_2 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 HNO_3 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 at120 °C for4 h. The product was filtered and dried for use.

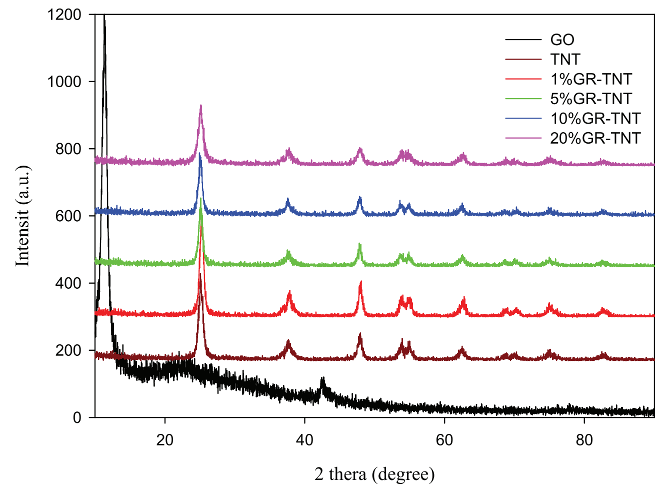


Fig. 1. XRD of different GR-TNT nanocomposites.

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 Kα radiation, $k = 1.1514$ nm.

2.4. Photocatalytic Measurements

The photocatalytic activity of the GR-TNTT 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 μm syringe filter to get a 3 mL aliquot at a certain time internal. 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 TiO_2 (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