Photocatalytic Degradation of Tannery Wastewater by Using MWCNTs/TiO_2 Nanocomposites

Yanqing Wang[1], Quanjie Wang[1, 2, 3,*], Lijie Hou[3], Yanyun Jiang[3], Danhua Du[1], Tao Du[3], Yanxing Liu[3]

[1] College of Resource and Environment, Shaanxi University of Science and Technology, Xi'an 710021, Shaanxi, P. R. China

[2] State Research and Promotion Center of Leather-making Technology, Yantai 264005, Shandong, P. R. China

[3] Department of Chemical Engineering, Yantai University, Yantai 264005, Shandong, P. R. China

Abstract: Coating carbon nanotube surface with TiO_2 as anatase and rutile types was performed by sol-gel method using $Ti(OBu)_4$ as raw material. The morphological structure of the composite photocatalyst particles was characterized by IR, XRD and TEM techniques. The results show that TiO_2 nanoparticles with about 15 nm in size are closely attached on the wall of MWCNTs. Under ultraviolet lamp, tannery wastewater was treated by the obtained catalyst to test the removal rates of COD_{Cr}. Within 6 h, CODcr value of the solution changes from the initial 3024 to 2000. As a comparison, more than 20 h are required to achieve similar effect for the pure TiO_2 catalyst. The results indicate that the nanocomposites exhibit high photocatalytic activity, showing potential application in the treatment of tannery wastewater.

Key words: photocatalytic degradation; carbon nanotubes; titanium dioxide; tannery wastewater

1 Introduction

Treatment of the industrial waste water, especially the organic pollutants hard to biochemically degrade is viewed as an active researching field currently [1-3]. Titanium dioxide (TiO_2) is an environmental-friendly photocatalyst material due to its high efficiency, thermal stability, strong oxidizing power, non-toxic, low cost, no secondary pollution and other unique advantages recently. However, its low photoefficiency and photoresponse are not suffcient. There is a measurable reduction in the photocatalytic activity for the recycled use. The most vital disadvantage of TiO_2 semiconductor is that it only absorbs a small portion of solar spectrum in the ultraviolet regions. So its applications are restricted in a large scale. Therefore, the development of new materials for modifying TiO_2 is urgently needed to increase the photocatalytic activity for the organic pollutants [4].

Carbon nanotubes (CNTs) are a new kind of carbon structure founded in 1991 by Iijima [5]. The ideal carbon nanotubes own seamless, hollow tube structure rolled by graphite surfaces slice layer composed of hexagon carbon atom. According to the number of graphite surfaces layer it can be divided into single walled and multi-walled types. Carbon nanotubes are considered to be ideal catalyst carriers owing to their huge specific surface area, remarkable chemical stability, unique electronic structure, nanoscale hollow tube property and good adsorbability [6-7].

This paper tries to introduce carbon nanotubes as the carrier of TiO_2 with the aim of improving the photocatalytic activity of TiO_2 effectively and make it easy to recycle. Coating carbon nanotube surface with TiO_2 was performed by sol-gel approach using $Ti(OBu)_4$ as raw material. Then the composite photocatalyst was used for the photocatalytic degradation research of polyphenols in leather wastewater.

* Corresponding author. Phone: +86-(0)535-6901722. E-mail: quanjie@vip.163.com

2 Experimental

2.1 Materials

MWCNTs (purity, >95 %; diameter, 10-20 nm; length, 1-2 μm; specific surface area, 40-300 m^2/g) were purchased from Shenzhen nanoport Co., Ltd. Tetrabutyl titanate (TBT) was purchased from Sino Pharm. Tannic acid was from Tianjin Kermel Chemical Reagents. Glacial acetic acid was from Tianjin University Chemical Experiment Plant. All the used reagents were reagent grade.

2.2 Purification of MWCNTs

For the purification, 1.0 g raw MWCNTs were added into the mixed solution of concentrated sulfuric (98%) and nitric acids (65%-68%) with a volume ratio of 3:1. By ultrasonicating at 70 ℃ for 3 h, MWCNTs were converted into acid form(designated as MWCNTs-COOH). Then the MWCNTs were filtered, washed with distilled water until pH=7, and finally dried at 100 ℃ in an oven.

2.3 Preparation of MWCNTs/TiO_2 Composites

In a typical experiment to prepare composites, titanium dioxide coated with MWCNTs was prepared by the following method. A certain amount of ethanol was taken in beaker added with a little glacial acetic acid as inhibitors and then the solution was added slowly by the tetrabutyl titanate which was used as a TiO_2 precursor under stirring. The resulting solution was designated as A. A certain proportion of surface modification of carbon nanotubes were dispersed in the mixture solution of nitric acid, deionized water and ethanol. After ultrasonic vibration for 20 min, the resulting suspension was added into A solution under stirring. The mixture was stirred constantly until the gel forms. The gel was placed for 48 h at room temperature and dried at 105 ℃ for about 8 h in air in order to vaporize water and ethanol in the gel, and then ground to a fine powder to obtain dried gel samples. The dried gel samples were calcined at 500 ℃ in air for 2 h to obtain MWCNTs/TiO_2 nanocomposites.

2.4 Photocatalytic Degradation Experiment of Vegetable Tannin Extract

In the self-made photocatalytic device, 200 mg obtained nanocomposites was added into 250 mL tannic acid solution with the concentration of 2.0 g/L (simulate vegetable tannin extract of tannery wastewater). After the pH value of degradation solution was adjusted to about 2, the solution under vigorous stirring was irradiated by a 300 W medium mercury lamp. A certain amount of aliquots was taken from solutions irradiated every 5 h and then COD_{cr} value of the sample was determined. The change of COD_{cr} value was regarded as the evaluation of vegetable tannin extracts in solution.

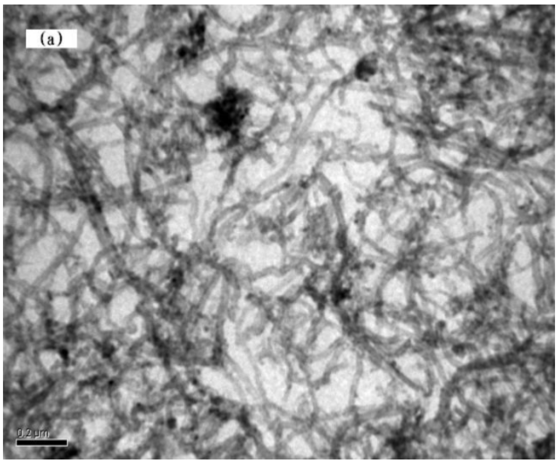
2.5 Characterization and Testing

The FT-IR spectra were recorded on a Shimadzu IR-440 type infrared spectrometer. The morphology of the particles was observed by JEM-1230 transmission electron microscope. The X-ray power diffraction (XRD) patterns were analyzed by a Panalytical X'pert PRO diffractometer (PANalytical B.V., Netherlands) operating at 50kv with Cu kα radiation. The intensity was measured by step scanning in the 2θ range 10°-70° with a step of 0.0167°.

3 Results and discussion

3.1 TEM Analysis of Nanocomposites

The morphology and microstructure of the nanocomposites were revealed by TEM investigations and the typical TEM images of MWCNTs/TiO_2 composites calcined at 500 ℃ are shown in Fig. 1. From Fig. 1a, a low magnification TEM micrograph, MWCNTs coated with TiO_2 nanoparticles are identified and little agglomeration of MWCNTs can be observed. Enlarged images of a segment of nanotube (Fig. 1 b) shows that the TiO_2 nanoparticles with about 15 nm in size are attached on the wall of MWCNTs, which is consistent with XRD results. However, TiO_2 nanoparticles did not cover all the surface of MWCNTs, since the active sites produced by the acid treatment are not sufficient.



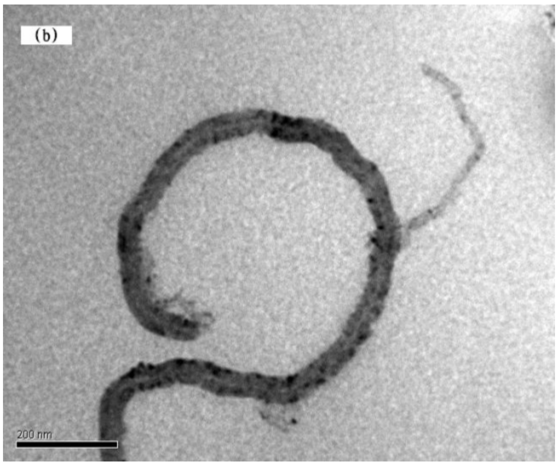


Fig. 1 TEM images of MWCNTs coated with TiO_2 nanoparticles

3.2 FTIR Analysis of Nanocomposites

Fig. 2 presents the FTIR spectra of MWCNTs/TiO_2 nanocomposites. The appearance of two strong absorption peaks at 2920cm^{-1} and 2850cm^{-1} is symmetrical and asymmetric telescopic vibration of methylene group(-CH_2-) of carbon nanotubes, which indicates the methylene structure of carbon nanotubes is not destroyed. Two absorption peaks at 1728 cm^{-1} and 1160 cm^{-1} show the formation of carboxyl groups and carbonyl groups. Additionally, a low frequency band in the range of 500-700 cm^{-1} in the spectra corresponds to the characteristic absorption of TiO_2.

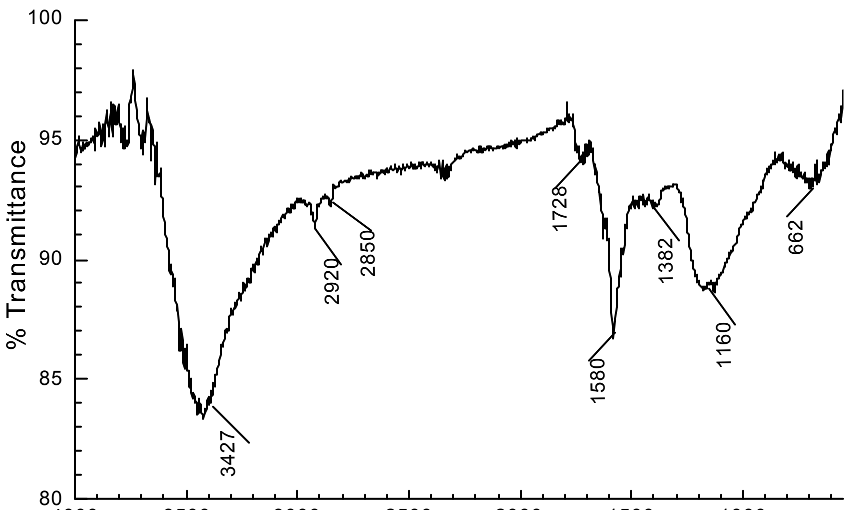


Fig. 2 FTIR spectra of MWCNTs/TiO_2 nanocomposites

3.3 XRD Analysis of Nanocomposites

To characterize the crystalline structure of the samples, the XRD patterns of MWCNTs and MWCNTs/TiO_2 composites are obtained (Fig. 3). Curve (a) is the pattern of carbon nanotubes and $2\theta=26.23$ is characteristic diffraction peak. Curve (b) is the XRD pattern of composites. Compared with (a), there is no apparent peak in the composites at the position of 26.23. Only anatase (2θ=25.33) and rutile (2θ=30.95) phases attributed to the existence of TiO_2. The reason may be that the main peak of nanotubes at 25.33 is overlapped with the main peak of anatase TiO_2 since their positions are so close. Moreover, the content of carbon nanotube is much lower than that of TiO_2, leading to the shielding of the peaks of nanotube by those of TiO_2. According to Scherrer analysis, the average size of TiO_2 is about 15 nm which agree with the TEM images.

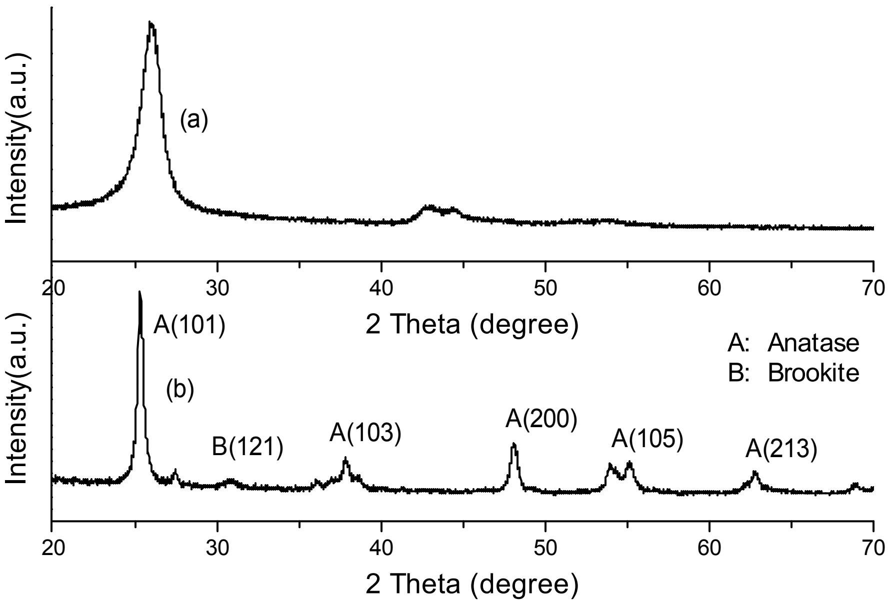


Fig. 3 XRD patterns of MWCNTs and composites

3.4 Treatment Effect of Photocatalytic Degradation of Tannery Wastewater

The photocatalytic degradation efficiencies of tannic acid over pure TiO_2 and MWCNTs/TiO_2 composites are illustrated in Fig. 4. The prepared composites have higher degradation efficiency than pure TiO_2. In less than 6 h, CODcr value of the solution changes from the initial 3024 to 2000. As a comparison, more than 20 h are needed to achieve similar effect for the pure TiO_2 catalyst. The photocatalytic activities of TiO_2 are much improved by the using of MWCNTs. The reasons can be concluded as follows. Firstly, MWCNTs can absorb dissolved oxygen and organic matter on the inside or outside of the surface due to its large surface areas and special aperture structure. Secondly, MWCNTs are eminent electronic conductors that can orderly export electron from TiO_2 and fleetly reduce electronic accumulation on TiO_2 particles. So the probability of electron hole recombination could be reduced effectively.

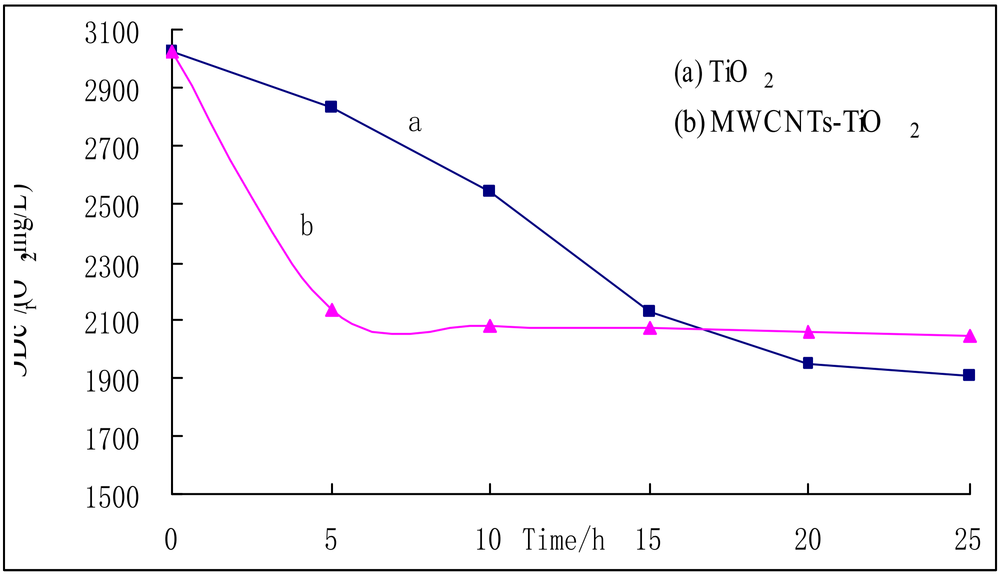


Fig. 4 Treatment effect of photocatalytic degradation of tannery wastewater by pure TiO_2 and MWCNTs/TiO_2 composites

4 Conclusions

The MWCNTs/TiO_2 nanocomposites were synthesized by surface coating of carbon nanotube with anatase and rutile types TiO_2 through a sol-gel route. TEM, XRD and FTIR analysis were employed to investigate the morphological structure of the hybrid photocatalyst particles. The results show that TiO_2 nanoparticles are closely coated on the surface of MWCNTs. The crystalling phase of titanium dioxide is mixed forms of anatase and rutile, with the particle size of about 15 nm. Under the irradiation of ultraviolet lamp, the composites can reduce the COD_{Cr} values of tannery wastewater more efficiently than pure TiO_2. Leather industry now faces a serious environmental problem with high concentration of oil and grease and polyhydric phenol in wastewater difficult to degrade in a single method. Photocatalytic technology, as an advanced oxidation technology with high catalytic efficiency, no secondary pollution and using solar energy in nature, will play an important role in the treatment of leather wastewater.

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