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Synthesis and Characterization of TiO_2 Nanoparticles Deposited on Porous Carbon Material for Dye Removal by Absorption and Photocatalytic Processes

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ABSTRACT

The disappearance of Methyl Orange (MO), Azo dye, in west water was studied using an absorption property from porous carbon and photocatalytic dye degradation using TiO_2 nanoparticles. Anatase TiO_2 was impregnated on porous carbon by a wet chemical process and post heat treatment at 400°C. The titania precursor concentrations, pH of the chemical solutions, and mixing techniques during the TiO_2 impregnation were studied. The MO dye's degradation using TiO_2 on porous carbon after saturated absorption revealed the porous carbon material's efficiency supported with TiO_2 nanoparticles for high photocatalytic activity. The degradation reaction was optimized with the catalyst amount. The impregnated porous carbon samples were characterized using powder X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and Energy Dispersive Spectroscopy (EDS). The photocatalytic reaction was studied under irradiation of UV light. The XRD, high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) results confirmed that the structure of TiO_2 nanoparticles was anatase with high crystallinity and no impurity. The porous carbon substate was amorphous carbon. The average particle diameter of TiO_2 nanoparticles measured by SEM and TEM images was 81 nm. Furthermore, the photocatalytic efficiency of as-synthesized samples was 95%, where 100 ml of 5 ppm methyl orange was used as initial concentration with 0.1 g of catalyst dosing for 6 hr under UV irradiation.

INTRODUCTION

The dying wastewater, rich in color and organic-containing residues of reactive dyes and other chemicals, requires proper treatment before being released into the environment. Nevertheless, textile dyeing wastewater can be treated by many technologies such as membrane filtration, electrochemical oxidation, ultrasonic or high energy physical process, sand filtration, aerobic and anaerobic pond [1] However, these technologies often have a very high investment cost and high energy consumption.

Photocatalysis is an alternative treatment that can be used for textile dyeing wastewater treatment. It is a photo-oxidation reaction using photocatalyst such as titanium dioxide, zinc oxide, etc. With this technology, most organic matter can be entirely oxidized to water, carbon dioxide, and other simple inorganic substances using light irradiation and the photocatalyst. The most apparent advantages of photocatalytic technology are energy efficiency and complete degradation of pollutants. The presence of either UV lamp or natural UV light (sunlight) can be used as a source of light for the system [2]. Photocatalyst can be reused results in a low operational cost. Moreover, treated wastewater can be reused in the dyeing process. Thus, zero discharge of water can also be achieved [3].

A photocatalyst is defined as a substance activated by adsorbing the photon energy and becoming capable of accelerating a reaction without being consumed. These substances are being called the semiconductors [4]. Several semiconductors (TiO_2, ZnO, Fe_2O_3, CdS, ZnS) can act as photocatalysts, but TiO_2 has been commonly studied due to its ability to break down organic pollutants, less toxic and its UV range application [3].

Many researchers had widely studied the immobilized TiO_2 (such as TiO_2 film on substrates) [2] to prevent the drawback of TiO_2 nanoparticles derived from the difficulty of TiO_2 separation from the treated wastewater. Thus, the immobilization of TiO_2 by coating it as a thin film on the substrate could result in a more comfortable separation process from the treated wastewater. There are several methods for TiO_2-based coating process such as electrochemical process [6], hydrothermal process [7], a modified sol-gel method [8] and chemical deposition technique [9], are costly and not suitable for practical production [4]. The wet chemical impregnation process is an appropriate technique to coat TiO_2 nanoparticles on the substrate due to low cost, uncomplicated method, and large scalable in the manufacturer. Porous carbon was considered as the TiO_2 supporter in this research. The porous carbon is a low cost, the intuitive capability of large-scale production,

high resistance at high temperature, and very high surface area, which show a superior for application in photocatalytic process. This research was conducted to prepare the TiO_2 nanoparticle immobilized on the porous carbon substrate. Finally, the materials will be tested for the absorption ability and photodegradation efficiency of Methyl Orange (MO) under UV-A light irradiation.

METHODOLOGY

Chemical

Titanium(IV)butoxide ($Ti(OCH_2CH_2CH_2CH_3)_4$,97%) was purchased from Sigma-Aldrich. Sodium hydroxide (NaOH, 98%), nitric acid and methanol were purchased from RCI-Labscan. Porous carbon was synthesized by water-in-oil emulsification coupled with sol-gel polymerization [4]. De-ionized (DI) water and methanol were used as the solvent in all reactions.

The effect of pH in the preparation methods

The titanium dioxide nanoparticles on a porous carbon substrate were synthesized via a wet impregnation process. The 0.1 mL titanium(IV) butoxide in 40 ml methanol solvent and 0.4 g porous carbon were mixed and stirred for 15 min. After that, 0.5 ml of 0.28M nitric acid, 0.5 ml of 0.28M NaOH and DI water were added into the solution as pH controller in each synthetic condition (pH 2, pH 8 and pH 6-7, respectively). The solution was stirred for 45 min, and then the yellow suspension was obtained. The filtrated powder was dried at 90 °C for 5 hr and calcined at 400 °C for 5 hr. The discrete TiO_2 nanoparticles on a porous carbon substrate were obtained. The name list of synthesized samples and their relative synthetic conditions were shown in Table 1.

The effect of Titanium(IV)butoxide concentrations and mixing processes.

The 0.02, 0.1, 1 ml of titanium(IV)butoxide in 40 ml methanol solvent and 0.1 g porous carbon were mixed and stirred or shake for 15 min. Then, 0.5 ml 0.28M nitric acid was added into the solution and stirred or shook for 45 min. The yellow suspension was filtrated and dried at 90°C for 5 hr. Finally, the products were calcined at 400°C for 5 hr to obtain the final product.

The photocatalytic degradation of dye

After immobilizing TiO_2 on porous carbon, the photodegradation of Methyl Orange (MO) under UV-A light was investigated. The experiments were conducted in the opaque box the reaction chamber placed on the lab jack at the center inside the box. In each reactor, 100 mL of 5 ppm Methyl Orange solution were mixed with 0.1 g of photocatalyst dosage. The catalyst was mixed in the dye solution without light irradiation for 12 hr to obtain the equilibrium absorption point. The solution was then exposed to UV-A light (2000 $\mu W/cm^2$) for 6 hours to investigate the photocatalytic activity.

Analytical methods

The composite materials were analyzed using the X-ray diffraction (XRD) analysis, which was performed by using an X-ray diffractometer (D8 Advance, Bruker). Furthermore, elemental composition and morphology of the catalytic materials were analyzed using the Field Emission Scanning electron microscopy (FE-SEM, JSM 6335 F) with an energy-dispersive X-ray spectroscopy (EDS). Transmission Electron Microscope (TEM, JEM 2010) was used to confirm the crystal structure of TiO_2 nanoparticles. The concentrations of MO dye in synthetic dyeing wastewater were measured the absorbance at 464 nm using UV–Vis spectroscopy (Lambda 365).

RESULTS AND DISCUSSION

The synthesized samples were investigated the crystal structure by XRD, as shown in Figure 1. The high intensity of TiO_2 (anatase) peaks on the XRD pattern of T1C1-A400 shows a better TiO_2 impregnation process than T1C1-B400 and T1C1-C400. In comparison between T1C1-A400-Sh0.1 (0.1 mL TTBD) and T1C1-A400-Sh0.02 (0.02 mL TTBD), the XRD pattern of T1C1-A400-Sh0.1 presents the intense peaks at 2θ=25.2° and 2θ=55.0° of TiO_2 over T1C1-A400-Sh0.02. This can imply that the amount of TiO_2 loading directly results in the quantity of impregnated TiO_2 on the surface of porous carbon. Moreover, the broad spectrum around 25° and 43° from bare carbon substrate can indicate the small amount of graphitic carbon. Two different mixing processes in T1C1-A400-St0.02 and T1C1-A400-Sh0.02 (Stirring and

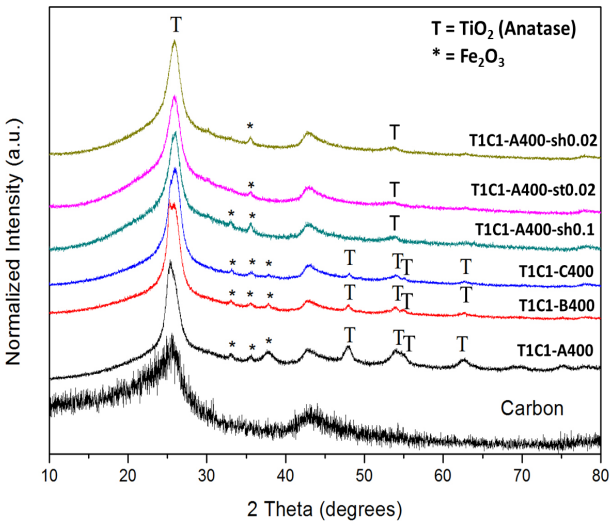

Figure 1. XRD results of porous carbon material supported with TiO_2 nanoparticles in many independent variables.

Table 1. List of Sample name and their relevant synthetic conditions.

Sample name	TTBD (ml)	Porous carbon (g)	pH condition	Mixing Method	Calcination temp (°C)
T1C1-A400	0.1	0.4	acid	stir	400
T1C1-B400	0.1	0.4	base	stir	400
T1C1-C400	0.1	0.4	control	stir	400
T1C1-A400-Sh0.1	0.1	0.1	acid	shaker	400
T1C1-A400-Sh0.2	0.02	0.1	acid	shaker	400
T1C1-A400-Sh0.2	0.02	0.1	acid	stir	400
T1C1-A400-St0.1	1.0	0.1	acid	shaker	400

Shaking) do not show a significant difference in XRD results. However, it might see little differences in the physical surface appearance of porous carbon, which can be confirmed by SEM results.

From Figure 2, a SEM image of (a) T1C1-A400 prepared *via* acidic solution illustrates a better dispersion and adhesion of TiO_2 nanoparticles on porous carbon materials than the other two (b) T1C1-B400 (basic condition) and (c) T1C1-C400 (neutral condition). EDS results of each sample showed a very high percentage of carbon composition (from porous carbon) and a small amount of titanium, which is reasonable to assume that TiO_2 nanoparticles are located on carbon's surface. In Figure 3, SEM images of (d), (e), (f) are not significantly different in dispersion and adhesion of TiO_2 nanoparticles on porous carbon. However, EDS results of (e) T1C1-A400-sh0.02 and (f) T1C1-A400-st0.02 indicate a high atomic percent of Ti element in the sample (e) more than (f) which can explain that the shaking method provides better dispersion and adhesion of TiO_2 than the stirring way.

Backscattered Electron (BSE) image of deposited TiO_2 nanoparticles on porous carbon substrate from T1C1-A400-sh0.02 samples as illustrated in Figure 4. The average particle diameter of TiO_2 nanoparticles was 81 nm (white particles). The small particle size of titanium dioxide on the porous carbon surface could provide more active sites for photocatalysis degradation. The porous carbon surface could be observed in Figure 4 in gray background. It can be clearly seen that the discrete TiO_2 nanoparticles distributed uniformly on the porous carbon surface.

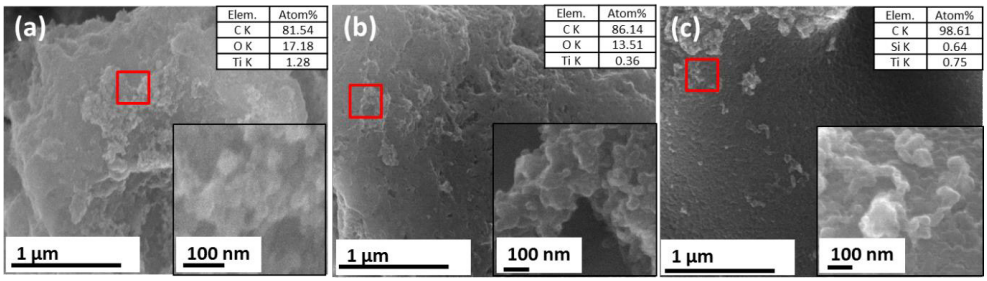

Figure 2. SEM images and EDS results of (a) T1C1-A400 (b) T1C1-B400 (c) T1C1-C400.

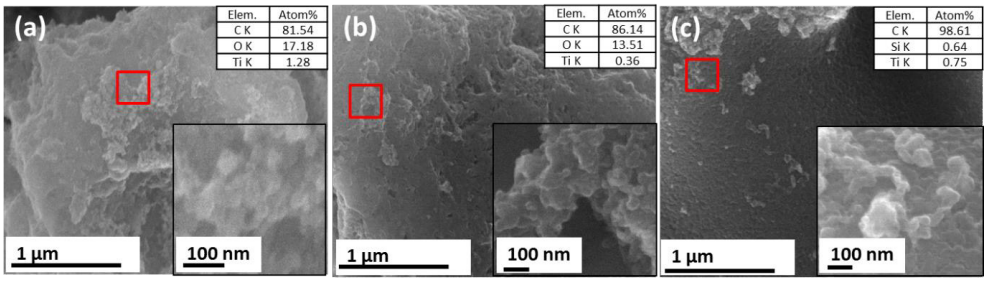

Figure 3. SEM images and EDS results of (d) T1C1-A400-sh0.1 (e) T1C1-A400-sh0.02 (f) T1C1-A400-st0.02.

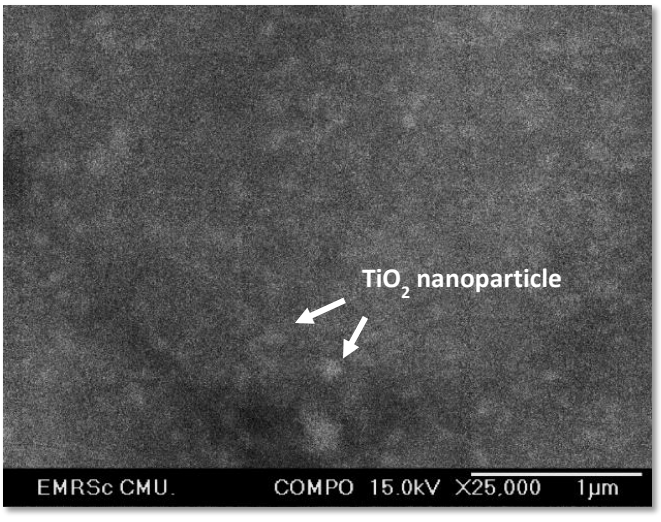

Figure 4. Backscattered Electron (BSE) image of the sample T1C1-A400-sh0.02.

The sample T1C1-A400-sh0.02 was selected to characterize by High-Resolution TEM (HR-TEM) technique and the Selected Area Electron Diffraction (SAED) pattern, as shown in Figure 5. HRTEM and SAED technique were confirmed the crystallinity of TiO_2 anatase. The SAED pattern from a group of particles exposed characteristic d-spacing of TiO_2 anatase, consisting mainly of (101), (103), (105), (213), (116), and (107) planes. Moreover, the HRTEM images reveal a d-spacing value of 0.352nm directly correlated with the (101) lattice plane of TiO_2 anatase.

The comparison in Methyl Orange removal efficiency from TiO_2 nanocatalyst on porous carbon substrates was shown in Figure 6. It can be seen that the % disappearance was reached to 85-95% after absorption for 12 hr combining with the photocatalytic process for 6 hr. At absorption period, the % disappearances were reach to 78%, 78% and 86% in T1C1-A400-sh0.1, T1C1-A400-sh1.0 and T1C1-A400-sh0.02 respectively. In the photocatalytic period, the disappearance of MO also continuously increased and reached to 95%, 93%, and 88% MO removal under UV-irradiation after 6 hr for T1C1-A400Sh0.1, T1C1-A400Sh0.02, and T1C1-A400Sh1, respectively. T1C1-A400Sh0.02 provides the highest %removal due to the appropriate ratio between TiO_2 nanoparticles and

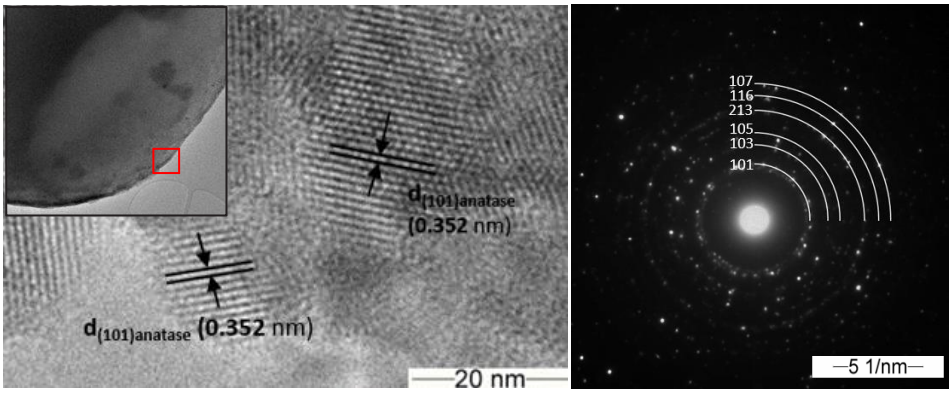

Figure 5. (a) HRTEM image of T1C1-A400-sh0.02 and (b) SAED pattern of T1C1-A400-sh0.02.

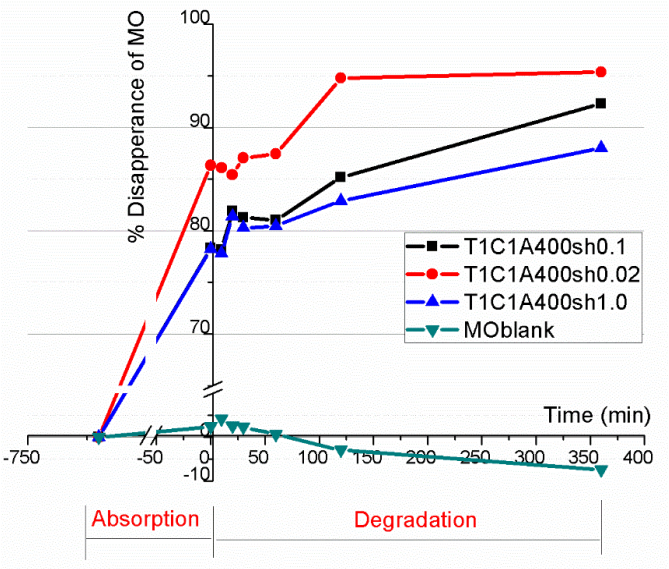

Figure 6. The Methyl Orange removal efficiency by using the as-prepared TiO_2 nanoparticles deposited on porous carbon material.

porous carbon substrate. The MO removal process possesses two steps. First, the MO organic dye molecules were absorbed within the hole in porous carbon structure and carbon surface leading to high %disappearance [4]. After that, titanium dioxide as a photocatalyst had the ability to generate radical species such as hydroxyl radical and superoxide radical, which can further degrade Methyl Orange [9].

CONCLUSION

Anatase TiO_2 nanoparticles were successfully impregnated on a porous carbon substrate by a wet chemical process and post heat treatment at 400°C. The acidic condition with the shaking process provided TiO_2 nanoparticles well impregnated on porous carbon with homogeneous dispersion. T1C1-A400-sh0.02 shows the highest efficiency on the disappearance of methyl orange. This research successfully combines the absorption property of porous carbon and the photocatalytic degradation of Dye using TiO_2 nanoparticles for wastewater treatment. The degradation of the MO dye using TiO_2 on porous carbon after saturated absorption revealed the porous carbon material's efficiency supported with TiO_2 nanoparticles for high photocatalytic activity.

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