Preparation of Ag/TiO_2/bamboo charcoal composite based on chemical and electrochemical synthesis: characterization and antibacterial study

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ABSTRACT

A combination of antibacterial, photocatalytic, and adsorption properties has been introduced as in a form of silver/titanium dioxide/bamboo charcoal ($Ag/TiO_2/BC$) composite where Ag nanoparticles incorporated with TiO_2 nanoparticles were previously immobilized on the BC support. The TiO_2 nanoparticles were synthesized by chemical method employing tetrabutyl orthotitanate, $Ti(OBu)_4$, as a precursor and subsequently wet impregnated on BC surface. The Ag nanoparticles were synthesized by electrochemical method in which the Ag^+ generated from silver electrolysis was reduced to Ag^0on the TiO_2/BC matrix. The obtained composite was studied in terms of morphologies using scanning and transmission electron microscopy (SEM and TEM, respectively) as well as in terms of light diffraction characteristics by X-ray diffractometer to confirm the presence of the desired product. The synergetic effect established from the three components in the composite was investigated by several approaches including dye removal, photodegradation, and antibacterial against *E. coli* and *S. aureus.*

Keywords: Titanium dioxide, bamboo charcoal, silver, nanoparticles

1 INTRODUCTION

Photocatalysts have been intensively studied to seek for benefits in wastewater treatment application. Most of organic substances dissolved in water can be eliminated toward the photocatalytic reaction involving oxidation and reduction of photocatalysts [1-2]. Titanium dioxide (TiO_2) is known as a photocatalyst for decades. It has several advantages, e.g. low cost, non-toxicity, and good stability [3]. One major limitation, however, is that TiO_2 nanoparticles cannot be recollected easily due to their very minute sizes. The TiO_2 immobilization on porous materials has been developed to overcome this problem [4]. Although the surface area of the immobilized TiO_2 is dramatically reduced when compared to its freely suspended spherical form, re-use of this TiO_2-coated porous media is much more practical.

Bamboo charcoal (BC) is of interest since its excellent adsorptivity. The incorporations of TiO_2 nanoparticles on BC have been demonstrated in a number of reports. Wang and coworker [5] studied the degradation of methyl orange by the composite photocatalyst obtained as TiO_2-immobilized activated carbon. They proposed that the adsorptivity of BC brought methyl orange molecules close to the immobilized TiO_2 nanoparticles, which is, therefore, the reason in enhanced photocatalytic activity of TiO_2/BC composite. Zhang et al. [6] also found that TiO_2 impregnated on BC exhibited greater photocatalytic degradation of dibenzothiophene toward the improvement of catalyst dispersity and transport of dibenzophenone.

The antibacterial effect by TiO_2 nanoparticles has also been investigated [7]. Interestingly, while pure TiO_2 nanoparticles exhibited significant impact on survival rate of microbial, the use of TiO_2-immobilized supports for bactericidal control are scarce [8]. In fact, the efficiency of the TiO_2-impregnated materials toward the killing activity on bacteria is quite low. It has been suggested by Srinivasan et al.[7] that the inaccessibility of microorganism to the TiO_2 active site, the diminution of specific surface area, and the limitation of oxygen over deep immobilized TiO_2 on the support surface may play as important causes to the ineffective photocatalytic antibacterial results.

Silver nanoparticles has been reported to be used in disinfecting microorganism effectively [9]. It releases silver ion (Ag^+) that affects the functions of protein in microorganism cells, hence inhibiting the replication abilities of DNA and thus destroy the microorganism, such as bacteria, fungi, etc [10].

Recently, some works relating to the incorporation of Ag with TiO_2 have been developed [11]. The metal doped-TiO_2 shows good photocatalytic results when compared to TiO_2-pure form. This is believed to involve the establishment of electron traps generated on the conduction bands, assisting electro-hole separation during the photocatalytic process [12]. Silver also enhances the antimicrobial property in the presence of TiO_2 through the increased surface area and its directly interacting with microorganism [13].

In this work, we prepared Ag/TiO_2/BC composite through the chemical and electrochemical process. The obtained product showed good adsorptivity, photocatalytic property, and antibacterial results.

2 EXPERIMENTAL

2.1 Preparation of TiO_2 nanoparticles

A 900 mL deionized water was acidified to pH 1.5 by adding concenctrated HNO_3 and cooled to 4 °C in a refrigerator for 12 h. To this solution was added drop-wise a mixture of titanium butoxide (10 mL) dissolved in isopropanol (90 mL) within 3 h with continuous stirring. The resulting mixture was further stirred for 2 h until a transparent colloidal solution of TiO_2 was obtained.

2.2 TiO_2 impregnation on bamboo charcoal

A 1 g of BC was dispersed in a 400 mL TiO_2 colloidal solution from 2.1 at room temperature, and the suspension was stirred at ambient temperature for 3.5h. The obtained mixture was concentrated at 60 °C under reduced pressure, yielding product as black precipitate. It was then heated from room temperature to 400 °C with heating rate at 20 °C/min and remained at that temperature for 1 h in N_2 atmosphere, giving TiO_2/BC product as grey powder.

2.3 Ag nanoparticles deposition on TiO_2/BC via electrochemical synthesis

A 1 g of TiO_2/BC sample was dispersed in 120 mL deionized (DI) water contained in a beaker, equipped with an electrochemical cell that was constructed as in the followings:

- Two silver electrodes were made by three-folded silver wire (0.4 mm diameter and 10 cm length). The distance between two electrodes was set at 5 cm where one end of the electrode (2 cm) was immersed in DI water.
- Electrolysis was performed at room temperature with a constant voltage at 15 V for 10, 30, and 60 min.
- The resulting suspension was magnetically stirred (500 rpm) throughout the end of electrolysis.
- The polarity of the direct current was switched every 3 min to reduce chance of silver deposition on the cathode.

The Ag/TiO_2/BC composite was washed with DI water, collected by centrifugation, and dried at 60 °C overnight.

2.4 Characterization method

The morphology and the particle distribution of the composites were analyzed by transmission electron microscopy (TEM: JEOL JEM 2010). Phase identification of composite was revealed using X-ray diffraction (JEOL JDX 3530) with Cu K$\propto$ radiation. Antibacterial efficacies against *S. aureus* (ATCC 6538) and *E.coli* (ATCC 25922) were determined by zone of inhibition method. The photocatalytic activity was examined by monitoring the removal of methylene blue solution through UV-Vis spectrophotometry.

3 RESULTS AND DISCUSSION

3.1 Impregnation of TiO_2 nanoparticles on BC matrix

TiO_2 nanoparticles were obtained by hydrolysis reaction of titanium butoxide, $Ti(OBu)_4$, followed by polycondensation with a complex reaction activity to form inorganic network ≡Ti-O-Ti≡. When hydrolysis is retarded, e.g. in a very acidic condition, the formation of TiO_2 particle is extremely slow, providing uniformity in size and shape of the particulates. The size of TiO_2 nanoparticles by this method can be in range of 10 nm approximately. This will allow them to be incorporated on any area of the BC matrix. Figure 1 shows the TEM image of TiO_2/BC composite obtained after calcination at 500 °C.

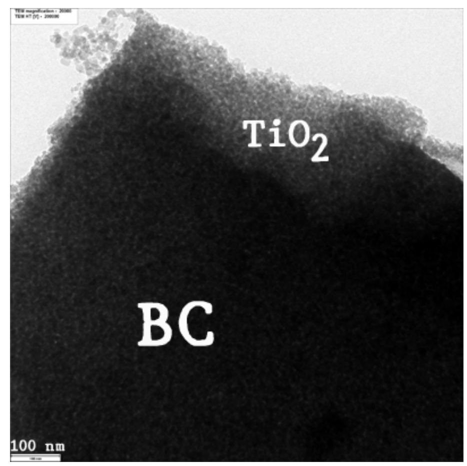

Figure 1: TEM image of TiO_2/BC

TiO_2 may be responsible for a significant decrease of surface area in BC, but this was sacrificed with photocatalytic ability in the composite.

3.2 Electrochemical deposition of Ag nanoparticles on TiO_2/BC matrix

Synthesis of Ag nanoparticles via electrochemical synthesis using two pure silver electrodes in DI water was studied earlier by Khaydarov et al. [14]. It involves several steps including oxidative and reductive reactions as follows:

$Ag^0 \rightarrow Ag^+ + e^-$	anode
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	anode
Ag^+	migrating to cathode
$Ag^+ + e^- \rightarrow Ag^0$	cathode
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	cathode

In the presence of suspending TiO_2/BC, Ag^+ that migrated from anode was adsorbed on the surface of the composite. It was then reduced to Ag nanoparticles by the electron-rich surface TiO_2/BC. In addition, Ag nanoparticles fallen off from the cathode by stirring activity were also attached on the composite surface with the adsorption driving force.

Figure 2 shows the TEM image of Ag/TiO_2/BC composite. The TiO_2 nanoparticles were formed as a thin layer, which covered most part of the BC surface. A larger particle size of Ag nanoparticles (ca. 200 nm), randomly distributed on the matrix of TiO_2/BC composite, was clearly observed.

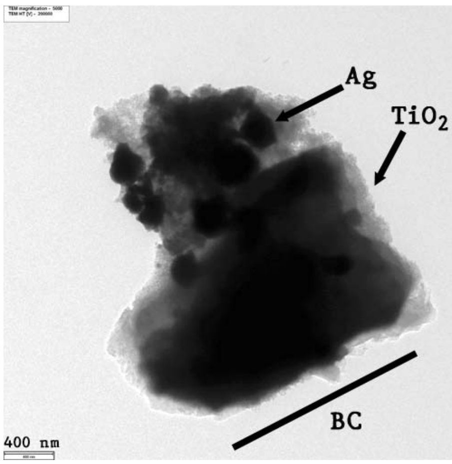

Figure 2: TEM image of Ag/TiO_2/BC

The Ag particle size could be controlled during the electrochemical synthesis. The longer the electrolytic period, the larger the Ag particle was formed. This is due to the continuous depositing of $Ag^{(0)}$ atom over the already nucleated Ag nanoparticles by van der Waals forces.

The XRD pattern of Ag/TiO_2/BC composite is shown in Figure 3. The diffraction peaks belongs to Ag, such as 111, 200, 220, 311 from left to right were observed beside the diffraction pattern of anatase TiO_2, indicating that this composite contained Ag and TiO_2 nanoparticles.

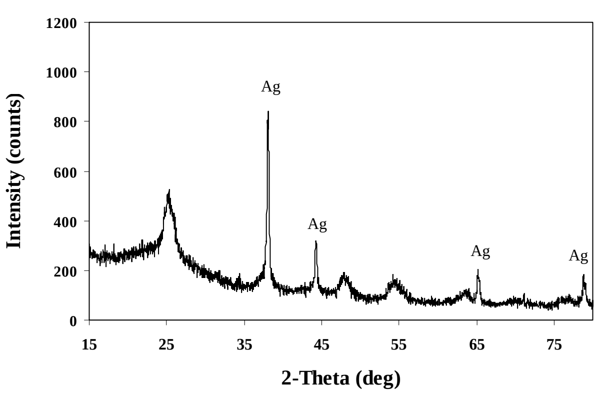

Figure 3: XRD pattern of Ag/TiO_2/BC

3.3 Antibacterial effect of Ag/TiO_2/BC

In this study, the zone of inhibition method was employed. It was carried out by swapping a standard inoculum of the test organism with 10^7 CFU on the surface of agar plate. Discs of filter paper coated with the sample, e.g. BC, TiO_2/BC, and Ag/TiO_2/BC were faced top over the agar. After incubation for one night at 37 ^oC, the sample plates were analyzed, and the clear zone around the discs were measured. Figure 4a-c show the results for zone of inhibition in TiO_2/BC and Ag/TiO_2/BC against *S. aureus* and *E.coli.* It appeared that the composite containing only TiO_2 and BC could not inhibit the growth of both bacteria.

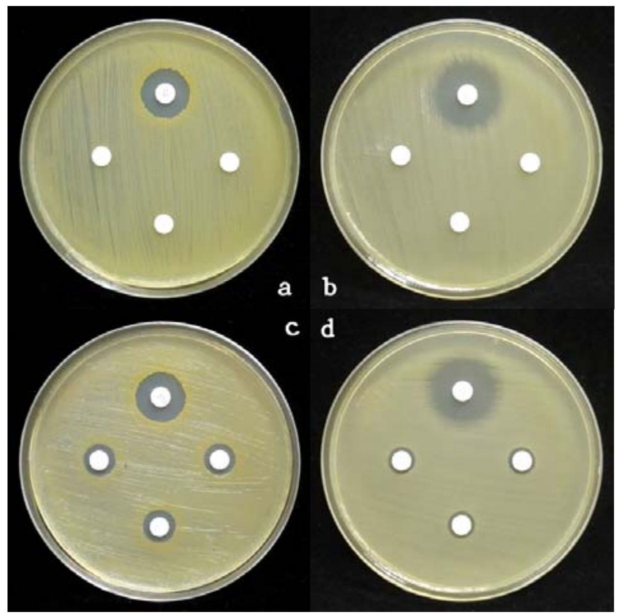

Figure 4: Photographs of agar plates for zone of inhibition in TiO_2/BC with *S. aureus* (a) and with *E. coli* (b); in Ag/TiO_2/BC with *S. aureus* (c) and with *E. coli* (d).

Table 1 reveals the zone of inhibition (mm) by the composite samples. Prolonging electrochemical synthesis from 10 to 60 minutes may increase the content of Ag nanoparticles on the composite, and thus it resulted in controlling bacteria more effectively. Note that when high Ag content was performed, the antibacterial activity against S. aureus became significant.

Table 1: Zone of inhibition (mm) against bacteria

Sample	Zone of inhibition (mm)	
	S. aureus	*E. coli*
BC	0	0
TiO_2/BC	0	0
Ag/TiO_2/BC (10 min)	0.2	0.5
Ag/TiO_2/BC (30 min)	1.5	1.0
Ag/TiO_2/BC (60 min)	1.5	1.0

3.4 Adsorption and photocatalytic activity of $Ag/TiO_2/BC$

Removal of methylene blue concentration by adsorption and photocatalytic property of $Ag/TiO_2/BC$ compared to the other composite (BC and TiO_2/BC) were investigated in two conditions, dark and light. In dark condition, the composite material was used to adsorb the methylene blue molecules in the solution under the absence of any light. This adsorption period was allowed for 3 ½ h in order to prove that $Ag/TiO_2/BC$ had adsorption ability to the target molecules. In light condition, the UV light (366 nm) was allowed to pass through the methylene blue solution at after 3 ½ h for 2 h. The photocatalyst, TiO_2, on the composite absorbed UV energy and began photocatalytic process. Figure 5 shows the comparative study of the dye removal by adsorption and photocatalytic reactions of different materials. It was found that the adsorptivity of composite reached limitation faster than that in the pure BC due to the loss of pore volume after TiO_2 impregnation.

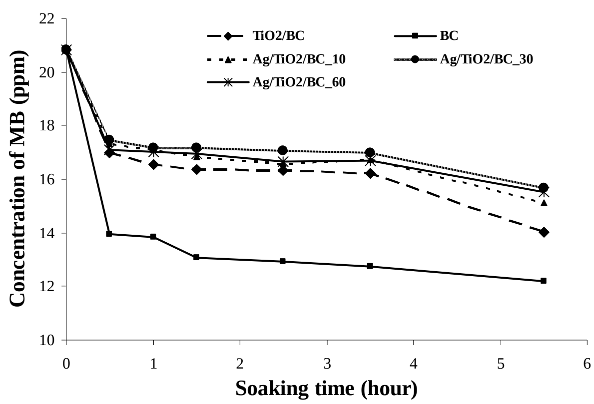

Figure 5: Dye removal efficiencies from different materials

The adsorption of BC was far more effective than other materials in methylene blue removal. It was almost two-time higher performance than that of the composites, which were all the same in adsorption character. Despite the fact that the photocatalytic of TiO_2/BC and $Ag/TiO_2/BC$ showed somewhat different tendency within the 2 h period, which was obviously contrast to the nearly flat photocatalytic result in BC, the efficiencies of their decomposing methylene blue molecules were not impressive. The TiO_2-impregnated materials may lose their photocatalytic active site in the process of Ag deposition. Another possibility is that synergetic effect between Ag and TiO_2 in $Ag/TiO_2/BC$ composite had induced the energy absorbed to be ranged in visible region.

4 CONCLUSION

A composite so-called $Ag/TiO_2/BC$ was prepared step-wise by chemical synthesis of TiO_2 nanoparticles on BC matrix, followed by electrochemical deposition of Ag nanoparticles. The morphology of this composite was also investigated by transmission electron microscope, revealing tiny TiO_2 nanoparticles in the size range of 10 nm were randomly attached with larger Ag nanoparticles (>200 nm). XRD result confirmed the presence of Ag nanoparticles in the composite. Antibacterial efficacy of $Ag/TiO_2/BC$ was examined against *S. aureus* and *E. coli*, which showed improvement from TiO_2/BC and BC. The adsorption and photocatalytic reaction were also observed in $Ag/TiO_2/BC$ although the latter was not shown efficiently. This combination of adsorption, photo-catalysis, and antibacterial property could be made possible in one composite material, and the results were promising for future need, especially in environmental application.

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