

Surface Modification of Natural Fiber using Bi₂O₃/TiO₂ Composite for Photocatalytic Self-cleaning

Ashiqur Rahman,^a Yern Chee Ching,^{a,*} Kuan Yong Ching,^{b,c} Nur Awanis,^d Ashok Kumar Chakraborty,^e Cheng Hock Chuah,^f and Nai-Shang Liou^g

A photocatalytic fiber was prepared by modifying the surface of jute fiber with a Bi₂O₃/TiO₂ composite. Maleic acid was used as an organic linker, and the coating process was conducted with heat-treatment at 240 °C. At first, the Bi₂O₃/TiO₂ composite was synthesized by incorporating TiO₂ nanoparticles onto a Bi₂O₃ phase. Subsequently, the photocatalytic fiber was prepared by incorporating the Bi₂O₃/TiO₂ composite onto the surface of the fiber. The Bi₂O₃/TiO₂ composite-modified fiber was characterized by field-emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and UV-visible spectroscopy. The synthesized composite exhibited notably high photocatalytic activity under visible light irradiation of λ up to 420 nm, whereby it could decompose organic pollutants in the aqueous and gaseous phases. Because of increasing environmental concerns, this photocatalytic system could be an important candidate for decomposing organic pollutants.

Keywords: Fiber; Bi₂O₃/TiO₂; Photocatalysis; Self cleaning; Organic pollutants

Contact information: a: Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia; b: National Centre for Advanced Tribology at Southampton, Faculty of Engineering and the Environment, University of Southampton, Southampton SO17 1BJ, United Kingdom; c: Department of Science, School of Foundation Studies, Southern University College, 81300 Skudai, Johor, Malaysia; d: Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia; e: Department of Applied Chemistry & Chemical Technology, Faculty of Applied Science & Technology, Islamic University, Kushtia-700, Bangladesh; f: Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia; g: Department of Mechanical Engineering, Southern Taiwan University of Science and Technology, Yungkuang Dist., Tainan City 710, Taiwan R.O.C;

* Corresponding author: chingyc@um.edu.my

INTRODUCTION

Titanium dioxide (TiO₂) could be a potential candidate for the degradation of organic materials because of its ability to initiate photocatalysis in the presence of UV light and its oxidant nature (*e.g.*, O₂/H₂O). To initiate the photocatalysis reaction, TiO₂ catalyst must undergo the photo excitation process. TiO₂, which acts as a semiconductor, requires photons with energy greater than their energy band gap (E_g), located within the UV-light range of the electromagnetic spectrum, to induce the reaction. TiO₂ is acknowledged as an excellent catalyst. However, when visible light is available as the energy input, its catalysis ability is limited because of its wide band gap of 3.2 eV (Sobana *et al.* 2006).

There are many studies on the modification of TiO₂. For instance, TiO₂ has been doped by metal and non-metal ions (Chao *et al.* 2003; Chatterjee and Dasgupta 2005;

Chang and Doong 2006; Venkatachalam *et al.* 2007; Gao *et al.* 2010), dye photo-sensitized on its surface (Fujishima *et al.* 2000; Hilal *et al.* 2007), sensitized by a narrow band gap semiconductor (Bai *et al.* 2010; Zhao *et al.* 2010; Zyoud *et al.* 2010), deposited with noble metals (Hufschmidt *et al.* 2002; Dobosz and Sobczykński 2003; Arana *et al.* 2004; Sobana *et al.* 2006), and combined with semiconductors. All of these studies aimed at extending the absorption range of TiO₂ into the visible range. Of the many approaches, noble metal-modified semiconductor nanoparticles have recently been recognized as one of the most viable solutions for maximizing the efficiency of photocatalytic reactions. Interestingly, noble metals doped or deposited on TiO₂ may act either singly or simultaneously, depending on the photoreaction conditions. Noble metals may (i) act as electron traps, which promote electron-hole separation; (ii) prolong light absorption in the visible range and promote surface electron excitation by plasmon resonances excited by visible light (Leong *et al.* 2014); and (iii) modify the surface properties of photocatalysts (Sobana *et al.* 2006; Moafi *et al.* 2011;). For TiO₂ to be photoactive under visible light, considerable efforts have been made to dope it with various metals (Ao *et al.* 2004; Abe *et al.* 2008; Mahdi *et al.* 2013) and non-metals (Arana *et al.* 2004; Brezesinski *et al.* 2010). A combination of semiconductors is considered an effective way to enhance the photostimulated electron-hole separation and effectively inhibit their recombination. The main feature of this technique is to assemble a heterojunction interface between wide and narrow band gap semiconductors with matching energy band potentials.

Consequently, an electric field assists in the transportation of charges from one particle to the adjacent one, which makes the catalysis process feasible at the interface of the electron-hole separations in the composite materials. Thus, the electron and hole can move to the surface of the semiconductors. The extensive research published on this composite system has mostly focused on TiO₂-based photocatalysts such as WO₃/TiO₂, In₂O₃/TiO₂, SiO₂/TiO₂, MgO/TiO₂, Fe₂O₃/TiO₂, Bi₂O₃/TiO₂, and FeTiO₃/TiO₂ (Houas *et al.* 2001; Dobosz and Sobczykński 2003; Kandavelu *et al.* 2004; Hameed *et al.* 2008; Kim *et al.* 2009; Chakraborty and Kebede 2012; Chakraborty *et al.* 2012). Bismuth (III) oxide Bi₂O₃, with a band gap of 2.8 eV, is known as p-type semiconductor and has proven to be a good photocatalyst for water treatment and the decomposition of pollutants under visible-light irradiation (Kun *et al.* 2006; Mozia *et al.* 2007; Salim *et al.* 2014).

In this study, Bismuth (III) oxide, Bi₂O₃ was used to increase the photoactivity of TiO₂. Bismuth (III) oxide is known as the most industrially important compound of bismuth. About half of the production of bismuth is for bismuth compounds. Bismuth compounds are used in cosmetics, pigments, and a few pharmaceuticals. Notably Pepto-Bismol is used to treat diarrhea. Bismuth's unusual propensity to expand upon freezing is responsible for uses in casting of printing type (typesetting). Bismuth can expand upon solidification, this makes it suitable to make castings for objects subjected to high temperatures. Scientific studies have confirmed that bismuth and most of its compounds are less toxic compared to other heavy metals such as lead, antimony, *etc.* Besides it is not bioaccumulative (Fujishima *et al.* 2000; Hilal *et al.* 2007; Chakraborty *et al.* 2012).

In the present study, a Bi₂O₃/TiO₂ system was developed by utilizing maleic acid as an organic binder. The role of maleic acid is to bind Bi₂O₃ and TiO₂ using two end carboxylic functional groups (Chakraborty *et al.* 2014). The prepared Bi₂O₃/TiO₂ was applied for the photocatalytic degradation of phenol in the aqueous phase and 2-propanol in the gaseous phase under visible-light irradiation. The capability of the non-toxic, inexpensive TiO₂ nanoparticles to exhibit self-cleaning properties in different textile materials has been widely studied (Ding *et al.* 2000; Fujishima *et al.* 2000; Chao *et al.*

2003; Stylidi *et al.* 2004; Fruth *et al.* 2005; Gan *et al.* 2007; Uddin *et al.* 2007; Venkatachalam *et al.* 2007; Uddin *et al.* 2008; Kim *et al.* 2009; Brezesinski *et al.* 2010; Gao *et al.* 2010). The compound of phenol and 2-propanol were selected as model pollutants in this study. This was due to the fact that both the phenol and 2-propanol are ubiquitous pollutants that cause pollutant to natural water resources. These pollutants come from the effluents of a variety of chemical industrial such as cool refineries, phenol manufacturing, pharmaceuticals and industries of resin paint, pulp mill, petrochemical, dying, textile wood, *etc.* (Gad and Saad 2008). These compounds can induce hematological, genotoxic, carcinogenic, immunotoxic, and physiological effects, and they have resulted in a high bioaccumulation rate along the food chain due to its lipophilicity. Thus, these pollutants represent a threat against the natural environment and also to human health (Hori *et al.* 2006). Bi₂O₃/TiO₂ composite can dissociate organic pollutants in the presence of UV-Visible light. For this reason, phenol and 2-propanol were selected as model pollutants in the photocatalytic and self-cleaning activity tests in this study.

In addition, self-cleaning materials have been explored for use in other applications, such as the windows of high-rise towers, automobile windshields, and even in industries that require this promising technique for sterilization, anti-fogging, room air cleaning, and deodorization (Houas *et al.* 2001). To enhance the catalyst's performance in self-cleaning applications, fine TiO₂ must be immobilized onto suitable substrates. However, fabrication methods such as chemical vapor deposition (CVD), anodization, and thermal oxidation of Ti metal, ultrasonic nebulization, and pyrolysis operate at high temperatures which may result in unwanted cracking and peeling of the TiO₂ film (Chao *et al.* 2003; Dobosz and Sobczyński 2003; Mozia *et al.* 2007). These defects are attributed to shrinkage during the crystallization of deposited amorphous films.

In this work, a facile and effective synthesis route to create self-cleaning coatings, based on titanium nanocomposites on fibers, was studied. The photocatalytic performance of the coated fibers was assessed. To the best of our knowledge, Bi₂O₃-doped TiO₂ films for self-cleaning applications have not been studied previously.

EXPERIMENTAL

Materials

Titanium dioxide (TiO₂), bismuth oxide (Bi₂O₃), maleic acid (C₄H₄O₄), absolute ethanol (CH₃CH₂OH), phenol (C₆H₅OH), and acetone were purchased from Evonik Degussa GmbH (Germany) and Sigma Aldrich (Germany) and were used without further refinement. Distilled water was used throughout the experiments. The fibers were extracted from the bark of a jute tree. The fibers were treated with water and detergent at 80 °C for 45 min to remove all impurities, fats, greases, waxes, and other residue before use. Then, they were washed repeatedly by a large amount of distilled water until the pH was constant. Acetone was used to clean the fiber again before they were dried at ambient temperature for 36 h (Ching *et al.* 2015).

Preparation of Bi₂O₃/TiO₂ Composite

In this study, a Bi₂O₃/TiO₂ composite was prepared in a ratio of 5/95, meaning that the Bi₂O₃/TiO₂ composite consisted of 5 mol% Bi₂O₃ (mean particle size 20 to 30 nm) and 95 mol% TiO₂ (mean particle size 4 to 13 nm). During preparation, 0.3070 g of Bi₂O₃ was first suspended in 40 mL of absolute ethanol. Then, 0.1987 g of maleic acid,

dissolved in absolute ethanol, was added to the suspension. Subsequently, 1 g of TiO₂ nanoparticles was added to the above suspension and stirred with a magnetic stirrer for 6 h at ambient conditions until the mixture was homogenous. After that, the suspension was centrifuged and the Bi₂O₃/TiO₂ composite was observed as the residue. Then, the Bi₂O₃/TiO₂ composite was washed several times with ethanol to remove unreacted maleic acid (Xu *et al.* 2008; Liu *et al.* 2010; Chakraborty *et al.* 2014). Next, the composite was dried at 60 °C in an oven overnight. Then, the Bi₂O₃/TiO₂ composite was annealed at 100 °C for 3 h to increase its bonding strength. The Bi₂O₃/TiO₂ composite obtained was then ready for coating on the surface of the jute fiber.

Coating of Bi₂O₃/TiO₂ Composite on Fiber

To prepare a Bi₂O₃/TiO₂ composite-coated fiber with ratio of 20 wt.% Bi₂O₃/TiO₂ and 80 wt.% fiber, 0.2 g of Bi₂O₃/TiO₂ composite was first suspended in 40 mL of absolute ethanol. Then, 0.1987 g of maleic acid and 0.8 g of fiber were added to the above suspension and stirred vigorously for 6 h at 25 °C. After that, the suspension was centrifuged and Bi₂O₃/TiO₂ composite-coated fibers were observed as the residue. Then, the fibers were washed several times with ethanol to remove unreacted maleic acid. Afterward, the coated fiber was dried at 60 °C for 6 h in an oven. The same procedure was repeated to prepare Bi₂O₃/TiO₂-coated fiber where fiber and Bi₂O₃/TiO₂ composite were present at ratios of 90:10; 65:35; 50:50; 35:65; and 20:80.

Photocatalytic Test

Photocatalytic degradation of adsorbed phenol and 2-propanol on Bi₂O₃/TiO₂ film coated fiber was investigated. The simulating solar light irradiation was carried out at 308 K by using a 300-W xenon lamp with a UV cutoff filter ($\lambda \leq 420$ nm, lamp spectrum: 220-2000 nm, Oriel Instrument, Singapore) was used for photocatalytic reactions (Fligge *et al.* 2001). The bulb and the H₂ filter together yield a spectrum ranging from ultraviolet to infrared radiation (similar to natural sunlight).

In this study, aqueous solutions (0.05%, w/v) of reagent grade phenol and gaseous 2-propanol were prepared for impregnation of the unmodified and of Bi₂O₃/TiO₂-coated fibers. The reaction medium was stirred by a magnetic stirrer for 30 min in darkness. The concentration of pollutants did not change after stirring for 30 min, which indicates that 30 min is enough to reach the adsorption equilibrium of organics (Chakraborty *et al.* 2014).

The phenol concentration was measured before the photocatalytic reaction. After that, the samples were remained overnight to complete the adsorption. The samples were then removed from phenol solution and gaseous 2-propanol and were dried at room temperature. From the decreased concentration value of phenol and 2-propanol, the concentration of pollutant compounds leave on the fiber was estimated to be 1.00×10^{-4} M. The samples containing adsorbed phenol and 2-propanol were then exposed to reproducible solar-like light (50 mW/cm²) for photoactivity test study. The phenol and 2-propanol photodecomposition reaction was monitored with a UV-Vis spectrometer in the reflectance mode by investigating the evolution of the absorbance upon light exposure (Uddin *et al.* 2007; Venkatachalam *et al.* 2007; Uddin *et al.* 2008). The remnant phenol and 2-propanol after the irradiation of visible light was analyzed from its characteristic absorption peak detected by UV-Vis spectroscopy (Chakraborty *et al.* 2014).

Characterization Methods

The morphologies of the pure and coated fibers were examined using a field-emission scanning electron microscopy (FESEM, FEI Quanta FEG 450, FEI Company, Redmond, USA). The elemental compositions of the Bi₂O₃/TiO₂-coated fibers were identified with energy-dispersive X-ray spectroscopy (EDX) attached to FESEM. For X-ray diffraction measurements, a D8 Bruker Avance X-ray diffractometer (Bruker, Germany) was used. FTIR analysis was performed using an FTIR Spectrum 400 spectrometer (Perkin Elmer, USA) to analyze the polymer chain quality of the fiber before and after treatment and after extended visible light exposure. UV-Vis reflectance spectra were recorded by a Shimadzu UV-1601 spectrophotometer (Shimadzu, Japan) to observe the photocatalytic dissociation of phenol and 2-propanol on the Bi₂O₃/TiO₂-coated fiber.

RESULTS AND DISCUSSION

Morphological and Compositional Analysis

Morphological analysis of the pure and treated fibers was conducted by FESEM. Figures 1a and 1b display the surfaces of the unmodified fibers. Figures 1c, d show the fiber surface after it was coated with the Bi₂O₃/TiO₂ (20 wt.%) composite in the presence of maleic acid. The samples were enclosed by discrete Bi₂O₃/TiO₂ agglomerates. The Bi₂O₃/TiO₂ agglomerates were irregular in shape, with dimensions of less than 100 nm. The Bi₂O₃/TiO₂ agglomerates were unevenly distributed over the fiber surface.

Figures 1e and 1f display the morphology of Bi₂O₃/TiO₂-coated fiber after 25 washings. There was no observed change in the surface of the Bi₂O₃/TiO₂-coated fiber. These figures demonstrate that the shapes of the particles were similar to each other and that these nanoparticles were irregular and likely to agglomerate. In general, the Bi₂O₃/TiO₂ composite with the presence of maleic acid showed good interfacial adhesion with the fiber surface. Figure 1g displays the morphology of Bi₂O₃/TiO₂-coated fiber without the presence of maleic acid. From the morphological result, no metal particle coating was observed on the jute fiber surface. This indicates that the maleic acid can play an important role as linker between the TiO₂ and Bi₂O₃ particles and between the Bi₂O₃/TiO₂ composite to fiber surface.

The EDX analyses of unmodified fibers, Bi₂O₃/TiO₂-coated fibers with a fiber-to-composite weight ratio of 80:20 before and after washing, and Bi₂O₃/TiO₂-coated fibers without maleic acid are presented in Table 1. The EDX result of Bi₂O₃/TiO₂-coated fiber without maleic acid was used as the control. Table 1 shows that the unmodified fiber contained high amounts of carbon and oxygen (Tan *et al.* 2015). After the fiber was coated with Bi₂O₃/TiO₂ composite, the elements Bi and Ti were observed. Thus, the Bi₂O₃/TiO₂-coated fiber consisted of C, Bi, Ti, and O. However, the Bi₂O₃/TiO₂-coated fiber without maleic acid did not show any element of Bi and Ti on the fiber surface. This indicates that maleic acid can play an important role to adhere the Bi₂O₃ and TiO₂ particles on the fiber surface. After 25 washing cycles, significant amounts of Bi and Ti were still observable on the Bi₂O₃/TiO₂-coated fiber surface. This shows that TiO₂ particles strongly adhered to the surface of the fibers. This might be due to the continuous and homogeneous configuration of the TiO₂ films. Thus, the pollutant molecules impinging on the fiber-TiO₂ composite could accumulate preferably with the TiO₂ phase covering the fibers.

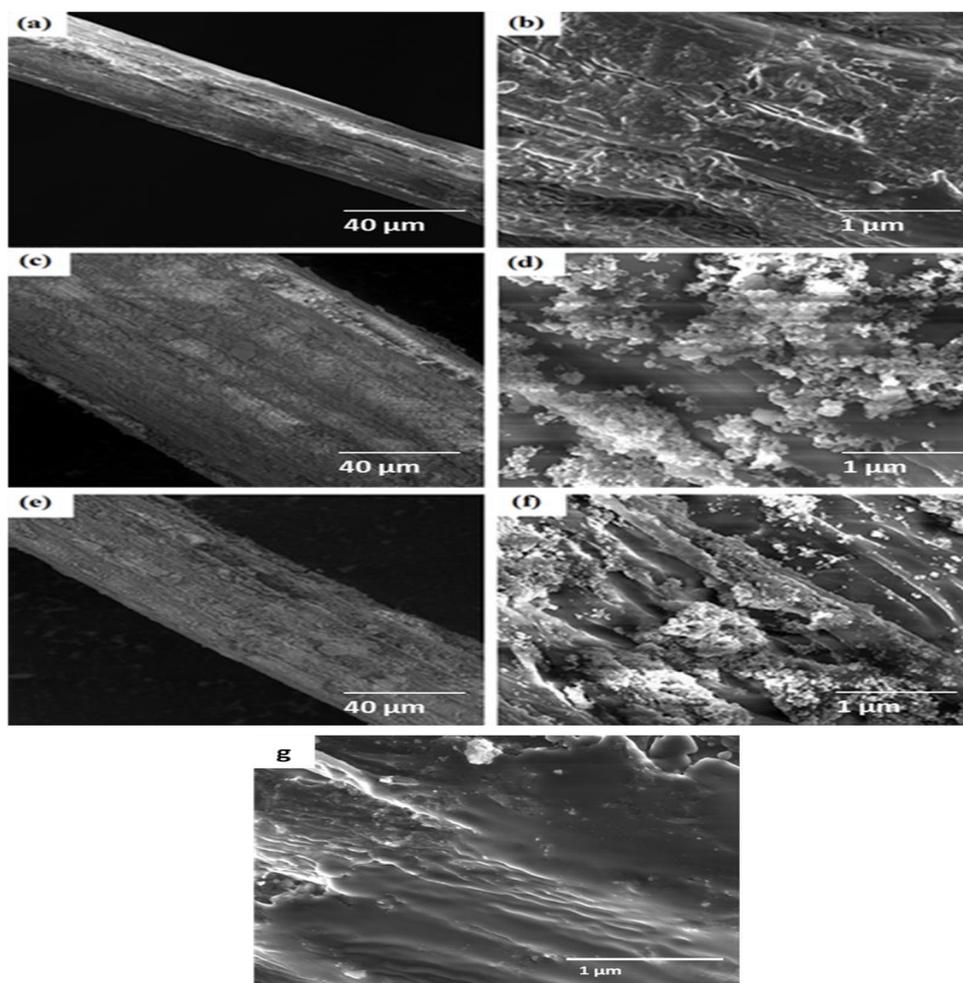


Fig. 1. FE-SEM images of (a, b) unmodified jute fiber, (c, d) $\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated fiber in the presence of maleic acid, (e, f) $\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated fiber (with maleic acid) after 25 washings (weight ratio of fiber: $\text{Bi}_2\text{O}_3/\text{TiO}_2 = 80:20$) and (g) $\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated fiber without maleic acid.

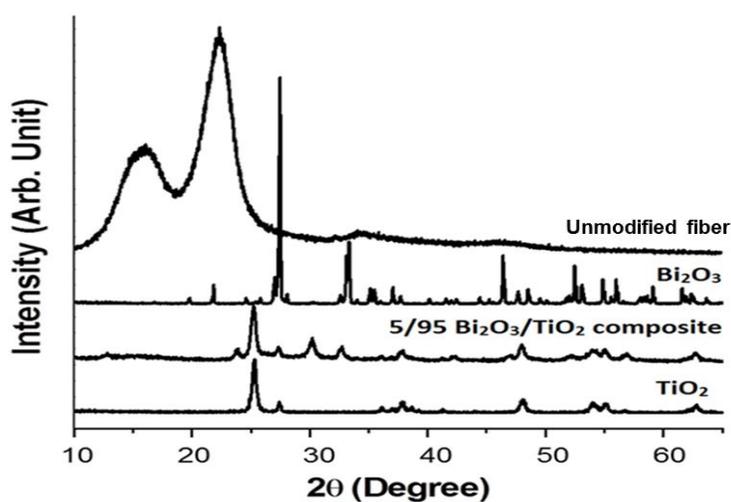
Table 1. EDX Data of Unmodified Fiber, $\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated Fiber (without maleic acid), $\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated Fiber (with maleic acid) before Washing, and $\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated fiber (with maleic acid) after 25 Washing Cycles

Element	Unmodified fiber		$\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated fiber (without maleic acid)		$\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated fiber (with maleic acid) before washing		$\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated fiber (with maleic acid) after 25 washing cycles	
	Wt. %	Atomic %	Wt. %	Atomic %	Wt. %	Atomic %	Wt. %	Atomic %
C	58.87	66.21	42.27	55.87	43.13	56.96	52.71	64.84
O	39.14	33.05	35.76	35.67	36.80	36.48	33.47	30.91
Ca	1.07	0.36	-	-	0.52	4.59	-	-
Bi	-	-	-	-	1.36	0.80	0.94	0.52
Ti	-	-	-	-	13.86	0.21	9.38	2.89

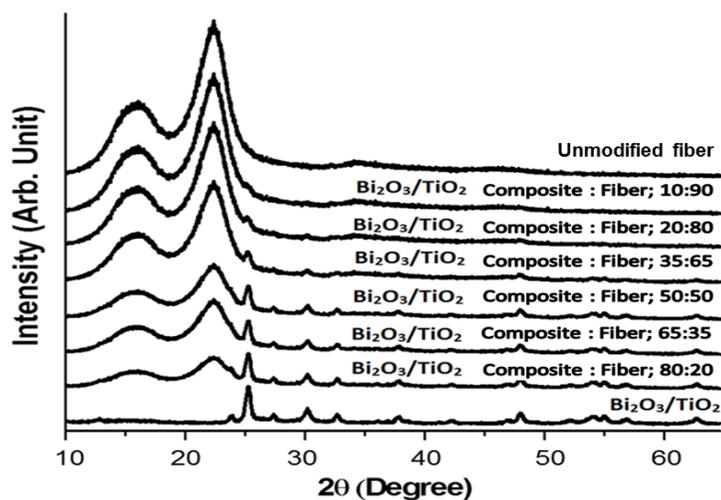
(Weight ratio of fiber: $\text{Bi}_2\text{O}_3/\text{TiO}_2 = 80:20$)

XRD Analysis

The XRD patterns of unmodified fiber, Bi_2O_3 , TiO_2 , and the $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite are shown in Fig. 2a. As shown from the typical XRD pattern of fibers, one intense peak at 23.1° was observed because of the crystalline phase and two broad peaks at 15.10° and 16.80° , respectively, were attributed to the amorphous phase. The Bi_2O_3 curve had diffraction peaks at 22.10° , 27.30° , 33.10° , 46.69° , and 54.10° . The TiO_2 curve exhibited peaks at 25.2° , 37.9° , 55° , and 62.70° , clearly designating the presence of an anatase phase, and at 44.10° , 57.80° , and 64.10° , establishing the existence of a rutile phase. The XRD patterns of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated fiber matched the diffraction peaks of Bi_2O_3 and TiO_2 phases without any other impurity phases. This indicates that there was no significant chemical reaction between Bi_2O_3 and TiO_2 during the preparation of the $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite and subsequent heat treatment at 100°C .



(a)



(b)

Fig. 2. XRD curves of (a) unmodified fiber substrate, TiO_2 , Bi_2O_3 , and $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite; and (b) $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite-coated fiber prepared with $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite ranging from 10 to 80 wt.%

The $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite-coated fiber with various weight percentages of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite exhibited the diffraction peaks of Bi_2O_3 and TiO_2 without any other impurity phases, as shown in Fig. 2b. This indicates that there was no chemical reaction place during the introduction of various weight percentages of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite onto the fiber. The intensity of the peaks of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ at 26.10° steadily diminished with reduction in the weight of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite applied to the fiber. This suggests that the annealing temperature of 100°C was sufficient to provide good interfacial adhesion between Bi_2O_3 , TiO_2 nanoparticles, and the fiber surface. This good interfacial bonding resulted in good interparticle electron transfer between Bi_2O_3 and TiO_2 .

FTIR Analysis

FTIR spectra of unmodified fiber, $\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated fiber, and $\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated fiber after 48 h of solar light exposure are shown in Fig. 3. The spectrum of fiber shows inter and intra chains of OH-O groups at 3600 to 3100 cm^{-1} . The attendance of interstitial or absorbed water, (H_2O) is indicated by the peak at 1600 cm^{-1} . The absorption at 300 to 2800 cm^{-1} and 1450 to 1350 cm^{-1} indicated the presence of $\nu(\text{CH})$ and $\delta(\text{CH})$, respectively. The most intense peak, located at 1200 to 900 cm^{-1} , specifies the existence of C-O-C groups on the fiber (Ali *et al.* 2015)

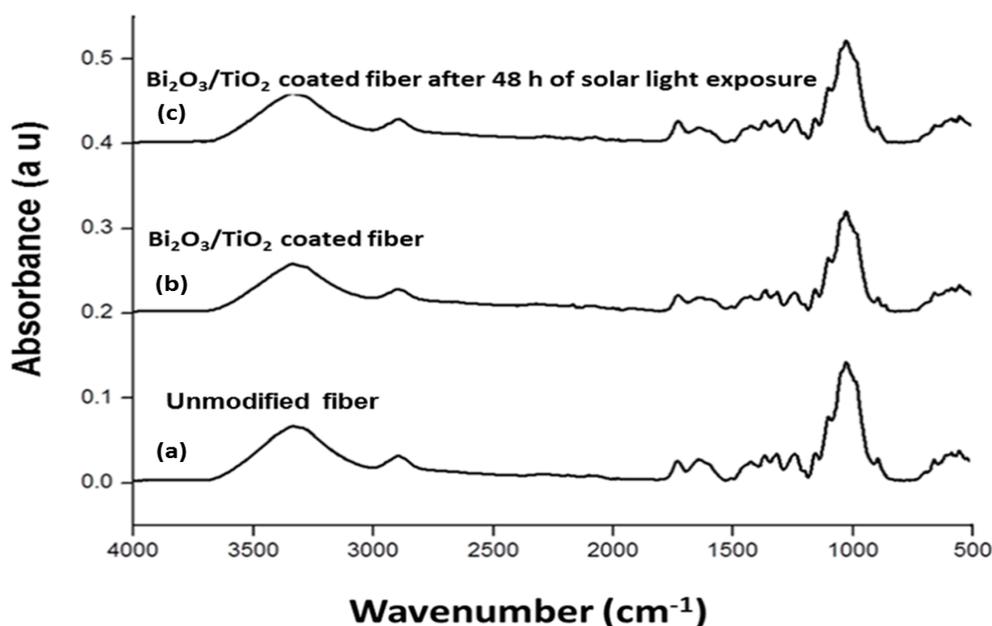


Fig. 3. FTIR spectra of unmodified fiber, $\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated fiber, and $\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated fiber after 48 h of solar light exposure (weight ratio of fiber: $\text{Bi}_2\text{O}_3/\text{TiO}_2 = 80:20$)

After introduction of a $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite coating on the surface of the jute fiber, there was no major change on the observed curve. This indicates that the $\text{Bi}_2\text{O}_3/\text{TiO}_2$ coating layer did not structurally change the fiber surface. Upon exposure to solar light, the $\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated fiber did not experience any chemical changes (Uddin *et al.* 2007). This might be because the contribution from the external alcoholic groups, which are expected to actively participate in the anchoring process and hence to be consumed by the coating procedure, was too small or negligible due to the small diameter of the fibers ($\sim 10\mu\text{m}$) (Uddin *et al.* 2007). This is demonstrated by the spectrum of the

Bi₂O₃/TiO₂-coated fiber (curve b), which is substantially unaltered. This means that due to the low external surface area of the supporting fibers, the use of FTIR spectroscopy is not informative and it is quite remarkable that the FTIR spectrum of the coated sample is only dominated by the spectrum of the fiber. The contribution of the Bi₂O₃/TiO₂ phase is also negligible.

The photostability of the Bi₂O₃/TiO₂-coated fiber after 48 h of solar light exposure is illustrated in curve c. From the curve, it can be seen that the absorption band at $\sim 3400\text{ cm}^{-1}$ and the complex absorption in the range $1650\text{ to }1050\text{ cm}^{-1}$ characteristic of the Bi₂O₃/TiO₂-coated fiber are mostly unchanged after 48 h of solar light exposure. This indicates that the chemical structure of Bi₂O₃/TiO₂-uncoated and -coated fiber was not substantially altered upon exposure to solar-like light. The homogeneous nature of the Bi₂O₃/TiO₂ film can protect the fibers from O²⁻ and OH• attack when exposed to sunlight (Uddin *et al.* 2007; Uddin *et al.* 2008).

UV-Vis Diffuse Reflectance Spectra

Figure 4 illustrates the UV-Vis diffuse reflectance spectra of the as-prepared Bi₂O₃/TiO₂ composite-coated fibers. The band gaps of Bi₂O₃ and TiO₂ were reported to be 2.8 and 3.2 eV, respectively (Hameed *et al.* 2008; Xu and Schoonen 2000). The optical absorptions of Bi₂O₃/TiO₂ composite-coated fibers start at about 400 nm due to the absorption edge of Bi₂O₃ composite.

The second absorption edge appearing at $\sim 387\text{ nm}$ is attributed to TiO₂ particles. Figure 4 illustrates that the absorption in visible-light of the coated fiber increased with the increasing of Bi₂O₃/TiO₂ component in the Bi₂O₃/TiO₂-coated fibers system. This result indicates that the Bi₂O₃/TiO₂ composite is efficient in absorbing the photon in the visible region of the solar spectrum.

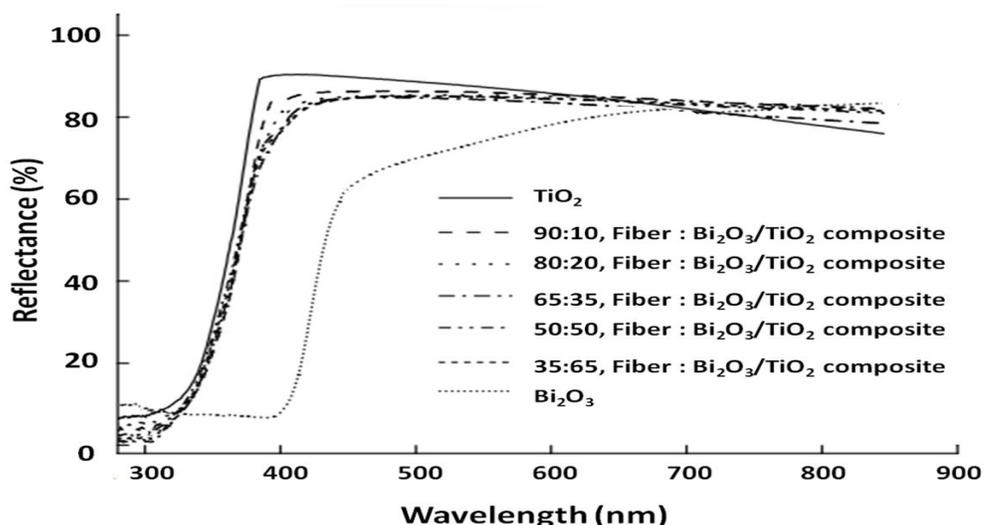


Fig. 4. UV-Visible diffuse reflectance spectra of Bi₂O₃, TiO₂ and Bi₂O₃/TiO₂ composite-coated fiber

Photocatalytic and Self-Cleaning Activity

The degradation of the organic compounds 2-propanol and phenol was used to determine the photocatalytic and self-cleaning activity of Bi₂O₃/TiO₂-coated fiber under visible light ($\lambda > 420\text{ nm}$). The remnant phenol and 2-propanol after irradiation with

visible light were analyzed from the characteristic absorption peaks detected by UV-Vis spectroscopy. The comparisons of the remnant of phenol and 2-propanol after visible light irradiation of both uncoated fiber and $\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated fiber are shown in Figs. 5a and 5b, respectively.

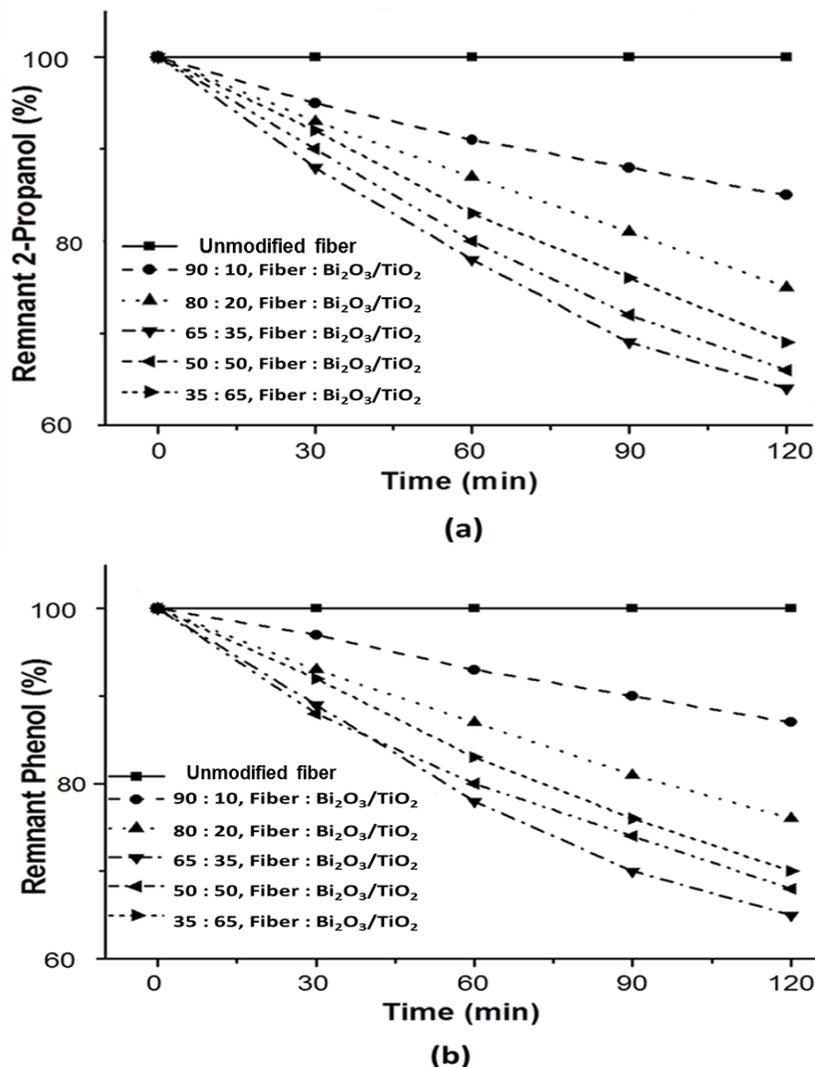


Fig. 5. Remnant organics after photocatalytic activity on unmodified fiber and $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite-coated fiber prepared with various composition ratios: (a) 2-propanol and (b) phenol

No phenol decomposition occurred in the aqueous phase of unmodified fiber. On the other hand, $\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated fibers with various weight ratios of composite coating to fiber increasingly degraded phenol with increasing irradiation time. As shown in Fig. 5, the $\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated fibers with 65 wt.% fiber and 35 wt.% $\text{Bi}_2\text{O}_3/\text{TiO}_2$ coating exhibited the highest degradation of phenol. In the case of the gaseous phase, the photocatalyst of uncoated fiber exhibited negligible activity for the decomposition of 2-propanol. However, $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite-coated fibers showed higher visible light-induced photocatalytic activity for the decomposition of 2-propanol with increasing irradiation time. Similar to the aqueous phase, the $\text{Bi}_2\text{O}_3/\text{TiO}_2$ -coated fibers with 65 wt.% fiber and 35 wt.% $\text{Bi}_2\text{O}_3/\text{TiO}_2$ coating demonstrated the highest degradation of 2-propanol in the gaseous phase.

CONCLUSIONS

1. Bi₂O₃/TiO₂-coated fiber was prepared utilizing maleic acid as an organic binder. The Bi₂O₃/TiO₂ composite has successfully coated firmly on the jute fiber.
2. The Bi₂O₃/TiO₂-coated fiber successfully exhibited photocatalytic self-cleaning activity for decomposition of phenol and 2-propanol under UV-visible light irradiation.
3. The prepared Bi₂O₃/TiO₂ composite coating performed effectively for the decomposition of organic pollutants on the jute fiber.

ACKNOWLEDGMENTS

The authors would like to acknowledge financial support from the High Impact Research MoE Grant UM.C/625/1/HIR/MoE/52 from the Ministry of Education Malaysia, RP024C-13AET, RU022A-2014, RG031-15AET and FP030-2013A, for the success of this project.

REFERENCES CITED

- Abe, R., Takami, H., Murakami, N., and Ohtani, B. (2008). "Pristine simple oxides as visible light driven photocatalysts: Highly efficient decomposition of organic compounds over platinum-loaded tungsten oxide," *Journal of the American Chemical Society* 130(25), 7780-7781. DOI: 10.1021/ja800835q
- Ali, M. E., Yong, C. K., Ching, Y. C., Chuah, C. H., and Liou, N.-S. (2015). "Effect of single and double stage chemically treated kenaf fibers on mechanical properties of polyvinyl alcohol film," *BioResources* 10(1), 822-838. DOI:10.15376/biores.10.1.822-838
- Ao, C., Lee, S., Yu, J., and Xu, J. (2004). "Photodegradation of formaldehyde by photocatalyst TiO₂: Effects on the presences of NO, SO₂ and VOCs," *Applied Catalysis B: Environmental* 54(1), 41-50. DOI: 10.1016/j.apcatb.2004.06.004
- Arana, J., Dona-Rodríguez, J., Gonzalez-Díaz, O., Tello Rendon, E., Herrera Melian, J., Colon, G., Navío, J., and Perez Pena, J. (2004). "Gas-phase ethanol photocatalytic degradation study with TiO₂ doped with Fe, Pd and Cu," *Journal of Molecular Catalysis A: Chemical* 215(1), 153-160. DOI: 10.1016/j.molcata.2004.01.020
- Bai, J., Li, J., Liu, Y., Zhou, B., and Cai, W. (2010). "A new glass substrate photoelectrocatalytic electrode for efficient visible-light hydrogen production: CdS sensitized TiO₂ nanotube arrays," *Applied Catalysis B: Environmental* 95(3), 408-413. DOI: 10.1016/j.apcatb.2010.01.020
- Brezesinski, K., Ostermann, R., Hartmann, P., Perlich, J., and Brezesinski, T. (2010). "Exceptional photocatalytic activity of ordered mesoporous β-Bi₂O₃ thin films and electrospun nanofiber mats," *Chemistry of Materials* 22(10), 3079-3085. DOI: 10.1021/cm903780m
- Chakraborty, A. K., Hossain, M. E., Rhaman, M. M., and Sobahan, K. M. A. (2014). "Fabrication of Bi₂O₃/TiO₂ nanocomposites and their applications to the degradation

- of pollutants in air and water under visible-light,” *Journal of Environmental Sciences* 26(2), 458-465
- Chakraborty, A. K., and Kebede, M. A. (2012). “Preparation and characterization of WO₃/Bi₃O₄Cl nanocomposite and its photocatalytic behavior under visible light irradiation,” *Reaction Kinetics, Mechanisms and Catalysis* 106(1), 83-98. DOI: 10.1007/s11144-012-0423-7
- Chakraborty, A. K., Ganguli, S., and Kebede, M. A. (2012). “Photocatalytic degradation of 2-propanol and phenol using Au loaded MnWO₄ nanorod under visible light irradiation,” *Journal of Cluster Science* 23(2), 437-448. DOI: 10.1007/s10876-012-0450-6
- Chang, S.-M., and Doong, R.-A. (2006). “Characterization of Zr-doped TiO₂ nanocrystals prepared by a nonhydrolytic sol-gel method at high temperatures,” *Journal of Physical Chemistry B* 110(42), 20808-20814. DOI: 10.1021/jp0626566
- Chao, H., Yun, Y., Xingfang, H., and Larbot, A. (2003). “Effect of silver doping on the phase transformation and grain growth of sol-gel titania powder,” *Journal of the European Ceramic Society* 23(9), 1457-1464. DOI: 10.1016/S0955-2219(02)00356-4
- Chatterjee, D., and Dasgupta, S. (2005). “Visible light induced photocatalytic degradation of organic pollutants,” *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 6(2), 186-205. DOI: 10.1016/j.jphotochemrev.2005.09.001
- Ching, Y. C., Rahman, A., Ching, K. Y., Sukiman, N. L., and Cheng, H. C. (2015). “Preparation and characterization of polyvinyl alcohol-based composite reinforced with nanocellulose and nanosilica,” *BioResources* 10(2), 3364-3377. DOI:10.15376/biores.10.1.1519-1527
- Ding, Z., Hu, X., Lu, G. Q., Yue, P.-L., and Greenfield, P. F. (2000). “Novel silica gel supported TiO₂ photocatalyst synthesized by CVD method,” *Langmuir* 16(15), 6216-6222. DOI: 10.1021/la000119l
- Dobosz, A., and Sobczynski, A. (2003). “The influence of silver additives on titania photoactivity in the photooxidation of phenol,” *Water Research* 37(7), 1489-1496. DOI: 10.1016/S0043-1354(02)00559-6
- Fligge, M., Solanki, S. K., Pap, J. M., Fröhlich, C., and Wehrli, C. (2001). “Variations of solar spectral irradiance from near UV to the infrared-measurements and results,” *Journal of Atmospheric and Solar-Terrestrial Physics* 63(14), 1479-1487. DOI:10.1016/j.jastp.2015.07.012
- Fruth, V., Popa, M., Berger, D., Ramer, R., Gartner, M., Ciulei, A., and Zaharescu, M. (2005). “Deposition and characterisation of bismuth oxide thin films,” *Journal of the European Ceramic Society* 25(12), 2171-2174. DOI: 10.1016/j.jeurceramsoc.2005.03.025
- Fujishima, A., Rao, T. N., and Tryk, D. A. (2000). “Titanium dioxide photocatalysis,” *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 1(1), 1-21. DOI: 10.1016/S1389-5567(00)00002-2
- Gad, N. S., and Saad, A. S. (2008). “Effect of environmental pollution by phenol on some physiological parameters of *Oreochromis niloticus*,” *Global Vet* 2, 312-319
- Gan, W., Chiang, K., Brungs, M., and Amal, R. (2007). “Dense TiO₂ thin film: Photoelectrochemical and photocatalytic properties,” *International Journal of Nanotechnology* 4(5), 574-587. DOI: 10.1504/IJNT.2007.014752
- Gao, B., Lim, T. M., Subagio, D. P., and Lim, T.-T. (2010). “Zr-doped TiO₂ for enhanced photocatalytic degradation of bisphenol A,” *Applied Catalysis A: General* 375(1), 107-115. DOI: 10.1016/j.apcata.2009.12.025

- Hameed, A., Montini, T., Gombac, V., and Fornasiero, P. (2008). "Surface phases and photocatalytic activity correlation of Bi₂O₃/Bi₂O_{4-x} nanocomposite," *Journal of the American Chemical Society* 130(30), 9658-9659. DOI: 10.1021/ja803603y
- Hilal, H., Majjad, L., Zaatari, N., and El-Hamouz, A. (2007). "Dye-effect in TiO₂ catalyzed contaminant photo-degradation: Sensitization vs. charge-transfer formalism," *Solid State Sciences* 9(1), 9-15. DOI:10.1016/j.solidstatesciences.2006.10.001
- Hori, T. S. F., Avilez, I. M., Inoue, L. K., and Moraes, G. (2006). "Metabolic changes induced by chronic phenol exposure in matrinxã *Brycon cephalus* (Teleostei: Characidae) juveniles," *Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology* 143(1), 67-72. DOI:10.1016/j.cbpc.2015.07.007
- Houas, A., Lachheb, H., Ksibi, M., Elaloui, E., Guillard, C., and Herrmann, J.-M. (2001). "Photocatalytic degradation pathway of methylene blue in water," *Applied Catalysis B: Environmental* 31(2), 145-157. DOI: 10.1016/S0926-3373(00)00276-9
- Hufschmidt, D., Bahnemann, D., Testa, J. J., Emilio, C. A., and Litter, M. I. (2002). "Enhancement of the photocatalytic activity of various TiO₂ materials by platinumisation," *Journal of Photochemistry and Photobiology A: Chemistry* 148(1), 223-231. DOI: 10.1016/S1010-6030(02)00048-5
- Kandavelu, V., Kastien, H., and Thampi, K. R. (2004). "Photocatalytic degradation of isothiazolin-3-ones in water and emulsion paints containing nanocrystalline TiO₂ and ZnO catalysts," *Applied Catalysis B: Environmental* 48(2), 101-111. DOI: 10.1016/j.apcatb.2003.09.022
- Kim, Y. J., Gao, B., Han, S. Y., Jung, M. H., Chakraborty, A. K., Ko, T., Lee, C., and Lee, W. I. (2009). "Heterojunction of FeTiO₃ nanodisc and TiO₂ nanoparticle for a novel visible light photocatalyst," *Journal of Physical Chemistry C* 113(44), 19179-19184. DOI: 10.1021/jp908874k
- Kun, R., Mogyorosi, K., and Dekany, I. (2006). "Synthesis and structural and photocatalytic properties of TiO₂ montmorillonite nanocomposites," *Applied Clay Science* 32(1), 99-110. DOI: 10.1016/j.clay.2005.09.007
- Kwon, Y. T., Song, K. Y., Lee, W. I., Choi, G. J., and Do, Y. R. (2000). "Photocatalytic behavior of WO₃-loaded TiO₂ in an oxidation reaction," *Journal of Catalysis* 191(1), 192-199.
- Leong, K.H., Gana, B.L., Ibrahima, S., Saravanan, P. (2014) "Synthesis of surface plasmon resonance (SPR) triggered Ag/TiO₂ photocatalyst for degradation of endocrine disturbing compounds," *Applied Surface Science* 319, 128-135
- Liu, Y., Xin, F., Wang, F., Luo, S., and Yin, X. (2010). "Synthesis, characterization, and activities of visible light-driven Bi₂O₃-TiO₂ composite photocatalysts," *Journal of Alloys and Compounds* 498(2), 179-184.
- Mahdi, E. M., Hamdi, M. and Yusoff, M.S. M. (2013). "The effect of sintering on the physical and optical properties of nano-TiO₂ synthesized via A modified hydrothermal route," *Arabian Journal for Science and Engineering* 38(7), 1701-1711. DOI: 10.1007/s13369-012-0384-1.
- Moafi, H. F., Shojaie, A. F., and Zanjanchi, M. A. (2011). "Titania and titania nanocomposites on cellulosic fibers: Synthesis, characterization and comparative study of photocatalytic activity," *Chemical Engineering Journal* 166(1), 413-419.
- Mozia, S., Toyoda, M., Inagaki, M., Tryba, B., and Morawski, A. W. (2007). "Application of carbon-coated TiO₂ for decomposition of methylene blue in a

- photocatalytic membrane reactor,” *Journal of Hazardous Materials* 140(1), 369-375. DOI: 10.1016/j.jhazmat.2006.10.016
- Salim, E., Al-Douri, Y., Al Wazny, M., and Fakhri, M. (2014). “Optical properties of cauliflower-like Bi₂O₃ nanostructures by reactive pulsed laser deposition (PLD) technique,” *Solar Energy* 107, 523-529. DOI: 10.1016/j.solener.2014.05.020
- Sobana, N., Muruganadham, M., and Swaminathan, M. (2006). “Nano-Ag particles doped TiO₂ for efficient photodegradation of direct azo dyes,” *Journal of Molecular Catalysis A: Chemical* 258(1), 124-132. DOI: 10.1016/j.molcata.2006.05.013
- Stylidi, M., Kondarides, D. I., and Verykios, X. E. (2004). “Visible light-induced photocatalytic degradation of Acid Orange 7 in aqueous TiO₂ suspensions,” *Applied Catalysis B: Environmental* 47(3), 189-201. DOI: 10.1016/j.apcatb.2003.09.014
- Tan, B. K., Ching, Y. C., Gan, S.N, and Shaifulazuar, R. (2015). “Biodegradable mulches based on poly(vinyl alcohol), kenaf fiber, and urea,” *BioResources* 10(3), 5532-5543. DOI:10.15376/biores.10.3.5523-5543
- Uddin, M., Cesano, F., Bonino, F., Bordiga, S., Spoto, G., Scarano, D., and Zecchina, A. (2007). “Photoactive TiO₂ films on cellulose fibres: Synthesis and characterization,” *Journal of Photochemistry and Photobiology A: Chemistry* 189(2), 286-294. DOI: 10.1016/j.jphotochem.2007.02.015
- Uddin, M., Cesano, F., Scarano, D., Bonino, F., Agostini, G., Spoto, G., Bordiga, S., and Zecchina, A. (2008). “Cotton textile fibres coated by Au/TiO₂ films: Synthesis, characterization and self-cleaning properties,” *Journal of Photochemistry and Photobiology A: Chemistry* 199(1), 64-72. DOI: 10.1016/j.jphotochem.2008.05.004
- Venkatachalam, N., Palanichamy, M., and Murugesan, V. (2007). “Sol-gel preparation and characterization of alkaline earth metal doped nano TiO₂: Efficient photocatalytic degradation of 4-chlorophenol,” *Journal of Molecular Catalysis A: Chemical* 273(1), 177-185. DOI: 10.1016/j.molcata.2007.03.077
- Xu, J., Ao, Y., Fu, D., and Yuan, C. (2008). “Synthesis of Bi₂O₃-TiO₂ composite film with high-photocatalytic activity under sunlight irradiation,” *Applied Surface Science* 255(5), 2365-2369
- Xu, Y., and Schoonen, M. A. (2000). “The absolute energy positions of conduction and valence bands of selected semiconducting minerals,” *American Mineralogist* 85(4), 543-556. DOI: 10.2138/am-2015-5170
- Zhao, W., Bai, Z., Ren, A., Guo, B., and Wu, C. (2010). “Sunlight photocatalytic activity of CdS modified TiO₂ loaded on activated carbon fibers,” *Applied Surface Science* 256(11), 3493-3498. DOI: 10.1016/j.apsusc.2009.12.062
- Zyoud, A. H., Zaatar, N., Saadeddin, I., Ali, C., Park, D., Campet, G., and Hilal, H. S. (2010). “CdS-sensitized TiO₂ in phenazopyridine photo-degradation: Catalyst efficiency, stability and feasibility assessment,” *Journal of Hazardous Materials* 173(1), 318-325. DOI: 10.1016/j.jhazmat.2009.08.093

Article submitted: April 15, 2015; Peer review completed: July 24, 2015; Revised version received and accepted: August 26, 2015; Published: September 17, 2015.

DOI: 10.15376/biores.10.4.7405-7418