Investigating the growth mechanism and photocatalytic properties of TiO_2/Bacterial Cellulose hybrid materials

Xiaoyu Lu, Guomin Jiang, Beibei Dai, Jiazhi Yang*
Chemicobiology and Functional Materials Institute, School of chemical engineering
Nanjing University of Science and Technology,
Nanjing, China.
suspect520@sohu.com, jgm1018@126.com, beibeidai0306@163.com,jzhyangb504@163.com

***Abstract*—A facile hydrothermal method was successful to synthesize the TiO_2 by using unique bacterial cellulose (BC) membranes as natural biotemplates. The three-dimensional networks of BC fibers coated with TiO_2 nanoparticles can be clearly observed, resulting in the formation of uniform and well-defined hybrid nanofiber structures. The content distribution of the titania on BC membranes were investigated using XPS depth profiling, it was revealed that the content of titania on the surface of the BC membranes was higher than the inside of the BC membranes. A molecular diffusion growth model was proposed to explain the formation process of the TiO_2/BC based on the crystal growth theory and molecule diffusion theory. In addition, the TiO_2/BC showed the high photocatalytic degradation efficiency for methyl orange.**

Keywords—TiO_2; growth mechanism; bacterial cellulose

I. INTRODUCTION

TiO_2 is a widely used semiconductor due to its suitable band gap energy, corrosion-resistant, environmentally friendly and abundant availability [1, 2]. It is the most investigated catalyst for photocatalytic and photoelectrocatalytic processes, which have gained increased interest in recent years within the scientific community. The synthesis of TiO_2 nanoparticles may be achieved by various routes including hydro/ solvothermal approachs [3], Sol-gel methods [4], electrochemical means [5] and template approachs [6, 7]. In particular, TiO_2 nanoparticles prepared by using templates have been demonstrated to be the versatile approach. Recently, a variety of templates have been reported to the synthesis of TiO_2 nanoparticles, such as organogel [8], block copolymer [9], colloidal crystals [10], BC membranes [11]. Especially, the TiO_2/BC shows the excellent photocatalytic activity due to the unique three-dimensional network structure and high mechanical strength of BC compared with the other templates. So BC has attracted much attention as the template or matrix for the synthesis of various inorganic nanostructures [12, 13]. However, the growth mechanism of TiO_2 including other inorganic nanoparticles on BC membranes templates is not clear. In the work, the content change of TiO_2 on BC membranes just a few nanometres thick was studied by using X-ray photoelectron spectroscopy (XPS) etching technique, assisted by electron microscopy and XRD, and a molecular diffusion model to explain the TiO_2 growth mechanism on BC membranes is proposed. In addition, the obtained TiO_2/BC showed enhanced photocatalytic activity than that of the TiO_2 without the template.

This work was supported by the National Natural Science Foundation of China (No.21206076, 21176111) and the Natural Science Foundation of Jiangsu Province (No. BE2012401 and BK2011715).

II. EXPERIMENTAL

Fresh BC pellicles (size about 2 cm×2 cm, 1 mm in thickness) were prepared and purified as previously reported [14]. The BC membranes were added to the mixed solution contained 85 ml ethanol, 10 ml tetrabutyl titanate, and 2 ml acetylacetone. Subsequently, the mixture was transferred into a 150 mL stainless steel autoclave with a Teflon tube attached. The autoclave was placed in a preheated oven 200 °C for 24 h. Then, the membranes were washed with ethanol and distilled water three times separately. The membranes held in air at room temperature for 48 h to complete the hydrolysis reaction and then followed by heating at 60 °C until the liquid evaporated.

The morphology of the samples was characterized by means of SEM (JSM-6380LV) and TEM (JEM-2100) microscopes. XRD (Bruker D8 ADVANCE) patterns of the prepared hybrids were measured with monochromatic Cu-Kα radiation. The nitrogen adsorption-desorption measurement was carried out on Micromeritics ASAP 2010. X-ray photoelectron spectroscopy (PHI Quantera II) was used to investigate the elemental composition and atomic configuration of the TiO_2/BC using Al-Kα non-monochromatic X-ray excitation. The present work made a XPS depth profile on the TiO_2/BC etched by Ar^+, the analyzing area was selected to be approximately 1um in diameter. The photocatalytic degradation experiments were performed using the quartz reactor with a 300W UV lamp. The titian catalyst and methyl orange (MO) were placed in the dark for 30min before illumination to allow sufficient adsorption of MO. During the photoreaction, samples were taken from the reaction mixture at the different periods for assessment of photocatalytic activity.

TABLE I. POROUS CHARACTERISTICS OF THE BC AND TiO_2/BC

Samples	S_{BET} (m^2g^{-1})	Total volume (cm^3g^{-1})	Average pore diameter (nm)
BC	30.85	0.0971	11.2
TiO_2/BC	153.67	0.194	6.4

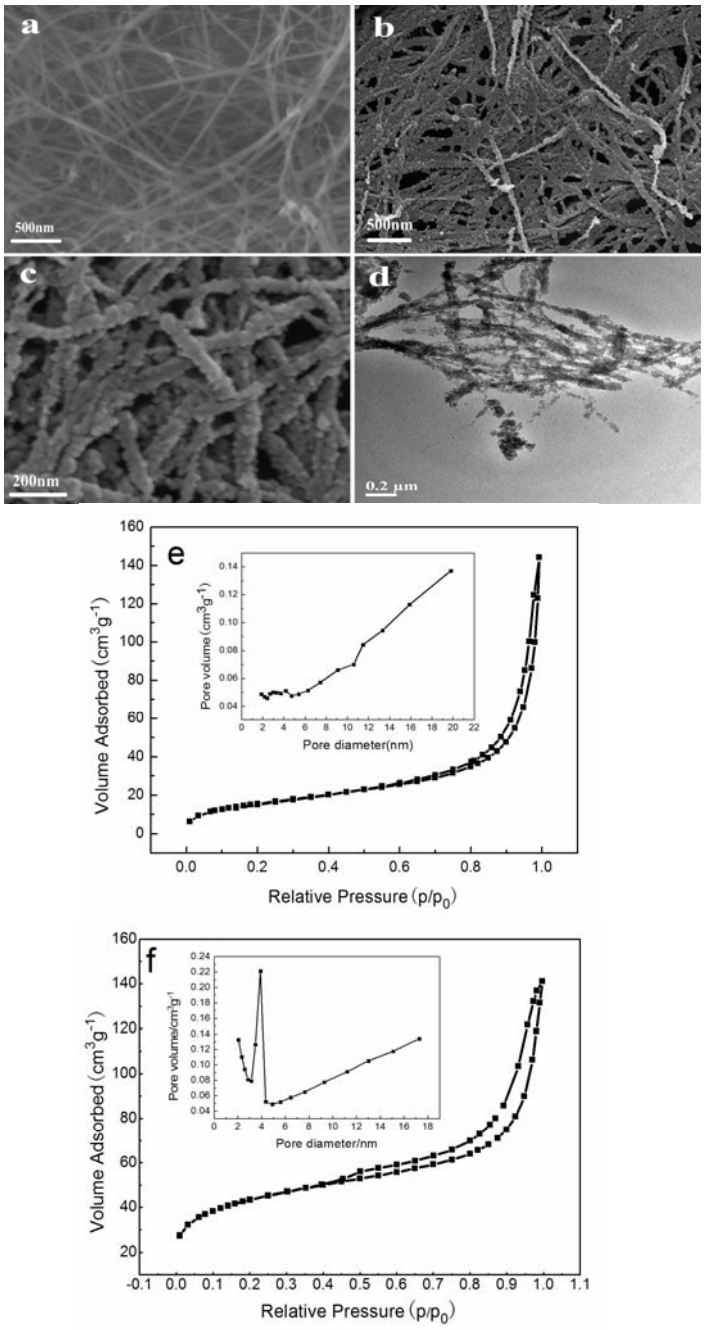

Fig. 1. SEM images of (a) BC and (b, c) TiO_2/BC. (d) TEM image of TiO_2/BC. Nitrogen adsorption-desorption isotherms of (e) BC and (f) TiO_2/BC. Insert shows the pore-size distribution determined from the desorption branch.

III. Results and Discussion

The SEM image of Fig. 1a shows that the BC membranes are the structure of the three-dimensional ultrafine network, with an average diameter of 50 nm, which is much smaller than the diameters of plant celluloses. Fig. 1b and Fig. 1c clearly show the TiO_2 nanoparticles deposited on the surface of BC fibers, with an average diameter of about 10 nm. It is noted that the uniform size distribution can be obtained. Fig. 1d shows a representative TEM image of the TiO_2/BC, it can be observed that the nanoparticles are dissociated outer of the fiber regularly, this can be attributed to the special structure of BC membranes. The data of specific surface area and pore size of the both samples are given in Table I. As compared with the BC membranes, the specific surface area and pore volume of TiO_2/BC are indeed greatly improved. Fig. 1e and Fig. 1f show the nitrogen adsorption-desorption isotherms and the Barret Joyner-Haienda (BJH) pore size distribution plot of the samples. According to the IUPAC classification, these isotherms are type IV, H1 hysteresis loop. As coated with the TiO_2, the slope of the N_2 adsorption–desorption isotherm increases significantly, indicating an increase in the surface area and the total pore volume. For the BC, the pore size distribution which ranging from 2 to 20 nm is very broad. Respectively, with the loading of TiO_2, which appear that the TiO_2/BC are basically mesoporous with pore size distribution predominantly focus on 4 nm, which is in good agreement with the SEM observations.

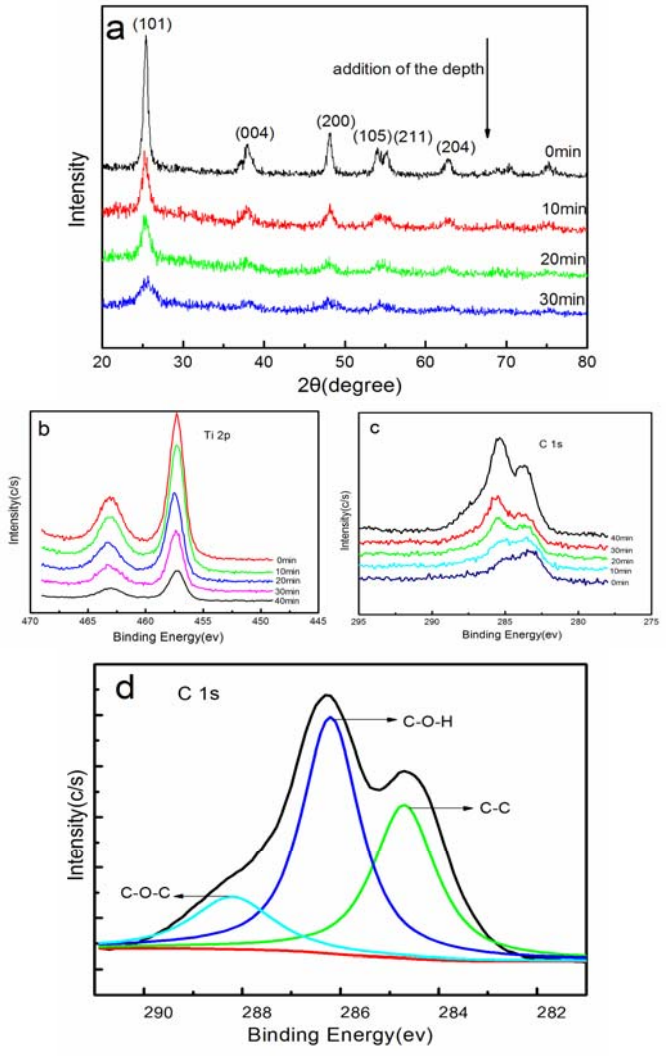

Fig. 2. (a) XRD patters of TiO2/BC at different depth. (b) Ti 2p and (c) C 1s XPS spectra of the TiO2/BC etched by Ar+ as a function of etching time. (d) C 1s core-level XPS spectra of the TiO2/BC

The XRD patterns of the TiO_2/BC are shown in Fig. 2a. The intensive diffraction peaks in TiO_2/BC pattern can be attributed to the anatase phase of TiO_2 (JCPDS89-4921), corresponding to the (101), (004), (200), and (204) planes. In order to understand the content of titania as the change of membrane depth, we do the analysis at the different depth after the XPS depth profiling. The peak intensity is gradually weakened as the addition of the depth, it is demonstrated that the content of titania on the surface of the membrane is higher than the interior of the membrane. An average crystallite size of about 6.2 nm was estimated according to line width analysis of the (101) reflection based on the Scherrer formula. Fig. 2b, c show the changes in the Ti 2p and C 1s spectra of TiO_2/BC after etched with 400 eV Ar^+ as a function of etching time. The intensity of the Ti 2p is gradually weakened while the intensity of the C 1s is stronger as the addition of the etching time. This is attributed to the different content distribution of TiO_2 nanoparticles on the BC. It is proved that the content of titania drops off as the addition of membrane depth. According to the structure of the bacterial cellulose membranes, Fig. 2d shows the overlapping peak resolving of C 1s.

According to the structure of the BC, we construct a model of diffusion between water molecules and tetrabutyl titanate molecules with the bacterial cellulose membrane as an interface in the mixture system (Fig. 3a). Due to the hydrogen bonding of hydroxyl on the bacterial cellulose surface, the system of the bacterial cellulose and water exists the oriented arrangement of water molecules layer. At the outside of the oriented water molecules layer, it can form a transition zone where water molecules from the bound state transition to the free state [14]. Tetrabutyl titanate and the free state water molecules are in a dynamic diffusion process when the tetrabutyl titanate is added into the system. The difussion rate of the tetrabutyl titanate molecules is V_0, The difussion rate of the water molecules is V_1. According to the results that the content of titania on the surface of the membrane is higher than the interior of the membrane, we deduce that the $V_0 > V_1$ which can be attributed to the hydrophilic materials of BC and stereo-hindrance effect. The free state water molecules transfer to the interface of the BC quickly and react with the tetrabutyl titanate molecules. On the other hand, the tetrabutyl titanate molecules also spread to the inner layer of the bacterial cellulose and interact with the water molecules. Because of the template effect, the tetrabutyl titanate molecules hydrolyze directionally and sequentially and disperse on the surface of the bacterial cellulose uniformly. It is precisely the unique structure of BC, we can prepare the hybrid materials with excellent morphology and superior performance [15].

Fig. 3b, c show the change of the largest ultraviolet absorption peak and the photocatalytic degradation efficiency of methyl orange in the presence of the TiO_2/BC under UV irradiation at a different time. We can see that the intensity of ultraviolet absorption peak faded away as the addition of UV irradiation. The photocatalytic efficiency of TiO_2/BC is higher than the TiO_2, Which may be attributed to the excellent morphology and larger specific surface areas. It is noted that the BC membranes provided the hydroxyl force as a soft chemical template, this avoids the agglomeration of nanoparticles. Therefore, the titania networks have larger accessible surface areas.

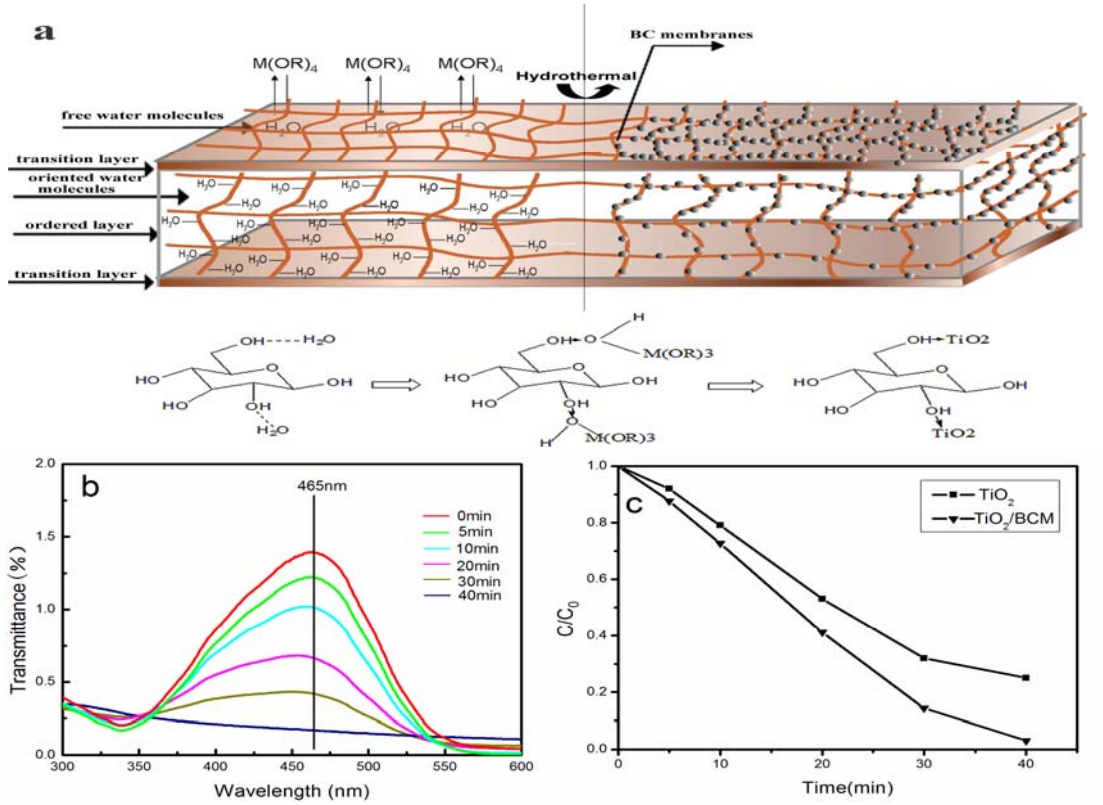

Fig. 3. (a)The model pattem of reaction mechanism about the titania on bacterial cellulose membranes.(b) The largest ultraviolet absorption peak of methyl orange at different time.(c)The comparison of photocatalytic activity of TiO_2 and TiO_2/BC.

IV. CONCLUSION

In summary, we have successfully synthesized the TiO_2/BC via a facile hydrothermal method. According to the results of research, we draw a conclusion that the content distribution of TiO_2 nanoparticles on the BC is different. A possible formation mechanism has been proposed using the molecule diffusion theory. The TiO_2/BC shows the higher photocatalytic activity than the TiO_2 nanoparticles.

REFERENCES

[1] K. Akihiko, and M.Yugo, "Heterogeneous photocatalyst materials for water splitting," Chem. Soc. Rev. vol. 38, no. 1, pp. 253-278, 2009.

[2] R. Poulomi, B. Steffen, and S. Patrik, "TiO_2 nanotubes: synthesis and applications," Angew. Chem. Int. Edit. vol. 50, no. 13, pp. 2904-2939, 2011.

[3] K. Tomoko, et al, "Titania nanotubes prepared by chemical processing," Adv. Mater. vol. 11, no. 15, pp. 1307-1311, 1999.

[4] M. Zhang, Y. Bando, and K. Wada, "Sol-gel template preparation of TiO2 nanotubes and nanorods," J. Mater. Sci. Lett. vol. 20, no. 2, pp. 167-170, 2001.

[5] K. Tetsuya, et al. "Crystal-face and illumination intensity dependences of the quantum efficiency of photoelectrochemical etching, in relation to those of water photooxidation, at n-TiO_2 (rutile) semiconductor electrodes," J. Elec. Chem. vol. 545, pp. 99-107, 2003.

[6] S.A. Lee, et al. "Use of ultrafiltration membranes for the separation of TiO2 photocatalysts in drinking water treatment," Ind. Eng. Chem. Res. vol. 40, no.7, pp. 1712-1719, 2001.

[7] X.Z. Li, et al. "Photocatalytic oxidation using a new catalyst TiO_2 microsphere for water and wastewater treatment," Environ. Sci. Technol. vol. 37, no. 17, pp. 3989-3994, 2003.

[8] H.J. Jung, et al. "Creation of novel helical ribbon and double-layered nanotube TiO_2 structures using an organogel template," Chem. Mater. vol. 14, no. 4, pp. 1445-1447, 2002.

[9] S. Bernd, et al., "Highly crystalline cubic mesoporous TiO2 with 10-nm pore diameter made with a new block copolymer template," Chem. Mater. vol. 16, no.15, pp. 2948-2952, 2004.

[10] Wijnhoven, Judith EGJ, and L.V. Willem, "Preparation of photonic crystals made of air spheres in titania," Sci. vol. 281, no. 5378, pp. 802-804, 1998.

[11] D. Zhang and L. Qi, "Synthesis of mesoporous titania networks consisting of anatase nanowires by templating of bacterial cellulose membranes," Chemical communications, vol. 21, pp. 2735-2737, 2005.

[12] J. Julasak, et al. "Creating hierarchical structures in renewable composites by attaching bacterial cellulose onto sisal fibers," Adv. Mater. vol. 20, no. 16, pp. 3122-3126, 2008.

[13] K. Dieter, et al., "Cellulose: fascinating biopolymer and sustainable raw material," Angew. Chem. Int. Edit. vol. 44, no. 22, pp. 3358-3393, 2005

[14] J. Yang, et al. "In situ deposition of platinum nanoparticles on bacterial cellulose membranes and evaluation of PEM fuel cell performance,"Elect. Acta, vol. 54, no. 26, pp. 6300-6305, 2009.

[15] D. Sun, J. Yang, and X. Wang. "Bacterial cellulose/TiO2 hybrid nanofibers prepared by the surface hydrolysis method with molecular precision," Nanoscale, vol. 2, no. 2, pp. 287-292, 2010.