Enhancement of methylene blue photo-degeneration by TiO_2/Carbon aerogel catalyst

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ABSTRACT

In this study, TiO_2/Carbon aerogel material (TiO_2/CA) synthesized by the sol-gel method has improved TiO_2 photocatalytic activity by trapping electrons and increasing the specific surface area. The success of material synthesis was characterized by X-ray diffraction (XRD), Nitrogen physisorption, Energy Dispersive X-Ray Analysis (EDS), and Fourier-transform infrared spectroscopy (FTIR). In particular, in TiO_2/CA sample, the uniform distributions of C, O, and Ti elements and the higher BET surface area compared with TiO_2 one have expressed the role of carbon aerogel carrier and the idea's correctness. Methylene Blue photo degeneration process happened under the following conditions: 3 UV-lamps (8 W per one), 0.015 g sample, and 50 ml MB solution 15 ppm, which showed a significant increase in the adsorption capacity, photocatalytic degradation, and the dynamic reaction of TiO_2/CA compared with initial TiO_2. Specifically, the MB degrading performance was up to 89% for the TiO_2/CA - more than 1.37 times as much as the TiO_2 sample, where the adsorption efficiency alone was about 11 times.

Keywords: TiO_2/Carbon aerogel; Methylene blue photo-degeneration; Photocatalysis.

1. INTRODUCTION

Textile dyeing wastewater treatment is one of the critical terms today due to the negative of this type of sewage consequence to the environment. Specifically, commercial dyes with complex structures and low biodegradation could cause harm to aquatic life or disturb the flora and fauna's ecological balance while being directly discharged outside, which leads to human health risks such as cancers or deformity. The color-contaminated receiving water source obstructs sunlight absorption and limits dissolved oxygen, consequently reducing photosynthetic activity [1]. But in fact, the textile industry plays an essential role in the economy by ensuring jobs for millions of people and is predicted to widen in the future [2]. So, with the goal of sustainable development, instead of banning or downsizing the textile industry, it is necessary for dye removal enhancement of the wastewater.

The photocatalytic technique has long been one of the most promising ways for textile dyeing wastewater treatment due to its low cost, high efficiency, and potential commercialization [3]. Unlike the usual methods such as adsorption, coagulation, membrane filtration, or sedimentation that only store the dyes, photocatalysis with free radical generation can eliminate them from wastewater by complete mineralization [3]. Because of some characteristics of low price, stabilization, and non-toxicity, titanium dioxide (TiO_2) has been a typical heterogeneous photocatalyst and applied widely in photochemical processes for cleaning sewage [4]. However, the two main existing drawbacks are the too-large band gap of TiO_2 (about 3.2 eV) makes it only be activated under ultraviolet (UV) irradiation leading to difficulties in low UV light source applications like being in sunlight with only 5% UV light, and the high recombination rate of electrons and holes causing low quantum efficiency as well poor photoactivity of TiO_2 even in

UV region [5]. Therefore, the TiO_2 photo-sensitive extension from UV light to the visible light range or the rapid electron-hole pair recombination reduction by the electron trap is significant in improving the photocatalytic ability of TiO_2 and widening its application fields.

Taking advantage of carbon - one of the most abundant elements in nature, during the past decades, carbon materials such as graphene, activated carbon, carbon aerogel, or carbon nanotubes have been focused on research and application [6]. Amongst, carbon aerogel (CA) is a potential candidate in different fields (biomedical, environmental, energy, ...) due to its attractive properties: ultralow density, excellent electrical conductivity, high surface area, and high porosity [7-9]. Moreover, the excellent electrical conductivity of carbon aerogel can make it become an electron trap with fast electronic transmission before that electron can recombine with the hole.

In this study, TiO_2/Carbon aerogel material (TiO_2/CA) has been synthesized by the sol-gel process and used for methylene blue treatment. In this case, carbon aerogel plays roles as an adsorbent with a high surface area, an electron trap with excellent conductivity, and a TiO_2 dispersant with 80-90% porosity. The combination of the advantage of carbon aerogel and TiO_2 material is expected for a higher result in methylene blue decolorization than individual materials.

2. EXPERIMENTAL SECTION

Materials. Chemicals, purity, and the company of purchase are listed as follows: formaldehyde solution (37 wt%, Xilong Co., Ltd.), resorcinol (≥99.5 wt%, Shanghai Xihua Scientific Co. Ltd.), Sodium carbonate (≥99.9 wt%, Xilong Co., Ltd.), absolute ethanol (≥99.7 wt%, Xilong Co., Ltd.), Tetrabutyl Titanate (≥98 wt%, Shanghai Zhanyun Chemical Co., Ltd.), and acid nitric (65-68 wt%, Xilong Co., Ltd.).

Preparation of carbon aerogel (CA). The carbon aerogel was synthesized by the sol-gel method. Firstly, the solution included 73.7 g formaldehyde solution, and 50 g was prepared in 160 mL distilled water as the solvent. In the synthesis reaction, Sodium carbonate (Na_2CO_3) was used as a catalyst. In particular, 24.2 g Na_2CO_3 solution 0.2 wt% was added into the obtained solution followed by stirring continuously for 15 minutes and sonicating in 5 minutes. Then, the final solution was aged at room temperature for 2 hours before the reaction at 80 ℃ for 24 hours until the gel was obtained. The gel was washed 3 times with acetone solvent before freeze-drying to form resorcinol-formaldehyde aerogel. The material was calcined at 800 ℃ in the nitrogen for an hour at a heating rate of 5 ℃/min. Finally, the sample was activated at 800 ℃ in CO_2 gas flow for 1.5 hours at the same heating rate.

Preparation of TiO2/carbon aerogel (TOCA). Two prepared premix A and B for the TiO_2/Carbon aerogel synthesis were as follows. The pale-yellow solution (A) was the result of stirring 30 mL absolute ethanol with 10 mL Tetrabutyl titanate for 15 minutes. The B solution was a mixture of 20 mL absolute ethanol, 10 mL distilled water, 1.5 mL HNO_3, and 1g carbon aerogel. The mixture created by adding drop by drop B to A was stirred for an hour before a room temperature rest for 2 hours and then a 70 ℃ reaction for 12 hours. Then, the sample was dried at 70 ℃ and calcined in nitrogen air at 500 ℃ for 1.5 hours with a heating rate of 5 ℃/min. Besides, the TiO_2 sample (TO) was also synthesized by a similar procedure with the carbon aerogel's absence.

Characterization of samples. Crystallization of materials was measured by Bruker D8 Advance instrument with CuKα radiation source (λ = 1.5418 Å) at 40 kV, 30 mA. Samples' morphologies and elements were photographed by JSM-IT200 InTouchScope™ Scanning Electron Microscope to obtain the SEM images and EDX distributions. The surface and pore properties of materials were determined by Nitrogen physisorption using PMI's BET-Sorptometer BET-201-A. The surface functional group of material using FT-IR method was conducted in Bruker ALPHA II Compact FT-IR Spectrometer.

Decolorization of Methylene blue. Methylene blue treatment experiments of the TOCA sample occurred under conditions with and without UV radiation. The specific amount of each experiment was 0.015 g of catalyst, 50 mL of MB solution 15 ppm, and 3 UVA lamps of 8 W per one. MB concentration was measured by Lovibond® Spectrophotometer XD 7000 (VIS) instrument at 640 nm of weight length.

3. RESULTS AND DISCUSSIONS

Figure 1 shows the XRD patterns of the TO and TOCA sample and the standard peaks of the anatase phase and rutile phase of TiO_2 based on JCPDS card 01-073-1764 (Anatase) and 01-078-1510 (Rutile). In both the TO and TOCA samples, the anatase phase's characteristic peaks appear at 2θ = 25.2º, 37.7º, 48.0º, and 55.0º corresponding to the (101), (004), (200), (105), (211) and (204) planes and a rutile phase's peak at 2θ value of 27.4º ((110) plane) also comes along in much the tinier qualities when observing the highest peak. Therefore, the synthetic materials are successful with the two simultaneously most popular TiO_2 phase presence where the anatase polymorph predominance expected higher photoactivity [10]. The absence of all carbon characteristic peaks on the TOCA sample indicates the amorphous form of carbon aerogel. Furthermore, the significantly higher peak intensity of the rutile phase in the TO sample compared with TOCA has proven an essential role of carbon in TiO_2 crystallization: the sintering avoidance and the anatase-rutile phase transformation inhibition [11]. On the other hand, the nitrogen calcination that causes the oxygen shortageis one of the reasons for the rutile formation impulse.

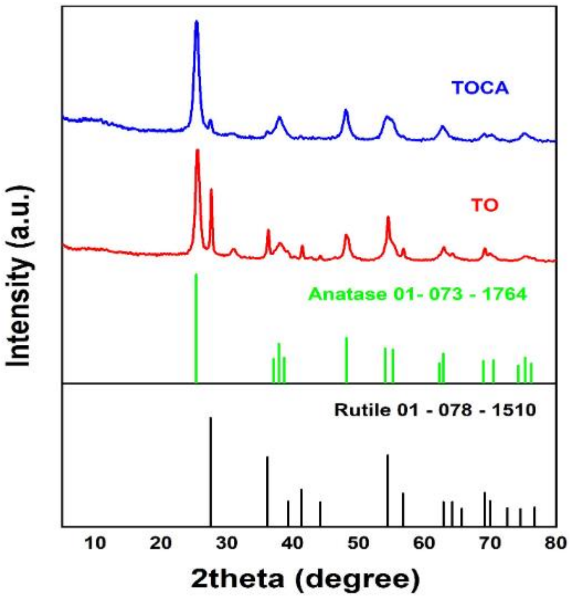

Figure 1. *XRD patterns of TiO_2 (TO) and Ti TOCA.*

Nitrogen physisorption results are expressed in figure 2 and table 1. As can be seen in figure 1, all the nitrogen adsorption-desorption isotherms of TiO_2, Carbon aerogel, and TiO_2/carbon aerogel have the shape of Type IV isotherm following IUPAC classification with the hysteresis loop attendance that characterizes for capillary condensation in mesoporous material. The listed information in table 1 includes: Brunauer-Emmett-Teller specific surface area (S_{BET}), Langmuir specific surface area ($S_{Langmuir}$), total volume (V_{total}) is the volume at P/P_0 nearest value 1, and average mesopore diameter (Da) from BJH pore size adsorption. Particularly, S_{BET} and V_{total} values of TO, CA and TOCA are 65.88 m^2/g, 813.08 m^2/g, 212.43 m^2/g and 0.0935 cc/g, 0.3428 cc/g, and 0.1604 cc/g respectively. It is easy to recognize that the CA sample has gotten the value of both S_{BET} and V_{total} higher than the TOCA one, which can be explained by the occupancy of TiO_2 molecules blocking or shrinking the aerogel pores [12].

Table 1. *Surface properties of TO, CA, and TOCA samples.*

Sample's name	S_{BET} (m^2/g)	$S_{Langmuir}$ (m^2/g)	V_{total} (cc/g)	Da (nm)
TO	65.88	-	0.0935	7.156
CA	813.08	1000.60	0.3428	3.460
TOCA	212.43	303.35	0.1604	9.228

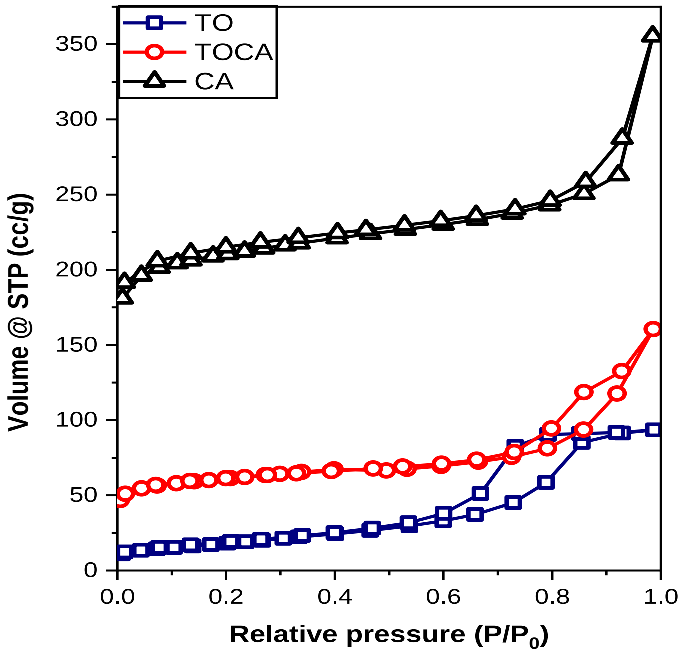

Figure 2. *Nitrogen adsorption-desorption isotherm curves of the CA, TOCA, and TO sample.*

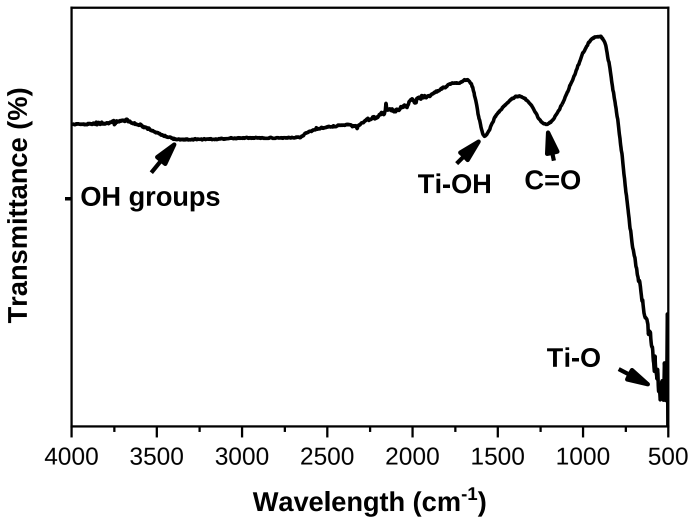

Figure 3. *FTIR spectra of TiO_2/Carbon aerogel in the wavenumber range of 500 to 4000 cm^{-1}.*

The surface functional groups of TOCA were determined by FT-IR spectra. According to the FT-IR spectrum of the TOCA sample (figure 3), in the range of 500 to 4000 cm^{-1}, there are four most clearly observed peaks (as marked on the spectra). Similar to the previous studies, the peaks at 1096 cm^{-1} and 3441 cm^{-1} are attributed to the stretching vibrations of C-O and hydroxyl groups, respectively [11]. The 1639 cm^{-1} peak is because of the bending vibration of the coordinated water or Ti-OH [13]. It can be reconfirmed that the priority of the anatase TiO_2 in the created sample with the adsorption band at 611 cm^{-1} ascribing to the Ti-O stretching and Ti-O-Ti bridging stretches are the contributions of anatase titania lattices [12].

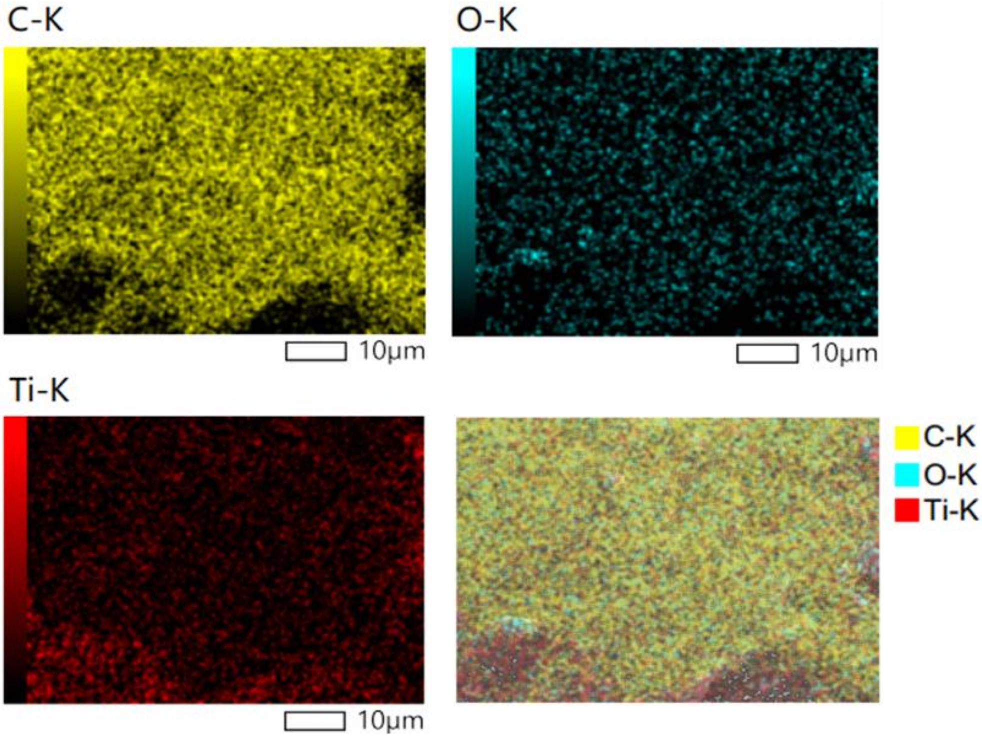

Figure 4. *EDS results of TOCA sample.*

Figure 4 expresses the elemental mapping of C, O, and Ti in the surface of the TOCA sample using EDS method. It is an obvious observation about the uniform distributions of the individual elemental distribution images and the mixed one, which indicates the correct original orientation with the even TiO_2 molecule dispersion of carbon aerogel supporter. In addition, according to the mixed image and the percentage composition table (table 2.), the carbon quantity accounts for a majority part (greater than Ti and O amount), showing the carrier role of carbon aerogel and the active site role of TiO_2 as well as the synthesized success.

Table 2. *The percentage of elements (C, O, Ti) of TOCA sample.*

Element	Line	Mass %	Atom %
C	K	77.98±0.11	87.28±0.12
O	K	11,68±0.11	9.81±0.1
Ti	K	10.34±0.2	2.9±0.06
Total		100.00	100.00

The MB preliminary removal outcomes are demonstrated in figure 5. The advantage of carbon aerogel in the adsorption process is impressed with the higher efficiency of the TOCA to TO sample (more than about six times). With the UV lamps' mutual contribution, the TOCA sample still has superior performance when compared with the TO sample. Specifically, after

210 minutes, the color of MB decreases by 88.7% at TOCA-UV, and only 64.1% at TO-UV. Moreover, the outstanding decolorization in both rate and capacity of TOCA material has authenticated the electron trap role of carbon aerogel and the correct initial idea.

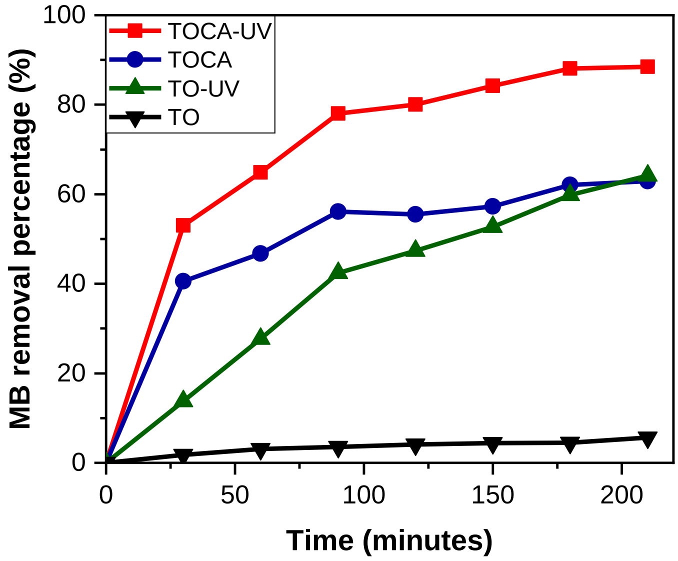

Figure 5. *Methylene blue removal percentage of TO and TOCA sample in 210 minutes (15 ppm, 0.015 g sample, 50 ml, and UVA lamps).*

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4. CONCLUSIONS

The TiO_2/carbon aerogel has been synthesized by the sol-gel method for the initial purpose of enhancing the photocatalytic ability of TiO_2. Taking advantage of the large surface area, high porosity, and wonderful conductivity, carbon aerogel is a good candidate to become a carrier in this case. The material characterizations include XRD, Nitrogen physisorption, FT-IR, and EDS, which give reasonable results for the initial idea and are similar to other research. Especially, the TiO_2/carbon aerogel has a higher BET surface area than TiO_2 without a carrier. The EDS images show the uniform distributions of elements (Ti, O, C) on the surface of TiO_2/carbon aerogel. Choosing methylene blue as a typical organic textile dyeing, after 15 minutes of treatment with the following conditions: 50 ml MB 15 ppm, 0.015 g catalyst, and 3 UVA lamps (8W per one), the TiO_2/carbon aerogel has gotten the highest MB performance (more than 88%), which indicates the success of this work.

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TÓM TẮT

Tăng cường hiệu quả xử lý methylene blue bằng chất xúc tác quang TiO_2/Carbon aerogel

Trong nghiên cứu này, vật liệu TiO_2/carbon aerogel tổng hợp bằng phương pháp sol – gel cải thiện hiệu quả xúc tác quang của TiO_2 nhờ vào sự giảm rộng vùng cấm và tăng đáng kể diện tích bề mặt riêng. Vật liệu tổng hợp được đặc trưng bởi phổ nhiễu xạ tia X (XRD), kính hiển vi điện tử quét – phổ tán sắc năng lượng tia X (SEM -EDX), phương pháp hấp phụ vật lý khí nito và phổ hồng ngoại chuyển đổi fourier (FTIR). Thử nghiệm xử lý Methylene blue thực hiện trong điều kiện: 3 đèn UVA (công suất mỗi đèn 8 W), 0.015 g mẫu và 50 ml dung dịch MB 15 ppm, cho thấy gia tăng đáng kể khả năng hấp phụ, sự phân hủy xúc tác quang và phản ứng động học của TiO_2/CA so với TiO_2 ban đầu. Cụ thể, tổng hiệu suất khử màu của MB đối với TiO_2/CA lên đến 89% - gấp hơn 1,37 lần so với mẫu TiO_2 tinh khiết, trong đó chỉ riêng hiệu suất hấp phụ là khoảng 11 lần.

Keywords: TiO_2/Carbon aerogel; Xử lý methylene blue; Quang xúc tác.