Preparation of black-TiO_2 and its application in photocatalytic removal of methyl orange dye

Dang Cam Vinh, Nguyen Quang Long*

Faculty of Chemical Engineering, Ho Chi Minh City University of Technology (HCMUT).
*Corresponding author: nqlong@hcmut.edu.vn.
Received 1 August 2021; Revised 15 November 2021; Accepted 12 December 2021.
DOI: https://doi.org/10.54939/1859-1043.j.mst.76.2021.68-73

ABSTRACT

For a few decades, Titanium Dioxide (TiO_2) has been the most studied photocatalyst due to its significant optical property. In the paper, TiO_2 pigment powder (Anatase form) was selected as a precursor to prepare a variety of Black-TiO_2 samples, and the typical material was then evaluated for its photocatalytic activity in organic pollutant treatment. Some properties of Black-TiO_2 were determined via common methods such as sensory analysis, X-Ray diffraction, and bandgap measurement obtained from UV-Vis spectroscopy. As a result, the material was successfully converted to more than 40% organic pollutant as Methyl Orange ($C_{14}H_{14}N_3NaO_3S$) for an hour, as two times higher than that of the amount converted by pristine TiO_2. In addition, Black-TiO_2 performed much better photocatalytic activity in an acidic medium in comparison with a neutral one, and the material also remained its activity as more than 90% after three time-continuous recycling operations.

Keywords: Photocatalysis; Black-TiO_2.

1. INTRODUCTION

At present, environmental pollution is still a challenge not only for developing countries but also for developed countries worldwide. Due to the diversity in industrial production activities, a large amount of wastewater containing many toxic substances has been directly discharged into the environment. Pollutants such as organic compounds and heavy metals exist mainly in wastewater from the cosmetic industry, pharmaceutical industry, landfill, agricultural cultivation, etc., which negatively affects the environment, makes water pollution increasingly serious [1]. Some effective methods have been applied to remove water pollutants, notably the photocatalytic oxidation process, using TiO_2 as a catalyst in the process. Since TiO_2 was first used in the photocatalytic process to treat Cyanide-containing wastewater, the material has been widely used in environmental treatment [2]. Thanks to outstanding properties such as optical stability, non-toxicity, low cost, and insoluble in water under most conditions, TiO_2 becomes a truly remarkable and attractive material in environmental applications. However, the major drawback of TiO_2 is that the recombination of the electron/hole pair takes place at a relatively fast rate, which reduces the efficiency of the material. In addition, the large bandgap energy leads to a limitation on the material's ability to absorb light radiation, and thereby energy consumption is likely high in providing radiation. To improve these demerits, scientists have studied the synthesis and modification of TiO_2 into new forms of materials with outstanding properties towards reducing the recombination rate, expanding the radiation absorption region, and thereby increasing the efficiency of pollutant treatment. Black-TiO_2 is the result of the successful modification of TiO_2 based on a number of procedures such as laser irradiation [3], H_2 reduction under high pressure [4] or high temperature [5], organic solvents [6], and $NaBH_4$ reduction [7].

In this study, Black-TiO_2 material was prepared via the method of reducing TiO_2 by $NaBH_4$ agent under various reaction conditions and applied in wastewater treatment, particularly Methyl Orange removal. The Black-TiO_2 evaluation is based on simple sensory perception through color and shape of the material. Next, a series of investigation were conducted to evaluate the Black-

TiO_2 material, including the investigation of TiO_2 preparation conditions (calcination time, calcination temperature, reagents ratio) and the investigation of reaction conditions (pH, concentration of Methyl Orange, Black-TiO_2 and Methyl Orange ratio).

2. EXPERIMENTAL

2.1. Preparation and characterization of materials

In this work, the preparation of Black-TiO_2 is based on the previous research [8] with modification. In detail, a commercial fine TiO_2 powder (Anatase form, from Van-Hai Company) was used as a starting material. The reduction agent $NaBH_4$ was purchased from Acros Company with high purity. In addition, all chemicals involved in the process were used without any further treatment. Generally, many different Black-TiO_2 materials were prepared by changing various conditions (TiO_2/$NaBH_4$ mass ratio, calcination temperature, and duration) in the research, as shown in table 1. The preparation of the samples was carried out by the following steps: Firstly, 2.0 g of pristine TiO_2 powder was mixed with 0.75 g of $NaBH_4$, followed by heating in the furnace under nitrogen atmosphere at different temperatures and times. The sample then cooled down, washed with distilled water and ethanol at least two times, and dried at 110 ^oC overnight. In this paper, the catalytic activity of the V22 sample, as a typical sample, was selected to report.

Table 1. *List of Black-TiO_2 materials (named as Vx) prepared in different conditions.*

Calcination Temperature / Duration	300^{o}C	350 ^{o}C	400 ^{o}C	450 ^{o}C
1h	V22	V26	V30	V17
2h	V23	V27	V31	V34
3h	V24	V28	V32	V35
4h	V25	V29	V33	V36
Mass ratio TiO_2/$NaBH_4$ (wt/wt)	5:0.5	5:0.75	5:1	5:1.25
	V39	V40	V37	V41

The crystalline structure of the above catalyst was analyzed by powder X-Ray diffraction using Advance D8 diffractometer, with Cu Kα radiation (λ = 1.5418Å) operated at 30 kV and 10 mA, measurement step of 0.01944^o over a 2θ range from 5° to 70° at a scan rate in 2θ about 4°/min. The crystallite sizes were estimated from the line broadening of the (111) peak obtained. The crystallite size D was calculated from the Scherrer equation in Eq (1):

$$D = \frac{0.9\times\lambda}{B\times\cos\theta} \qquad (1)$$

Where λ is the wavelength of the X-rays, θ is the diffraction angle, and B is the corrected full width, at half-maximum of the peak. In order to confirm the size as well as the size distribution of Au particles, we used transmission electron microscopy (TEM) by using JEOL – JEM 1400 operated at 100 kV.

2.2. Methyl Orange removal test

The efficiency for Methyl Orange removal of the Black-TiO_2 materials in this work was carried out in a continuous system with an annular reactor that included an interconnected quartz tube. An 11W UV-C radiation lamp was put inside the quartz tube. The outside diameter of the quartz tube was 35 mm with a thickness of 1mm. The outlet of the reactor was connected with a container storing a mixture of 500 mL Methyl Orange solution and 0.1 g Black-TiO_2, and the inlet was connected with a simple pump before the mixture. The Methyl Orange solution was prepared with various concentrations (50, 100, 200 ppm) depending on the investigation, while the amount of Black-TiO_2 remained at 0.1g. After every 10 minutes, the mixture was diluted and analyzed by UV-Vis spectroscopy at 463 nm, Spectrony Genesys 2pc, to determine Methyl Orange concentration.

3. RESULTS AND DISCUSSION

3.1. Characterization

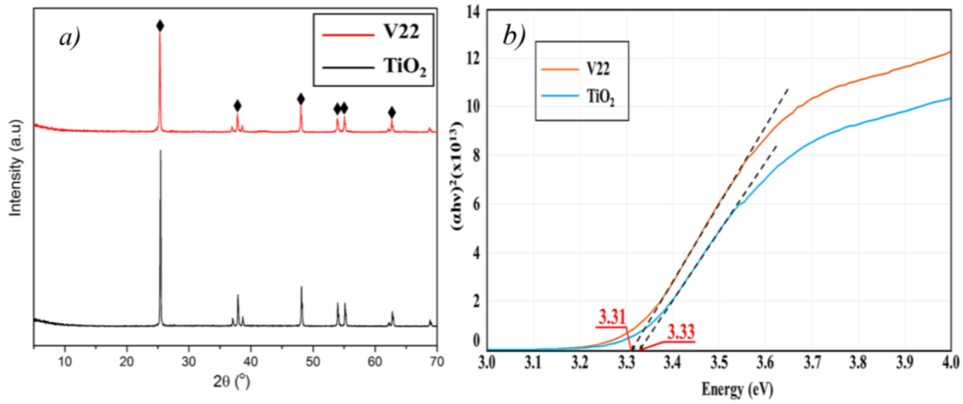

Figure 1. *a) XRD pattern of Black-TiO_2 V22 sample and standard sample (JCPDS 21-1272); b) Restricted energy of V22 sample and pristine TiO_2.*

The standard XRD plot was used to determine the crystal structure corresponding to the peak that appeared on the measurement result. The 2θ peaks at 25.3°; 36.9°; 37.8°; 38.6°; 48°; 53.9°; 55.1°; 62.7° were characteristic of the Anatase form in Black-TiO_2 V22 sample. The peaks emerge at the same 2θ values as the standard TiO_2 sample JCPDS 21-1272, and no new peak was detected, indicating no phase conversion after the preparation.

Based on the Tauc method, the bandgap energy of the material was theoretically calculated. Among the Black-TiO_2 samples, the V22 sample particularly exhibited a stronger light absorption than the pristine TiO_2, and thus determining the bandgap energy of these two samples. It could be referred that the restricted energy of V22 sample was successfully reduced compared to the pristine sample, which was confirmed by the improvement of photocatalytic activity of V22 sample compared to the pristine sample in the next section.

3.2. The effect of preparation conditions on materials

In the study, there were three main types of experiments carried out to investigate the appearance of the Black-TiO_2 materials after preparation via the sensory method. From which, it was possible to predict the light absorption of the prepared sample through the color of the materials with simple steps and the least cost. The first experiment was conducted to evaluate the effect of calcination time on the product. In this experiment, the temperature and the mass ratio between TiO_2 and $NaBH_4$ were kept constant while the calcination time increased exponentially, particularly 1 h, 2 h, 3 h, and 4 h (as shown in figure 2.a,b,c,d). The image shows that at the same temperature, the longer the calcination time, the darker the color would be. The next experiment was performed with the aim of observing the effect of the temperature on the Black-TiO_2 samples. In this experiment, the calcination time and mass ratio between TiO_2 and $NaBH_4$ were maintained unchanged while the temperature increased to 300 ^oC, 350 ^oC, 400 ^oC, and 450 ^oC respectively (as shown in figure 2.e,f,g,h). The picture exhibits that the higher the heating temperature is, the darker the Black-TiO_2 samples are. This can be explained by the fact that due to the high temperature, $NaBH_4$ decomposes more, and the hydrogenation reaction is far easier, making the TiO_2 much more defective resulting in a darker color. The final experiment was designed to evaluate the effect of the number of reactants on the product. Specifically, the mixture was constantly calcined at 35 ^oC in 1h. Meanwhile, the mass ratio between TiO_2 and $NaBH_4$ was changed for each experiment. The mass ratios of TiO_2:$NaBH_4$ selected for investigation were 5:0.5, 5:0.75, 5:1, and 5:1.25 (g/g). figure 2.k) shows the gradual darkening in color of the Black-

TiO_2 samples when the amount of $NaBH_4$ was increased in the reaction mixture.

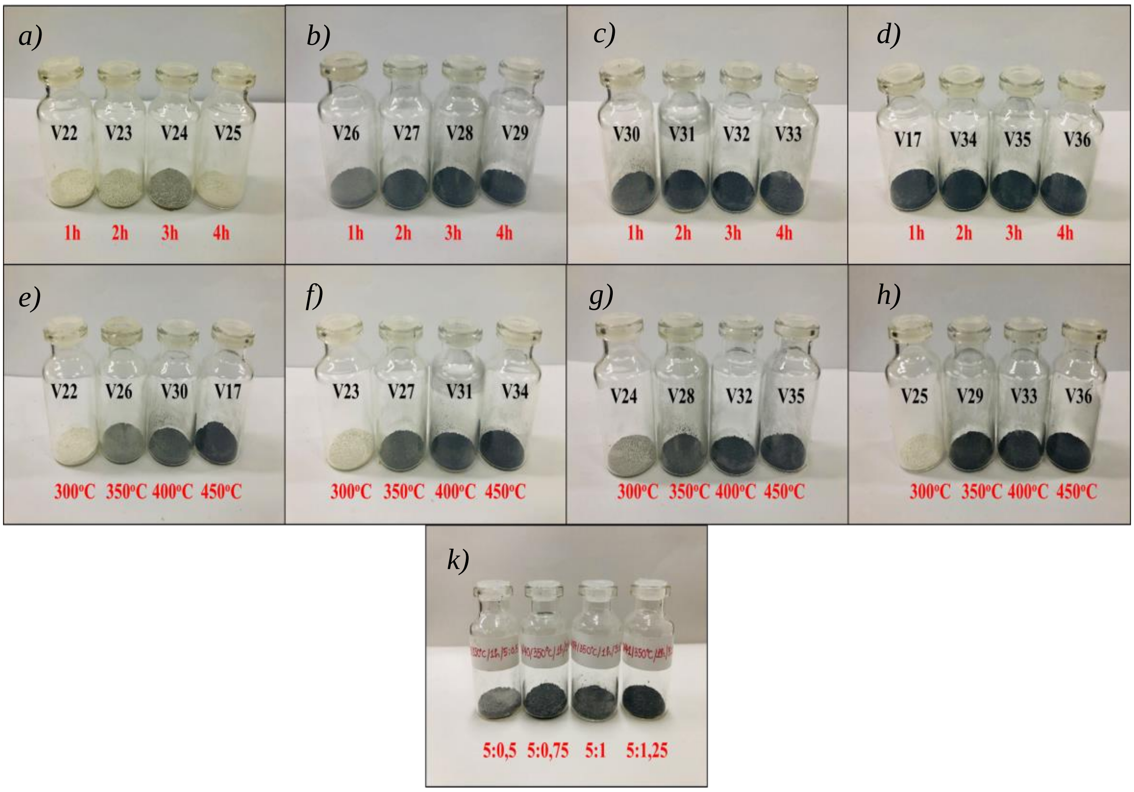

Figure 2. *a,b,c,d) Prepared samples at 300 °C, 350 °C, 400 °C, and 450 °C, respectively; e,f,g,h) Prepared samples at calcination time of 1 h, 2 h, 3 h, and 4 h, respectively; k) Prepared samples with different mass ratio $TiO_2/NaBH_4$.*

3.3. The effect of reaction conditions on photocatalytic activity

Figure 3.a) shows that the photocatalytic activity of the Black-TiO_2 V22 sample was significantly improved compared to pristine TiO_2. Specifically, the material was able to convert approximately 45% of Methyl Orange in a period of 1 hour, twice as compared to the amount of Methyl Orange converted by pristine TiO_2. This result supported the result obtained in the Tauc method to determine the bandgap energy of the prepared sample. In acidic and alkaline mediums, Methyl Orange absorbed light of different wavelengths. In this experiment, the MO degradation was evaluated in acidic (pH3 and pH5), neutral (pH7), and alkaline (pH9) medium. The conversion of Methyl Orange in an acidic medium was higher than that in a neutral and alkaline medium, as shown in figure 3.b). This result could be explained based on the PZC theory. In the acidic medium, Black-TiO_2 tended to be positively charged at the surface, which increased the electrostatic interaction with Methyl Orange in the solution and thus increased the conversion. In contrast, in neutral or alkaline medium, Black-TiO_2 was negatively charged and the conversion was approximately 45% of Methyl Orange.

Figure 3.c) exhibits the process of investigating the effect of Methyl Orange concentration on the photocatalytic efficiency of the V22 sample. The experiment was carried out with a concentration of Methyl Orange of 50, 100, and 200 ppm. In general, all experiments showed a general trend toward process conversion rate. The efficiency of the reaction decreases with the increase in the initial Methyl Orange concentration. As shown in figure 3.d), the experiment was established to investigate the effect of mass/volume ratio between V22 sample and Methyl

Orange solution on the efficiency of the reaction. The conversion of Methyl Orange increased when there was an addition of Black-TiO_2 sample. The difference was considerable in half period of reaction time. Figure 3.e) shows the recycling ability of the V22 sample after three continuous runs (only counted the recycling runs). The results implied that the photocatalytic activity of the sample V22 decreased slightly after the operation. At the third recycling, the photocatalytic activity remained at more than 90% compared to that of the original V22 sample.

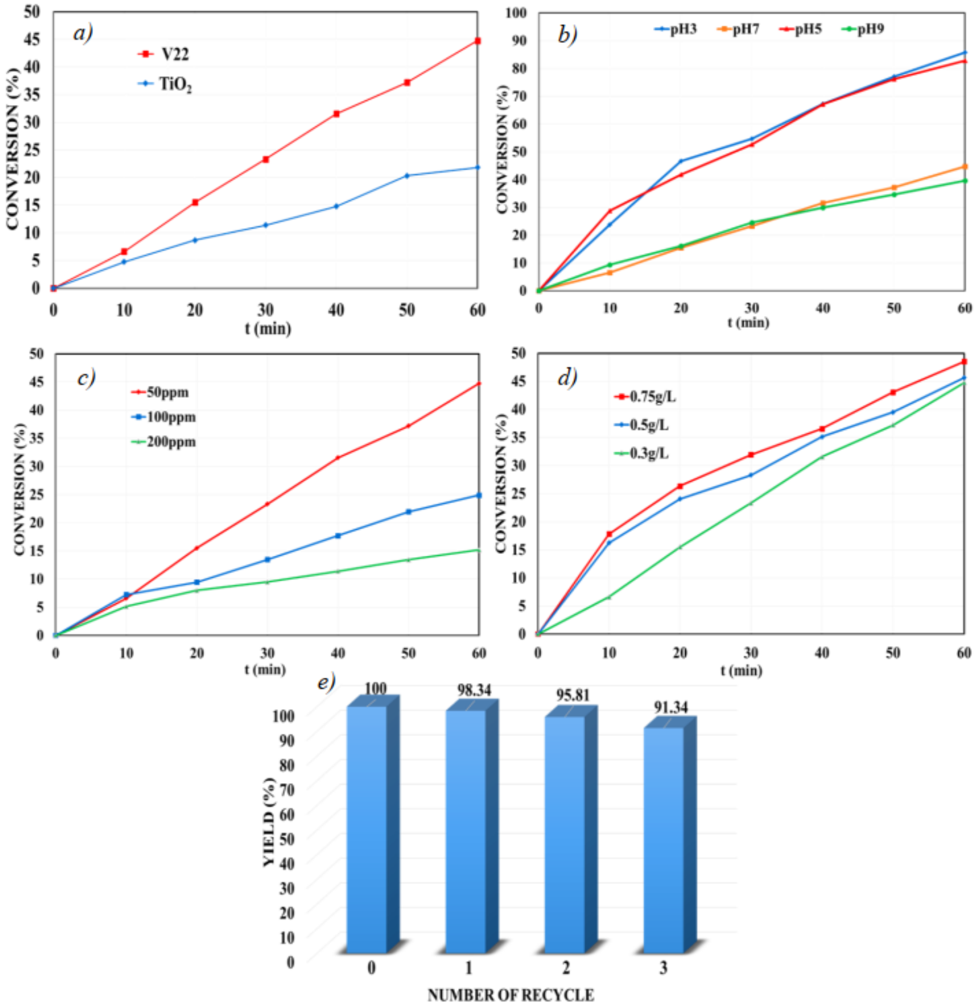

Figure 3. *a) The photocatalytic efficiency of pristine TiO_2 and V22 sample in a neutral medium; b) The photocatalytic efficiency of V22 sample at different pH; c) The photocatalytic efficiency of V22 sample at different Methyl Orange concentration; d) The photocatalytic efficiency of V22 sample with different mass/volume ratios between V22 sample and Methul Orange solution; e) The recycling operation of V22 sample.*

4. CONCLUSION

The Black-TiO_2 material was successfully prepared via the $NaBH_4$ reduction method. Furthermore, its characteristics were investigated through the sensory method, XRD, and bandgap energy measurement. The results had provided a deep understanding about the properties of prepared materials. The photocatalytic activity of Black-TiO_2 was investigated based on the change of factors: pH of the medium, Methyl Orange concentration, and mass/volume (g/L) ratio between Black-TiO_2 and Methyl Orange. Results showed that the Black-

TiO_2 material was able to decompose Methyl Orange under the effect of UV light better than pristine TiO_2, which was explained by the improvement of light absorption and the reduction in restricted energy. There are various defects on Black-TiO_2 reported previously. This study should also be conducted to investigate the presence of which kind of defects on the Black-TiO_2 surface via XPS method. These defects show many practical applications. Some of the conditions of the experiments in this study were not practical. In order to apply the result of this research, a study of the application of Black-TiO_2 material in the visible light region should be conducted. The light intensity in the study was considered a constant to simplify the process of research. However, this value could not be maintained the same in practical use over time. Therefore, the effect of light intensity on the ability of Methyl Orange treatment should be observed. The prepared material has exhibited a reduction in efficiency over time. It is critical to research regenerating the catalysts to save operating costs when applied to an industrial scale.

Acknowledgments: *We acknowledge the support of time and facilities from Ho Chi Minh university of Technology (HCMUT), VNU-HCM for this study.*

REFERENCES

[1]. S. R. Wild, T. Rudd, and A. Neller, *"Fate and effects of cyanide during wastewater treatment processes,"* Sci. Total Environ., vol. 156, no. 2, pp. 93–107, Nov. 1994.

[2]. S. N. Frank and A. J. Bard, *"Heterogeneous photocatalytic oxidation of cyanide and sulfite in aqueous solutions at semiconductor powders,"* J. Phys. Chem., vol. 81, no. 15, pp. 1484–1488, Jul. 1977.

[3]. C. Langlade, B. Vannes, T. Sarnet, and M. Autric, *"Characterization of titanium oxide films with Magnéli structure elaborated by a sol–gel route,"* Appl. Surf. Sci., vol. 186, no. 1–4, pp. 145–149, Jan. 2002.

[4]. X. Chen, L. Liu, P. Y. Yu, and S. S. Mao, *"Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals,"* Science (80), vol. 331, no. 6018, pp. 746–750, Feb. 2011.

[5]. A. Naldoni *et al.*, *"Effect of Nature and Location of Defects on Bandgap Narrowing in Black TiO 2 Nanoparticles,"* J. Am. Chem. Soc., vol. 134, no. 18, pp. 7600–7603, May 2012.

[6]. F. Zuo, L. Wang, T. Wu, Z. Zhang, D. Borchardt, and P. Feng, *"Self-Doped Ti 3+ Enhanced Photocatalyst for Hydrogen Production under Visible Light,"* J. Am. Chem. Soc., vol. 132, no. 34, pp. 11856–11857, Sep. 2010.

[7]. S. Tominaka, *"Facile synthesis of nanostructured reduced titanium oxides using borohydride toward the creation of oxide-based fuel cell electrodes,"* Chem. Commun., vol. 48, no. 64, p. 7949, 2012.

[8]. D. Ariyanti, L. Mills, J. Dong, Y. Yao, and W. Gao, *"NaBH4 modified TiO2: Defect site enhancement related to its photocatalytic activity,"* Mater. Chem. Phys., vol. 199, pp. 571–576, Sep. 2017.

TÓM TẮT

TỔNG HỢP TiO_2 ĐEN VÀ ỨNG DỤNG TRONG QUÁ TRÌNH QUANG XÚC TÁC XỬ LÝ METYL DA CAM

Hiện nay, TiO_2 là một loại xúc tác quang đã và đang được nghiên cứu rộng rãi nhờ vào những tính chất đặc trưng của vật liệu. Trong nghiên cứu này, TiO_2 dạng chất màu (pigment, Anatase 100%) được lựa chọn nhằm tổng hợp vật liệu Black-TiO_2 và khảo sát khả năng ứng dụng trong phản ứng xúc tác quang xử lí chất ô nhiễm trong môi trường lỏng. Các tính chất của vật liệu tổng hợp Black-TiO_2 được đánh giá thông qua phương pháp cảm quan đơn giản và các phương pháp khác như nhiễu xạ tia X (XRD), xác định mức năng lượng vùng cấm vật liệu từ phổ hấp thu ánh sáng vùng UV-Vis. Kết quả là, vật liệu Black-TiO_2 đã thành công chuyển hóa hơn 40% chất ô nhiễm Methyl da cam ($C_{14}H_{14}N_3NaO_3S$) trong 1 giờ, gấp đôi so với lượng được chuyển hóa bởi tiền chất TiO_2 ban đầu. Bên cạnh đó, khả năng chuyển hóa của vật liệu trong môi trường axit tốt hơn hẳn so với môi trường trung tính và hoạt tính quang hóa của Black-TiO_2 vẫn đạt trên 90% sau 3 lần tái sinh liên tục.

Từ khoá: Xúc tác quang; Black-TiO_2; Xử lý môi trường.