



Preparation of Black-Titanium Dioxide Nanotubes by Thermal Decomposition of Sodium Borohydride

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Abstract – Titanium dioxide is a very attractive material in catalysis. Although the titanium dioxide exhibits superior properties in ultra violet radiation, activity of the catalyst can be improved by some modifications specially for daylight radiation. Titanium dioxide was colored by thermal decomposition of sodium borohydride at 400 °C. The gray colored nanotube-titanium dioxide obtained where the molar ratio of titanium dioxide to sodium borohydride, 1.2 and 0.6. The black nanotube-titanium dioxide was prepared by making the ratio 0.3. While heterogeneous dispersion observed after coloring of commercial titanium dioxide, all photocatalysts prepared from nanotube-titanium dioxide were perfectly homogeneous after coloring. Structural properties of photocatalysts analysed by using XRD, BET and SEM. The nanotube form of titanium dioxide prepared by hydrothermal method. The nanotube photocatalysts are anatase and have high surface area. The activities of colored nanotubes investigated according to these structural properties. Photocatalysts could not be colored homogeneously with the hydrogen reduction process but efficient reduction and coloration obtained with sodium borohydride. The visible region activities of photocatalysts increased by coloring with sodium borohydride compared to coloring by hydrogen. While the surface structure is important, all prepared nanotube-titanium photocatalysts exhibited more efficient color removal yield with regard to commercial one. More active catalysts prepared for absorption of daylight energy and 98.4 % color removal yield from 30 ppm methylene blue solution obtained with black nanotube-titanium dioxide photocatalyst.

Keywords – Black nanotube-titanium dioxide, Color removal, Photocatalysts, Sodium borohydride, Visible region

1. Introduction

Titanium dioxide (TiO₂) is utilized in the range of electronic material applications, environmental and energy-related uses. Due to its high chemical stability, high availability and low cost, different usage areas are still being investigated by scientists (Haider, Jameel, & Al-Hussaini, 2019). Especially in the last decade, hydrogen (Sinhamahapatra, Jong-Pil Jeon & Yu, 2015) and hydrocarbon production processes (Suprun, Lutecki, Haber, & Papp, 2009), wastewater treatment by degradation of organic pollutants (Kerkez-Kuyumcu et. al., 2015) and removal of bacteria and pollutants from air and water (Zhu, Cai, & Sun, 2018; León-Ríos et. al. 2016), carbon dioxide removal (Nikokavoura & Trapalis, 2017) have become very important processes.

The most important feature of TiO₂ as a photocatalyst is that it forms electron-hole pairs when excited by an external energy. The incoming beam causes excitation on the TiO₂ surface, thus enabling oxidation and reduction reactions to occur with the surrounded environment of TiO₂. If the mechanism of photoreactions is examined in detail, it can be seen that it takes place in three steps. 1) the semiconductor photocatalyst absorbs the beam to form an electron-hole pair. 2) These electron-hole pairs are separated from the bulk and migrate to the surface of the photocatalyst to form the active centers of the photocatalyst. 3) Oxidation and reduction reactions take place in these surface regions. UV light is the source of energy for the formation of the specified

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mechanism, but since only 4% of solar energy is UV light, this situation plays a limiting role in TiO₂ excitation efficiency. Although many advantages are given above, the inability of TiO₂ to be used efficiently in daylight appears as a disadvantage. The low energy of daylight beam is not able to excite the electrons of TiO₂ phases where the bandgap of anatase and rutile are 3.0 eV and 3.5 eV, respectively. In addition, excited electrons want to quickly return to their low energy orbits, this process called recombination that causes the photoactivity to decrease. In the presence of these information, two main issues have been focused on to increase the photocatalytic activity of TiO₂. The first one is the development of methods to reduce the disadvantage of broad band gap and the second is to slow down the recombination rate (Liu et. al. 2016). In order to increase the photocatalytic activity of TiO₂ in the visible region, it has great importance to improve its optical absorption capacity (Ariyanti, Mills, Dong, Yao, & Gao, 2017, Quingli et. al., 2015, Matsunami, Yamanaka, Mizoguchi, & Kojima, 2019). There are some methods to increase the visible region activity of TiO₂. Traditionally, metal, nonmetal or oxidized forms of metal/nonmetal species are loaded to TiO₂. Thus, these dopants in the bulk photocatalyst take place in the band gap energy level and partially reduce the band gap value. The beam response of TiO₂ can be increased in visible light region (Li et. al., 2016). Another method is coloring of TiO₂ in order to increase the beam absorption capacity. As it is known that, if a substance absorbs 100% of the light coming in the visible region, the substance appears in black color. In partial absorption, the visible color becomes in the gray-black range. If there is no absorption of light the material will be white and while the absorption at different wavelengths creates different colors of the color scale such as yellow, brown, green and blue. The blackening mechanism of TiO₂ can be summarized by structural changes such as defect formation, formation of Ti⁺³/oxygen hole and loading of hydrogen. With the realization of this mechanism, the surface functionality of TiO₂ evidently changes according to the electronical structures (Ren et. al., 2015). There are various studies in the literature in which sunlight absorption capacity is increased such as hydrogenated black TiO₂ (Chen, Liu, Yu, & Mao 2011), black nanotube TiO₂ in high pressure hydrogen environment (Liu et. al., 2014), blue rutile at 40 bar hydrogen pressure and 450 °C (Qiu et. al., 2014), hydrogenated blue-gray anatase TiO₂ at atmospheric pressure and 700 °C (Yu, Kim & Kim, 2013), gray microspheres (Li, Zhang, Peng, & Chen, 2013), and TiO₂ in the form of green-black nanowires (Wang et. al., 2011). Black TiO₂ preparation methods can be categorized by hydrogenated heat treatments (high-pressure hydrogen, atmospheric or low-pressure hydrogen, atmospheric pressure hydrogen-argon, atmospheric pressure hydrogen-nitrogen, atmospheric argon), hydrogen plasma, chemical reduction (aluminum (Al), zinc (Zn), imidazole (C₃H₄N₂), sodium borohydride (NaBH₄), calcium hydride (CaH₂)), chemical oxidation, electrochemical reduction, and anode-annealing (Ullattil, Narendranath, Pillai, & Periyat, 2018). While NaBH₄ thermally decomposed, the generated hydrogen reacts with the lattice oxygen of TiO₂. The removed oxygen makes vacancies in the structure where the vacancies are called defects. The formation of Ti³⁺ is also possible by transferring excess electrons to the vacancies of removed oxygen. According to this reduction procedure the white TiO₂ turns black. Apart from traditional methods, surface morphology of TiO₂ is also a factor involved in photoactivity, such as in the oxidation and reduction reactions by facilitating the electron transfer to the surface of the catalyst. The amount of active electrons and holes on the surface of the photocatalyst is directly proportional to the crystalline phase, crystallinity, surface structure and defects on the surface. For instance, the source of the super hydrophilic property of TiO₂ is related with the chemical conformation changes that occurs on the surface. For this reason, tube, fiber, nano-rod, sphere, sheet forms of TiO₂ have become very attractive in photoactivity that these forms can be produced at the nano or micro levels. Different forms of TiO₂ inherently have different properties such as size, surface area, pore volume, pore structure, phase of crystals that are directly related to the photoactivity of TiO₂ (Chen et. al., 2010).

In this study, the coloring of TiO₂ was achieved by thermal decomposition of NaBH₄ to enhance the activity of the catalyst by improving the absorption capacity of daylight energy. During the thermal decomposition of NaBH₄, defects were formed in TiO₂, at the same time chemical reduction was achieved and black TiO₂ was prepared. Also, where the surface morphology is an important parameter, the photocatalysts were prepared in

nanotube form from commercial TiO₂ and colored. The process of decolorization depending on the degradation of methylene blue was investigated with the prepared colored catalysts.

2. Materials and Methods

2.1. Preparation of Nanotubes

1 gram of commercial TiO₂ (Acros, Thermo Fisher Scientific, USA) mixed with 150 mL of 10 M NaOH (Merck, Germany) solution and kept in ultrasonic bath (Bandelin, Sonorex RK106, Germany) for 30 min. After ultrasonic treatment, the suspension of TiO₂ taken into the homemade hydrothermal reactor with teflon liner and treated at 130 °C for 24 hours. After filtration of the suspension, the solid washed with 0.1 M, 150 mL HCl (Merck, Germany) solution for 15 min on a magnetic stirrer (Heidolph, 3001K, Germany). This procedure repeated four times according to the pH value of the residue. After acid treatment the solid washed with distilled water until the pH of the residue was 7. The remaining nanotube catalyst dried in a furnace (Nüve, FN500, Turkey) for 24 hours at 105 °C and calcined at 500 °C for 2 hours in a muffle furnace (Protherm, PLF 120/5, Turkey).

2.2. Coloring with NaBH₄

The commercial TiO₂ mixed with NaBH₄ at a molar ratio of 1.25 ($n_{\text{TiO}_2} / n_{\text{NaBH}_4} = 1.25 \text{ (mol/mol)}$) and was subjected to heat treatment at 400 °C under argon flow rate of 100 mL / min. To determine the coloring potential of NaBH₄, the time dependency of thermal decomposition was also studied. At the first part of the studies, TiO₂-NaBH₄ mixture was heated to 400 °C with a ramp rate 50 °C/min. After 60 min treatment the power of the tubular furnace turned off and let the catalyst cool down under argon flow for 24 hours. This catalyst was named TB1. Similar conditions applied to TB2 except ramp rate and cooling time, the ramp rate of TB2 was 10 °C/min and cooling time was 120 min. The last study with commercial TiO₂ was named TB3 with the cooling time parameter was 24 hours. According to the changes in color, TiO₂/NaBH₄ molar ratios were also carried out as 1.2-0.6 and 0.3 (mol/mol). The studies with nanotubes were named as nTB1, nTB2 and nTB3 related to the similar conditions of commercial TiO₂ counterparts. The parameters and working conditions were given in Table 1. After heat treatment the catalysts washed with ethanol/water mixture (1/2 v/v) for three times and then dried at 105 °C for 24 hours.

Table 1

Experimental design and naming of the catalysts

Catalyst	TiO ₂ /NaBH ₄ molar ratio (mol/mol)	Heating rate (°C/min)	Heat treatment (min)	Cooling time (h)
TB1	1.25	50	60	24
TB2	1.25	10	60	2
TB3	1.25	10	60	24
nTB1	1.20	10	60	24
nTB2	0.60	10	60	24
nTB3	0.30	10	60	24

2.3. Activity Tests

Activity tests were carried out for decolorization of 30 ppm methylene blue solutions with 100 mL. In each experiment, 0.1 g of photocatalyst was used and the concentration value of the solution obtained by filtering the catalyst after the reaction. Since the catalysts are porous materials the adsorption of methylene blue on the surface has to be considered. To determine the methylene blue adsorption capacity of the catalysts, the reaction conditions were performed in the dark. To obtain the real reaction yield the desorption of adsorbed methylene

blue on the catalysts was conducted with the distilled water in an ultrasonic bath. The removal yield of the reaction calculated related to difference between reaction conversion and adsorbed-unreacted parts. Blank experiments in daylight and in the ultraviolet C (UV-C, 254 nm) region were also conducted with both commercial and prepared nanotube TiO₂s for comparison.

2.4. Characterization

X-ray diffractometer (XRD) (Miniflex 2; Rigakku, Japan) used to determine the crystalline phases of catalysts. 2θ values determined in the range of 10° - 80° with Cu K α radiation ($\lambda = 0.1541$ nm) and a step size of 0.02. Standard BET method used to evaluate the data for total surface area and BJH method was used to evaluate the pore size distribution plot in nitrogen adsorption (Micromeritics, ASAP 2020, USA). To emphasize the morphology of the samples FEI Quanta 250 environmental scanning electron microscopy (ESEM) and JEOL 6060 scanning electron microscopy (SEM) were used. The absorbance values obtained with UV-spectrophotometer (Hach Lange, DR5000, Germany).

3. Results and Discussion

Although there are many different methods to synthesize nanoscale TiO₂, the frequently used method is the hydrothermal method. Factors affecting nanotube synthesis by hydrothermal method can be examined under five categories. First, the choice of titanium source (anatase, rutile, alkoxide salt, etc.), second, ultrasonic pretreatment (dispersion of nanoparticles, growth of crystals, etc.), third, hydrothermal reaction time and temperature, fourth, the washing process (water, acid, etc.) and the fifth is the calcination conditions (temperature, time etc.). For instance, the hydrothermal reaction temperature determines the formation nanosphere or nanotube form of TiO₂. The SEM images of commercial and nanotube TiO₂ were given in Figure 1.

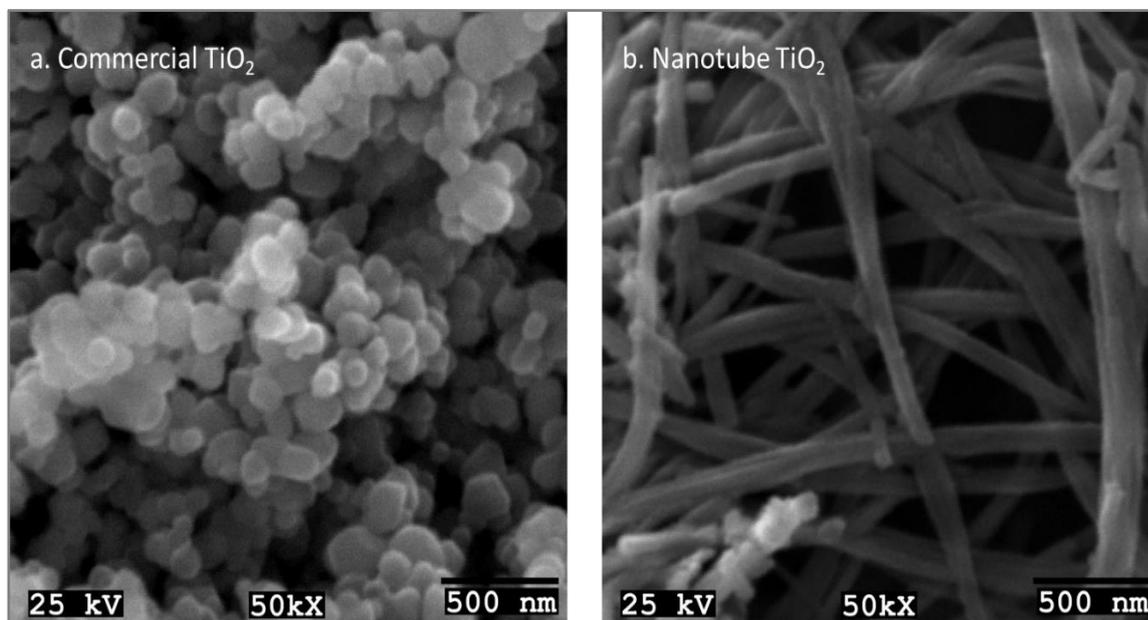


Figure 1. SEM images of a) commercial and b) prepared nanotube TiO₂

As seen in Figure 1., the nanotubes were produced successfully by chemical treatment of commercial TiO₂. At the end of the process, partially agglomerated nanotubes with diameters between 10 to 20 nm, not homogeneous in length (100-500 nm) but compatible with the literature (Guo, Wang, & He, 2016) were obtained. In Figure 2., the change in pore distribution and consequently the total surface area of commercial and nanotubes are shown.

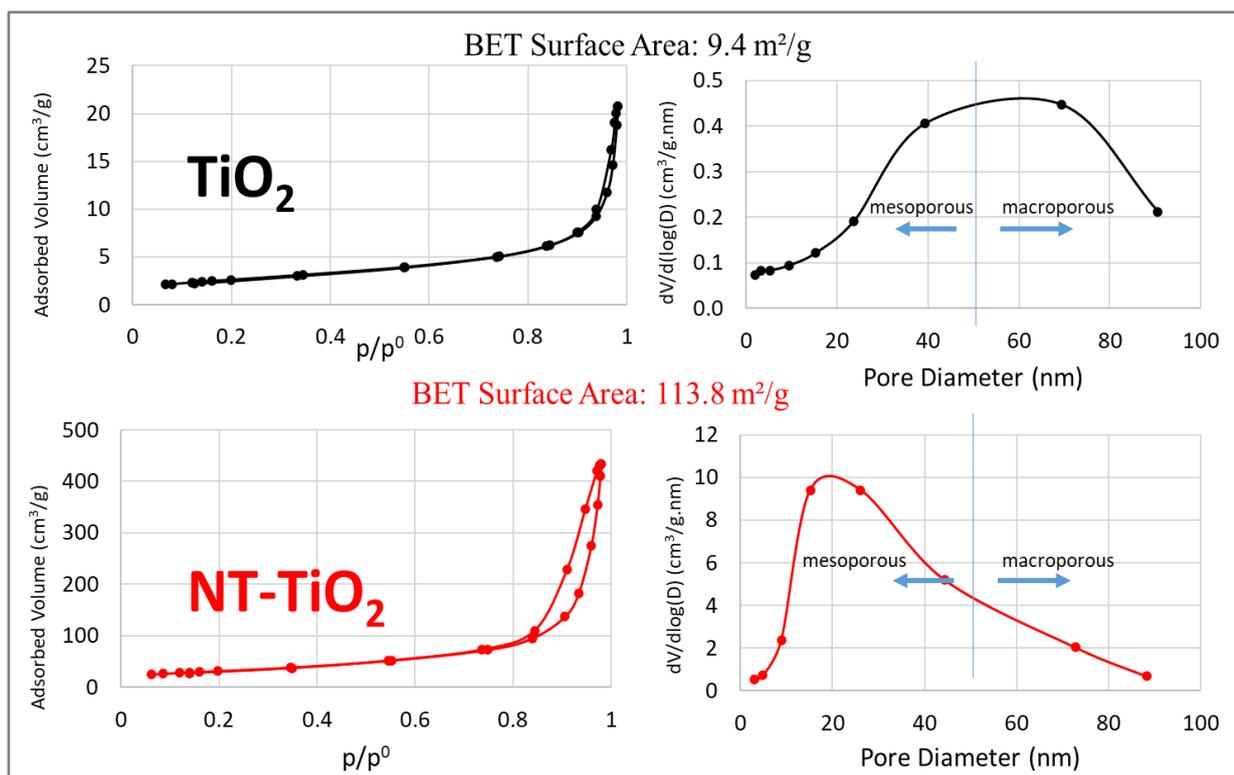


Figure 2. Adsorption-desorption isotherms, pore volume distribution and total surface area values of commercial and prepared NanoTube-TiO₂

According to Figure 2., nanotubes with a high surface area of 113.8 m²/g were produced by modifying the morphological properties. At the same time, the synthesis parameters allowed the formation of a mesoporous structure from the macroporous structure. Adsorption-desorption isotherms of nanotubes are typically Type II with H3 hysteresis loop. Thus, as expected, nanotubes with a morphological property of plate like were obtained by chemical methods. As a result, mesoporous nanotubes with increased surface area were efficiently prepared to be used for decoloring of methylene blue solution. As mentioned before, TiO₂ is active in ultra violet region. The use of colored TiO₂ is important to overcome this limitation that the catalyst can absorb energy including the visible region and increase the efficiency of electron transfer. Due to the obtained results, major problems in providing homogeneous coloration revealed the need to investigate alternative methods of coloring TiO₂. It has been observed that the most prominent method among the possible methods in the literature also given is the use of NaBH₄ according to its high reduction capacity. In Figure 3., the photographs of colored commercial TiO₂ were given for 1.25 (mol/mol) molar ratio with different heating rates and cooling time.

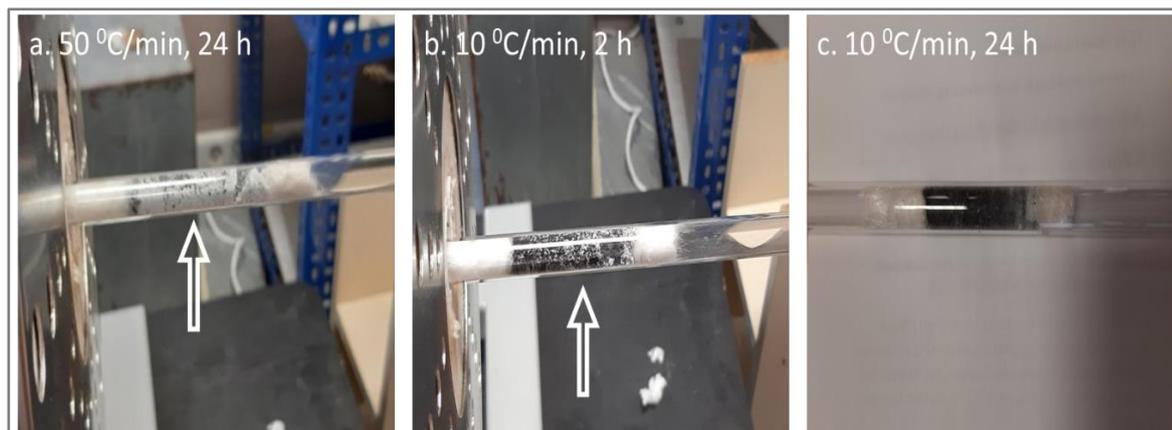


Figure 3. Coloring of commercial TiO_2 at $400\text{ }^\circ\text{C}$ by thermal decomposition of NaBH_4

As seen in Figure 3.a., heterogeneously colored catalyst was obtained while the heating rate was high. Coloring efficiency was also very low and mostly the catalyst was white. It was observed that commercial TiO_2 turned into a very high amount of black color by decreasing the heating rate, but in this sample with limited cooling time, homogeneity (Figure 3.b.) could not be achieved completely. Also, this catalyst started to burn while it was taken out from the reactor by the contact with oxygen. Therefore, it has been concluded that besides the cooling time, it is necessary to remove the hydrogen from the environment, which is released by thermal decomposition of sodium borohydride that was not used for reduction of TiO_2 . The homogeneous and black TiO_2 was obtained where the heating rate was slow, cooling and sweeping period was long (Figure 3.c.). Coloring studies have been done with the optimized conditions on nanotube TiO_2 catalysts, and in Figure 4, photographs of catalysts prepared with different nanotube- TiO_2 / NaBH_4 (mol / mol) ratios are given.

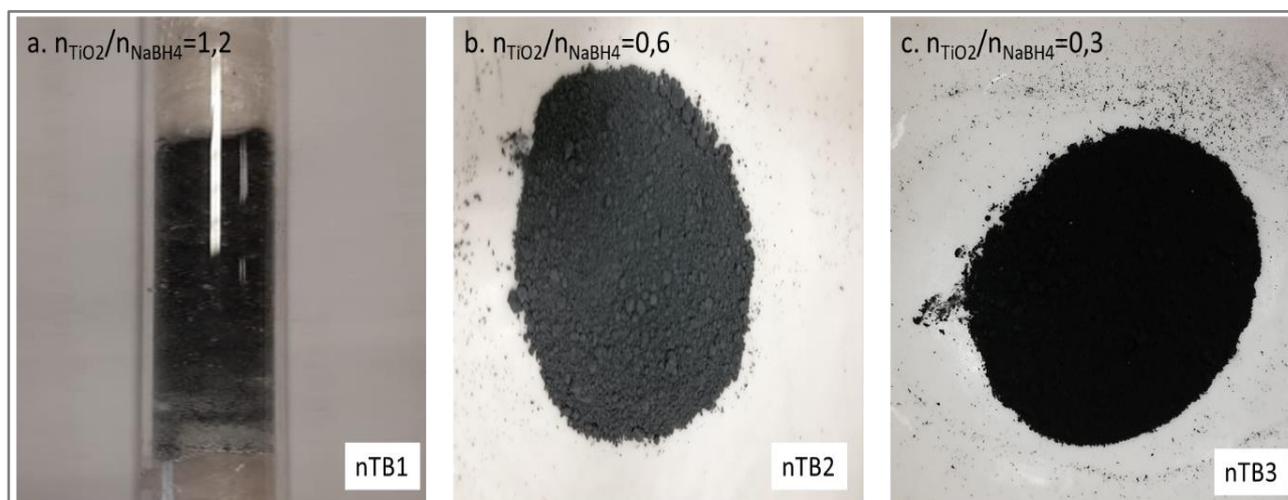


Figure 4. Effect of NaBH_4 amount on nanotube TiO_2 coloring

As given in Figure 4.a and 4.b, the catalysts were homogeneous and the color of them were dark gray. While the maximum amount of NaBH_4 was used to prepare the catalyst, black and homogeneous catalyst was obtained (Figure 4.c.). Thus, by means of NaBH_4 , the heterogeneity in the reduction process with hydrogen was prevented and homogeneous catalysts in the gray-black color range were prepared.

In Figure 5, XRD spectra of commercial, nanotube and black nanotube of TiO_2 were given.

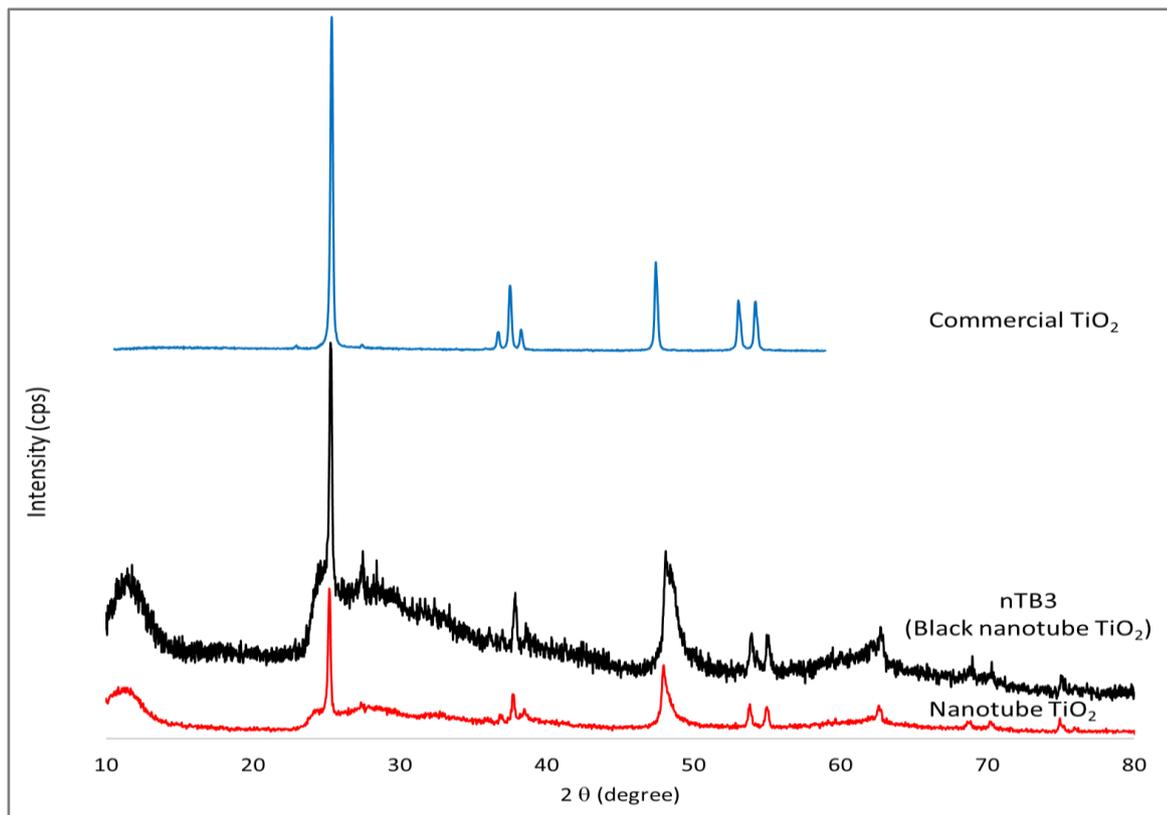


Figure 5. XRD spectra of commercial, nanotube and black nanotube TiO₂ catalysts

XRD spectra of the catalysts exhibit that the crystalline phase is anatase for all with PDF No. 99-101-0957. Additional peaks were observed for nTB3 (black nanotube TiO₂) at the angles 27° and 28° which was attributed to the deformation of the lattice due to hydrogen atoms from NaBH₄ and which is also used for the reduction of Ti⁺⁴ to Ti⁺³ (Ariyanti, Mills, Dong, Yao, & Gao, 2017). To observe the effects of blackening process on total surface area and pore size distribution, the results are given in Figure 6.

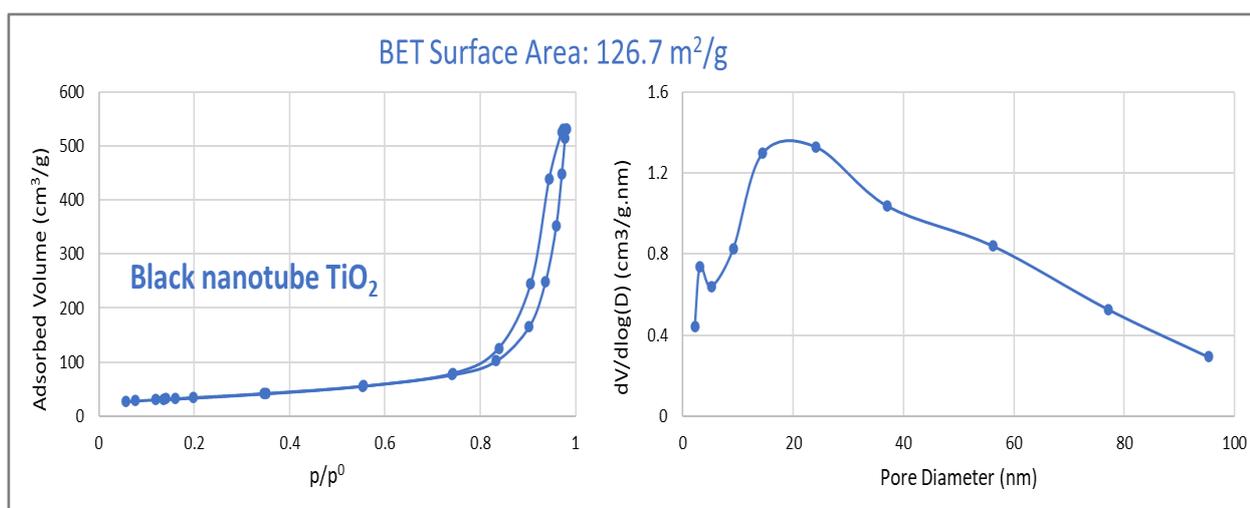


Figure 6. Adsorption-desorption isotherms, pore size distribution and total surface area values of black NanoTube-TiO₂

After blackening the nanotube TiO_2 , total surface area of the sample is almost constant. A little increase on total surface area is probably due to creation of some pores during the thermal degradation of NaBH_4 where some pore formations are observed at narrower pore ranges from pore size distribution results compared to the white nanotubes. Adsorption-desorption isotherms of black nanotubes exhibit typically Type II with H3 hysteresis loop as obtained for prepared nanotubes TiO_2 . In Figure 7., the ESEM results are given to investigate the microstructure of the of black TiO_2 .

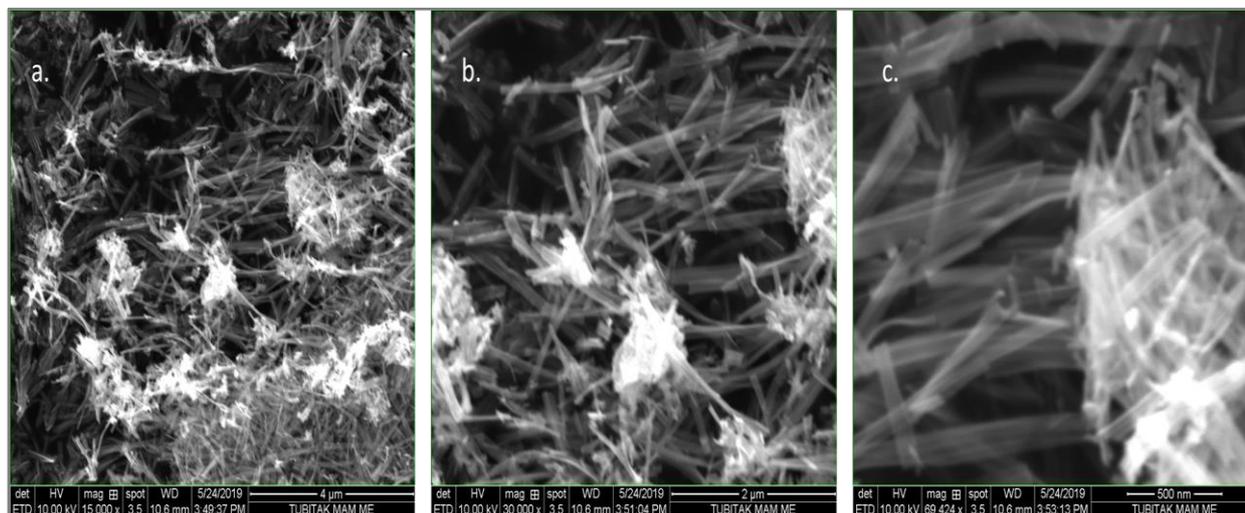


Figure 7. ESEM images of black TiO_2 a) $4\mu\text{m}$, b) $2\mu\text{m}$ and c) 500 nm

Although agglomeration was observed, the similar shapes and size of nanotubes were obtained after blackening process. This result shows that the role of NaBH_4 is to lead the formation of oxygen vacancies in the nanotubes by keeping the morphology similar that overlap with the XRD results.

The prepared photocatalysts were performed on degradation of methylene blue and in Table 2., the removal yields were given for methylene blue where the energy source was daylight.

Table 2

Color removal efficiency

Catalyst	Catalyst color and appearance	Removal Yield (%)
Commercial TiO_2	White-Homogeneous	83.7
*Commercial TiO_2	White-Homogeneous	88.6
TB1	White-Black-Heterogeneous	91.2
TB2	White-Black-Heterogeneous	93.1
TB3	Black- Homogeneous	93.7
Nanotube TiO_2	White- Homogeneous	95.6
*Nanotube TiO_2	White- Homogeneous	96.8
nTB1	Dark Gray- Homogeneous	97.9
nTB2	Dark Gray- Homogeneous	97.9
nTB3	Black- Homogeneous	98.4

*: Blank experiments at UV-C (254 nm)

When the activity test results are examined, the superiority of the prepared nanotubes over the commercial one is revealed. Although homogeneity was not achieved in commercial TiO_2 , the coloring process worked and a catalyst with increased activity under visible light was prepared. The high performance of colored catalysts are the result of enhancement of daylight absorption capacity of the catalysts. Colored catalysts used the low energy from daylight to excite the electrons in the structure. Photocatalysts were obtained homogeneously in all nanotube coloring studies. When the amount of NaBH_4 is limited, gray catalysts were prepared. Under all

conditions, the simultaneous coloration of nanotubes and color removal where the sign of methylene blue degradation have ensured that the process is completed with high efficiency. Maximum removal yield, 98.4%, was obtained with black nanotube TiO₂ catalyst.

4. Conclusion

In the nanotube preparation process, the transition from macroporous structure to mesoporous structure has increased the retention of solar energy on the surface and act as a trap for the energy absorption. Thus, the beam hitting the surface was refracted many times, the distance it traveled was extended and the retention time of the beam was increased. Photocatalysts could not be colored homogeneously with the hydrogen reduction process but efficient reduction and coloration obtained with sodium borohydride. In addition to coloring, it has been observed that the surface structure has an important role in activity and the nanotube structure has an important place in the preparation of photocatalysts. The photoactivity in the visible area is increased with colored photocatalysts with increased sunlight absorption capacity. As a result highly active photocatalysts were prepared by thermal decomposition of sodium borohydride with increased beam absorption capacity.

Acknowledgement

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Conflicts of Interest

The author declare no conflict of interest.

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