Characterization and Comparison of Photocatalytic Activity Silver Ion doped on TiO$_2$(TiO$_2$/Ag$^+$) and Silver Ion doped on Black TiO$_2$(Black TiO$_2$/Ag$^+$)

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Abstract. Titanium dioxide (TiO$_2$) is one of the representative ceramic materials containing photocatalyst, optic and antibacterial activity. The hydroxyl radical in TiO$_2$ applies to the intensive oxidizing agent, hence TiO$_2$ is suitable to use photocatalytic materials. Black TiO$_2$ was prepared through reduction of amorphous TiO$_2$ conducting under H$_2$ which leads to color changes. Its black color is proven that absorbs 100% light across the whole-visible light, drawing enhancement of photocatalytic property. In this study, we aimed to compare the photocatalytic activity of silver ion doped on TiO$_2$(TiO$_2$/Ag$^+$) and silver ion doped on black TiO$_2$(black TiO$_2$/Ag$^+$) under visible light range. TiO$_2$/Ag$^+$ was fabricated following steps. 1) TiO$_2$ was synthesized by a sol-gel method from Titanium tetraisopropoxide (TTIP). 2) Then AgNO$_3$ was added during an aging process step for silver ion doping on the surface of TiO$_2$. Moreover, Black TiO$_2$/Ag$^+$ was obtained same as TiO$_2$/Ag$^+$ except for calcination under H$_2$. The samples were characterized X-ray diffraction (XRD), UV-visible reflectance (UV-vis DRS), and Methylene Blue degradation test. XRD analysis confirmed morphology of TiO$_2$. The band gap of black TiO$_2$/Ag$^+$ was confirmed (2.6 eV) through UV-vis DRS, which was lower than TiO$_2$/Ag$^+$ (2.9 eV). The photocatalytic effect was conducted by methylene blue degradation test. It demonstrated that black TiO$_2$/Ag$^+$ had a photocatalytic effect under UV light also visible light.

1. Introduction
The Sol-gel synthesis method is one of the suitable methods for producing metal oxides having better purity and uniformity under specific conditions. In this synthesis method, necessary nanoparticles can be produced by a relatively simple method and synthesis can be performed even at a low temperature. Among the metal oxides obtained by this synthesis method, Titanium dioxide has optical effects,
photocatalyst, antibacterial effect, etc. as one of the typical ceramic materials commonly used. It has a particularly excellent photocatalytic effect, but synthesizes superoxide anion and hydroxy radical which are activated by ultraviolet light and have high oxidizing power [1,3]. TiO$_2$ which is a semiconductor material having a strong oxidizing power has three forms of rutile, anatase and brookite, and generally has a band gap of 3.0 eV. In order to lower the band gap of TiO$_2$, which has a high oxidizing power and a relatively large band gap energy, in this study, after synthesis by the same method, one is the general atmospheric atmosphere, and calcined in an H$_2$ gas atmosphere [2,3]. TiO$_2$ calcined in a hydrogen atmosphere draws black, unlike general TiO$_2$. Since black absorbs light, unlike white TiO$_2$ which is not good in the visible light region, it can be seen in the hope that it will absorb light in the visible light region to produce photocatalytic effect [4,5].

2. **Experimentals**

2.1. **Materials**
Titanium tetra-isopropoxide (TTIP) and Silver nitrate were purchased from Sigma-Aldrich (97%). Isopropyl alcohol was bought from Junsei Co. Ltd, Japan. Polyethylene glycol 600 (PEG 600) were procured from Daejung Chemical and Material Co Ltd, South Korea. The solution of 0.5 M Nitric acid (Daejung) was prepared by dissolving concentrated nitric acid in deionized (DI) water.

2.2. **Synthesis of Ag-doped TiO$_2$**
Ag-doped TiO$_2$ was synthesized using one-step sol-gel method process from TTIP. As following these steps: A basis solution was prepared by dispersing 2.0 g of PEG in 120 ml of Isopropyl alcohol. Then, 20 ml of TTIP was mixed with the basic solution using magnetic stirrer for 1 h, on 60 °C. The mixed solution was titrated with 0.5 M HNO$_3$ to pH 1,3,5 and 7 as well as the temperature was maintained. After titration, an Ag solution (0.2 M) that silver nitrate was dispersed in DI water was added to the titrated composite. And the composite was aged under constant stirring and heating for 6 h, keeping temperature. The aged composite was filtered by DI water and Ethanol for 3 times using an aspirator. The filtered composite was dried at 70 °C. Finally, the obtained powder was calcined at 550 °C for 2 h using tube furnace. An Ag-doped black TiO$_2$ was obtained from general Ag-doped TiO$_2$. The fabricating method significantly similar to the previous process except for final step. The substance which after drying was calcined at 550 °C for 2 h in the H$_2$ atmosphere. This powder was modified from white to black (Figure 1).

2.3. **Photodegradation of Methylene blue**
The photocatalytic activities of calcined Ag-doped TiO$_2$ and Ag-doped black TiO$_2$ was evaluated by measuring degradation rates of Methylene blue. A certain amount of sample was placed in a methylene blue aqueous solution (100 ml), and then light was irradiated with a halogen lamp. From the initial methylene blue solution, Absorbance was measured using a UV-visible instrument at intervals of 30 minutes.

2.4. **Characterization**
The acquired material was characterized via a X-ray diffraction (XRD, Rigaku D/MAX-2500/PC) to decide crystallinity. The XRD was measured by using Cu Kα radiation in the 20 range from 20° to 80 ° with a scanning rate of 4°/min. The Photocatalytic activity was confirmed through Methylene blue degradation. Lastly, it was able to calculate the band gap energy of synthesized nanoparticles from UV-vis diffuse reflectance spectroscopy (UV-vis DRS).
Figure 1. This flow chart showed synthesis method of two types Ag-TiO₂.

3. Results

3.1. Crystal structure and morphology
Through a series of experimental processes, White Ag-doped TiO₂ and black Ag-doped TiO₂ were synthesized. In Figure 2 you can see the nanopowder made from other colors. Nanoparticles synthesized under general air conditions showed white, and nanoparticles calcined in H₂ atmosphere gave black. As a result of measurement at these speeds of 4 ° per minute at a rate of 20 ° to 80 ° for structural analysis, the Anathase shape such as 550 ° C, whichever is lower, 1, 3, etc., the black Ag - TiO₂ is rutile day Anathase shape was shown. The higher the value of pH, the higher the percentage of rutile was shown. The crystallite size of particles through Scherrer equation is on average 13 - 15 nm for white TiO₂ and
black TiO$_2$ about 31 - 35 nm in size. And also, it can be confirmed through Figure 3.

![Image](a) white TiO$_2$/Ag$^+$, and (b) black TiO$_2$/Ag$^+$

![Image]

Figure 2. (a) white TiO$_2$/Ag$^+$, and (b) black TiO$_2$/Ag$^+$

Figure 3. XRD analysis of Ag doped on TiO$_2$: (A) calcined at 550 ℃, and (b) 550 ℃ in H$_2$ atmosphere

3.2. Photocatalytic studies

In order to investigate photocatalytic activity, methylene blue decomposition experiment was conducted. Place a specimen to investigate the photocatalytic effect in a solution diluted appropriately with methylene blue and irradiate the light through a light source. (Figure 4), white TiO$_2$ on anatase shows better decomposition reaction than black TiO$_2$. It was confirmed that black TiO$_2$/Ag$^+$ has a photocatalytic activity lower than that of general TiO$_2$/Ag$^+$, but the photocatalytic activity also showed on the surface reduced black TiO$_2$/Ag$^+$. Figure 5 was showed degradation ratio from Figure 4, Although the reduction rate of (b) is gentle compared to (a), you can see that it is a shape that is decreasing compared with the initial stage. Photocatalytic activity can be confirmed also with this black Ag-doped TiO$_2$. 

![Image]
Figure 4. MB degradation analysis of (a) Ag doped TiO$_2$ calcined at 550 °C, and (b) calcined at 550 °C in H$_2$ atmosphere.

3.3. UV-visible diffuse reflectance spectroscopy
The synthesized Ag-doped TiO$_2$ band gap was confirmed via UV-visible diffuse reflectance spectroscopy. Looking at Figure 5 (a), it can be confirmed that they represent pH 1, 3, 5, 7 in order and absorb a small amount of light even in the visible light region. Based on the results of Reflectance, the bandgap energy was calculated using the Kubelka-munk equation. (equation 1, 2).

\[
F(R) = \frac{[(1-R)^2]}{2R} \quad \text{------------------------- (1)}
\]

\[
[F(R)hv]^{\frac{1}{n}} = A(hv - E_g) \quad \text{------------------------- (2)}
\]

- $R$: percentage of reflected light
- $h$: Plank constant ($4.13566733 \times 10^{-15}$ eV·s)
- $v$: Radiation frequency
- $E_g$: Bandgap
- $A$: Constant
- $n$: indirent bandgap = 2, direct bandgap=1/2
- $\lambda$: Wavelength
- $c$: Light velocity (3.0×10$^8$ m/s)
Figure 5. UV-vis DRS analysis of Ag doped TiO$_2$. (a) calcined at 550 C, (b) calcined at 550 C in H$_2$ atmosphere.

4. Conclusion

TiO$_2$/Ag$^+$ is one of the well-known ceramic materials for the photocatalytic activity. We synthesized TiO$_2$/Ag$^+$ with general TiO$_2$/Ag$^+$ (white TiO$_2$/Ag$^+$) and black TiO$_2$/Ag$^+$ to confirm the characteristics. Black TiO$_2$/Ag$^+$ shows the black part as the part of the table is reduced. In general, black TiO$_2$/Ag$^+$ has anatase and rutile mixed phase. In the degradation experiment of methylene blue, both photocatalytic activities of TiO$_2$/Ag$^+$ were shown. As a result, the white TiO$_2$/Ag$^+$ showed better photocatalytic characteristics, but the black TiO$_2$/Ag$^+$ absorbs light even in the visible light range.

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