NI-DOPED TiO₂ THIN FILM FOR PHOTO DEGRADATION OF METHYLENE BLUE BY SOL-GEL ELECTROPHORESIS DEPOSITION

Yoshiki kurokawa¹, Dang Trang Nguyen², Kozo Taguchi³

¹,²,³ Ritsumeikan University, Department of Science and Engineering, Kusatsu, Japan

Email: re0057kp@ed.ritsumei.ac.jp

https://doi.org/10.26782/jmcms.spl.9/2020.05.00019

Abstract

Titanium oxide (TiO₂) is used as photocatalyst. It has wide band gap of 3.2eV, so it can absorb only ultraviolet light. In this paper, we tried to make visible light response for TiO₂ by doping Ni using Sol-Gel method. For photocatalyst experiments (methylene blue degradation), we made some sample types from handmade TiO₂ powder, handmade Ni-doped TiO₂ powder, and commercially TiO₂ powder (P25). Based on experimental results, the Ni-doped powder mixed with P25 powder can absorb the low range of visible light, as a result, it achieved highest methylene blue degradation ability.

Keywords: Photocatalyst, Ni-doped TiO₂ powder, Sol-Gel method, Electrophoresis deposition

I. Introduction

In the 1970s, Honda and Fujishima discovered water was decomposed into oxygen and hydrogen by irradiating light to a titanium dioxide (TiO₂) electrode. This is called Honda & Fujisima effect. Research in this field has been developed rapidly and has become a boom in photocatalyst research. It turned out that it can be applied to the degradation of organic matter in the 1980s [I], [II], [III]. The working principle of photocatalyst is as follows; when the photocatalyst is irradiated by light having energy higher than the energy band-gap, electrons in the valence band are excited to the migrate to the conduction band. At this time, electrons are present in the conduction band, and holes that are scavenges of electrons are generated in the valence band. Hole has a strong oxidizing power and takes away electrons from OH⁻ (hydroxide ion). OH⁻ deprived of electrons becomes an OH radical in an unstable state. It has a strong oxidizing power and deprives electrons from nearby organic matter. Then, it becomes stable condition. The organic matter deprived electrons break the bond and causes a degradation reaction. In this way, organic matter degradation occurs by the photocatalyst as shown in Fig 1 [IV], [V], [VI]. Various materials such as tungsten oxide (WO₃), zinc oxide (ZnO), zinc sulfide (ZnS) can also be used as the photocatalyst. Among them, TiO₂ is most used as a photocatalyst.
It is widely used substance in familiar products such as cosmetics and rubber. It has three crystal forms (Rutile, Anatase, Brookite). Rutile is generally used for white pigment, food additives, and anatase is used as a photocatalyst because of its large specific surface area. Brookite is not used for industrial purposes but is used for research purposes. TiO$_2$ has four characteristics (1) it is very stable physically and chemically, (2) High photocatalytic activity, (3) non-toxic and environmentally friendly, and (4) low price [VIII], [IX]. The light is an important element in the photocatalytic reaction. Sunlight is the light which we can easily use and exists infinitely. The light reaching the ground from the sun contains 290 nm to 4000 nm wavelength ray. The range from 100 nm to 400 nm wavelength light is called ultraviolet light (UV light), from 400 nm to 800 nm wavelength light are called visible light. TiO$_2$ used as a photocatalyst has 3.2 eV band gap, so light having a wavelength shorter than 380 nm is required for photocatalytic activity (Eq (1)). However, sunlight contains only about 5% of ultraviolet light and research for effective use of sunlight is necessary [X]. Furthermore, most of the light emitted from light sources used in everyday life, such as fluorescent lamps and incandescent bulbs, is visible light. Therefore, it is difficult to use titanium oxide in everyday life. In order to solve this problem, doping elements to TiO$_2$ by a sol-gel method has been paid attention. Sol-gel method is one of the methods used for manufacturing thin films and powder catalysts. This method is a method used to adjust the TiO$_2$ based photocatalyst because it can produce low cost, simplicity, high purity. Easily doping is possible for substances with changes in the combination of sol solutions. Doped materials broaden the operation of photocatalysts. Doping a noble metal is effective for improving the photocatalyst, but it is not practical because of rare and high-cost materials. Therefore, doping of transition metals such as Fe, Ni, Cu and the like has attracted attention. Among them, nickel has some characteristics, such as resistance to corrosion and oxidation, easy to alloy, coverable by electroplating, catalyst characteristics. Therefore, study of Ni doped TiO$_2$ thin film for photocatalyst is highly necessary [XI], [XII].

In this study, a photocatalyst nickel doped TiO$_2$ powder was developed by sol-gel method and we try to realize visible light response of TiO$_2$. We fabricated photocatalyst TiO$_2$ thin films in combination with handmade powder (No doped sol-gel powder (SP) and Ni doped sol-gel powder (Ni-SP)) and commercially available TiO$_2$ powders (P25) for improving the photocatalytic reaction. Five thin films were prepared: P25, SP, Ni-SP, P25 + SP, P25 + Ni-SP. The characteristics of the powder and thin films were evaluated by Scanning Electron Microscope (SEM), X-ray diffraction (XRD) and UV-vis spectrophotometer. Furthermore, photocatalytic reaction was evaluated through methylene blue (MB) degradation under UV light with a little visible light.

$$\lambda = \frac{1240}{E_g}$$  \hspace{2cm} (1)
II. Experiment Method

II.i. How to Make Titanium Sol-Gel Powder (SP) and Ni-Doped Titanium Sol-Gel Powder (Ni-SP)

We mixed titanium tetraispropoxide (TTIP) (6ml), ethanol (20mL) and water (1mL) in a plastic vessel using a magnetic stirrer (ASONE, RS-6DN) rotating at speed of 500 rpm for 1 hour. In case of making of Ni-doped Titanium Sol-Gel Powder, nickel nitrate (Ni(NO$_3$)$_2$·6H$_2$O) (0.01mol) was added to Sol as nickel source. Then the mixed sol was dried at 100°C for about 3 hours and moved to plastic bottle because of stirring to make small powder. After making small powder, it was annealed at 650°C for 1 hour to crystallize powder. So, we obtained titanium sol-gel powder and Ni-doped sol-gel powder [XIII].

II.ii. How to Make Titanium Thin Film by Electrophoresis Deposition

To do electrophoresis deposition (EPD), we mixed some materials shown in Table 1 using magnetic stirrer (ASONE, RS-6DN) rotating at speed of 700rpm for 1 hour. EPD has been used as a method for decorating ceramic because it is easy to prepare a dense film. This method is based on particles in EPD solution charged positively or negatively. Positively charged particles will move to the anode. In contrast, negatively charged particles will move to the cathode. Through experiments, it has been confirmed that the TiO$_2$ particles are positively charged and move in the negative direction due to the electric field as shown in Fig. 2. EPD method has advantages of low cost, short deposition time and high reproducibility. EPD is usually used in biochemistry field. For example, separation of protein deoxyribonucleic acid (DNA).Fig 3.shows EPD device. For EPD setting, aluminum plate (20×20×1mm) was used as EPD anode electrode and fluorine doped SnO$_2$ coated glassed (FTO) was used as EPD cathode electrode with a distance of 10mm
fixed by silicon plate. EPD current from current source (AVDANTEST, R6144) was set at 0.12mA and EPD time was set at 100 second. After EPD process, fabricated TiO₂ thin film was annealed by an electric furnace (ASONE,SMF-1) at 400℃ for 1 hour.

Table 1: EPD materials

| sample     | Powder      | Solution   |
|------------|-------------|------------|
| P25        | P25 0.1g    | EtOH 20mL  |
| SP         | SP 0.2g     | EtOH 20mL  |
| Ni-SP      | Ni-SP 0.2g  | EtOH 20mL  |
| P25+SP     | P25 0.1g, SP 0.02g | EtOH 20mL |
| P25+Ni-SP  | P25 0.1g, Ni-SP 0.02g | EtOH 20mL |

Fig. 2: How to move particles

Fig. 3: EPD device
II.iii. Measurement

Fabricated TiO$_2$ thin films (10×20mm) were measured by Scanning Electron Microscope (SEM) (HITACHI, S4300), X-ray diffraction (XRD) (PAnalytical) and spectrophotometer (SHIMADZU, UV-3600). SEM was used to observe the sol-gel powder and particle condition. The XRD pattern was used to measure crystalline morphology and microstructures of obtained powder. In this measurement, it was confirmed that titanium oxide was doped. Spectrophotometer was used to measure the transmittance and reflectance of the thin films. The photodegradation activities were determined by methylene blue (MB) degradation under UV light (TOSHIBA, FL20S-BL). The MB test is used widely as an effective method for the determination of the photocatalytic activity of photocatalyst materials. This experiment was carried out in a dark room space. Used UV lamp has ultraviolet light and slight visible light (400-500 nm). MB is a dye for coloring cloth, cell nuclei and blood corpuscle. In this study, it was used as a model of stain. The initial concentration of MB was 1.0×10^{-5} M. Plastic case was filled with 5ml MB and the TiO$_2$ thin films were lay inside as shown as Fig. 4. The TiO$_2$ thin films were illuminated by the UV lamp keeping distance of 5cm. After illumination, MB solution color became lighter. After every hour, we took out 1 ml MB solution for measurement by a spectrophotometer (measured at $\lambda_{\text{max}}$=664nm). After the measurement, we returned the taken-out MB solution to the plastic case. We repeated the measurement six times in total, and the MB decomposition rate was obtained from the measurement. Absorbance was calculated using the following equation (Eq. (2)).

\[
\text{Absorbance (abs)} = \ln \left( \frac{T_0}{T_t} \right)
\]

(Where, $T_0$: Initial Transmittance and $T_t$: Transmittance at time)

Fig. 4: Measurement setup of MB degradation (left; before light irradiation, right; after light irradiation)
III. Results and Discussion

III.i. SEM (Scanning Electron Microscope)

We observed the handmade sol-gel powder (SP) by SEM as shown in Fig. 5. It can be seen that the particle diameter is about 100 nm and handmade particles are in a roughly round condition. The particle diameter of commercially available P25 powder is about 20 nm, so the sol-gel powder is about 5 times as large as P25 powder. It is thought that the large particle has an influence on the photocatalytic reaction, and the photocatalytic ability improvement will be studied by only SP and a combination with P25.

![SEM image of Sol-Gel](image)

Fig. 5: SEM image of Sol-Gel

III.ii. XRD (X-Ray-Diffraction)

We analyzed five types of powders using XRD. These powders were annealed in an electric furnace at 450°C for 1 hour. Fig. 6 depicts XRD pattern of five samples. Each sample has strong peaks of the anatase crystals at 25.27°, 37.76°, 38.56°, 48.05°, 53.88°, 55.0°, 62.1°, 68.7°, 70.3°, 75.1°. Furthermore, two samples containing Ni-SP (Ni-SP and P25 + Ni-SP) have other peaks compared with TiO₂ (P25, and SP). Based on the analysis, it turned out that they contain TiNiO₃ (Nickel TiO₂) (peaks at 33.1°, 49.4°). Based on the quantitative analysis, Ni-SP contains 14% TiNiO₃ and P25+Ni-SP contain 10% TiNiO₃. This is the evidence of that TiO₂ can be doped with nickel by the sol-gel method. This handmade powder can be expected to improve the photocatalytic reaction.
III.iii. Absorption Spectrophotometer

Fig. 6: X-ray diffraction of P25, SP, P25+SP, P25+Ni-SP and Ni-SP

![X-ray diffraction](image)

Fig. 7: UV-visible absorbance spectra of P25, SP, P25+SP, Ni-SP, P25+Ni-SP

![UV-visible absorbance spectra](image)
Fig. 8: Photocatalytic degradation of Methylene blue dye in the presence of (a) P25, (b) SP, (c) Ni SP, (d) P25+SP, (e) P25+Ni SP, (f) absorbance of methylene blue when the light irradiation time is 6 hours.

We measured the absorptivity of fabricated TiO$_2$ thin films using a spectrophotometer. Fig. 7 shows the absorptivity of the TiO$_2$ thin film from 300 nm to 500 nm wavelength light. From Fig. 7, three types of thin films (P25, SP, P25 + SP) without Ni doping absorb light of wavelength shorter than 400 nm wavelength, but hardly absorb light of wavelength longer than 400 nm. Regardless of with SP or without SP, it became clear that there was almost no change in the crystal properties of TiO$_2$ in three kinds. Two kinds of TiO$_2$ thin films containing Ni-doped SP (Ni-SP, P25 + Ni-SP) absorb UV light and further absorb visible light in 400 nm to 500 nm wavelength. TiNiO$_3$ in Ni-SP is more than TiNiO$_3$ in P25 + Ni-SP, so it is considered...
that Ni-SP absorptivity of light of 400 to 500 nm wavelength is higher than that of P25 + Ni-SP. Thus, produced Ni-SP can change the light absorptive property of TiO$_2$, that is considered to contribute greatly to the photocatalyst under sunlight.

Figure 8. Photocatalytic degradation of Methylene blue dye in the presence of (a) P25, (b) SP, (c) Ni SP, (d) P25+SP, (e) P25+Ni SP, (f) absorbance of methylene blue when the light irradiation time is 6 hours

Fig. 8 shows the results of MB absorbance (from 400nm to 800 nm wavelength light) and MB degradation rate. MB solution was measured every hour for a total of 6 hours. Fig. 8 (a) - (e) were calculated using equation (2). The light we used was an UV lamp containing ultraviolet light and a little visible light. Regarding others four samples, it is also confirmed that MB is decomposed by light irradiation due to decrease in absorbance in (b) to (e). Fig. 8 (f) shows the absorbance of methylene blue when the light irradiation time is 6 hours. It can be seen that after 6 hours of irradiation, the two samples (P25 and P25+Ni SP) recorded lower absorbance. So, obviously, these samples have relatively high degradation ability. Fig. 9 shows MB degradation rate and light irradiation time (1 to 6 hours) by handmade five TiO$_2$ thin films. MB degradation was obtained from the ratio of the absorbance of maximum absorption wavelength (664nm). In case of measurement of P25, it showed 62.31% MB degradation after 6 hours light irradiation. This value is base value. P25 + Ni-SP showed 68.84% MB degradation after 6 hours light irradiation, which was the maximum degradation value in five samples. Furthermore, only this sample recorded higher degradation than P25 thin film. After light irradiation for 6 hours, Fig. 8 (g) showed degradation rate of 51.11% for SP, 47.83% for Ni-SP, and 55.13% for P25 + SP, respectively, indicating a MB degradation amount lower than P25. As a result, it was found that a small amount of Ni-SP improves the original photocatalytic capability of P25. It is thought that the photocatalyst function was improved by absorption of light having a wavelength of about 400-500 nm which P25 does not originally own (Fig. 7).

![Fig. 9: The variation of photocatalytic degradation rate of MB dye under exposure](image)

**IV. Conclusion**

*Copyright reserved © J. Mech. Cont.& Math. Sci.*
*Yoshiki kurokawa et al*
In this paper, we prepared a Ni-doped TiO₂ powder by sol-gel method and tried to apply it to photocatalytic reaction. Originally, TiO₂ only has the UV light absorbing property. The produced nickel-doped powder (Ni-SP) contained 14% Ni-doped TiO₂, but it has large particle diameter (100nm). The nickel-doped powder changed the absorptive property of commercially available TiO₂ powder (P25) and succeeded absorbing a narrow band of visible light (400 nm to 500 nm). The Ni-SP thin film recorded the lowest degradation ability, but the thin film containing a small amount of Ni-SP (P25 + Ni-SP) showed the highest degradation ability. It was confirmed that Ni-SP changed the absorption characteristics of the TiO₂ powder (P25) and enhanced the photocatalytic activity of P25. The doped powder can increase possibility of daily use of the photocatalytic reaction of TiO₂. In the future we will try to further reduce the particle size of the produced powder.

V. Acknowledgment

The authors wish to thank to Minemoto laboratory of Ritsumeikan University. We got to use XRD (PANalytical), step gauge (BRUKER DektakXT) and spectrophotometer (SHIMADZU, UV-3600) from Minemoto laboratory.

References

I. Ahmed (2012). Synthesis and structural features of mesoporousNiO/TiO2 nanocomposites prepared by sol–gel method for photodegradation of MB dye. Journal of Photochemistry and Photobiology A: Chemistry 238, 63–70

II. Ali SepharShikoh, Zubair Ahmad, FaridTouati, R.A. Shakoor, Shaheen A. Al-Muhtaseb (2017). Optimization of ITO glass/TiO2 based DSSC photo-anodes through electrophoretic deposition and sintering techniques. Ceramics International 43, 10540–10545

III. Guoguang Liu, Xuezhi Zhang, YajieXu, XinshuNiu, LiqingZheng, Xuejun Ding (2005). The preparation of Zn2+-doped TiO2 nanoparticles by sol–gel and solid phase reaction methods respectively and their photocatalytic activities. Chemosphere 59, 1367–1371

IV. Ho Chang, Hung-Ting Su, Wei-An Chen, K. David Huang, Shu-HuaChien, Sih-Li Chen, Chih-Chieh Chen (2010). Fabrication of multilayer TiO2 thin films for dye-sensitized solar cells with high
conversion efficiency by electrophoresis deposition. Solar Energy 84, 130–136

V. HU Hai, XIAO Wen-jun, YUAN Jian, SHI Jian-wei, CHEN Ming-xi, SHANG GUAN Wen-feng (2007). Preparations of TiO2 film coated on foam nickel substrate by sol-gel processes and its photocatalytic activity for degradation of acetaldehyde. Journal of Environmental Sciences 19, 80–85

VI. Hua Yu, Xin-Jun Li, Shao-Jian Zheng, Wei Xu (2006). Photo-catalytic activity of TiO2 thin film non-uniformly doped by Ni. Materials Chemistry and Physics 97, 59–63

VII. Ibram Ganesh, A. K. Gupta, P. P. Kumar, P. S. C. Sekhar, K. Radha, G. Padmanabham, and G. Sundararajan (2012). Preparation and Characterization of Ni-Doped TiO2 Materials for Photocurrent and Photocatalytic Applications. The Scientific World Journal 1-16

VIII. Jian-Hui Sun, Shu-Ying Dong, Jing-LanFeng, Xiao-Jing Yin, Xiao-Chuan Zhao (2011). Enhanced sunlight photocatalytic performance of Sn-doped ZnO for Methylene Blue degradation. Journal of Molecular Catalysis A: Chemical 335, 145–150

IX. Jixiang Chen, Na Yao, Rijie Wang, Jiyan Zhang (2009). Hydrogenation of chloronitrobenzene to chloroaniline over Ni/TiO2 catalysts prepared by sol–gel method. Chemical Engineering Journal 148, 164–172

XI. K. Pomoni, A. Vomvas, Chr. Trapalis (2008). Electrical conductivity and photoconductivity studies of TiO2 sol–gel thin films and the effect of N-doping. Journal of Non-Crystalline Solids 354, 4448–4457

XII. L.S. Yoong, F.K. Chong, Binay K. Dutta (2009). Development of copper-doped TiO2 photocatalyst for hydrogen production under visible light. Energy 34, 1652–1661

XIII. Larissa Grinis, Snir Dor, Ashi Ofir, Ari Zaban (2008). Electrophoretic deposition and compression of titania nanoparticle films for dye-sensitized solar cells. Journal of Photochemistry and Photobiology A: Chemistry 198, 52–59

XIV. Ludwig Gutzweiler, Tobias Gleichmann1, Laurent Tanguy, Peter Koltay, Roland Zengerle, Lutz Riegger (2017). Open microfluidic gel electrophoresis: Rapid and low cost separation and analysis of DNA at the nanoliter scale. Electrophoresis, 38, 1764–1770