CRYSTAL GROWTH OF TITANIA BY PHOTOCATALYTIC REACTION

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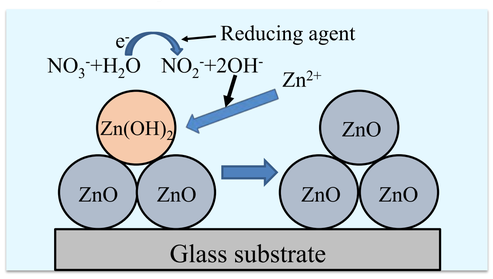
Introduction

Photocatalytic activity can be improved by surface modification and morphology control of original photocatalyst particles. Zinc oxide particles were previously deposited from an aqueous solution of zinc nitrate on a titania thin film by a photocatalytic reaction [1,2]. In this study, titania nanoparticles were also formed from an aqueous solution of titanium (III or IV) chloride containing nitrate ion on a substrate plate with a titania thin film by a photocatalytic reaction.

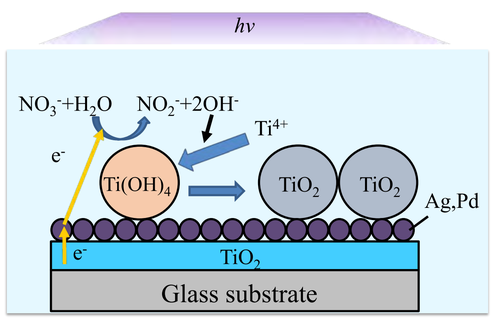
[1] Nagaya, S.; Nishikiori, H. *Chem. Lett.* **2012**, *41*, 993-995.
[2] Nishikiori, H. et al. *Appl. Catal. B: Environ.* **2014**, *160-161*, 651-657.

Preparation method in this study

Previous study



Formation of ZnO by electroless deposition

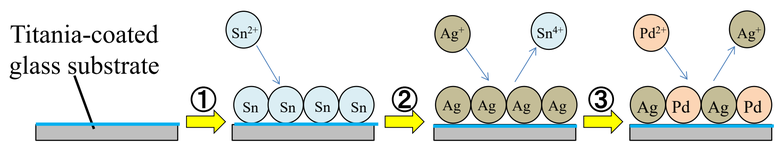


Formation of TiO_2 using photocatalytic reaction

Advantages
- Low temperature
- No requirement of conducting substrates, electrical power, or strong reducing agent.

① $TiO_2 + h\nu \rightarrow TiO_2 + e^- + h^+$
② $NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$
③ $Ti^{4+} + 4OH^- \rightarrow Ti(OH)_4$
④ $Ti(OH)_4 \rightarrow TiO_2 + 2H_2O$

Production of co-catalysts



① Dipping in sensitizer aqueous solution ($SnCl_2$)
Adsorption of Sn^{2+} on glass substrates.

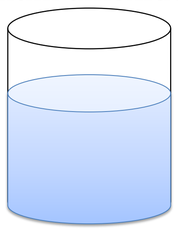
② Dipping in first activator aqueous solution ($AgNO_3$)
$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$
$2Ag^+ + 2e^- \rightarrow 2Ag$

③ Dipping in second activator aqueous solution ($PdCl_2$)
$2Ag^+ \rightarrow 2Ag^+ + 2e^-$
$Pd^{2+} + 2e^- \rightarrow Pd$

Ag and Pd particles were formed on surface as the co-catalysts for the TiO_2 photocatalyst.

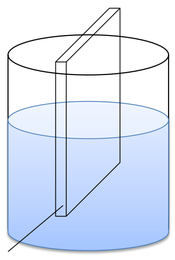
Experimental

①Preparation of titanium alkoxide sol



TTIP	5.0 mL
C_2H_5OH	25.0 mL
Nitric acid(69 %)	0.21 mL
H_2O	0.21 mL

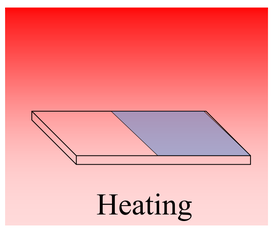
②Dip-coating



Dip-coating 10 times
Lifting speed 160 μm s^{-1}

TTIP = Titanium tetraisopropoxide

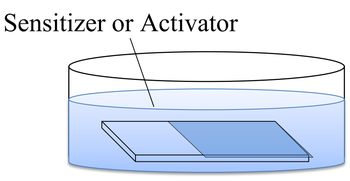
③Heating



Temperature 500ºC
Time 30 min

※Titania film was prepared.

④Preparation of co-catalysts



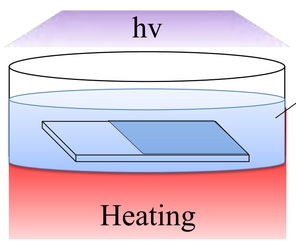
Sensitizer
$SnCl_2$ 1.8 g
HCl (0.1 mol dm^{-3}) 40 mL

First activator
$Zn(NO_3)_2$ 30 mg
H_2O 40 mL

Second activator
$PdCl_2$ 4.2 mg
HCl (0.1 mol dm^{-3}) 40 mL

※Substrates were immersed for 10 min in each solution

⑤Irradiation of UV light



High-pressure mercury lamp
Wavelength Centered at 365 nm
Time 2 or 4 h
Temperature 78±3ºC

Material solution

• $TiCl_3$, $TiCl_4$	5.0 mL
• 1 mol·L^{-1} HCl	18.8 mL
• H_2O	16.2 mL
• $LiNO_3$	1.40 g

<Characterization>
- **XRD analysis**
- **SEM observation**
- **FT-IR (ATR) measurement**

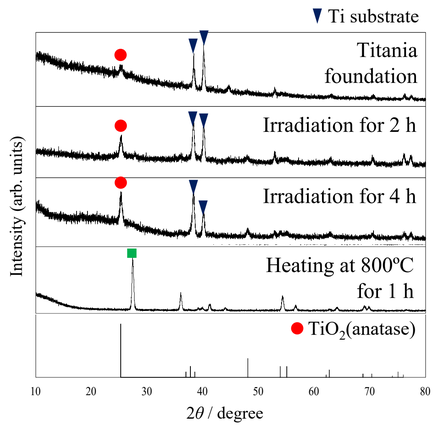
<Photocatalytic activity examination>
- **Methylene blue degradation**
- **Photocurrent measurement**

Results and discussion

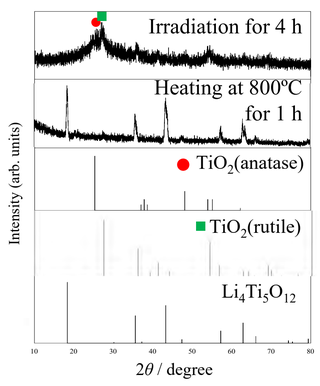
$TiCl_3$ system

Characterization

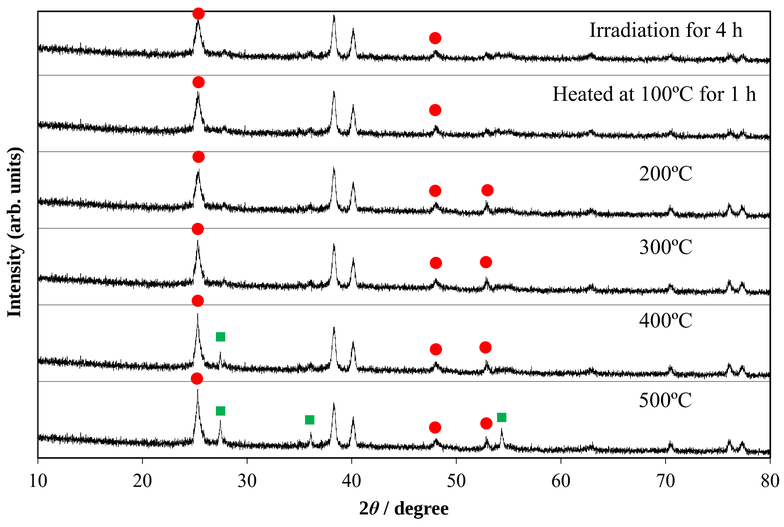
◆Substrate surface (thin films)



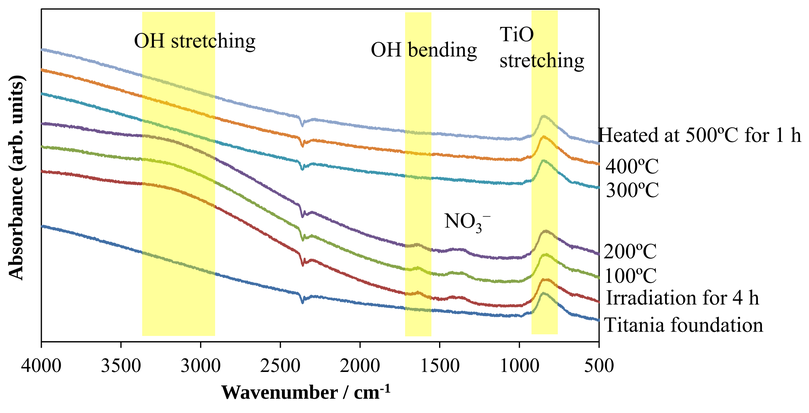
◆Precipitate (powders)



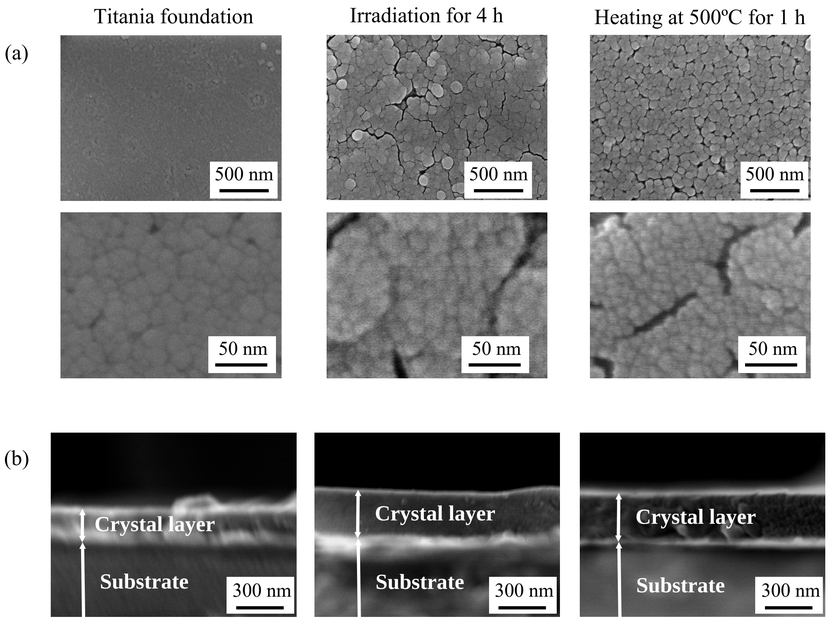
XRD patterns of the titania foundation and the titania films prepared by UV irradiation for 2 and 4 h and then heated at 800ºC for 1 h and the powers produced by UV irradiation for 4 h and then heated at 800ºC for 1 h.



XRD patterns of the titania films prepared by UV irradiation for 4 h and then heated at 100ºC–500ºC for 1 h



FTIR (ATR) spectra of the titania foundation and the titania films prepared by UV irradiation for 4 h and then heated at 100ºC–500ºC for 1 h.

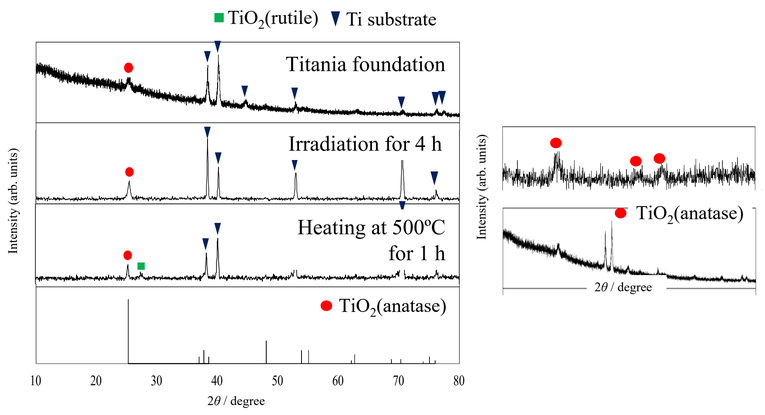


SEM images of the (a) surface and (b) cross section of the titania foundation and the titania films prepared by UV irradiation for 4 h and then heated at 500ºC for 1 h.

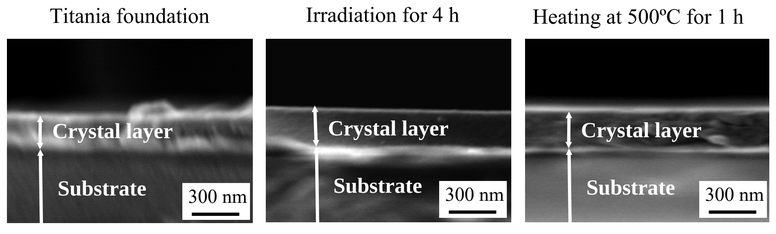
$TiCl_4$ system

◆Substrate surface (thin films)

◆Precipitate (powders)

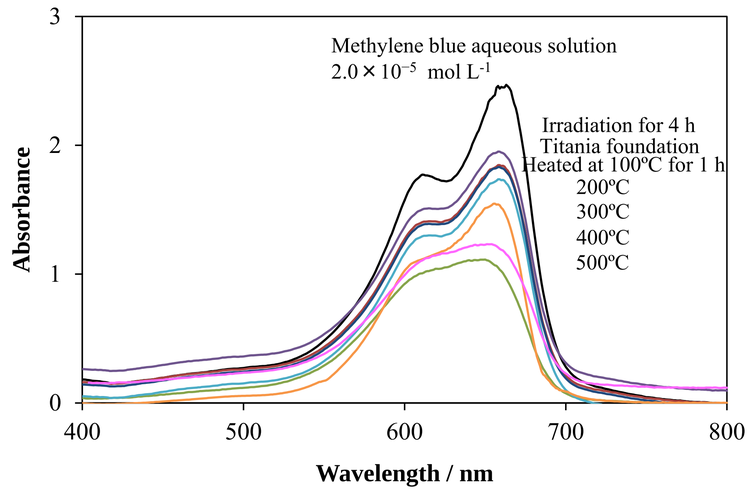


XRD patterns of the titania foundation, titania films prepared by UV irradiation for 4 h and then heated at 500ºC for 1 h and the powers produced by UV irradiation for 4 h.



SEM images of the cross section of the titania foundation and the titania films prepared by UV irradiation for 4 h and then heated at 500ºC for 1 h.

Photocatalytic activity



UV-Vis absorption spectra of methylene blue aqueous solution before and after UV (black lamp) irradiation for 24 h using the titania foundation and the titania films prepared by UV irradiation for 4 h and then heated at 100ºC–500ºC for 1 h.

Photocurrent spectra of the titania foundation and the titania films prepared by UV irradiation for 4 h and then heated at 100ºC–500ºC for 1 h.

Conclusions

- Nitrate ions in the solution were reduced to nitrite ions, and water was transformed into hydroxide ions by a photocatalytic reaction on the original titania film.
- The pH value increased on the substrate surface with the film, which caused the titanium hydroxide formation on the film.
- The titanium hydroxide were then dehydrated and transformed into titania because the substrate surface was heated by the irradiation.
- The titania particles formed on the substrate exhibited photocatalytic activity similar to the original titania.
- The activity was improved by annealing at 300ºC–500ºC.