



Presented at the Research Congress 2013
De La Salle University Manila
March 7-9, 2013

THE EFFECT OF IRON AND NIOBIUM CO-DOPING RATIO ON THE PHOTOCATALYTIC ACTIVITY OF SOL-GEL DERIVED TITANIUM DIOXIDE

Dave Patrick Opec¹, Susan Gallardo¹, Carl Renan Estrellan¹, Hirofumi Hinode², Chris Salim²

¹ De La Salle University

² Tokyo Institute of Technology

Abstract: As metal co-dopants, Fe and Nb have been reported to improve the photoquantum efficiency of TiO₂ by simultaneously lowering the band gap energy and improving charge separation. In this study, the effects of varying the co-doping ratio of Fe and Nb on the physico-chemical properties and photocatalytic activity of TiO₂ photocatalysts prepared using a temperature-controlled sol-gel method were investigated. The combined co-dopant molar loading was held constant (0.25%) while the co-doping ratio of Fe and Nb was varied. The physico-chemical properties of TiO₂ were monitored by characterizing the photocatalysts in terms of crystallite phase (XRD), band gap energy (UV-Vis Spectrophotometry), specific surface area (3-point BET), and surface morphology/composition (SEM-EDX). Measurement of the band gap energy confirmed the band gap-lowering effect of Fe, but the lower band gap energy of Nb-TiO₂ compared to pure TiO₂ indicated that Nb also exhibits a band-gap lowering effect. After 6 hours of photocatalytic testing, 1:2 Fe:Nb-TiO₂ displayed the highest photocatalytic activity among the photocatalysts with 64.78% decolorization of the lignin model pollutant under UV illumination and 38.02% under visible light illumination. All co-doped photocatalysts exhibited higher photocatalytic activity compared to pure TiO₂ under visible light illumination, confirming the cooperative effects of Fe and Nb towards improving the photocatalytic activity of TiO₂.

Keywords: TiO₂ photocatalysis; Metal co-doping; Sol-gel method

1. INTRODUCTION

The ability of titanium dioxide (TiO₂) to decompose organic pollutants into CO₂, H₂O, and mineral acids under ultraviolet light (UV) illumination has attracted a substantial amount of research pertaining to potential applications in environmental cleanup. However, the wide band gap energy (3.2 eV) and the rapid recombination of generated electron-hole (e⁻/h⁺) pairs in TiO₂ prevent the effective utilization of solar energy (4-5% UV, 45% visible light) in photocatalytic processes. In order to enhance the photocatalytic activity and shift the



absorption edge of TiO_2 towards the visible light region, modification by metal co-doping can be done.

As metal co-dopants, iron (Fe) and niobium (Nb) have been reported to improve the photoquantum efficiency of TiO_2 by simultaneously lowering the band gap energy and improving charge separation. The study of Estrellan et al. (2009) determined the combined molar loading of Fe and Nb to be a crucial factor affecting the photocatalytic activity of TiO_2 . Holding the co-doping ratio of Fe and Nb constant (1:1) at different molar loading values, 0.25%Fe:Nb- TiO_2 exhibited the highest activity among the co-doped samples under visible light irradiation. Moreover, higher values of combined molar loading proved to be detrimental to the photocatalytic activity of TiO_2 , which could be attributed to the negative effect of excess metal ions in the process of electron transfer.

In this study, the effects of varying the co-doping ratio of Fe and Nb on the photocatalytic activity and physico-chemical properties of TiO_2 were investigated, while holding the combined molar loading constant at 0.25% based on the results of the previous study Estrellan et al. (2009).

2. METHODOLOGY

The TiO_2 -based photocatalysts co-doped with Fe and Nb were prepared using a temperature-controlled sol-gel method. Titanium tetraisopropoxide [$\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$] was used as the TiO_2 source while ferric nitrate nonahydrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] and ammonium niobium oxalate [$\text{C}_4\text{NH}_4\text{NbO}_9 \cdot 10\text{H}_2\text{O}$] were used as Fe and Nb metal precursors respectively. The co-doping ratios of Fe and Nb were varied at 1:1, 1:2, 2:1, 1:3, and 3:1. Pure TiO_2 , Fe-doped TiO_2 , and Nb-doped TiO_2 were also prepared.

180 mL of isopropyl alcohol ($\text{C}_3\text{H}_8\text{O}$) and 10 mL of deionized H_2O (10:1 volume ratio) were put together in an ice bath (0-5°C). 50 mL of $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ was added drop-wise into the $\text{C}_3\text{H}_8\text{O}$ - H_2O solution under vigorous stirring. The pH of the solution was then reduced to 2.5 by adding HNO_3 in order to facilitate sol formation.

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{C}_4\text{NH}_4\text{NbO}_9 \cdot 10\text{H}_2\text{O}$ were dissolved in 88 mL $\text{C}_3\text{H}_8\text{O}$ - H_2O solution (10:1 volume ratio) and added to the sol. The pH was then increased to 9 by adding an ammonia solution [NH_4OH] to facilitate gel formation. The resulting gel was left under vigorous stirring for 24 hours and then subjected to vacuum filtration. The residue obtained

was dried at 110°C for 12 hours. The dried gels were crushed and sieved to obtain powders which were then calcined under an air stream at 450°C for 3 hours.

The synthesized TiO₂ powders were characterized in terms of crystallite phase using X-ray diffraction (Rigaku Corp., Japan), specific surface area using 3-point BET method (Quantachrome, USA), and surface composition with elemental mapping using SEM-EDX (JEOL JED-2140). The absorption profile of TiO₂ was determined using a UV-Vis spectrophotometer (UV-VIS 1700 Shimadzu, Japan) with BaSO₄ reference and the band gap energy was estimated using the methodology of Kumar et al. (1999) with modifications.

The batch photoreactor (effective volume 1900 mL) used in this study was equipped with a high pressure mercury lamp (254 nm) located at the axial center of the reactor vessel. Two types of water cooling circulation system were used for the photoreactor: (1) quartz, which transmits both UV and visible light; and (2) glass, which transmits visible light only. An aqueous solution of lignin model pollutant (80 ppm, pH 3, 27°C) was prepared by dissolving alkali lignin powder (Aldrich Chemical Co., USA) in deionized H₂O. The concentration of the lignin model pollutant was then determined by its absorbance at maximum wavelength (291 nm) using a UV-Vis spectrophotometer (UV-VIS 1700 Shimadzu, Japan) for photolysis and photocatalytic activity testing runs.

3. RESULTS AND DISCUSSION

The incorporation of Fe and Nb on the sol-gel derived TiO₂ was found to have significant effects on both the physico-chemical properties and photocatalytic activity. As shown in the XRD patterns of the synthesized photocatalysts (Figure 1), only peaks corresponding to the anatase phase were observed, confirming the results of Ahmed et al. (2008) which showed that higher concentrations of Nb in TiO₂ results in the stabilization of the anatase phase which hinders the transformation of anatase to rutile.

Similarly from Table 1, Nb was found to have a positive effect on the specific surface area of TiO₂. Although all co-doped photocatalysts exhibited higher specific surface area compared to pure TiO₂ and single-doped photocatalysts, Fe:Nb co-doped TiO₂ with higher Nb loading exhibited the highest values for specific surface area.

Energy Dispersive X-Ray Spectroscopy (EDS) was used to analyze the elemental composition of the photocatalyst surfaces and detected the only presence of Ti, O, Fe, and Nb, which confirms that the TiO₂ nanoparticles were free of contaminants. The EDS analysis indicates that the substitution for Ti in the TiO₂ lattice or deposition on the TiO₂ surface could occur regardless of the differences in the atomic radii of Fe and Nb, an improvement of the result from the previous study of Estrellan et al. (2009).

The band gap energy of the TiO₂ photocatalysts was measured to determine if the optical absorption edge was shifted towards the visible light region. As shown in Table 1, all doped photocatalysts exhibited band gap energies that were lower than that of pure TiO₂ which corresponds to an absorption wavelength near the visible light region. While there is a tendency for co-doped photocatalysts with high levels of Fe to exhibit a lower band gap, the band gap-lowering cannot be solely attributed to Fe due to the fact that Nb-doped TiO₂ exhibited lower band gap energy compared to pure TiO₂. Both Fe and Nb exhibited band-gap lowering effects, with Fe playing a more significant role compared to Nb.

Dark adsorption was performed prior to photocatalytic activity testing. As shown in Table 1, 1:3 Fe:Nb-TiO₂ and 1:2 Fe:Nb-TiO₂ displayed the highest percentage of decolorization at 3.14 and 2.94% respectively while the lowest percentage decolorization was obtained from 2:1 Fe:Nb-TiO₂ which could be attributed to the specific surface area of the photocatalysts. The decolorization brought about by adsorption of lignin onto the TiO₂ surface was minimal compared to the decolorization brought about by the photocatalytic degradation.

After 6 hours of photocatalytic activity testing under combined UV and visible light irradiation, the highest percentage decolorization was obtained using 1:2 Fe:Nb-TiO₂ (64.78%) which could be attributed to the high specific surface area of the photocatalyst providing an increased number of active sites available for the reaction on the photocatalyst surface. Pure TiO₂ outperformed all of the other photocatalysts except for 1:2 Fe:Nb-TiO₂ and 1:3 Fe:Nb-TiO₂, which could have been a result of excess metal ions hindering the process of electron transfer on the photocatalyst surface. Excess amounts of Fe in the co-dopants also appeared to have a negative effect on the photocatalytic activity of TiO₂ with Fe-TiO₂ resulting to only 38.07% decolorization.

Similar to that of the UV-Vis Testing, the highest percentage decolorization was obtained using 1:2 Fe:Nb-TiO₂ (38.02%). However, contrary to the UV-Vis testing, Fe-TiO₂ (25.16%)

appeared to perform better under Vis irradiation compared to pure TiO₂ (24.62%), which could be attributed to the band gap-lowering effect of Fe on TiO₂.

Table 1. Physico-chemical properties of photocatalysts

Photocatalyst	BET Surface Area (m ² /g)	Band Gap Energy (eV)	% Decolorization		
			Dark Adsorption	Visible	UV-VIS
Pure TiO ₂	134.9	3.25	2.78	24.64	54.28
Fe-TiO ₂	110.1	3.18	2.53	25.16	38.07
3:1 Fe:Nb-TiO ₂	211.1	3.09	2.88	27.17	47.36
2:1 Fe:Nb-TiO ₂	91.61	3.12	2.33	29.33	51.22
1:1 Fe:Nb-TiO ₂	157.8	3.18	2.68	29.67	53.13
1:2 Fe:Nb-TiO ₂	251.9	3.14	2.94	38.02	64.78
1:3 Fe:Nb-TiO ₂	245.3	3.15	3.14	35.97	56.57
Nb-TiO ₂	105.3	3.16	2.78	24.89	45.28

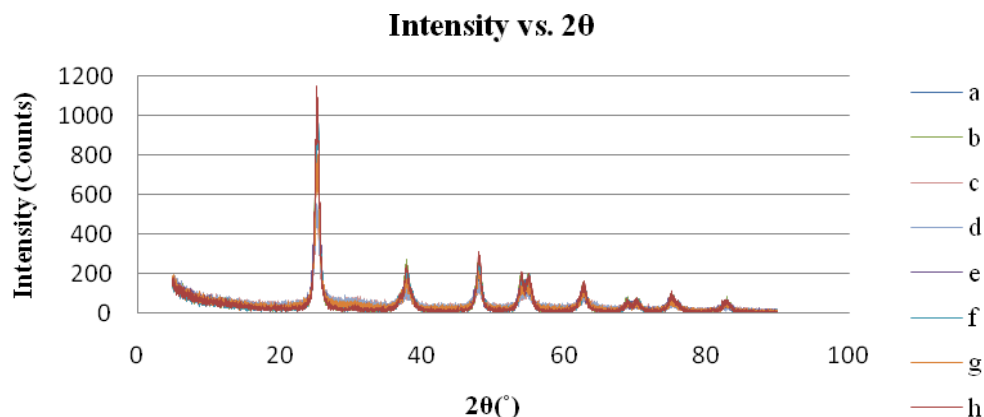


Figure 1. XRD patterns of photocatalysts: a) Pure TiO₂, b) Nb-TiO₂, c) 1:3 Fe:Nb-TiO₂, d) 1:2 Fe:Nb-TiO₂, e) 1:1 Fe:Nb-TiO₂, f) 2:1 Fe:Nb-TiO₂, g) 3:1 Fe:Nb-TiO₂, h) Fe-TiO₂

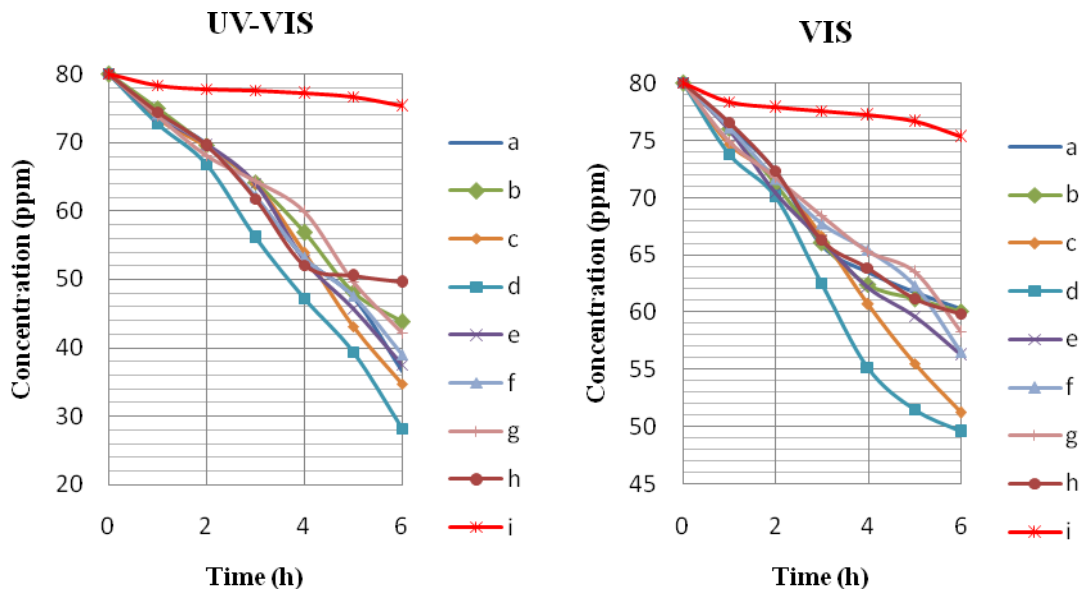


Figure 2. Concentration profile of lignin model pollutant under combined UV-VIS and VIS irradiation only: a) Pure TiO₂, b) Nb-TiO₂, c) 1:3 Fe:Nb-TiO₂, d) 1:2 Fe:Nb-TiO₂, e) 1:1 Fe:Nb-TiO₂, f) 2:1 Fe:Nb-TiO₂, g) 3:1 Fe:Nb-TiO₂, h) Fe-TiO₂, i) Photolysis

4. CONCLUSIONS

The photocatalyst that provided the highest degradation of the lignin model pollutant was 1:2 Fe:Nb-TiO₂ for both combined UV-Vis and visible light irradiation only. It can be concluded that 1:2 is the best co-doping ratio for Fe and Nb at 0.25% molar loading.

The incorporation of Fe and Nb co-dopants greatly affected the physico-chemical properties of TiO₂. Both Fe and Nb have been shown to exhibit band gap-lowering effects, with Fe presenting a more significant role. Furthermore, the positive effect of Nb on the surface area and stabilization of the anatase phase as stated in previous studies were confirmed. However, the band gap-lowering effect of Nb has never been mentioned before in literature and must be considered as a subject of further research.



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5. ACKNOWLEDGEMENTS

This research was a collaboration between the Department of International Development Engineering, Tokyo Institute of Technology and the Department of Chemical Engineering, De La Salle University. The project was partially funded by the Japan International Cooperation Agency (JICA) under the AUN/SEED-Net program.

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