

# Enhancing Photocatalytic Performance of Silver-Decorated Titanium Dioxide via Nanocolumnar Thin Films Produced by Oblique Angle Deposition

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Titanium dioxide (TiO<sub>2</sub>) has been widely studied in various applications especially in photocatalysis due to its stability, non-toxicity and high photocatalytic activity. Although it exhibits favorable properties, its activity is only limited in the ultraviolet range due to its relatively high band gap. [1] In general, sputter deposited TiO<sub>2</sub> thin films offer good mechanical stability and high reusability when it comes to wastewater treatment. However, the relatively dense characteristics of thin films limit the surface area accessibility. Oblique angle deposition (OAD) provides a simple way to make nanostructure columnar films with high porosity. In this process, the substrate is placed at an angle large enough (~70° to 85°) to the direction of the coating vapor flux. During film growth, line-of-sight shadowing prevents the subsequent incoming atoms from impinging on the area directly behind these initial nuclei. The result, tall columns grow at the expense of smaller columns due to self-shadowing. [2] In this work, visible light active silver-decorated TiO<sub>2</sub> nanocolumnar thin films (Ag-TiO<sub>2</sub> NCTFs) were fabricated using a custom-built magnetron sputter deposition using OAD technique followed by a calcination step to form a high surface area NCTFs. The TiO<sub>2</sub> NCTFs are then decorated with metallic Ag nanoparticles through wet impregnation and subsequent plasma reduction to shift the activity of TiO<sub>2</sub> films to the visible light region.

The composition and crystalline phases of the NCTFs were identified using Raman spectroscopy. Figure 1(a) presents the Raman spectra of the fabricated NCTFs. No significant peaks were observed for as-deposited TiO<sub>2</sub> NCTFs due to its amorphous structure. Peaks observed at 145 cm<sup>-1</sup>, 197 cm<sup>-1</sup>, 396 cm<sup>-1</sup>, 515 cm<sup>-1</sup>, and 639 cm<sup>-1</sup> for annealed NCTFs confirms the presence of anatase characteristic peaks of TiO<sub>2</sub>. Incorporation of Ag shows an increase in intensity of the characteristic

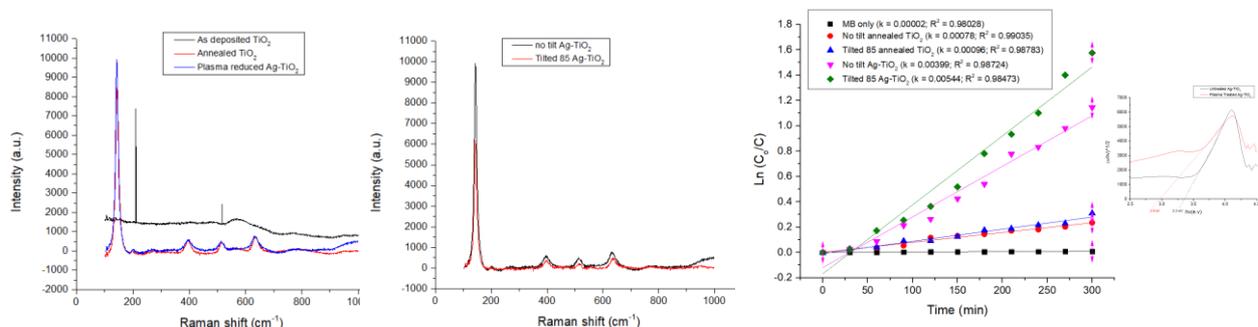
peaks of anatase TiO<sub>2</sub> due to surface plasmon resonance (SPR) phenomenon where the CB electrons on the surface undergo oscillation when excited by light at a specific wavelength, resulting in the strong scattering and absorption of light. [3]

Figure 1(b) shows the Raman Spectroscopy measurements of TiO<sub>2</sub> NCTFs tilted at different angles (0° and 85°). Both films show anatase characteristic peaks of TiO<sub>2</sub> but intensity decreases as tilting angle is increased due to differences in film thickness. Figure 1(c) shows methylene blue (MB) photodegradation under visible light irradiation. In comparison, NCTFs tilted at 85° show higher rate constant as compared to the untilted ones. This suggests that more structured columnar films with higher porosity are produced when tilting angle is set at 85° due to self-shadowing.

Degradation experiments also revealed that MB removal efficiency of TiO<sub>2</sub> NCTFs increased from 26% to 79% upon decorating with Ag. The inset plot also shows a decrease in band gap energy from 3.3 eV to 2.9 eV upon Ag decoration. This improvement was due to SPR effect in which electrons from the conduction band (CB) of Ag were efficiently transferred to the CB of TiO<sub>2</sub> improving the oxidation-reduction process needed for photocatalysis as well as the improvement of local electric field near Ag-TiO<sub>2</sub> for faster generation of charge carriers.

## References

- [1] D. Kim, N. Han, J. B. Lee, and H. T. Kim. *Scripta Materialia* 54, p. 143–146, (2006).
- [2] Y. P. He, Z. Y. Zhang, and Y. P. Zhao. *JVST B* 26, p. 1350 (2008)
- [3] A.S. Montallana and M.R. Vasquez. *Res. in Phys.* 25 p. 104205 (2021)



**Figure 1.** (a) Raman Spectroscopy measurements of as deposited amorphous TiO<sub>2</sub> NCTFs, TiO<sub>2</sub> NCTFs annealed at 450 °C, and plasma-reduced Ag on TiO<sub>2</sub> NCTFs. (b) Raman Spectroscopy measurements of TiO<sub>2</sub> NCTFs tilted at different angles (0° and 85°). (c) Plots of ln(C<sub>0</sub>/C) versus time and corresponding linear fits (inset: Tauc's Plot derived from UV-Vis Absorbance Spectra of annealed TiO<sub>2</sub> and Ag-TiO<sub>2</sub>).