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Plasma-assisted reduction of silver ions on titanium dioxide film for visible-light photocatalysis

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TiO_2 serves as a widely utilized photocatalyst due to its non-toxic nature, cost-effectiveness, potent photocatalytic capabilities, and thermal stability. However, its effectiveness is primarily limited to the UV spectrum owing to its sizable bandgap (~3.2 eV), restricting its application in visible light-driven photocatalysis [1]. Incorporating noble metallic nanoparticles such as silver (Ag) has been shown to enhance TiO2's performance and expand its functionality into the visible light spectrum through the surface plasmon resonance (SPR) effect [2]. One efficient method for Ag reduction involves ion exchange via the wet impregnation technique, followed by plasma reduction using a Capacitively-Coupled Plasma (CCP) system, converting Ag ions into metallic Ag. Unlike conventional metal reduction methods reliant on chemical agents, plasma reduction mitigates environmental risks associated with chemical reducing agents [3]. In this study, visible light-responsive Ag NP-decorated TiO_2 (Ag- TiO_2) films were synthesized by fabricating TiO_2 films using a DC magnetron sputtering system followed by annealing. Subsequently, metallic Ag NPs were deposited onto the films via wet impregnation in a silver nitrate ($AgNO_3$) solution and plasma reduction of silver ions using a custom-built CCP system.

The presence of Ag in the Ag-TiO_2 sample was confirmed by subjecting it to Argon (Ar) plasma and analyzing the optical emission spectra (OES). Full spectra at 350-1000 nm show typical Ar peaks for both samples. However, at 290-350 nm (Figure 1a), a distinct Ag peak at approximately 328 nm was observed, indicating the successful plasma reduction of Ag and the presence of loosely bound metallic Ag on the TiO_2 surface. This observation aligns with findings from previous research by Osonio and Vasquez [3]. Plasma treatment also revealed a shift from Ag oxide peaks to metallic Ag peaks at 38.16°, 44.34°, and 64.43° 2-theta angles in the X-ray Diffraction (XRD) pattern as shown in Figure 1b which was achieved after the 30 min plasma treatment.

Figure 1c presents Raman spectroscopy results for Ag-TiO_2 films pre- and post-plasma treatment, indicating the presence of anatase TiO_2 with no distinct peaks corresponding to $AgNO_3$, likely due to its low concentration. After plasma treatment, TiO_2 peaks intensify, suggesting enhanced local electronic fields near Ag-TiO_2 junctions induced by the SPR effect. Reflectance spectra measurements show a decreased band gap energy from 3.25 eV to 3.05 eV for Ag-TiO_2 films, indicating increased sensitivity in the visible range. Photodegradation studies (Figure 1d) under white light irradiation demonstrate improved methylene blue (MB) removal efficiency from 40.98% to 71.37% upon Ag decoration. This enhancement is attributed to the SPR effect, facilitating efficient electron transfer from the conduction band of Ag to TiO_2, enhancing the local electric field near Ag-TiO_2 for accelerated charge carrier generation, and improving the photocatalytic oxidation-reduction process [4].

References

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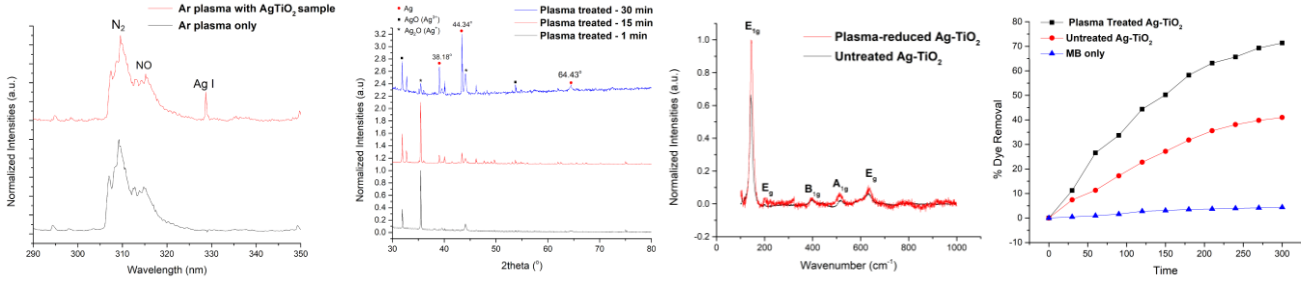

Figure 1. (a) OES spectra of an Ar discharge with and without Ag-TiO_2 sample at 290-350 nm. (b) XRD spectra of plasma-treated Ag NPs at varying treatment times. (c) Raman spectra of untreated and plasma-treated Ag-TiO_2 films. (d) Comparison of MB degradation using TiO_2 and Plasma-reduced Ag- TiO_2 films under white light irradiation.