

## Photodeposition of Me/MeO<sub>x</sub> Cocatalysts on TiO<sub>2</sub> Thin Films: Effects on Photocatalytic Activity and Quantum Efficiency

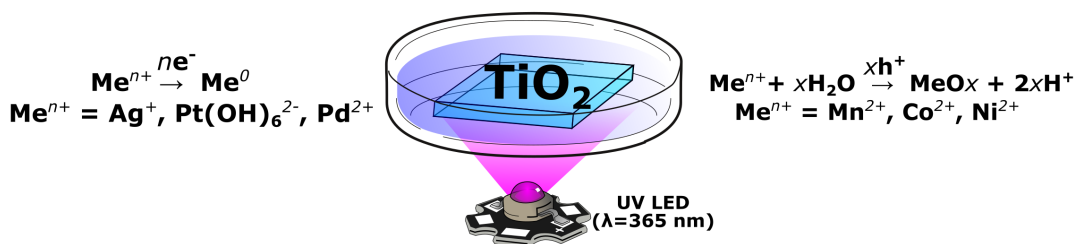
Bozhidar Stefanov

*Department of Chemistry, Faculty of Electronic Engineering and Technology,  
Technical University of Sofia, 8 Kl. Ohridski Blvd., 1756 Sofia, Bulgaria.*

E-mail: b.stefanov@tu-sofia.bg

**Keywords:** TiO<sub>2</sub>, Thin Films, Photodeposition, Cocatalysts, Photocatalysis.

Titanium dioxide (TiO<sub>2</sub>) is a versatile photocatalyst, finding a plethora of applications in emerging “green” technologies [1]. The photocatalytic action of TiO<sub>2</sub> is driven by absorption of photons, of energy higher than its bandgap ( $E_g = 3.2$  eV,  $\lambda \leq 384$  nm), leading to the excitation of electron-hole ( $e^- - h^+$ ) pairs, also known as excitons, that in turn participate in redox reactions with surface-adsorbed chemical species. However, the quantum yield of this photochemical process is hindered by  $e^- - h^+$  recombination losses (> 90%) [2]. A promising strategy for minimizing recombination losses, while simultaneously improving surface charge transfer, is through the introduction of cocatalysts on the TiO<sub>2</sub> surface. These are often noble metals (Me-type), or transition metal oxides (MeO<sub>x</sub>-type), that form either Schottky-, or heterojunctions with TiO<sub>2</sub>, thus selectively accumulating either of the photogenerated charge carriers. Cocatalyst-modification may be carried through simple procedure, of impregnating the pristine catalyst with a cocatalyst precursor salt solution, followed by a thermal treatment, however, it is possible to use photocatalytic activity of TiO<sub>2</sub> itself, for direct photodeposition of the of Me or MeO<sub>x</sub>-type cocatalysts [3], as shown in Figure 1.



**Figure 1.** Simplified mechanism of photodeposition of Me/MeO<sub>x</sub> type cocatalyst from precursor ions.

Photodeposition-functionalization is a beneficial modification strategy, since both photoreduction of metal ion, to Me-type species and their photooxidation – to MeO<sub>x</sub>-type products takes place on specific sites, facets, and defects that express differential redox activity on the TiO<sub>2</sub> surface. This way, photodeposited cocatalysts are preferentially located on surface-sites which already accumulate the photogenerated charges able to pass through the TiO<sub>2</sub>|cocatalyst junction. It has been demonstrated in literature that photodeposition-

functionalized TiO<sub>2</sub> yields improved quantum efficiency, compared to impregnation-functionalized TiO<sub>2</sub>, e.g., in the case of CoO<sub>x</sub>/Au/TiO<sub>2</sub> [4].

This work contributes to the topic, presenting results on the effects of Me/MeO<sub>x</sub> photodeposition on the photocatalytic activity of TiO<sub>2</sub> thin films. Optically-transparent TiO<sub>2</sub> layers were dip-coated on a glass substrate from a titanium tetraisopropoxide (TTIP) – salicylic acid (SA) – isopropanol (IP) based sol (1:3:15 TTIP:SA:IP molar ratio). Five coating cycles were applied, with an intermediate heat-treatment (1h @ 450°C), to afford 250-nm-thick anatase layers. The as-prepared photocatalyst was surface-functionalized, in liquid phase, via photodeposition under UV illumination (LED source,  $\lambda=365\pm 5$  nm,  $\approx 12\pm 0.5$  mW cm<sup>-2</sup>). Aqueous solutions (5 mM precursor ion content) of: Pd<sup>2+</sup>, Ag<sup>+</sup>, and Pt(OH)<sub>6</sub><sup>2-</sup> were used to deposit Pd, Ag, and Pt (Me-type), respectively; while Co<sup>2+</sup>, Ni<sup>2+</sup>, and Mn<sup>2+</sup>, with equimolar electron scavenger (IO<sub>3</sub><sup>-</sup>) content, were used for the deposition of CoO<sub>x</sub>, NiO<sub>x</sub>, and MnO<sub>x</sub> (MeO<sub>x</sub>-type). Photodeposition was carried at varied UV dose (1.25 – 15 J cm<sup>-2</sup>) and reference samples were prepared via impregnation with the same electrolytes, in darkness, followed by heat treatment (1h @ 350°C). All samples were characterized by SEM-EDX to observe any morphology changes and measure the cocatalyst content. The effects of functionalization on the photocatalytic activity were studied in the liquid-phase photooxidation of Methylene blue (MB) dye model contaminant, providing both information of the change of available MB adsorption sites (by measuring the equilibrium MB coverages during dark adsorption) and an estimate of the quantum efficiency of the functionalized TiO<sub>2</sub> layers (by screening the MB removal rate at varied UV illumination intensity at 0.5 – 1.5 mW cm<sup>-2</sup>).

Briefly, in all cases the functionalization led to a decrease in the MB saturation coverage, which was proportional to the UV dose in the photodeposition strategy. The impregnation approach had, in general, detrimental effect on MB removal rate for all of the six Me/MeO<sub>x</sub> cocatalysts. In the photodeposition case – an improved photocatalytic activity was observed in the Me-type case (Pt > Ag > Pd); while the MeO<sub>x</sub> functionalization had a detrimental effect in the case of MnO<sub>x</sub>, and a modest increase in the other two cases (NiO<sub>x</sub> > CoO<sub>x</sub>).

## References

1. Z. Li, S. Wang, J. Wu, W. Zhou, *Renewable Sustainable Energy Rev.* 156 (2022) 111980.
2. J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, D. Bahnemann, *Chem. Rev.* 114 (2014) 9919-9986.
3. T. Butburee, P. Kotchasarn, P. Hirunsit, Z. Sun, Q. Tang, P. Khemthong, W. Sangkhun, W. Thongsuwan, P. Kumnorkaew, H. Wang, K. Faungnawakij, *J. Mater. Chem. A* 14 (2019) 8156-8166.
4. M. Okazaki, Y. Suganami, N. Hirayama, H. Nakata, T. Oshikiri, T. Yokoi, H. Misawa, K. Maeda, *ACS Appl. Energy* 3 (2020) 5142-5146.

*Acknowledgements:* This work was possible through financial support from the Bulgarian National Science Fund, under project КП-06-H59/11 “Photocatalytic activity of thin films with selectively photodeposited cocatalysts”, which is greatly acknowledged.