The Effect of Nano-Sized Metal Deposits on TiO_2 on the Photocatalytic Activity and Mechanism

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 TiO_2 photocatalysis has been extensively studied for its environmental applications and demonstrated to be a technically viable clean-up process (1). The main drawbacks of the low quantum yields and the lack of visible-light utilization, however, hinder its widespread acceptance as a practical remediation technology. Various approaches have been attempted to enhance the photocatalytic efficiency of TiO₂, which include metal-ion doping, metallization, and sensitization.

In this study, we investigated and compared the effects of depositing nano-sized metal particles (M: Pt, Au) on TiO₂ in three different aquatic photocatalytic systems: (1) dye-sensitized M/TiO₂ for the visible light photocatalytic degradation of perchlorinated compounds, (2) M/TiO₂ photocatalyst for ammonia removal, and (3) M/TiO₂ photocatalyst for trichloroacetate (TCA) degradation. The Pt and Au particles were photodeposited on TiO₂ (Degussa P25) with a typical loading of ca. 0.2 wt%. The transmission electron microscopic (TEM) images showed that Pt particles with a size range of 1-2 nm were well dispersed on TiO₂ particles (20-30 nm diameter).

Figure 1 exhibits the dramatic effect of the platinization of the sensitized TiO_2 on the visible light-induced dechlorination of CCl_4 . The dechlorination initiates by the conduction band electron transfer to CCl_4 (2).

 $\text{CCl}_4 + e_{cb}^{-}(\text{Pt}) \rightarrow \text{\bullet}\text{CCl}_3 + \text{Cl}^{-}$

The presence of Pt deposits on TiO_2 in this case reduces the fast back electron transfer to the oxidized dye and enhances the interfacial electron transfer to CCl₄. The Pt/TiO2 was also very effective in photocatalytic denitrification of ammonia as shown in Figure 2. While the pure TiO₂ almost quantitatively transformed ammonia into nitrite and nitrate (Fig. 2a), Pt/TiO₂ converted NH₃ into N₂ with reducing the total nitrogen concentration in the suspension (Fig. 2b). The evolution of N_2 gas was confirmed by detecting ${}^{30}N_2$ using GC/MS from ${}^{15}NH_3$ conversion. Au/TiO2 did not exhibit such denitrification effect. The photocatalytic degradation of TCA on Pt/TiO₂ was significantly different from that on pure TiO₂ with showing different product distribution. In the above three photocatalytic systems, both the photocatalytic activity and mechanism changed when Pt was deposited on TiO₂. Although the platinization of TiO₂ has been widely studied, its effect on the photocatalytic mechanism is not well understood. The role of metals and their effect on the photocatalytic reaction system will be discussed.

REFERENCES

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Figure 1. Chloride production from CCl_4 degradation on $TiO_2/Ru^{II}L_3$ and $Pt/TiO_2/Ru^{II}L_3$ under visible light illumination. The experimental conditions were: $[TiO_2] = 0.5 \text{ g/L}$, $[Ru^{II}L_3]_i = 10 \text{ }\mu\text{M}$, $[CCl_4]_i = 1 \text{ }m\text{M}$, $pH_i = 3$, and initially N₂-saturated.



Figure 2. Photocatalytic degradation of NH_3 on (a) pure TiO_2 and (b) Pt/TiO_2 under UV irradiation. The experimental conditions were $[NH_3]_0 = 100 \ \mu M$, $[TiO_2] = 0.5 \ g/L$, pH = 10, and air-equilibrated.