Scanning electrochemical microscopy (SECM) as a new approach for measuring photomineralization kinetics at an illuminated titanium dioxide film

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Scanning electrochemical microscopy (SECM) technique has been developed as a new approach to investigate the kinetics of interfacial photoelectrochemical processes at the microscopic level. This system employed a finely polished and smooth quartz fiber of 250 μm diameter, which guides the light flux to sensitize a thin film of TiO₂ (deposited on to the polished fiber surface from a 13.0 % colloidal slurry of TiO₂) by back-illumination. This initiates the local photoelectrochemical process. The SECM probe (either a potentiometric or an amperometric microdisc UMEs of 25 μm diameter) was positioned with high precision in close proximity to the TiO₂ surface to monitor the reactants or products of the ongoing photo degradation process.

The initial emphasis of this newly developed technique covered investigations in a very localized region during the TiO₂-sensitized photomineralisation of 4-chlorophenol (4 -CP) and the photoelectrochemical reduction of O₂ in different substrate solutions, utilizing both potentiometric and amperometric approaches respectively. These photoelectrochemical reactions were investigated at the tip electrode by measuring the time-dependent response after suddenly stepping the light flux.

Semiconductors are activated by absorbing a photon of ultra band gap energy which causes the transfer of an electron from the valence band (VB) to the conduction band (CB). A hole, h⁺, is formed in the VB. These photogenerated holes oxidize H₂O (or OH⁻) to form OH⁻ which initiates the photomineralization process at the surface of the catalyst, while photogenerated electrons are captured by O₂ to produce superoxide anion, which also oxidizes the organic pollutant. The net process for the complete oxidative mineralisation of 4-CP by semiconductor photosensitizers is given by the following reaction [1]:

\[
\text{semiconductor} + 4 \text{-CP} + 6.5O_2 \rightarrow 6\text{CO}_2 + 2\text{H}_2\text{O} + \text{HCl} \quad [1]
\]

The degradation pattern of 4-CP was monitored at the Ag/AgCl detector electrode in terms of Cl⁻ production and the kinetics of the photomineralization process was assessed through model studies using the well-defined properties of the SECM. A typical SECM image of Cl⁻ distribution at the illuminated TiO₂ surface is shown in Figure 1.

A significant depletion in [O₂] was evident at the TiO₂ surface as a result of illumination, indicating that dissolved O₂ plays a key role in controlling the photodegradation process even at the microscopic level. A typical transient response recorded during the photoelectrochemical reduction of O₂ at the amperometric tip electrode is depicted in Figure 2.

Figure 1 Potentiometric image of the Cl⁻ distribution formed at the TiO₂ / aqueous interface during the photomineralization of 4-CP

Figure 2 Phototransient response at the tip UME for the reduction of O₂ detected at a tip/substrate distance of 8.50 μm

References

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