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

Samina Ahmed[*], *Terence J. Kemp* and *Patrick R. Unwin*
Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK.

Scanning electrochemical microscopy (SECM) technique has been developed as a new approach to investigate the kinetics of interfacial photo electrochemical 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 TiO_2 (deposited on to the polished fiber surface from a 13.0 % colloidal slurry of TiO_2) by back-illumination. This initiates the local photo electrochemical process. The SECM probe (either a potentiometric or an amperometric micro disc UMEs of 25 μm diameter) was positioned with high precision in close proximity to the TiO_2 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 TiO_2-sensitised photomineralisation of 4-chlorophenol (4 -CP) and the photo electrochemical reduction of O_2 in different substrate solutions, utilizing both potentiometric and amperometric approaches respectively. These photo electrochemical 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 H_2O (or OH^-) to form $OH^\bullet$ which initiates the photomineralization process at the surface of the catalyst, while photogenerated electrons are captured by O_2 to produce superoxide anoin, which also oxidizes the organic pollutant.[1,2,3] The net process for the complete oxidative mineralisation of 4-CP by semiconductor photosensitizers is given by the following reaction [1]:

$$4\text{-CP} + 6.5O_2 \xrightarrow[h\nu \geq E_{bg}]{\text{semiconductor}} 6CO_2 + 2H_2O + HCl \qquad [1]$$

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.[4,5] A typical SECM image of Cl^- distribution at the illuminated TiO_2 surface is shown in Figure 1.

A significant depletion in $[O_2]$ was evident at the TiO_2 surface as a result of illumination, indicating that dissolved O_2 plays a key role in controlling the photodegradation process even at the microscopic level. A typical transient response recorded during the photoelectrochemical reduction of O_2 at the amperometric tip electrode is depicted in Figure 2.

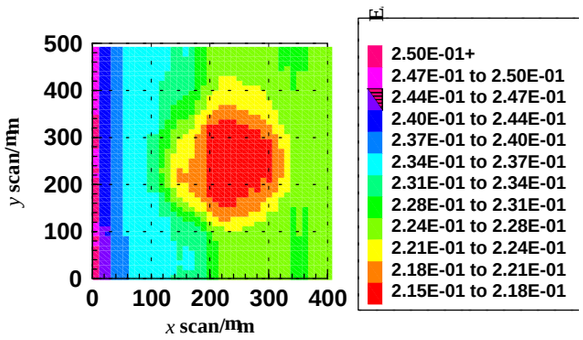

Figure 1 Potentiometric image of the Cl^- distribution formed at the TiO_2 / aqueous interface during the photomineralization of 4-CP

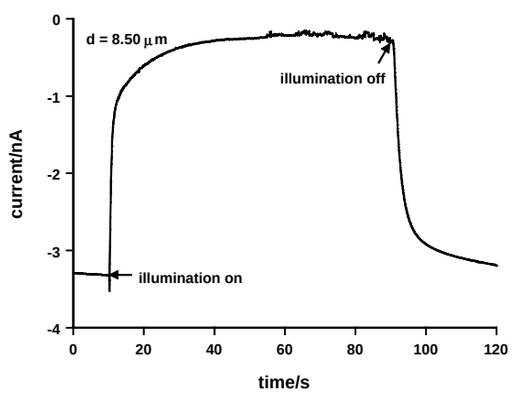

Figure 2 Phototransient response at the tip UME for the reduction of O_2 detected at a tip/substrate distance of 8.50 μm

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[*]Present address: Institute of Glass and Ceramic Research & Testing (IGCRT), Bangladesh Council of Scientific and Industrial Research (BCSIR), Dr. Kudrat-i-Khuda Road, Dhanmondi, Dhaka-1205, Bangladesh
(e-mail: bcsir@yahoo.com)