ChemComm
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Direct observation of oxygen depletion and product formation during photocatalysis at a TiO_2 surface using scanning electrochemical microscopy

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Received (in Cambridge, UK) 11th December 2002, Accepted 6th March 2003
First published as an Advance Article on the web 24th March 2003

Using scanning electrochemical microscopy (SECM) we have measured quantitatively the depletion of O_2 during the photodegradation of 4-chlorophenol at supported TiO_2 films for the first time and established the connection between Cl^- formation and O_2 depletion rates.

The use of TiO_2 as a photocatalyst for a variety of processes, including the photomineralisation of organic pollutants in water, continues to be of considerable interest.[1] In this process, photogenerated holes mineralise the organic, *via* the rapid formation of hydroxyl radicals, and the photogenerated electrons are captured by O_2. The role of O_2 in TiO_2 photocatalysis has been the focus of several previous studies.[2–4] As well as acting as an electron scavenger, oxygen species may also be involved in the oxidation reaction pathway.[5,6] The photomineralisation of 4-chlorophenol (4-CP) by oxygen, at TiO_2, has been the subject of numerous studies, both in suspensions[7,8] and at immobilised films,[9,10] and is established as a model system. Immobilisation of TiO_2 onto a solid support eliminates the need to separate and recycle the catalyst, but introduces the possibility of solution phase transport limitations on the overall reaction rate. To assess the importance of such effects, it is essential to have knowledge of the interfacial kinetics. However, rate constants for O_2 reduction at illuminated TiO_2 films have never been reported nor has there been any correlation between the rate of O_2 consumption and the formation of products.

Ultramicroelectrodes (UMEs) have recently emerged as powerful tools for investigating surface photocatalytic processes, particularly when operated as probes in SECM.[11–13] Here, we study the initial stages of the photodegradation of 4-CP, using SECM to investigate the rate of Cl^- formation and O_2 loss. We establish, for the first time, the link between these processes.

In the SECM system developed, an UME is positioned above a TiO_2-coated quartz fibre (250 µm diameter) secured vertically in the base of a cell. A TiO_2 film was deposited on the smooth, polished end of the fibre from a suspension of Degussa P25 TiO_2 powder.[14] The TiO_2 films were 12 ± 1 µm thick. The light from a xenon lamp was focused onto the uncoated end of the fibre, and a manual shutter was used to switch the light on and off.

To investigate the role of O_2 in the photodegradation process, a 25 µm diameter Pt disk-shaped UME was positioned above the TiO_2 film in an aqueous aerated 1 mM 4-CP solution, with 0.1 M $NaClO_4$ as supporting electrolyte. The potential of the UME was held at -1.0 V *vs.* silver quasi reference electrode (AgQRE) to effect the diffusion-limited reduction of O_2, which is a 4-electron process on the timescale of these measurements.[15] In the dark, the TiO_2 surface is inert and the resulting steady-state current for the hindered diffusion of O_2 to the UME provided information on the distance between the UME and the TiO_2 surface, *i.e.* on the tip–substrate separation.[16] The transient UME current response for O_2 reduction was subsequently recorded after stepping the illumination at the TiO_2 surface on and off. Typical transients, at different light intensities, are shown in Fig. 1. The full light intensity, I_0, of ultra band gap photons was 2.13×10^{16} q cm^{-2} s^{-1} and this was varied through the use of neutral density filters. When the TiO_2 film was illuminated, the UME current decreased significantly, and quickly attained a steady value, indicating that less O_2 was detected by the UME. This is because illumination causes the photogenerated electrons to be captured by O_2, thus depleting the O_2 concentration at, and near, the catalyst surface. When the illumination was suddenly stopped, the transient current response gradually increased again towards the dark value, consistent with no photocatalytic reaction, and O_2 reaching the UME by hindered diffusion. A schematic of the reduction of O_2 at the UME probe, with and without illumination, is shown in Fig. 2 to illustrate these processes. These experiments demonstrate that O_2 is significantly depleted at the illuminated TiO_2 surface during photocatalysis. The magnitude of the diminution in the steady-state O_2 reduction current, due to the reaction of O_2 at the TiO_2 surface, was closely proportional to the light intensity. We attempted to identify intermediates of the O_2 reduction process voltammetrically at the Pt UME, but none were evident, suggesting that O_2 reduction at illuminated TiO_2

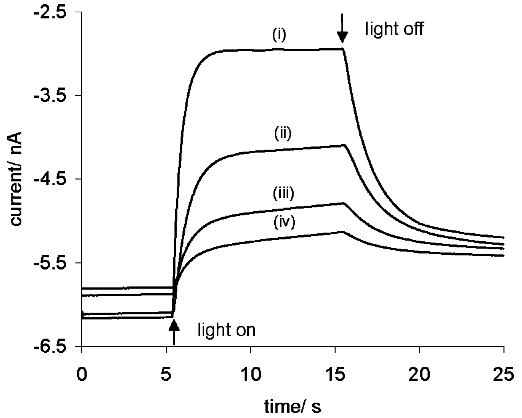

Fig. 1 Phototransient responses at the Pt UME for the reduction of O_2 in an aerated 1 mM 4-CP solution: (i) 100% I_0, (ii) 50% I_0, (iii) 25% I_0 and (iv) 12.5% I_0. The tip–substrate distance was *ca.* 20 µm.

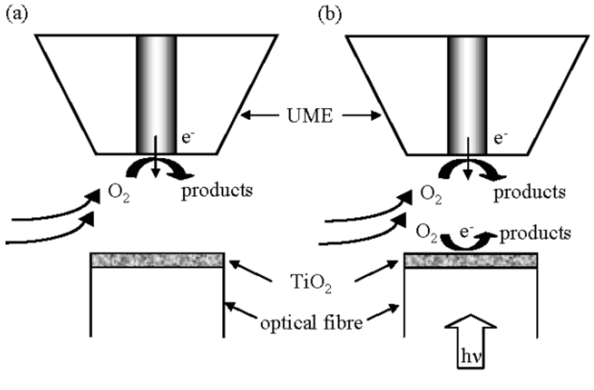

Fig. 2 Schematic representation (not to scale) of the detection of O_2 at an UME, in the dark (a) and with illumination (b). The UME (25 µm diameter) was typically *ca.* 20 µm from the TiO_2 surface.

DOI: 10.1039/b212222g

occurs predominantly *via* a 4-electron process on the timescale of these measurements.

To monitor Cl^- generation during the photodegradation of 4-CP, the Pt UME was replaced by a 25 μm diameter Ag/AgCl potentiometric UME, which acted as an indicator electrode in a simple potentiometric circuit with a saturated calomel reference electrode. The UME was again placed close to the catalyst surface. The response of the potentiometric electrode was recorded before and during illumination. Illumination had no effect on the electrode response in the absence of either 4-CP or TiO_2. A calibration curve[17] was used to convert the observed potential differences into Cl^- concentration, resulting in the profiles shown in Fig. 3 for four different light intensities. The rate of photogenerated Cl^- formation was again found to be closely proportional to the light intensity.

Photomineralisation kinetics have generally been interpreted using a Langmuir–Hinshelwood kinetic scheme in which O_2 and 4-CP adsorb non-competitively at the TiO_2 surface.[1] Under the conditions of our experiments 4-CP is initially in excess of O_2 and the concentration of 4-CP did not decrease noticeably on the timescale of these studies. This was ascertained by detecting 4-CP oxidatively at a Pt UME, with and without illumination, using fast transient measurements.[18] Consequently, we write the expression for the heterogeneous reaction (flux) of O_2 at the TiO_2 surface as:

$$j_{O_2} = \frac{k' K_{O_2} c_{O_2,\mathrm{int}}}{1 + K_{O_2} c_{O_2,\mathrm{int}}} \qquad (1)$$

where $c_{O_2,\mathrm{int}}$ is the concentration of O_2 close to the interface and K_{O_2} is the equilibrium adsorption constant for O_2 (9.63×10^6 $\mathrm{mol^{-1}\ cm^3}$).[19] The rate constant k' is that determined experimentally at the specific light intensities and [4-CP] defined herein.

We are interested in comparing the initial rate of O_2 loss and Cl^- formation, which we also treat as a heterogeneous process:

$$j_{Cl^-} = -f\, j_{O_2} \qquad (2)$$

where f is a factor which defines the relationship between the O_2 and Cl^- fluxes.

The time-dependent diffusion equations for O_2 and Cl^- were solved numerically in the axisymmetric cylindrical geometry of SECM with the usual conditions.[20] The rate constants for the depletion of O_2 deduced from the responses in Fig. 2 and the f values obtained by fitting the curves in Fig. 3 are summarised in Table 1. It can be seen that k' is closely proportional to the light intensity. These data are the first quantitative measurements of O_2 depletion, and its dependence on light intensity, under photomineralisation conditions. It appears that O_2 reacts significantly, so that transport of O_2 to the TiO_2–aqueous interface is likely to be an important consideration when designing practical photomineralisation systems.

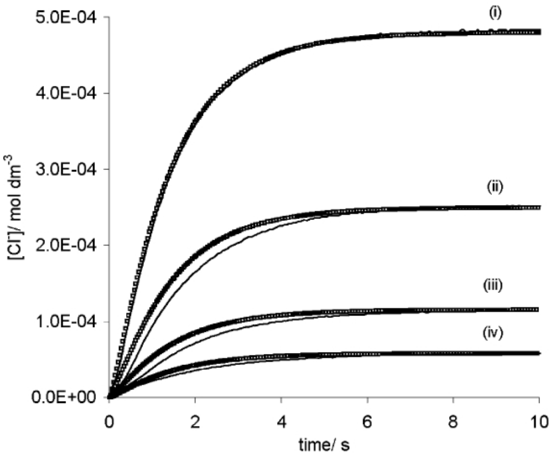

Fig. 3 Photogenerated [Cl^-] detected at the Ag/AgCl UME (—), compared with the best fit simulations (□), during the photodegradation of an aerated 1 mM 4-CP solution: (i) 100% I_0, (ii) 50% I_0, (iii) 25% I_0 and (iv) 12.5% I_0. The tip–substrate distance was 17.5 μm.

Table 1 Values of the best-fit rate constants for the depletion of O_2 during the photodegradation of 4-CP and f values

I_0/q $\mathrm{cm^{-2}\ s^{-1}}$	$k'/10^{-10}$ $\mathrm{mol\ cm^{-2}\ s^{-1}}$ (O_2 reduction)	f
2.13×10^{16} (100%)	3.5 ± 0.05	1.8
1.07×10^{16} (50%)	1.9 ± 0.05	1.6
5.33×10^{15} (25%)	0.99 ± 0.04	1.4
2.66×10^{15} (12.5%)	0.59 ± 0.04	1.2

Although there is a small systematic shift to lower f values as the light flux decreases, the data also demonstrate that Cl^- and O_2 fluxes are correlated. Since the hole and electron transfer rates at the TiO_2 surface must balance, at steady-state, and the O_2 process is predominantly 4-electron, while each 4-CP will react with one $^{\cdot}OH$ radical (produced by one hole), our results suggest that only a fraction (albeit significant) of 4-CP releases Cl^-, based on this reaction stoichiometry. This is consistent with work in suspensions[21,22] which has established that the predominant initial intermediates in the oxidative degradation of 4-CP are hydroquinone (involving Cl^- loss) and 4-chlorocatechol (no Cl^- loss), formed primarily in amounts of the same order, but with secondary intensity and wavelength effects that influence the precise distribution.

S. M. F. gratefully acknowledges a scholarship from the Portuguese Foundation for Science and Technology.

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