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A novel electrochemical device for the disinfection of fluids by OH radicals

P. A. Christensen,*[a] T. A. Egerton,[a] W. F. Lin,[a] P. Meynet,[a] Z.-G. Shao[a] and N. G. Wright[b]

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This paper describes a novel, composite device, based not on optical excitation but on the transfer of holes from Si to the TiO_2/air or TiO_2/water interface, for the disinfection and detoxification of fluid streams.

It is well known that electron/hole pairs can be thermally generated in Si due to the relatively small bandgap of the semiconductor. In a fabricated metal–insulator–semiconductor structure, such as TiO_2/Si with a metal contact on the surface of the TiO_2, current flow will occur when a relative potential exists between the metal and the semiconductor due to defect states in the TiO_2. Application of a negative potential on the metal with respect to the Si will typically result in an electron current from the metal to Si, particularly as it has been reported that metal deposition onto TiO_2 results in the creation of surface states *ca.* 1 eV below the conduction band edge which facilitate electron transfer into the conduction band.[1,2] However, hole conduction has also been reported in HfO_2 and TiO_2,[3] and hence it was postulated that a hole current may be induced *via* injection from the Si to the TiO_2 surface, and that this would be facilitated by rendering the metal overlayer on the TiO_2 negative. By fabricating the metal overlayer in the form of a grid, holes may be generated at the open surface of the TiO_2 and such carriers may be available for reactions in an external fluid.

The design of such a device (in terms of suitable grid hole spacing) was performed in the first instance by modelling a 500 μm Si/120 nm TiO_2/Au device in which the Au was in the form of a 120 nm metal grid. The device was modelled using semiconductor industry standard 2D simulation software (Atlas from Silvaco Corp). This is finite element software which performs a fully coupled solution of the Poisson equations, hole and electron continuity equations and the modified Boltzmann transport equation to give a self consistent solution of the electric field and potential inside the device, the carrier concentrations and the hole and electron currents. These simulation results showed quite clearly that with a suitable grid hole spacing and under the correct grid bias conditions, a significant hole conduction to the TiO_2 electrode surface would be expected – in fact up to 25% of the holes generated in the Si are predicted to reach the surface of the TiO_2.

Any holes reaching the TiO_2/moist air or TiO_2/water interface would be expected to generate OH radicals, as is observed with more conventional systems where TiO_2 powders or electrodes are irradiated with UV light.[4–6] Hence, the electrically biased Si/TiO_2/Au device should be able to disinfect air or water streams under electrical stressing, and without the requirement for a remote counter electrode or any optical excitation. To test this conclusion, a device was fabricated which consisted of thin TiO_2 films deposited onto n-Si wafers by a modified physical vapour deposition (PVD) method; in turn, a gold grid was deposited directly onto the TiO_2 also using PVD. The device consisted of a ¼ of 10.0 cm diameter (*i.e.* 18 cm^2), 500 μm thick Si wafer, n-type (100) substrate, of resistivity of 1–10 Ω cm, coated with a 120 nm TiO_2 layer and a Au grid formed of wires 120 nm thick, 0.375 mm wide and 1 mm apart, total area of Au 6.6 cm^2 and total length of the TiO_2/Au perimeter 218 cm, see Fig. 1. The Au grid was deposited on a 1 nm Ti 'wetting' layer.

The disinfection activity of a n-Si(100)/TiO_2/Au-grid was assessed using an 18 cm^2 section placed in 100 cm^3 suspension of *ca.* 10^7 cfu ml^{-1} of the K-12 strain of *E. coli* (NCMB 8277) in 100 ml 1.4 mM Na_2SO_4 solution stirred by a magnetic bar and enclosed by a thermostatically controlled water jacket. The concentration of bacteria in suspension was monitored by serial dilution followed by growth on agar gel and colony counts (average of six).[6] As may be seen from Fig. 2, clear, potential-dependent disinfection activity was demonstrated. As a further check, the experiment depicted in Fig. 2 was repeated, first with visible radiation and then with the Au grid positive with respect to the Si. In neither case was disinfection activity observed.

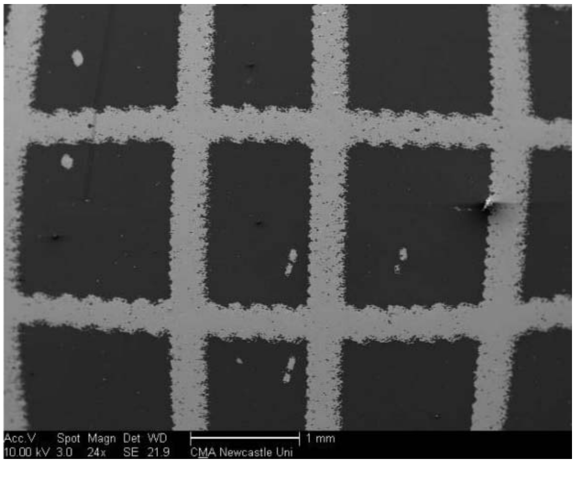

Fig. 1 SEM of the Si/TiO_2/Au device; bar = 1 mm. The light areas represent the Au grid deposited on the TiO_2 overlayer on Si.

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[a] *School of Chemical Engineering and Advanced Materials, Newcastle University, Newcastle upon Tyne, UK NE1 7RU.*
E-mail: p.a.christensen@ncl.ac.uk; Fax: +44 (0) 191 222 5472;
Tel: 44 (0) 191 222 5472
[b] *School of Electrical, Electronic and Computer Engineering, Newcastle University, Newcastle upon Tyne, UK NE1 7RU.*
E-mail: n.g.wright@ncl.ac.uk; Fax: +44 (0) 191 222 8180;
Tel: 44 (0) 191 222 8665

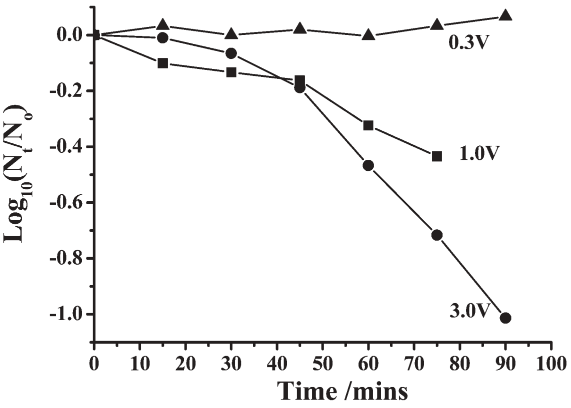

Fig. 2 Disinfection of *ca.* 10^7 cfu ml^{-1} *E. coli* in 100 ml 1.4 mM Na_2SO_4 by an 18 cm^2 n-Si (100)/TiO_2/Au grid.

Since hydroxyl radicals are known to partially destroy the outer membrane and the peptidoglycan layer of *E. coli* membrane walls,[7] and as we have previously shown that the effect of carbonate/bicarbonate on both the photocatalytic and photoelectrocatalytic disinfection of *E. coli* is consistent with a hydroxyl radical mechanism,[8] the disinfection results support the postulated hole transfer to the TiO_2/water interface and subsequent generation of OH radicals. Further support for the generation of hydroxyl radicals was provided, during exploratory measurements, by the development of a 460 nm shoulder to the 390 nm fluorescence spectrum of coumarin excited by 332 nm radiation. This has been reported by Hashimoto and co-workers[9] to be a specific monitor of hydroxyl radicals.

Because the object of this exploratory work has been to test our initial postulate, and since the geometry of the present quarter-disc electrode is so different to the cylindrical electrodes previously used,[5,8] we have not directly compared the activity of the present device with conventional photoelectrocatalysis. However, the results in Fig. 2 demonstrate near complete disinfection of a 100 cm^3 suspension in 90 min for an applied potential of 3 V. This compares with the disinfection of 500 cm^3 in 10 min (by thermal electrodes) or 25 min (sol–gel electrodes) using mesh electrodes with a significantly larger ($\times \sim 10$) geometric area. A crude normalization suggests that, although the order of activity is thermal > sol–gel > Si/TiO_2/Au-grid, the activities of all three systems are the same, within a factor of 5. This is a remarkable result since, unlike the conventional electrodes, the Si/TiO_2/Au electrodes have not been optimized and require neither visible nor UV excitation.

The presence of harmful bacteria in water is a major hazard to public health in many developing countries and is a recognised health risk even in first world societies. For over 20 years UV/TiO_2 has been put forward as a novel and potentially effective technology to disinfect and detoxify water and air. However, real progress has been incremental and slow, and the significant disadvantage of the poor quantum yield for OH radical generation at irradiated TiO_2[10] remains a major challenge. The preliminary results presented in this paper offer, in principle, a radically new approach to the detoxification and disinfection of water and air. If this potential is to be realised, the activity of the device must be understood, optimised (typical current densities through the devices at 3 V are of the order of tens of mA cm^{-2}) and benchmarked, first against conventional UV/TiO_2 approaches, and then against other novel electrochemical devices such as those based on conducting paints and TiN.[11]

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