Effect of pH on the Stability of TiO_2 Coatings on Glass Photocatalysis Reactors for Water Purification

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TiO_2 coated glass shows excellent stability in the range pH 2–9, however, there is rapid and complete stripping of the TiO_2 coating between pH 11 and 12.

Semiconductor photocatalysis offers a promising route to decontaminate polluted waste waters[1–4] of a wide range of organics. In this technique, ultra-band-gap excitation of the semiconductor produces electron-hole pairs. The photogenerated electron is able to reduce any O_2 present to H_2O_2 or H_2O and the photogenerated hole produces surface $OH^{\cdot}$ radicals, which bring about the complete oxidation of the pollutant to its minerals. The overall photocatalytic reaction may be summarised by eqn. (1)

$$\text{Organic pollutant} \xrightarrow[O_2,\ \text{semiconductor}]{h\nu > \text{band gap}} CO_2 + H_2O + \text{mineral acids} \quad (1)$$

The semiconductor TiO_2, which is biologically and chemically inert, has proved to be highly effective in reaction (1) for an extensive range of organic contaminants.[4] It is generally agreed, that the most likely way semiconductor photocatalysis will emerge as a commercially viable method of water purification, is one in which TiO_2 is immobilised as a photocatalytic film, on a glass substrate in a photoreactor and the polluted water is flowed past.[5] This approach has attracted a great deal of research and commercial interest and pilot plants are already being developed and tested. TiO_2 readily adheres to glass and it is this feature which has been used to create most of the flow photoreactors for water purification developed to date. However, to our knowledge, the stability of these TiO_2-on-glass films towards aqueous solutions of different pH has not been investigated. The initial results of such a study are reported below and have major implications on the extensive current work on flow systems using a TiO_2 photocatalyst.

A slurry of TiO_2 (Degussa P25) was prepared by dispersing 10 g of TiO_2 in 200 ml water using a direct immersion sonic horn, followed by stirring for 12 hours. The slurry was poured through a glass tube [borosilicate or sodalime glass: 1.5 m × 7 mm (od)/5 mm (id)] and the resultant TiO_2-on-glass film was dried by passing a rapid air stream through the tube. The process was repeated five times and after the final coating the film was dried for 10 hours at 250 °C.

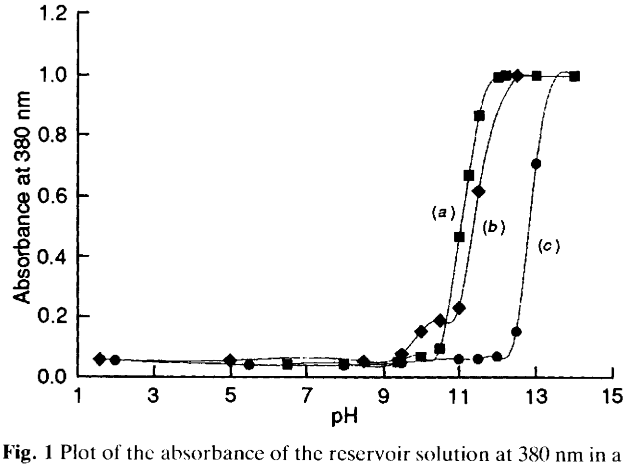

Fig. 1 Plot of the absorbance of the reservoir solution at 380 nm in a 1 cm cell as a function of the solution pH; (*a*) borosilicate glass, no ionic strength buffer, (*b*) borosilicate glass, with 0.1 mol dm^{-3} $NaNO_3$ ionic strength buffer, (*c*) sodalime glass, no ionic strength buffer

In order to assess the stability of the TiO_2 coating to aqueous solutions of different pH, a flow system was set up in which a peristaltic pump was used to circulate 200 ml of a water reservoir around a loop incorporating two 1.5 m coated tubes coupled in series. The pH of the reservoir was controlled using an autoburette and monitored via a chart recorder using glass pH indicator electrode/saturated calomel reference electrode combination. At each pH a period of 30 min was allowed before the next addition of alkali was made. The stability of the coating was monitored as a function of pH by measuring, at 380 nm, the absorbance of samples of the aqueous solution in the reservoir using a 1 cm cell. Any particular level of TiO_2 present in the reactor solution gives it a certain opacity. By comparison of the absorbance of this solution at 380 nm with that of standard solutions of TiO_2, which exhibit a linear absorbance/concentration relationship in this concentration range, the concentration of TiO_2 in the aqueous solution of the flow reactor can be determined.

The observed variation in the absorbance of the reservoir solution as a function of pH is illustrated in Fig. 1, curve (*a*). It can be seen that while the coating is stable in the range pH 2–9, it is rapidly stripped off in the pH range 11–12. In identical experiments the pH was varied in the presence of an ionic strength buffer (0.1 mol dm^{-3} $NaNO_3$) and the results of this work are illustrated in Fig. 1, curve (*b*). From this work it appears that stability of the TiO_2 coating is independent of the ionic strength, which suggests that its removal is not a surface charge related phenomenon. Additional experiments were performed in which sodalime glass tubing, as opposed to borosilicate tubing, was used as the support. In this case there is a shift in the pH, from pH 10.5 to 12.5, at which TiO_2 stripping is observed as illustrated by the data in Fig. 1, curves (*a*) and (*c*).

It is well established[6–8] that glass will dissolve at high pH, indeed the onset of glass dissolution occurs at a very similar pH to the stripping of the TiO_2 coating illustrated in Fig. 1. This evidence indicates that it is the dissolution of the surface layers of the glass tubing which is responsible for the poor stability of these coatings at high pH.

From the absorbance of the flow reactor solution at pH 12 after 30 min it appeared that *ca.* 70% of the TiO_2 coating on the tubes had been stripped off and this extended to 100% when the exposure time was increased to 2 hours. In blank experiments it was found that there was no TiO_2 stripping from an identical coated glass tube when a solution of pH 5 was flowed through it for 10 hours.

In conclusion, whilst TiO_2 photocatalytic purification of water is a very promising method, these results show that the physically adsorbed TiO_2-on-glass films commonly employed in flow reactors are not stable at high pH. Further work on the effectiveness and pH stability of chemically bound TiO_2-on-glass films is needed.

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