Sustained production of H_2O_2 on irradiated TiO_2 – fluoride systems

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Received (in Cambridge, UK) 15th December 2004, Accepted 18th March 2005
First published as an Advance Article on the web 6th April 2005
DOI: 10.1039/b418789j

UV irradiation of fluorinated TiO_2 suspensions in water, in the presence of oxygen and a hole scavenger, leads to the production of H_2O_2 with steady state concentration levels up to 1.3 millimolar; the H_2O_2 formation rate follows the TiO_2 surface speciation, being maximum when the surface is completely covered by ≡Ti–F groups; these results outline the importance of surface speciation on the photocatalytic process.

In recent years photocatalytic reactions over semiconductor oxides have been investigated in depth.[1,2] The formation of reactive oxygen species, namely $OH^\bullet$, O_2^-, H_2O_2, during catalytic processes on metal oxide semiconductors is of paramount importance for practical application of both photocatalysis (*e.g.* water and air detoxification, self cleaning and self disinfecting surfaces) and metal oxide catalysed oxidation of organic compounds.[3,4] Formation of H_2O_2[5–9] and superoxide[5,9,10] from irradiated TiO_2 particles has been reported. Concentration levels of H_2O_2 noticed so far are in the micromolar range. Although now there is a consensus on the reductive mechanism involving O_2 reaction with a conduction band electron (e_{CB}),[7,8] the detailed pathway of H_2O_2 production and the influence of parameters like pH, the presence of anions, the nature and concentration of hole scavenger, are still missing. Recently the strong influence of surface adsorbed ions on the photocatalytic oxidation mechanism of organic substrates over TiO_2 was demonstrated.[11–13] Surface complexation by the redox inactive fluoride ion leads to an increase in the degradation rate of organic substrates that react mainly through an $OH^\bullet$ radical mediated pathway, with a bell shaped dependence on pH, reflecting the distribution of ≡Ti–F;[11] a kinetic analysis of competition experiments with different $OH^\bullet$ scavengers allowed the quantification of the relative role of direct electron transfer and mediated oxidation through $OH^\bullet$ radical (free or adsorbed) in the photocatalytic degradation of phenol, showing that over TiO_2/F the transformation proceeds almost entirely through mediated oxidation by free $OH^\bullet$, whereas on naked TiO_2 about 10% is due to a direct hole oxidation and the 90% to $OH^\bullet$ (adsorbed).[12] In this note we present the results of the surface fluorination of TiO_2 on the reductive processes started by e_{CB}, specifically the production of H_2O_2 through oxygen reduction.

The irradiation experiments were carried out on 5 ml of aqueous suspension containing the hole scavenger (formic acid or phenol) and 0.5 g L^{-1} of catalyst (TiO_2 P25 powder, Degussa), using a 40 W fluorescent lamp (TL K 40W 05 Philips, max. emission at 360 nm). Fluorides were added as HF. The pH before irradiation was adjusted by adding HNO_3 or NaOH solutions. Total photonic flux was 1.0×10^{-5} Ein min^{-1}. The filtered suspensions were analysed by the appropriate analytical technique (HPLC, ion chromatography or spectrophotometry). A careful cleaning of TiO_2 powder to eliminate organic and ionic impurities was carried out by irradiating in air a TiO_2 suspension for two days, then washing the powder until no chloride ions were detected. The H_2O_2 was quantified by the peroxidase-catalysed oxidation of either *p*-phenylenediamine[14a] or phenol/4-aminoantipyrine[14b] (when phenol is employed as hole scavenger).

The first striking feature of photocatalytic processes over TiO_2/F in the presence of a hole scavenger is the production of H_2O_2 with steady state concentration levels in the millimolar range (Fig. 1).

These concentrations are at least 100 times higher than those reported so far. The maximum photonic efficiency attained for H_2O_2 photoproduction is 1.25% (pH 3.2, $[HF] + [F^-] = 10$ mM). Without fluoride, the H_2O_2 in the photocatalytic system is not detectable (below 0.1 μM). A possible role in the enhancement of oxygen adsorption over TiO_2/F could be relevant.[15] The second feature is the bell shaped pH dependence of the initial rate of H_2O_2 production (Fig. 2). The maximum rate is obtained around pH 3.1 and the curve is very similar to the dependence on the pH of ≡Ti–F coverage.[11] Similar results were obtained by using phenol as hole scavenger. However, the ratio between the initial rates of H_2O_2 production and phenol degradation is half of that observed with formic acid (0.16 *vs.* 0.31 at pH 3.2). This result can be explained by the reducing ability of the radical generated by the one electron oxidation of HCOOH, which could give the current doubling effect in photoelectrochemical systems, or, as in the present case, produce an additional molecule of O_2^- from the reduction of O_2.[16]

No H_2O_2 is formed in the absence of: 1) fluoride ions; 2) a hole scavenger; 3) oxygen, even in the presence of fluoride and Ag^+ as

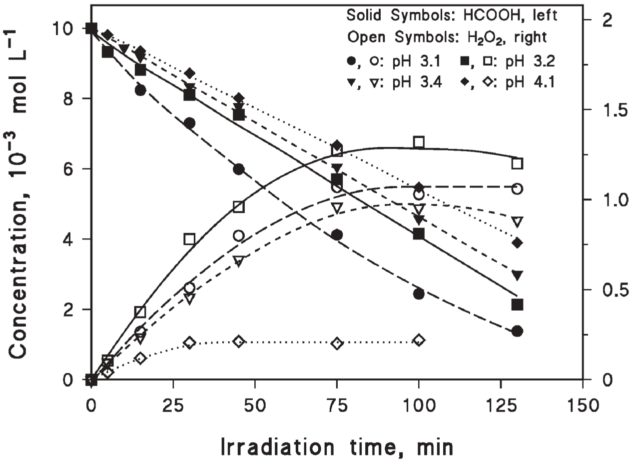

Fig. 1 H_2O_2 production in the photocatalytic degradation of formic acid over fluorinated TiO_2. Conditions: TiO_2 0.5 g L^{-1}, HCOOH 1.0×10^{-2} M, $[HF] + [F^-] = 1.0 \times 10^{-2}$ M. Air saturated suspension.

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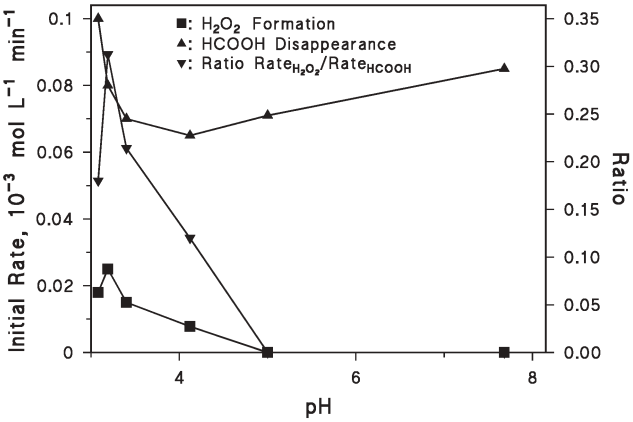

Fig. 2 Influence of pH on the initial rate of the photocatalytic H_2O_2 production. Data are obtained from experiments like those reported in Fig. 1.

electron scavenger. On the other hand, the loss of H_2O_2 under photocatalytic conditions is inhibited by the presence of fluoride. Fig. 3 reports the disappearance curves of H_2O_2 at pH 4. The ratio of the initial rate of H_2O_2 disappearance in the absence and in the presence of fluoride ions (1×10^{-2} M) is $R^{deg}{}_{H_2O_2} = 19$.

The ability of peroxides to complex Ti(IV) compounds[17] and the surface of titanium dioxide has long been known.[18] However, no equilibrium adsorption data are reported. Recently it was noticed that there was a pH dependence of the formation of ≡Ti–OOH species.[19] The insert of Fig. 3 reports the adsorption isotherms of H_2O_2 at pH 4 over TiO_2 P25 in the absence and in the presence of fluoride ions (1×10^{-2} M). The competition of fluoride with H_2O_2 for the TiO_2 surface sites is evident. Interestingly, the ratio of the H_2O_2 adsorbed in the absence and in the presence of fluoride, when $[H_2O_2]_{free} = 1 \times 10^{-3}$ M, is $R^{ads}{}_{H_2O_2} \approx 22$ (Fig. 3, insert). Thus, a possible role of the redox inert ligand is the inhibition of the formation of surface superoxo/peroxo species. When these are produced from O_2 reduction by e_{CB}, in the presence of F^- a release in solution of $HO_2^{\bullet}/H_2O_2$ is achieved:

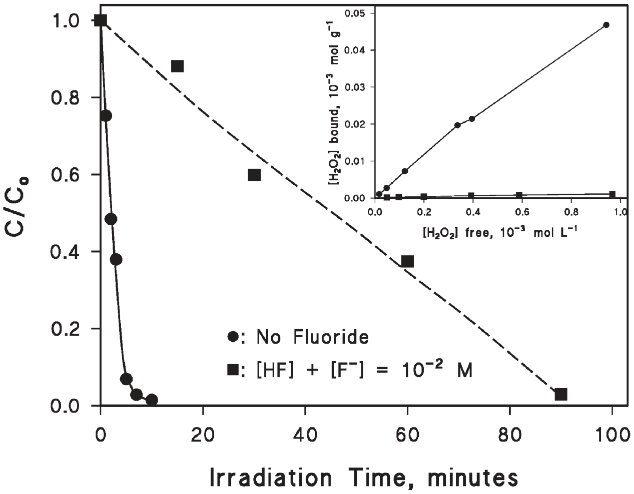

Fig. 3 Photocatalytic degradation of H_2O_2 ($C_o = 1 \times 10^{-3}$ M) in the presence and in the absence of fluoride. Conditions: TiO_2 0.5 g L^{-1}, pH 4.0. Air saturated suspension. Insert: H_2O_2 Adsorption isotherm on TiO_2 at pH 4 in the presence and the absence of fluoride. Conditions: TiO_2 5 g L^{-1}, pH 4.0.

$$\equiv Ti–OH + O_2 + e_{CB} + H^+ \rightarrow \equiv Ti–OO^{\bullet} + H_2O$$

$$\equiv Ti–F + O_2 + e_{CB} \rightarrow \equiv Ti–F + O_2^{\bullet -}(aq) \rightarrow H_2O_2$$

The ratio between $R^{deg}{}_{H_2O_2}$ and $R^{ads}{}_{H_2O_2}$ is $19/22 \approx 0.86$, suggesting that the photocatalytic transformation of H_2O_2 involves almost entirely the reaction of the surface ≡Ti–OOH complexes and not free H_2O_2. Anions without surface complexing abilities (*e.g.* nitrate) do not lead to H_2O_2 formation. These results are consistent with the reported production of H_2O_2 over irradiated ZnO,[7] the surface of which is not complexed by H_2O_2.

In conclusion, the modification of the TiO_2 surface through anion complexation has a strong influence on the reductive pathways started by photogenerated e_{CB}. The major effect of the presence of oxygen as electron scavenger is the sustained production of hydrogen peroxide, with steady state concentration levels of 1–1.3 mM, nearly 100 times the levels reported so far. Experimental results are explained in terms of a competition of the fluoride with superoxide/peroxide species for the surface sites of TiO_2, thus inhibiting H_2O_2 degradation.†

The authors are grateful to MIUR (PRIN03, Contract No. 20030335534) and Università di Torino (Ricerca locale) for financial support.

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Notes and references

† Presented in part at "XIV Congresso Nazionale di Catalisi – GIC2004", Lerici, La Spezia, Italy, 6–10 June 2004 and "The 9th Conference on TiO_2 Photocatalysis", San Diego, CA, USA, 24–28 October 2004.

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