

Enhancement of Photocatalytic Oxygen Evolution in Aqueous TiO₂ Suspensions by Removal of Surface-OH Groups

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The activity of TiO₂ particles for photocatalytic oxygen evolution in the presence of Ag⁺ ions as an electron acceptor is increased 10 times by the removal of surface hydroxy groups through thermal treatment.

It is well known that surface hydroxy groups play an important role in the photoadsorption of O₂ on TiO₂.¹ This reaction has been suggested to account for the difficulties in observing O₂ release in water decomposition experiments involving TiO₂ dispersions in closed systems.² Electrochemical experiments have confirmed the importance of hydroxy groups in mediating electron transfer from the conduction band of TiO₂ to acceptors in solution.³ On the other hand, little is known about the role of surface-OH in the reaction of holes with

water to yield oxygen. While scrutinizing these effects, we discovered a remarkable enhancement in the oxygen evolution rate associated with the removal of surface-OH groups on which we report in the following.

The degree of hydroxylation of TiO₂ powder was adjusted by thermal treatment. In order to avoid a phase transformation during this procedure, rutile (Brunauer-Emmett-Teller surface area 80 m²/g) was used as a starting material, and heated (7 h) at various temperatures in a stream of Ar or

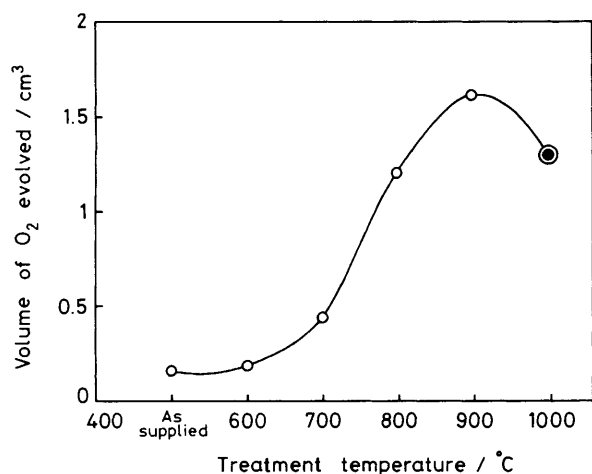


Figure 1. Volume of O₂ (standard temperature and pressure: s.t.p.) evolved after 5 h of reaction over TiO₂ treated at various temperatures. ○, treated in Ar stream; ●, treated in O₂ stream. Conditions: TiO₂ (rutile), 100 mg; AgNO₃, 1 mmol.

O₂. AgNO₃ (Merck, analytical grade) was used as an electron acceptor.⁴ Other chemicals were at least reagent grade and were used as supplied. Samples of 25 ml volume containing invariably 1 mmol AgNO₃ and 100 mg TiO₂ were irradiated in a Pyrex glass vial closed with a septum. Prior to irradiation, the dispersion was freed from O₂ by purging with Ar. Irradiation was carried out with a Hanau suntest lamp (global irradiance 70 mW/cm²) whose emission spectrum closely mimics solar radiation. Oxygen was determined by gas chromatography using a molecular sieve 5 Å column and Ar as a carrier gas. Ag⁺ was determined by potentiometric titration with HCl on a Metrohm Titroprocessor 636 and Dosimat 635. The amount of surface-OH was determined by an Na⁺ adsorption method⁵ with NaOH_{aq} (2 × 10⁻³ M).

Figure 1 shows the effect of treatment temperature on the amount of oxygen evolved during the first 5 hours of illumination. The volume of O₂ increases drastically for rutile powders treated at 700 °C and above. TiO₂ heated at 900 °C exhibits the highest activity. The volume of O₂ obtained is here 10 times higher than that observed with the untreated powder. The fact that there is no difference in the activity of TiO₂ treated at 1000 °C in Ar and O₂ shows that doping (partial removal of lattice oxygen rendering the TiO₂ particles n-conducting) cannot explain the observed phenomena, because TiO₂ cannot be n-doped in a stream of oxygen (1 atm).

Further analysis showed a correlation between photocatalytic activity for O₂ generation and surface hydroxy density. A positive and nearly linear relationship is obtained between the initial rate of O₂ production and the reciprocal concentration of OH groups present at the surface of the rutile powder, which indicates that a low hydroxy density favours liberation of O₂, Figure 2.

The molar ratio of silver ions reduced and oxygen evolved during the photoreaction was also found to be affected by the surface hydroxy density. (The amount of Ag deposited onto the TiO₂ powder was determined by oxidation with K₂S₂O₈ and quantitative analysis of Ag⁺ with a silver ion specific electrode.) Thus, TiO₂ powders with a low OH density resulting from thermal treatment at high temperature gave a molar ratio of 4 which is expected from the stoichiometry of reaction (1). For example, TiO₂ powder treated at 1000 °C under Ar produced after 21 hours of photolysis 101 μmol of O₂ while, at the same time, 417 μmol of Ag were deposited. On

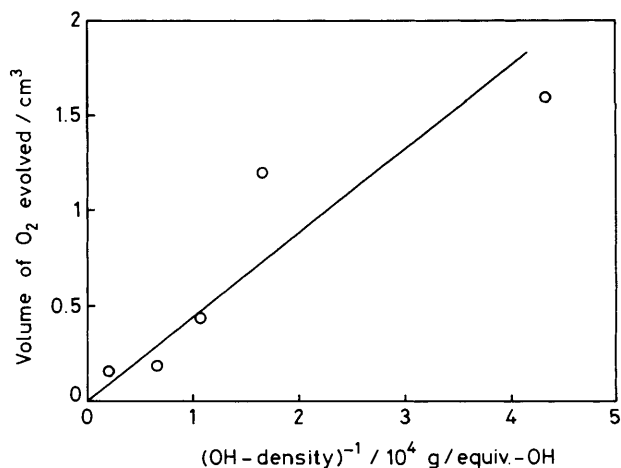
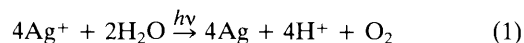


Figure 2. Dependence of volume of O₂ (s.t.p.) evolved after 5 h of reaction on the reciprocal of OH density.

the other hand, TiO₂ powders with high hydroxy density gave a molar ratio ($r = [\text{Ag}]/[\text{O}_2]$) exceeding significantly the value 4. Thus, for untreated rutile 9.2 μmol of O₂ were formed in 21 hours of irradiation and 61 μmol of Ag deposited, indicating $r = 6.6$. It can be excluded that the $r > 4$ values observed with highly hydroxylated powders are due to the presence of carbonaceous impurities acting as hole scavengers since elemental analysis showed the carbon content of the TiO₂ employed to be negligible (≤ 0.01 wt %). Other impurities, such as Cl or S, were only present in trace amounts and were not affected by the high temperature treatment. Elemental analysis gave 34 p.p.m. of Cl and <14 p.p.m. of S in the TiO₂ samples as received. After treatment at 1000 °C 26 p.p.m. of Cl and <13 p.p.m. of S were still present.



Finally, it should be pointed out that the effects observed here are not unique to Ag⁺ since with other electron acceptors, *i.e.* PtCl₄²⁻ and BrO₃⁻, a similar correlation between oxygen yields and surface hydroxy density was obtained. This would indicate that the effect of surface-OH on the efficiency of photocatalytic oxygen generation arises from the valence rather than the conduction band process. It appears, therefore, that the hole reaction in the case of highly hydroxylated TiO₂ does not lead directly to oxygen but rather to an intermediate, presumably a peroxo titanium complex,² whose decomposition is slow.

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References

- 1 G. Munuera, V. Rives-Arnau, and A. Sancedo, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 736.
- 2 E. Yesodharan and M. Grätzel, *Helv. Chim. Acta*, 1983, **66**, 2145.
- 3 B. Parkinson, F. Decker, J. F. Juliao, M. Abramovich, and H. C. Chagas, *Electrochim. Acta*, 1980, **25**, 521; P. Salvador and L. Gutierrez, *Chem. Phys. Lett.*, 1982, **86**, 131.
- 4 S. Nishimoto, B. Ohtani, H. Kajiwarra, and T. Kagiya, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 2685.
- 5 H. P. Boehm, *Faraday Discuss., Chem. Soc.*, 1971, **52**, 264.