# Photooxidation of Sulfur Dioxide by a Polymer Supported Porphyrin on Platinized $TiO_2$ Particles

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Received March 21, 1984

## Introduction

Recently, photooxidation of $SO_2$ on the surface of an n-doped $SnO_2$ electrode coated with a film of polyvinylpyridine(PVP) supporting zinc tetraphenylporphyrin(ZnTPP) as a chromophore was reported from this laboratory [1]. The efficiency was interesting in that the overall utilization of absorbed white light was approximately 2% efficient and the estimated monochromatic quantum yield was as high as 0.06. It is of interest to compare the photoelectrochemical configuration to a 'photocatalyst' configuration were the opportunity to apply a voltage no longer exists. In this note we report the preparation of the ZnTPP/PVP system on 10 micron particle size commercial pigment $TiO_2$ loaded with 0.7% Pt ($Pt/TiO_2$) and its exploitation in the oxidation of $SO_2$. The comparison of the two systems is important. Parallel behaviour would be quite useful. The photoelectrode allows the use of all of the tools of electrochemistry including the current-voltage curve and control of hydrodynamics to be brought to bear on the analysis of mechanism. The particle dispersion, however, represents the more promising fom for 'synthetic' photochemistry.

## Experimental

$Pt/TiO_2$ was prepared by method 'B' drawn from the critical comparison of platinization methods given by Mills [2] using '10 micron' particle size $TiO_2$ supplied by Tioxide Canada. The solution of PVP (Aldrich 10% polystyrene) was prepared by dissolving 104 mg of PVP in 100 ml of $CHCl_3$ along with 24 mg of ZnTPP (Eastman). The coating of the particles was accomplished by addition of 5 ml of the ZnTPP/PVP solution to 25 ml of $CH_2Cl_2$ containing 100 mg of $Pt/TiO_2$ dispersed by sonication. The solution is initially reddish in colour. The solid was isolated by evaporation of the volatile solvents at room temperature with occasional stirring. The solid is greenish in colour as was the photoelectrode [1] after polarization cycling.

The spectrum of the powder was obtained for comparison with the transparent electrode by preparing a 2% by weight KBr disk analogous to the technique used for IR of solids. We have previously used this method to obtain satisfactory qualitative absorption spectra of transition metal ions in zeolite powders [3]. Spectra were recorded on a Cary 14 UV-Vis spectrophotometer.

Reaction media were prepared by sonication of 100 mg of the 'catalyst' powder into 25 ml of water, deaerating with nitrogen and saturating with sulfur dioxide. The reaction was conducted in a 50 ml round bottom flask irradiated for 12 h with a 1000 W Hg lamp filtered through water to remove IR and a through a 420 nm cutoff filter to remove UV.

Light intensity was measured using reineckate actinometry [4] on a solution of potassium *trans*-diaminotetraisothiocyanatochromate(III) of a concentration 0.050 *M* which should be sufficient to absorb more than 90% of the light across the visible. Titration of $SO_2$ used conventional iodimetry.

## Results

The initial concentration of sulfur dioxide in the reaction solution was measured as 0.80 *M* after 12 hours of irradiation; the average residual $SO_2$ was estimated as 0.50 ± 0.01 *M*. (The probable reduction product is hydrogen at Pt) In blank runs with the photocatalyst omitted, the maximum loss of $SO_2$ concentration was 0.032 *M*. The calculated average yield of sulfuric acid is 7.5 mmol according to actinometry, the light entering the sample was 10.8 einstein.

The chromophore present in the reaction vessel corresponds to 0.6 mmol. Thus, on the assumption that all chromophoric molecules are participant, a minimum of 12 mol of sulfuric acid are produced per mole of chromophore.

The overal 'efficiency' of conversion of light to oxidizing power is only 0.07%. This appears to imply that the efficiency of the dispersed 'catalyst' is significantly lower than that of the photoelectrode, lower by a factor of 20 or more by comparison with the electrode polarized to an optimal voltage or by more than 10 at zero applied potential between the tin oxide and Pt electrodes. However, it is necessary to account for the 'non-optimum' geometry of the irradiation and light scattering losses from the particle dispersion. In the actinometry experiment, no significant scattering reduces the intensity of light available for chemistry inside the flask. However, study of the light scat-

0020-1693/84/$3.00

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tered by the oxide dispersion using a spectrofluorimeter as a 'nephelometer' shows that light scattered out of a 1 cm cell is very large. Comparison with scattered light loss from the dispersion after coating with the chromophore did not reveal a significant reduction in scattering. This indicated that the dye on the dispersion does not act efficiently to reabsorb scattered light within the 1 cm path. We estimate that scattering loss from the 50 ml flask exceeds 90%. Thus, the apparent reduction in efficiency may be entirely attributable to scattering and the major problem for design of a 'catalytic' system will be to develop an efficient reactor geometry.

The spectrum of the dye on the oxide dispersion in KBr pellets shows a maximum at 560 nm with a shoulder at 605 nm. The previously reported spectrum of the transparent electrode had peaks at 565 and 605 nm whereas a solution of the dye in the presence of excess PVP has bands at 562 and 602. The intensity ratio for the latter two cases is 565/605 = 1.8–1.9. Correcting for scattering approximately suggests a ratio on the catalyst particles of 1.6–1.7. Qualitatively, the spectra are equivalent.

## Discussion

The very close parallel between the results for the present dispersed 'photocatalyst' and the transparent photoelectrode discussed earlier [1] illustrates a useful tactical device for the development of system for operation of photochemistry on dispersions. The complicated combinations needed to produce interesting reactions at attractive efficiency are difficult to study. Here, for example, we have the porphyrin as a chromophore, a metal oxide semiconductor with a conduction band edge below the level of the excited state of the chromophore as an electron acceptor and mediator and Pt as a catalyst for the reduction step. (The role played by the PVP is not yet so clearly specifiable.) The information extractable from a current voltage curve, especially where this can be coupled with information about mass transport in the solution from variation of flow of solution near the electrode permits much more detailed analysis of reaction and charge transport mechanisms than are possible from studies of particle dispersion chemistry. On the other hand, economic utilization of solar energy for photochemical conversion may depend on the low cost of dispersions as light harvesting systems. Consequently, it is very useful to be able to pursue the study of the two related systems in close coordination. At least in the case of the photooxidation of sulfur dioxide, this appears to be possible.

## Acknowledgement

We thank the Natural Sciences and Engineering Research Council of Canada and Les Fonds FCAC du Québec for financial support.

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