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TiO_2 catalysed photo-oxidation of water in the presence of methylene blue

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Photolysis of an aqueous solution of methylene blue in the presence of TiO_2 is found to generate O_2 with reduction of methylene blue to the lecuo form. The rate of O_2 evolution and the rate of reduction of the dye is monitored and the kinetics are determined. The study shows that certain organic molecules adsorbed on TiO_2 can be reduced with concomitant oxidation of water.

1. Introduction

Catalysis of photochemical reactions by semiconductor particles continues to be an active area of research [1–7]. Much effort has been given to adopt semiconductor photocatalysis as a means of initiating economically important chemical reactions [1–7] such as (a) photodecomposition of water, (b) photofixation of nitrogen, (c) photoreduction of carbon dioxide, and (d) mineralization of organic contaminants in water. The quantum yields obtained for the processes (a), (b) and (c) are several orders of magnitude lower than the limits of practical viability [1–7]. However, the continuation of the above studies could contribute much to the fundamental knowledge needed for the development of future practical systems. A point noted by the earlier workers in the above field is that hydrogen evolution from water under sacrificial conditions is a relatively easier task, compared to oxygen evolution [7–10]. Oxygen photogeneration from water necessitates rapid consumption of photogenerated electrons by the sacrificial agent, so that the accumulated holes can be readily transferred to water (generation of one molecule of O_2 requires the transfer of 4 electrons). It was noted, that with a few inorganic electron acceptors (e.g., bromate, persulphate, silver nitrate) O_2 is photoproduced from water in the presence of TiO_2 [7–10]. On the other hand most organic compounds (with TiO_2 as the catalyst) act as electron donors and undergo oxidation with concurrent H_2 evolution via electron transfer to water [11]. Here, we report our observations on photolysis of an aqueous solution of methylene blue in the presence of TiO_2. In contrast to the expected behavior of most organic

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compounds, methylene blue was found undergo reduction to the lecuo form with O_2 evolution. It is suggested that the observed effect results from the trapping of photogenerated electrons by methylene blue adsorbed at the TiO_2 surface.

2. Experimental

In all experiments TiO_2 (Aldrich, surface area = 3.5 m^2/g) and methylene blue (BDH) were used without further purification. Photolysis experiments were carried out in a 500 ml photochemical reactor (Applied Photophysics) with a water cooled (26°C) cylindrical quartz jacket, where a 400 W medium pressure mercury lamp is housed. A pyrex thimble which covers the lamp was used to cut-off light of wavelength $\geqslant 300$ nm. The photolysis solution was 300 ml aqueous methylene blue (2.5×10^{-4} M) containing 25 mg TiO_2. The solution was rapidly purged with pure (99.99%) argon for 30 min to remove dissolved O_2, the lamp is switched on and a slower purging rate (3 ml min^{-1}) is maintained. The out-going gas was monitored for O_2 and other gases by gas chromatography (Shimadzu GC-9AM gas chromatography, molecular sieve 5A column, thermal conductivity detector). Extreme precautions were taken to prevent leakage of atmospheric oxygen into the reactor. The extent of air leakage was assessed by the detection of N_2 in the out-going gas and necessary corrections were made. To estimate the total amount of O_2 evolved in a given duration of time (50 min), the solution was kept purged with argon after switching off the lamp, until the O_2 signal disappear in the gas chromatograph. The photolysis experiment was also conducted in a reactor fitted with a polarographic detector (Applied Photophysics) and the O_2 evolution was confirmed. The reduction of methylene blue was monitored spectrophotometrically by drawing aliquots of the solution from the reactor.

3. Results and discussion

Fig. 1 gives the time development of the rate of O_2 evolution during photolysis. In about 40 min the solution turns colourless owing to a nearly complete reduction of methylene blue, subsequently a decrease of O_2 in the out-going gas is noted as a result of reductive consumption of the dye. Fig. 2 shows the decrease in methylene blue concentration with the progress of photolysis. when the photolysed solution is exposed to atmospheric O_2, the colour is quickly regained and spectrophotometric estimation revealed that the initial amount of methylene blue is almost completely regenerated. The photochemical reaction occurring can be summarized as

$$(MB)^+ + 2\,H_2O \xrightarrow{TiO_2/h\nu} (MB)H_3^{3+} + OH^- + \tfrac{1}{2}\,O_2, \qquad (1)$$

where MB^+ and $(MB)H_3^{3+}$ denote methylene blue and lecuo-methylene blue cations. The total amount of O_2 generated is in good agreement with the

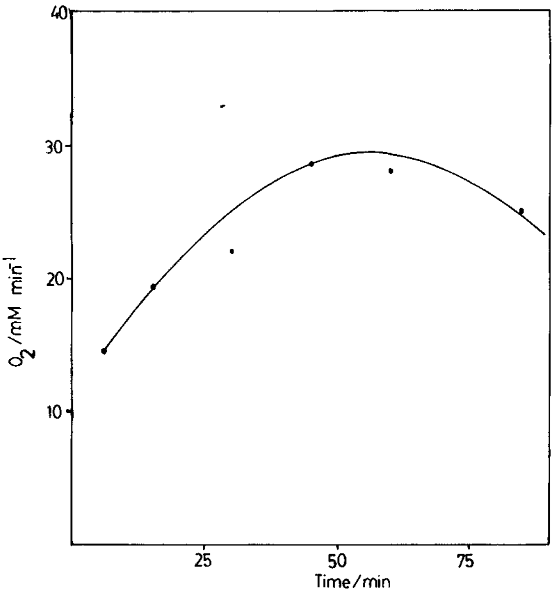

Fig. 1. Plot of the rate of O_2 evolution versus time.

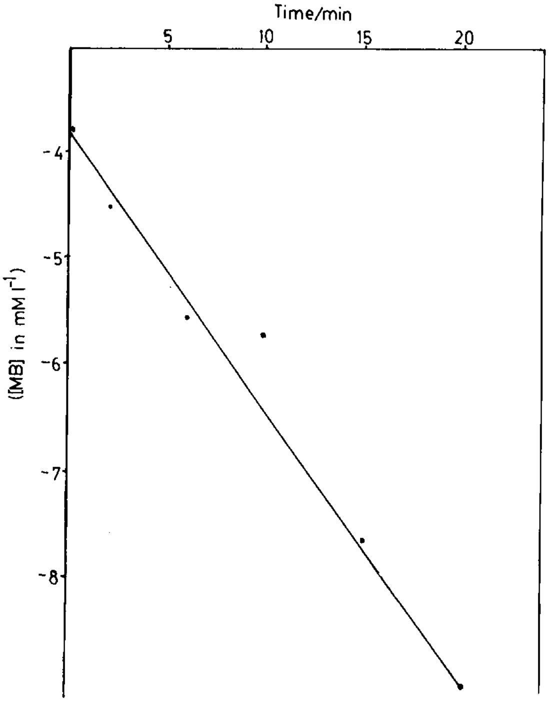

Fig. 2. Plot of [MB] ([MB] = concentration of methylene blue) versus time.

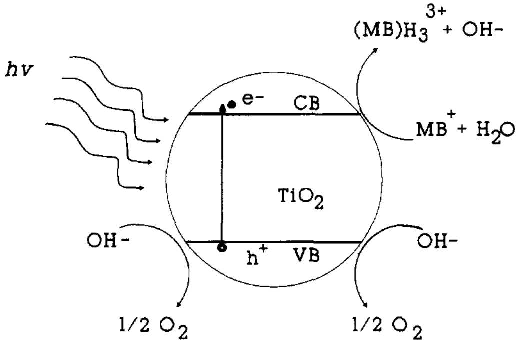

Fig. 3. Energy band diagram showing electron and hole transfer.

stoichiometry of eq. (1). Electron and hole transfer reactions leading to (1) are (see fig. 3)

$$\underset{\overset{\uparrow}{\text{CB TiO}_2}}{(\text{MB})^+ + 3\,\text{H}_2\text{O} + \text{e}^-} \rightleftharpoons (\text{MB})\text{H}_3^{3+} + 3\,\text{OH}^-, \tag{2}$$

$$2\,\text{OH}^- + \underset{\overset{\uparrow}{\text{VB TiO}_2}}{2\,\text{h}^+} \longrightarrow \text{H}_2\text{O} + \tfrac{1}{2}\text{O}_2. \tag{3}$$

The alternative electron transfer scheme, where holes are transferred to methylene blue and electrons to water is completely suppressed possibly because $(\text{MB})^+$ adsorbed onto the surface of TiO_2 acts as an electron attracting site (fig. 3). The above methylene blue reduction reaction is initiated by TiO_2 band gap radiation. Visible light that excites the dye molecules was found to have no detectable effect. If the pyrex filter was not used, methylene blue undergoes detectable direct photodegradation by energetic UV photons.

At low concentrations of methylene blue, the rate equation governing its disappearance is

$$\frac{\mathrm{d}}{\mathrm{d}t}[\text{MB}] = -k[\text{MB}] \tag{4}$$

and the plot of ln[MB] versus time fits into a straight line (fig. 2). The rate constant depends on light intensity and concentration of the catalyst.

4. Conclusion

It is well known that noble metals coated on semiconductor particles act as sites for accumulation of photogenerated electrons. The above observation shows that certain organic molecules adsorbed on semiconductor particles behave in the same manner. Furthermore it is known in photolysis of organic compounds in the presence of semiconductor catalysts, the generally favoured reaction mode is oxidative degradation. In this case electron transfer is directed towards adsorbed dye and prevents oxidative degradation as a result of hole consumption. As quantum yields are small present system will not lead to practical solar energy conversion. Nevertheless it clearly demonstrate the potential of organic compounds in achieving directional electron transfer in solar energy conversion devices.

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