Zirconium Dioxide: A New Photosensitizer under UV Irradiation

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A new colloidal semiconductor, ZrO_2, is used as sensitizer for photocleavage of water under UV irradiation.

There has been much recent interest in the photocleavage of water using semiconductor particle dispersions.[1] Aqueous dispersions of ultrafine semiconductor particles as light harvesting units in solar energy conversion devices have several advantageous features such as high absorption coefficients, electron storage and hydrogen generation *etc.* A number of semiconductors are used for this purpose: TiO_2,[2] ZnO,[3] CdS,[4] ZnS,[5] Fe_2O_3[6] *etc.* When a semiconductor absorbs photons, electrons are excited to the conduction band and holes are generated in the valence band. These electrons and holes can be used to induce reduction and oxidation, respectively. The energy level of the bottom of the conduction band is a measure of the reducing ability of the photoexcited electrons, the higher the energy level the stronger the reductive power of the semiconductors. Accordingly, the new semiconductor, ZrO_2, appears to be promising as a light harvesting agent since its conduction band is at a much higher level[7] than that for previous studied semiconductors. Preparation of a stable form of colloidal ZrO_2 under illumination is an important problem, and we now report our attempts to prepare a stable form of zirconium dioxide sol. The band gap and the size of the semiconductor particles have been determined. Zirconium dioxide colloid is used as photosensitizer in water splitting under UV irradiation and the amount of hydrogen produced has been estimated.

For preparation[8] of the sol, aqueous $ZrOCl_2$ was treated with aqueous oxalic acid (both analytical grade), and the precipitate of zirconyl oxalate filtered off. This white precipitate was hydrolysed by heating with doubly distilled water at 90 °C for 48 h. The resulting zirconium dioxide sol was purified by dialysis. Its conductivity was 4–6 µS and its pH (Elico Li-120 pH meter) 7.51. Its concentration was measured by lyophilization followed by weighing the dried sample. Absorption spectra were measured on a Perkin-Elmer Spectrophotometer-554, and the sol particle size was determined by transmission electron microscopy (TEM) using a Hitachi 600

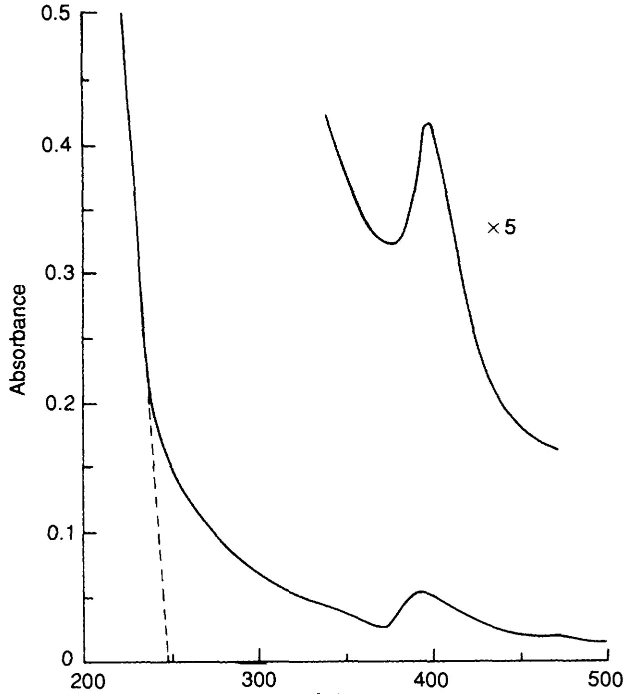

Fig. 1 Absorption spectra of ZrO_2 sol (1.42×10^{-3} mol dm^{-3})

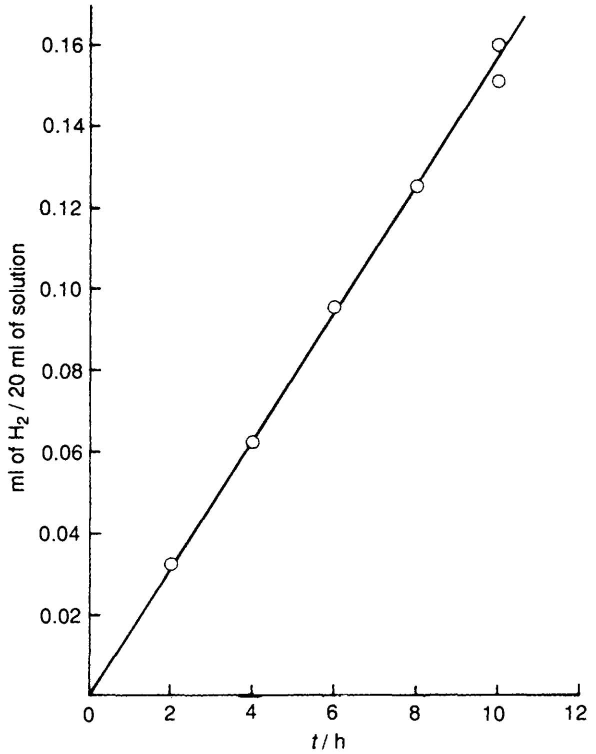

Fig. 2 Variation of amount of hydrogen evolved on UV irradiation of ZrO_2 sol with time (pH 7.51; 3.5 mg ZrO_2 in 20 ml)

instrument following lyophilization and resuspension in water. The particles were of uniform dimensions with diameters in the range 30–40 nm.

The absorption spectra of ZrO_2 sol (Fig. 1) show a weak maximum at 395 nm, whose origin is unclear. It has no appreciable absorbance in the visible region (>400 nm) and it is UV-active. Extrapolation of the rising portion of the spectra to zero absorbance (dotted line in Fig. 1) gives the band gap[6b] of ZrO_2 as 5.0 eV, in good agreement with the literature value.[7]

Table 1 Amounts of H_2 produced from ZrO_2 sol following UV irradiation for 10 h using different filters

Sol sample	Sol vol./ml	Filter	Amount of H_2 detected
1	20	None	0.151 ml
2	20	None	0.160 ml
1	20	425 nm	None
2	20	425 nm	None
1	20	345 nm	13.46 μl
2	20	345 nm	13.51 μl

Argon was bubbled through the sol (20 ml, containing 3.5 mg of ZrO_2) in a quartz cell for at least 1 h. The magnetically stirred sol was then irradiated with a 450 W Xenon lamp (Oriel) under argon for 10 h and the gaseous products were analysed by GC, using a Shimadzu GCR1A chromatograph with a 5 Å molecular sieve column to estimate hydrogen (column temp. 75 °C; carrier gas argon). The amounts of hydrogen produced from two identical samples under different conditions are given in Table 1.

The results indicate that the ZrO_2 sol is capable of producing hydrogen in appreciable amounts under UV irradiation. The amount of hydrogen production decreases with increase in the wavelength, none being produced in the visible region. The direct production of hydrogen from water by the conduction band electrons of the ZrO_2 sol is in agreement with the characteristics of the conduction band as discussed earlier. It is also expected[7] that water would be oxidised by the holes in the valence band and the formation of oxygen has been detected in the system, but it has not been studied in detail since our primary interest was the production of hydrogen from water.

Fig. 2 shows that the production of hydrogen gas increases linearly with irradiation time, showing that the ZrO_2 sol is quite stable under UV irradiation.

The ZrO_2 would not be effective for harnessing solar radiation, but injection[9] of electrons to the conduction band of ZrO_2 from a suitable photosensitizer could make it active with visible light. This and the influence of relay systems, scavengers, catalysts *etc.* are being studied.

Received, 30th June 1992; Com. 2/03465D
Received in revised form 25th January 1993

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