

Efficient Water Cleavage with Visible Light by a System mimicking Photosystem II

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Efficient visible light cleavage of water with simultaneous evolution of hydrogen and oxygen has been achieved by a system mimicking photosystem II, composed of a CdS photoanode modified with a polymer membrane incorporating a highly active water oxidation catalyst.

In the past decade water cleavage by visible light has attracted much attention with respect to chemical conversion of solar energy.^{1–3} This involves an important water oxidation reaction which is the key process in photosystem II of photosynthesis. Water cleavage with a TiO₂ photoanode⁴ occurs only with u.v. light, and there are only a few reports on water photolysis with visible light to give hydrogen and oxygen simultaneously;^{5–12} the photochemical conversion yield in these cases is not high or often not reported. One problem in water photolysis is oxygen evolution, which is normally catalysed by metals or metal oxides such as RuO₂^{5–7,9,10} and Ni;⁸ these are not ideal to achieve efficient water oxidation. In photosystem II of photosynthesis, efficient water oxidation is realized by an oxygen evolving centre composed of a protein complex containing at least two Mn ions. In order to attain a high conversion yield in water photolysis, an efficient water oxidation catalyst should be combined with a photoreaction centre. Some metal complexes have been reported as water oxidation catalysts in homogeneous solution,^{13–15} but their activity and stability were insufficient. We have developed highly active water oxidation catalysts such as Mn and Ru complexes which mimic photosystem II. These catalysts were active even under heterogeneous conditions.^{16–18}

We have reported that a CdS photoanode can be used for visible light water cleavage when the holes formed under irradiation are transported effectively to the water oxidation catalyst to evolve oxygen.¹⁰ Further, it was found that a trinuclear Ru complex (Ru-red), [(NH₃)₅RuORu(NH₃)₄ORu(NH₃)₅]⁶⁺, which was one of the active water oxidation catalysts studied,¹⁶ can stabilize the liquid-junction n-CdS photoanode against photocorrosion, leading to efficient water cleavage to give hydrogen and oxygen simultaneously, when incorporated into a polymer membrane coated on the semiconductor.

A surface (3–4 mm²) perpendicular to the <0001> surface of a single crystal of n-CdS (Cleveland Crystals, Inc.) was used. Ohmic contact with a copper lead wire was made with Ga–In eutectic. A Nafion (perfluorinated cation exchange polymer, Aldrich Chemical Co. Inc.) membrane was coated on the CdS surface, by casting 4 μl of a 5 wt% solution of Nafion, and then dried. The Nafion-coated CdS was dipped in a 0.1 mM Ru-red aqueous solution (10 ml) for 10 min to adsorb

the complex into the membrane; the details are reported elsewhere.¹⁹ The Nafion-coating and the complex-adsorption procedures were repeated twice. The thickness of the Nafion membrane was estimated to be about 50 μm. The irradiation was done with monochromatic light, 496 nm, from a 500 W xenon lamp using an interference filter (Toshiba KL-50) and a u.v. cut-off filter (Toshiba VY-42).

The cyclic voltammogram of a bare CdS electrode measured in an aqueous solution containing 0.5 M KNO₃ and 0.01 M HNO₃, under irradiation, showed an anodic peak at –0.46 V (*vs.* Ag–AgCl) which is typical for a bare CdS electrode.²⁰ The anodic photocurrent obtained at this electrode decreased drastically during repeated cyclic scanning owing to photocorrosion. The cyclic voltammogram of a Ru-red/Nafion-coated CdS electrode, in contrast, did not show a peak originating from corrosion and gave stable photoanodic currents, indicating a distinct stabilization by the modification. Nafion-coating alone without the complex was not effective for stabilizing the CdS photoanode. Electrochemical oxygen evolution, by water oxidation through Ru-red adsorbed in a Nafion membrane coated on a graphite electrode, has been confirmed and reported elsewhere.¹⁹ This result suggested that a Ru complex coated on CdS could accept corrosive holes formed on the CdS surface and lead to water oxidation.

Water photolysis was carried out using a Ru-red/Nafion-coated CdS electrode with a platinum wire counter and silver wire reference electrode. The silver reference electrode was used in order to have a gas-tight cell; its potential was 0.458 V [*vs.* normal hydrogen electrode (NHE)] in the same electrolyte solution. A 4.5 ml aqueous solution containing 0.5 M KNO₃ and 0.01 M HNO₃ was used. Before irradiation, argon gas was bubbled through the solution for 2 h. A potential of 0.36 or 0.46 V (*vs.* NHE) was applied to the CdS electrode, which was then irradiated under argon with monochromatic light at 496 nm (intensity 2.05 mW cm^{–1}). The photocurrent usually increased ~20–30% in the first 10–30 min, and then reached a constant value. Gas bubbles were observed both at the CdS and counter electrodes during the irradiation. After irradiation, the gas phase was analysed by a g.c. system (Shimadzu GC-4C) equipped with a 1.5 m column of molecular sieve (5 Å) and using argon carrier gas at room temperature. The net amount of oxygen evolved was calcu-

Table 1. Water photolysis with an n-CdS photoanode coated with a Nafion membrane incorporating Ru-red.^a

Run	Reaction time /h	Gases evolved			Efficiency/%		
		H ₂ /μl	O ₂ /μl	H ₂ /O ₂	Photocurrent ^b	A ^c	Photolysis ^d
1	4.0	7.4	3.8	1.9	25	64	16
2	7.9	14.0	7.5	1.9	21	71	15

^a Electrode area, 4.7 mm² (run 1); 3.2 mm² (run 2). Applied potential, 0.46 V (run 1); 0.36 V (run 2) (*vs.* NHE). ^b Based on the total irradiation with monochromatic light at 496 nm. ^c Water cleavage efficiency based on the photocurrent. ^d Total photolysis efficiency based on the irradiation light.

lated by subtracting the oxygen content of a blank experiment, for which the blank O₂/N₂ ratio was measured very carefully under exactly the same conditions without irradiation.

The results of water photolysis (Table 1) show that the ratio of the evolved H₂/O₂ is almost 2 for each run. High yields of the photocurrent, 25 and 21%, were obtained with respect to the irradiated monochromatic light. The yields of water cleavage based on the photocurrent, 64 and 71%, seem to be rational in the present preliminary stage. High yields of the total water photolysis, 16%, were obtained based on the irradiated light. The coated amount of the Ru-red was estimated as about 2.5×10^{-6} mol cm⁻² from a cyclic voltammogram of a Ru-red/Nafion-coated graphite electrode. From this, the turnover numbers of the Ru-red catalyst were calculated as 14 (run 1) and 40 (run 2). Almost no leaching of the Ru-red into the solution was observed during each experiment. Thus, visible light water photolysis has been successfully carried out by a system mimicking photosystem II.

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