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Stabilization of Platinum-Loaded CdS Photocatalyst by Addition of EDTA

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The photocatalytic activity of platinum-loaded CdS powder in sulfite solutions declined by illumination over 200 h, and became half the initial activity at 600 h. By addition of small amount (2 mM) of ethylenediaminetetraacetic acid (EDTA) to the solution, however, the photocatalyst was guarded from deterioration. The effect of EDTA is to prevent the platinum part of photocatalyst from the impurity metal deposition by forming stable metal-EDTA complexes in the solution. The reactivities of sulfite ions, EDTA, and metal-EDTA complexes on illuminated CdS are examined electrochemically by use of CdS-sinter electrodes.

A variety of photocatalytic reactions are induced by semiconductor particles. Hydrogen and many organic compounds are produced from aqueous solutions of organic materials, such as alcohols, aromatic hydrocarbons, etc., over the illuminated semiconductor particles loaded with noble metals.[1,2] Hydrogen production occurs also from aqueous solutions of inorganic materials, such as sulfide ions.[3,4] Efficient hydrogen production from aqueous solutions of sulfite was reported by use of noblel metal loaded CdS powder,[5-8] the sulfite ions being oxidized to sulfate and dithionate ions. This photocatalytic reaction is interesting from the viewpoint of industrial waste disposal.

The platinum-loaded CdS photocatalyst used for the hydrogen production from sulfite solutions was stable for 65 h in our previous experiment.[5] Ciba-Geigy group reported that the photocatalyst was deactivated after 6 d.[7] In this paper, the durability of the photocatalyst and its stabilization by addition of EDTA to the solution is reported.

Experimental

Photocatalytic Reaction. CdS powder of 99.999% purity purchased from Furuuchi Chemical Co., Inc. was used after heat treatment at 700 °C for 2 h under a nitrogen stream. The particle size after the heat treatment was ca. 2 μm. For the platinum loading, the CdS powder was shaken with platinum powder (Japan-Engelhard) in a glass vessel for 1 h. Aqueous solutions were prepared by use of deionized water having resistivities higher than 3.3 MΩ cm. The pH was adjusted at 8.4 by addition of boric acid (0.3 M, 1 M=1 mol dm^{-3}) and sodium hydroxide. All chemicals used were of reagent grade.

In a 100-ml glass flask, 0.5 g photocatalyst was suspended in a 50 ml sodium sulfite solution. The suspension was illuminated with a 500-W high-pressure mercury lamp, after it was deaerated by bubbling with high purity nitrogen gas for 15 min. The evolved hydrogen gas was introduced into a measuring cylinder.

Electrochemical Measurements. The CdS sintered disks for use as electrodes were prepared from CdS powder by use of a hot press under pressure of 1×10^7 Pa at 750 °C for 6 h in a nitrogen atmosphere. Electrochemical measurements were performed in a three-electrode cell with a sintered CdS electrode, a platinum counterelectrode, and an Ag/AgCl reference electrode under potentiostatic and galvanostatic conditions. A tungsten-halogen lamp was used as the light source for the photoelectrochemical measurements.

Results

The photocatalytic hydrogen evolution from sulfite solutions proceeded in our experimental conditions at the initial rate of ca. 2.7×10^{-3} mol h^{-1}. It declined to nearly zero after 50 h as shown in Fig. 1, as the sulfite ions were consumed, and the pH shifted to ca. 13. The decline of the hydrogen evolution rate was also due to the shift of pH, because the hydrogen evolution is inefficient in alkaline solutions.[5] The rate of hydrogen evolution recovered to the initial value by renewing the solution as shown by an arrow in Fig. 1.

The long-term stability of the photocatalyst was tested, renewing the solution at every 45 h. The rate of hydrogen evolution measured at 4 h after each of the renewal of the solution is shown by a solid line in Fig. 2. The rate of hydrogen evolution began to decline at ca. 200 h, and dropped to half the initial value at 600 h. However, the activity of the photocatalyst after illumination for 650 h recovered to 95% of the initial value by washing it in 0.4 M HCl for 30 min.

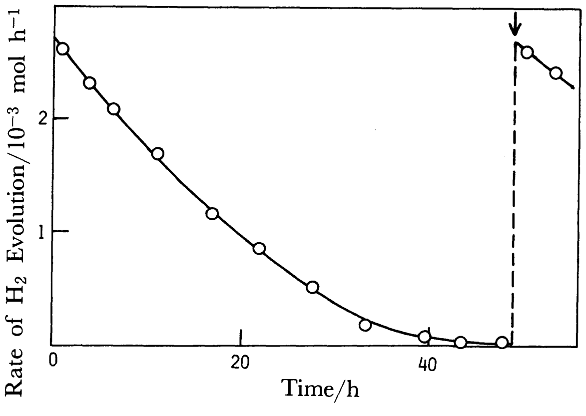

Fig. 1. Time-course of the rate of hydrogen evolution for the solution of 1 M sodium sulfite buffered at pH 8.4; the solution was renewed at the arrow.

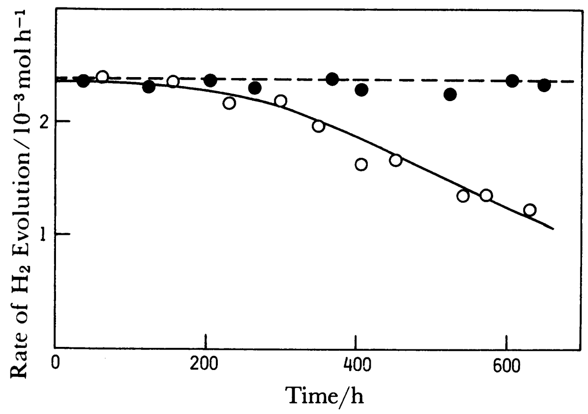

Fig. 2. Time-course of the rate of hydrogen evolution for the solutions of 1 M sodium sulfite buffered at pH 8.4 without EDTA, solid line, and with 5 mM EDTA, broken line.

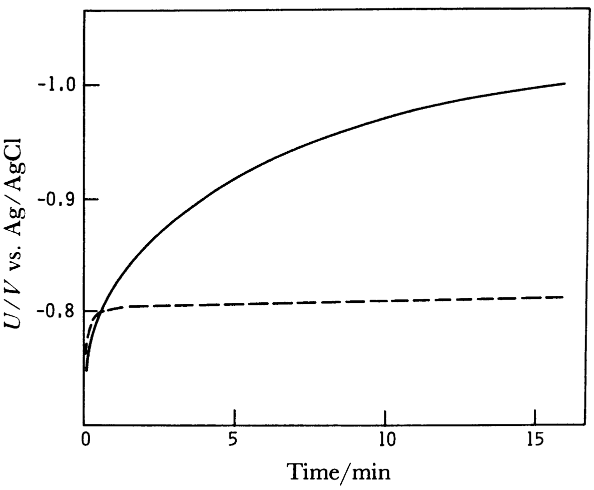

Fig. 3. Time-course of the potential of a platinum electrode observed under galvanostatic conditions at the current density of $-0.5\,\mathrm{mA\,cm^{-2}}$ in the solutions of 0.5 M sodium sulfite buffered at pH 8.4 without EDTA, solid line, and with 5 mM EDTA, broken line.

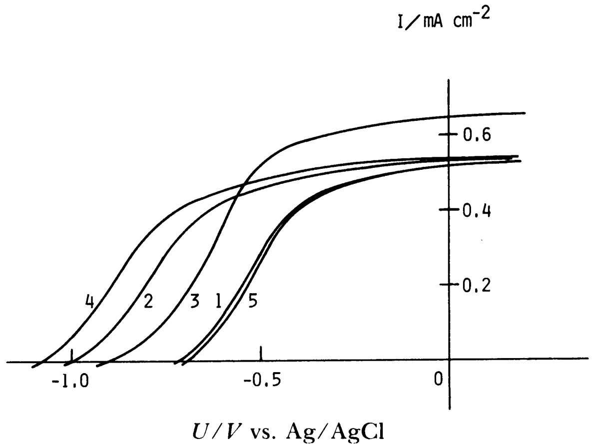

Fig. 4. I–U curve of a CdS sinter electrode measured under illumination with a tungsten-halogen lamp in 0.5 M sodium sulfate (curve 1), and those obtained by the addition of 0.1 sodium sulfite (curve 2), 0.1 M EDTA (curve 3), 0.1 M sodium sulfite and 0.1 M EDTA (curve 4), and 0.1 M cadmium chloride and 0.1 M EDTA (curve 5); the pH of the solutions is adjusted to 8.4.

When a small amount of ethylenediaminetetraacetic acid (EDTA, 5 mM) was added to the sulfite solution, the photocatalyst showed no decay of the activity even after illumination over 650 h, as shown by a broken line in Fig. 2. The amounts of hydrogen evolved during 650 h illumination from the solutions with and without EDTA were 13.6 and 10.7 l, respectively. Platinum-loaded CdS powder has been reported to photocatalyze hydrogen evolution from the aqueous solution of EDTA.[9] However, the rate of hydrogen evolution was negligibly small from the solution of 5 mM EDTA without sulfite. Therefore, the oxidation of EDTA at the illuminated CdS surface is excluded from the reasons of the stabilization of the photocatalyst and the increase of the amount of evolved hydrogen. By addition of 2 mM EDTA to the sulfite solution, practically the same stability of the photocatalyst was obtained as the case of 5 mM EDTA. The lower limit of the concentration of EDTA needed to stabilize the photocatalyst has not been determined.

In order to clarify the reason for the enhancement of the durability of the photocatalyst by the addition of EDTA and the deactivation of the photocatalyst in the absence of EDTA, we measured the potential of a hydrogen-evolving platinum electrode under galvanostatic conditions in 1 M sodium sulfite with and without EDTA. In the solution without EDTA, the potential of the platinum electrode shifted to negative rapidly as shown by a solid line in Fig. 3. This suggests that the catalytic activity of the platinum electrode for the hydrogen evolution decays with time. The shift of the potential of the platinum electrode was retarded drastically by addition of EDTA as shown by a broken line.

In Fig. 4 are shown the I–U curves of the illuminated CdS electrode in various solutions. The photocurrent in a sodium sulfate solution (curve 1) is caused by the dissolution of the CdS electrode. By addition of sulfite ions (curve 2) or EDTA (curve 3), the photocurrents now start at −1.0 and −0.91 V, respectively, which are caused by the oxidation of these species by the photogenerated positive holes in CdS. The higher reactivity of sulfite ions than that of EDTA is suggested by comparing curves 2 and 3. The increase of the saturated photocurrent density by the addition of EDTA (curve 3) is attributed to the "current doubling effect"[10] arising from the oxidation of EDTA. The disappearance of the "current doubling effect" in the presence of both EDTA and sulfite ions (curve 4) suggests that the sulfite ions are solely oxidized on the illuminated CdS electrode due to their higher reactivity than that of EDTA. The negative shift of the onset potential of the photocurrent by the addition of EDTA to the sulfite solution (compare curves 2 and 4) is probably due to the shift of the flat band potential of the CdS electrode caused by the chemisorption of EDTA on the surface of CdS.11) In the solution containing both EDTA and heavy metal ions, such as cadmium ions, at the same concentrations (0.1 M), the *I-U* curve nearly coincided with that measured in sodium sulfate solution (curves 1 and 5). This suggests that the heavy metal ions present in the solution are complexed with EDTA and that the complexes have very low reactivities with the positive holes photogenerated in CdS.

Discussion

The properties of the platinum-loaded CdS photocatalyst are well explained by assuming that each photocatalyst particle works as a photoelectrochemical cell having a CdS electrode and a platinum electrode.12) Then, the deposition of metals on the platinum from impurity metal ions existing in the solution is likely to occur electrochemically in competition with the hydrogen evolution. Therefore, the deactivation of the photocatalyst by illumination in the absence of EDTA is attributable to the deposition of impurity metals on a platinum part of the photocatalyst. The recovery of the photocatalytic activity by the washing treatment of the deactivated photocatalyst in hydrochloric acid suggests the removal of metals deposited on platinum.

The metal ions which deteriorate the activity of the photocatalyst are supposed to come from water, sodium sulfite, or the photocatalyst itself. The shift of the potential of the hydrogen-evolving platinum electrode under galvanostatic conditions was accelerated by addition of CdS powder to the solution. This suggests that not only the impurities in the solution but also impurities, probably cadmium ion, from the surface of CdS powder also deactivate the photocatalyst.

It is plausible to conclude that EDTA forms stable complexes with metal ions, prevents them from depositing on the platinum, and raises the durability of the photocatalyst. The electrochemical activity of EDTA itself with positive holes photogenerated in CdS is lowered by the formation of metal complexes as shown by curve 5 in Fig. 4. This gives a good reason why the effect of EDTA is sustained for the solutions containing EDTA at low concentrations. The low reactivity of the metal-EDTA complexes is presumably due to the stabilization of the lone-electron pair of nitrogen atoms in EDTA by formation of coordination bonds with the metal ions.

On the basis of these properties of EDTA and metal-EDTA complexes, it is expected that the stability of many photocatalysts other than platinized CdS, e.g., TiO_2, ZnO, etc., and also the hydrogen-evolving electrodes of photoelectrochemical cells can be improved by addition of small amounts of EDTA or other chelating agents to the solutions. The present results for the effect of EDTA on the platinum-loaded CdS photocatalyst are, aside from aforementioned practical significances, interesting from the viewpoint of the elucidation of the working mechanism of the photocatalysts.

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