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SYNERGETIC ELECTROCATALYST FOR EFFICIENT PHOTOELECTROCHEMICAL GENERATION OF HYDROGEN AT p-InP

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The efficient photoelectrochemical generation of hydrogen was achieved at p-InP modified with Co-Mo synergetic catalysts. The highest efficiency (8%) was achieved by the galvanostatic cathodic treatment ($\approx$ 0.5 mA) for 150 s in a solution containing 1 M NaOH, 10^{-2}M $Co(en)_3Cl_3$ and 10^{-4}M Na_2MoO_4 followed by etching in concd HCl for 5-30 s.

The photoelectrolysis of water is a very attractive method to convert solar energy to chemical energy and has been studied very extensively.[1)] Recently, the significant improvement of photoelectrochemical hydrogen generation efficiency at p-type semiconductors has been reported. The key to this improvement is the modification of the semiconductor surface by metals which catalyze the hydrogen evolution reaction (H.E.R.).[2)] However, all the catalysts used were noble metals such as Pt, Ru, Rh, Pd, and Re and it is of interest to find non-noble metal catalyst for this reaction.

The slow kinetics of photoelectrochemical H.E.R. at p-type semiconductors is attributed to the fact that the energy of adsorption of hydrogen atom, which is the intermediate of H.E.R., on the semiconductors is small.[1b)] The existence of metals which adsorb hydrogen atom strongly accelerates the first step of H.E.R. ($H^+ + e^- \rightarrow H(a)$) but the too strong adsorption of hydrogen atom lowers the rate of the second step ($H(a) + H(a) \rightarrow H_2$ or $H(a) + H_3O^+ + e^- \rightarrow H_2 + H_2O$). Thus, a volcano shape curve between log of exchange current density of H.E.R. at metal electrode and metal-hydrogen bond strength exists.[3)] The Pt group metals are on the top of this curve. It was suggested that the surface which had similar characteristics to that of Pt group metals could be provided by the *in situ* codeposition of two metals from the two branches of the volcano curve such as Co and Mo and, indeed, it was reported that the overpotential of H.E.R. at metal and carbon electrodes was decreased by this treatment.[4)] In this communication, we demonstrate that this strategy is applicable for photoelectrochemical H.E.R. at p-type semiconductors.

The photocurrent-potential (i_{ph}-V) relation of a p-InP electrode in 1 M NaOH is shown in Fig. 1 (curve 1).[5)] Since the overpotential of H.E.R. at metal and carbon electrodes was reported to be reduced by the *in situ* generation of a Co-Mo synergetic catalyst in a solution containing Co and Mo ions, the i_{ph}-V relations of the p-InP electrode in 1 M NaOH containing 10^{-2}M $Co(en)_3Cl_3$[6)] (solution 1), 10^{-4}M

Na_2MoO_4 (solution 2) or 10^{-2}M $Co(en)_3Cl_3$ + 10^{-4}M Na_2MoO_4 (solution 3) were also studied and are shown in Fig. 1 (1 M = 1 mol·dm^{-3}). The photocurrent onset potential in solution 1 (curve 2) was more positive than that in 1 M NaOH and that in solution 3 (curve 3) was even more positive that in solution 1. The i_{ph}-V relation in solution 2 was exactly the same as that in 1 M NaOH. The photocurrents seemed to be mainly due to H.E.R. as vigorous gas evolution from the electrode surface was observed. Thus, the *in situ* generation of Co and Co-Mo was effective for reducing the overpotential of photoelectrochemical H.E.R. at p-InP electrodes and the existence of synergetic effect was confirmed. Unfortunately, however, the rather large hysteresis was observed in i_{ph}-V curves in solution 1 and in solution 3 and maximum currents in these solutions were even smaller than that in 1 M NaOH. Furthermore, the photocurrent at a constant potential diminished very rapidly in these solutions. Etching in HNO_3-HCl (1:1) recovered the original i_{ph}-V curves. These results suggest that a part of the photocurrents was derived from the cathodic deposition of Co in solution 1 or of Co-Mo in solution 3 and that these films absorbed most of light so that the photocurrent decreased. Thus, it was concluded that the *in situ* generation of these catalysts was not suitable for the photoelectrochemical H.E.R.

The reduction of the overpotential of this reaction by the deposition of Co or Co-Mo was so significant that we tried the surface modification prior to the photoelectrochemical experiments to avoid the growth of the catalyst during H.E.R., although it was said that these synergetic catalysts were active only when they were deposited *in situ* during hydrogen evolution and dissolved immediately when current stopped.$^{4b)}$ The methods employed for surface modification of p-InP electrodes were dipping in 1 M NaOH containing 10^{-2}M $Co(en)_3Cl_3$ (solution 1), 10^{-4}M Na_2MoO_4 (solution 2) or 10^{-2}M $Co(en)_3Cl_3$ and 10^{-4}M Na_2MoO_4 (solution 3) and the galvanostatic cathodic treatment in the above mentioned solutions. Typical results

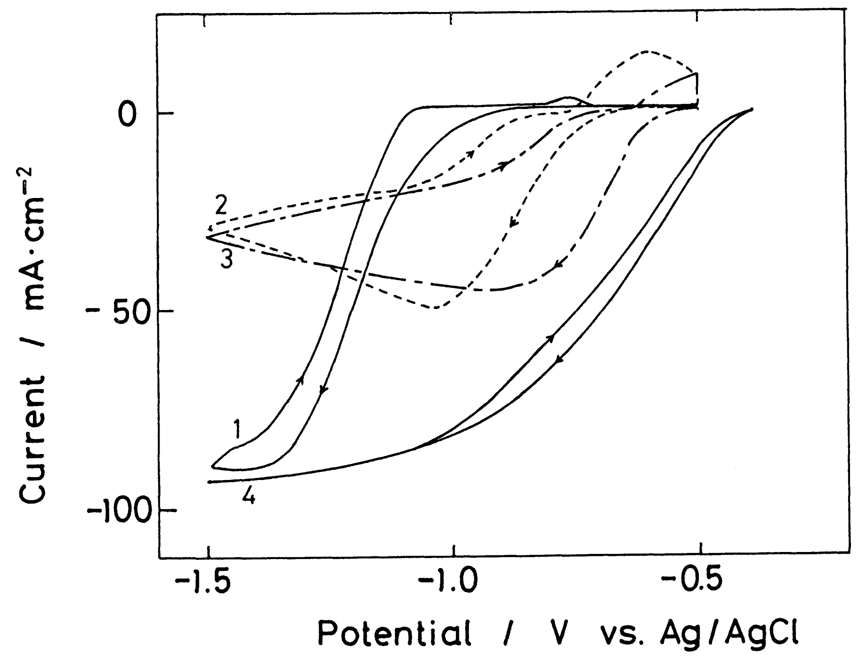

Fig. 1. The current-potential (i-V) relations of p-InP under illumination of a 500 W Xe lamp with an IR absorbing filter (IRA-20). Curve 1, p-InP thoroughly etched in HCl-HNO_3 (1:1) measured in 1 M NaOH. Curve 2, p-InP thoroughly etched in HCl-HNO_3 (1:1) measured in 1 M NaOH with 10^{-2}M $Co(en)_3Cl_3$. Curve 3, p-InP thoroughly etched in HCl-HNO_3 (1:1) measured in 1 M NaOH with 10^{-2}M $Co(en)_3Cl_3$ and 10^{-4}M Na_2MoO_4. Curve 4, p-InP cathodically treated (0.5 mA) for 150 s in 1 M NaOH with 10^{-2}M $Co(en)_3Cl_3$ and 10^{-2}M Na_2MoO_4 followed by etching in conc. HCl for 10 s measured in 1 M NaOH. Sweep rate = 50 mV/s. Light Intensity = 250 mW·cm^{-2}.

are summarized in Table 1. Except for the treatments in solution 2, the open circuit voltage (V_{oc}), currents at reversible hydrogen electrode potential (I_{sc})

Table 1. Photoelectrochemical characteristics of surface treated p-InP electrodes

Treatment[a)]	ΔV [b)] / V	I_{sc} [c)] / $mA \cdot cm^{-2}$	Fill factor [d)]	W_{max} [e)] / $mW \cdot cm^{-2}$	η [f)] / %
————	0.30	19	0.11	0.63	0.25
Dipped for 30 s in solution 1	0.45	56	0.19	4.8	1.9
Dipped for 30 s in solution 2	0.30	19	0.11	0.63	0.25
Dipped for 30 s in solution 3	0.45	70	0.25	7.9	3.2
Cathodic treatment (0.5 mA) for 30 s in solution 1	0.58	81	0.29	14	5.6
As above followed by etching in concd HCl for 10 s	0.58	70	0.31	13	5.2
Cathodic treatment (0.5 mA) for 30 s in solution 2	0.30	19	0.11	0.63	0.25
Cathodic treatment (0.5 mA) for 30 s in solution 3	0.58	81	0.31	15	6
As above but for 150 s	0.55	44	0.44	11	4.4
As above followed by etching in concd HCl for 10 s	0.70	86	0.33	20	8

a) Before each treatment, p-InP was thoroughly etched in HNO_3-HCl (1:1). This etching recovered the fresh p-InP surface. Solution 1: 1 M NaOH with 10^{-2}M $Co(en)_3Cl_3$. Solution 2: 1 M NaOH with 10^{-4}M Na_2MoO_4. Solution 3: 1 M NaOH with 10^{-2}M $Co(en)_3Cl_3$ and 10^{-4}M Na_2MoO_4.

b) The potential difference between the reversible hydrogen electrode potential (RHE) and the open circuit potential.

c) The photocurrent at RHE.

d) ΔV, I_{sc}, and fill factor were determined for the sweep of negative direction.

e) $W_{max} = \Delta V \times I_{sc} \times$ fill factor.

f) Input power density was 250 mW/cm^2. $\eta/\% = W_{max}/250 \times 100$.

and the fill factor were improved by these treatments. The efficiency of p-InP electrodes treated in 1 M NaOH containing both 10^{-2}M $Co(en)_3Cl_3$ and 10^{-4}M $NaMoO_4$ was better than that of p-InP treated in the same manner but in 1 M NaOH containing only 10^{-2}M $Co(en)_3Cl_3$. Although the concentration of Na_2MoO_4 was relatively small compared with that of $Co(en)_3Cl_3$, the deposition of Mo after these treatments was confirmed by XPS measurements. The treatments in solution 2 did not affect the efficiency. These results support the synergetic effect of the Co-Mo couple. The best efficiency was obtained when p-InP was cathodically treated in solution 3 and then etched in concd HCl for 5-30 s. The i_{ph}-V relation of this electrode is shown in Fig. 1 (curve 4). The photocurrent onset potential was -400 mV vs. Ag/AgCl which was about 700 mV more positive than that of reversible hydrogen electrode potential and the quantum efficiency for 600 nm light at -1.1 V was about 0.60. The maximum power conversion efficiency was about 8%. Although the fill factor was little less than those reported by Heller et al. for p-InP modified with Pt group metal catalyst,[2a-c] it is very encouraging that the efficient photoelectrochemical generation of hydrogen was achieved at p-InP electrodes modified with non-noble metal catalysts. The photocurrent at -1.1 V declined from the initial value of 160 mA/cm^2 to 60 mA/cm^2 after 20 h illumination by a 500 W Xe lamp without an IR absorbing filter but the original photocurrent was recovered by just keeping the electrode at -0.4 V in dark for 30 s. Details of the role of the catalyst and of synergetic effect are under investigation.

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5) Wafers of p-InP doped with Zn were obtained from Varian Associates. The samples had a carrier density of 3.4×10^{17} cm^{-3}, a mobility of 362 $cm^2/V \cdot s$ and resistivity of 0.045 $\Omega \cdot cm$. Ohmic contact to the crystals was made by using In-Zn alloy. The $(\bar{1}\bar{1}\bar{1})$ face of the crystals was always exposed to the electrolytes and the surface area of the electrodes was 0.08 cm^2.

6) $Co(en)_3Cl_3$ was synthesized and purified by the method suggested in Ref. 4b.

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