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Near-infrared Photocurrent of a Zinc Oxide Electrode Covered with Silver Atoms

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Synopsis. A near-infrared photocurrent has been observed in a sintered ZnO electrode whose surface was covered with Ag atoms. The photocurrent became more evident when silver deposition was carried out with a relatively large charging current. The importance of H^+ reduction which competed with silver reduction is pointed out.

We have studied the electrochemistry of sintered zinc oxide (ZnO) electrodes to clarify the mechanism of the photoreduction of silver ions (Ag^+) at the surface of ZnO.[1] In the course of this research, it was noted that the ZnO surface suffered some changes in its physicochemical properties after the deposition of a considerable amount of Ag atoms. Kolb *et al.* have reported a near-infrared photocurrent regarding a ZnO single crystal electrode covered with a monolayer of Ag atoms.[2] It is worthwhile to examine the nature of the near-infrared photocurrent of ZnO electrodes in more detail.

A ZnO electrode was prepared from a ZnO powder, SASEX-4000, (Sakai Kagaku Co., Ltd.,) in the same manner as reported previously.[1] The surface area of the electrode was about 1 cm^2. The electrochemical cell contained a ZnO electrode, a platinum counter electrode, and a saturated KCl, Ag, AgCl reference electrode. The electrode potential in this Note referred to a saturated KCl, Ag, AgCl electrode. A Hokutodenko HA-104 potentiostat/galvanostat with an electronic picoammeter TR-8641 (Takeda Riken Co., Ltd.,) was used for the measurement of the photocurrent. As a light source, a 45-W tungsten-iodide lamp (Shimadzu Seisakusho Co., Ltd.,) was used in combination with a grating monochromator (Shimadzu Seisakusho Co., Ltd.,) and a glass filter, VR-67 (Toshiba Co., Ltd.,). The ratio of the number of incident photons was determined by means of a calibrated thermopile (Nihon Bunko Co., Ltd.,). The optical absorption spectrum of the electrolyte solution was taken into account in order to calibrate the number of incident photons at the electrode surface. The action spectrum of the photocurrent was corrected to a constant photon flux incident to the electrode surface at the wavelength, λ=700—1200 nm. All the measurements were carried out at the room temperature. Before the measurements, the ZnO surface was etched with 85% H_3PO_4 and washed in water. Dissolved oxygen in the electrolyte solution was purged by the introduction of high-purity nitrogen gas. We employed a galvanostatic method with a controlled charging current, i_{ch}, to deposit Ag atoms at the ZnO surface (electrochemical charging).

Cyclic current-voltage curves for the ZnO electrode were measured in the dark in 0.5 M KNO_3 (1 M=1 mol dm^{-3})(Fig. 1). On the cathodic scan, the current began to rise at about −0.7 V due to hydrogen evolution. When $AgClO_4$ was added to the solution, the Ag deposition was seen by a current rise of around +0.2 V on the cathodic scan. It was noticed that at the Ag-covered ZnO surface, hydrogen evolution commenced about 0.3 V earlier than at a bare electrode surface. Catalytic action of metal atoms at the semiconductor surface has been discussed by Kolb *et al.*[2] On the anodic scan, the photocurrent began to rise at *ca.* −0.2 V when the ZnO electrode in the electrolyte solution containing Ag^+ was illuminated with λ=365 nm light. The absence of a well-defined stripping peak of Ag indicates that photo-generated holes are consumed with the dissolution of ZnO.

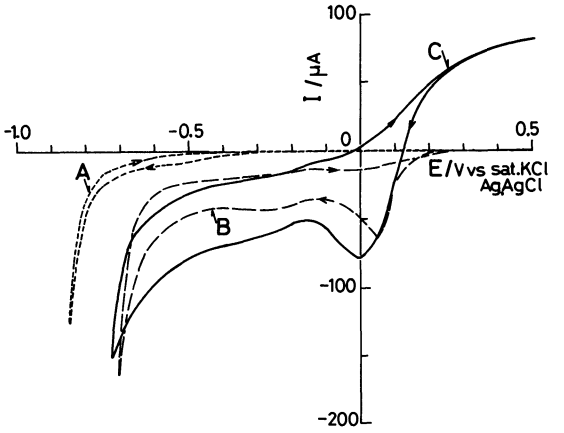

Fig. 1. Cyclic current (I)-voltage(E) curves of ZnO electrode.
Electrolyte: A: 0.5 M KNO_3 (------), B, C: 0.5 M KNO_3 and 10^{-3} M $AgClO_4$.
Curve B (— — —) is obtained in the dark, curve C (———) by illumination with λ=365 nm light from 500 W xenon lamp. Scan rate is 20 mV s^{-1}.

We deposited the Ag atoms at the ZnO surface in an electrolyte solution composed of 0.5 M KNO_3 and 10^{-3} M $AgClO_4$. As the electrode potential during charging, E_{ch}, with i_{ch}=5 μA was about +0.2 V, a greater part of the charging current contributed to the reduction of Ag^+. The action spectra of the anodic photocurrent at +0.5 V are given in Fig. 2. The increase in the photocurrent, ΔI, being defined as the subtraction of the photocurrent before silver deposition, I_0, from that after silver deposition, I_{ch}, is also shown in Fig. 2. The dark anodic current was less than 1 nA at +0.5 V. The near-infrared photocurrent increased several times after charging the electrode by the quantity of electricity, Q_{ch}=6.0 mC. ΔI at λ=800—900 nm was about 2.5 nA. We next employed a relatively large i_{ch} of 200 μA. As E_{ch} was *ca.* −0.75 V, the reduction of both Ag^+ and H^+ was possible in view of Fig. 1. Some of the evolved hydrogen was absorbed inside of ZnO and silver layers. The action spectrum of the photocurrent (Fig. 3) shows that ΔI at λ=800—900 nm was *ca.* 30 nA for Q_{ch}=6.0 mC, which is about one order larger than ΔI of case C in Fig. 2. Figure 4 shows the

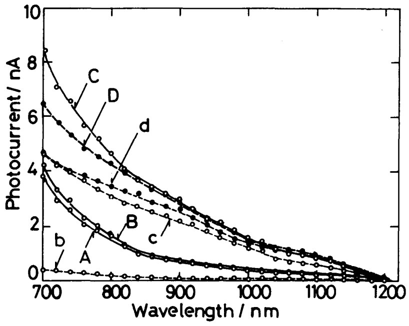

Fig. 2. Action spectra of anodic photocurrent of ZnO electrode.
Electrolyte: 0.5 M KNO_3 and 10^{-3}M $AgClO_4$, Electrode potential: +0.5 V.
A: Before charging, I_0, B: after electrochemical charging with i_{ch}=5 μA for 120 s (Q_{ch}=0.6 mC), I_{ch}, C: after electrochemical charging with i_{ch}=5 μA for 1200 s (Q_{ch}=6.0 mC), I_{ch}, D: after photochemical charging with λ=365 nm light (Q_{ch}=*ca.* 6.0 mC), I_{ch}.
The dashed lines b, c, and d denote the increase in photocurrent, $\Delta I=I_{ch}-I_0$, for B, C, and D, respectively. The magnitude of the photocurrent, D and d is reduced by one-half.

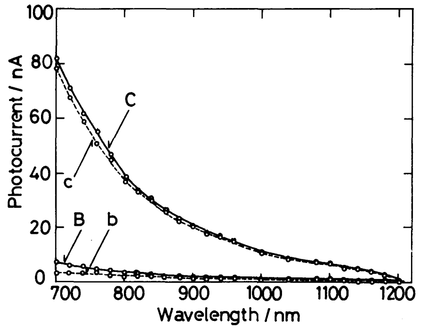

Fig. 3. Action spectra of anodic photocurrent of ZnO electrode.
Electrolyte, electrode potential: the same as in Fig. 2.
B: After electrochemical charging with i_{ch}=200 μA for 3 s (Q_{ch}=0.6 mC), I_{ch}, C: after electrochemical charging with i_{ch}=200 μA for 30 s (Q_{ch}=6.0 mC), I_{ch}.
The dashed lines b, c denote ΔI for B, C, respectively.

action spectrum after charging the electrode in a 0.5 M KNO_3 solution with i_{ch}=200 μA. The main electrode reaction was the reduction of H^+, as E_{ch} was *ca.* −0.9 V in this case. ΔI for Q_{ch}=6.0 mC was only about 0.1 nA at λ=800—900 nm. We then tried to superpose hydrogen on the silver layer. In the first place, the ZnO electrode was charged in the same electrolyte solution as in Fig. 2 with i_{ch}=5 μA for 1200 s (silver deposition). Then, the second charging was carried out in a 0.5 M KNO_3 solution with i_{ch}=200 μA for 30 s (hydrogen evolution). The action spectrum of the photocurrent after two-step deposition is added to Fig. 4. The magnitude of ΔI proved to be smaller than that of case C in Fig. 3: ΔI at λ=800—900 nm was *ca.* 2.5 nA.

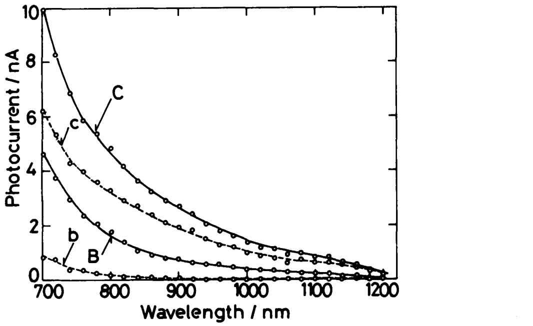

Fig. 4. Action spectra of anodic photocurrent of ZnO electrode.
Electrode potential: +0.5 V.
B: After electrochemical charging in 0.5 M KNO_3 with i_{ch}=200 μA for 30 s (Q_{ch}=6.0 mC), I_{ch}, C: after electrochemical charging firstly in 0.5 M KNO_3 and 10^{-3} M $AgClO_4$ with i_{ch}=5 μA for 1200 s (Q_{ch}=6.0 mC) and secondly in 0.5 M KNO_3 with i_{ch}=200 μA for 30 s (Q_{ch}=6.0 mC), I_{ch}.
The dashed lines, b, c denote ΔI for B, C, respectively.

Kolb *et al.* have ascribed the near-infrared photocurrent to an optical interfacial electron transfer between Ag adatoms and the ZnO electrode.[2] It has often been observed that extrinsic surface states are introduced to a semiconductor surface when some chemical species are adsorbed on it.[3] We could assume that electronic excitation from the surface states to the conduction band of ZnO is important as an additional mechanism of the near-infrared photocurrent of the ZnO electrode covered with Ag atoms. The enhanced photocurrent in Fig. 3 is probably due to a relatively large i_{ch}. It has been found that the current efficiency of Ag^+ reduction amounts to *ca.* 100% for an i_{ch} smaller than 20 μA and is less than 50% for an i_{ch} greater than 100 μA.[4] As the photocurrent of the electrode after the superposition of silver and hydrogen in Fig. 4 was not so large, we can state that extrinsic surface states responsible to the near-infrared photocurrent are introduced to the ZnO surface during the co-deposition of silver and hydrogen under relatively large i_{ch} conditions. As the distinct structure of the action spectra in Figs. 2—4 is blurred, it seems that occupied energy levels of the surface states are located in a diffuse manner within the forbidden energy band of ZnO.

We finally examined the possibility of the increase of near-infrared photocurrent as a result of the photodeposition of Ag atoms at the ZnO surface (photochemical charging). The ZnO electrode in a solution composed of 0.5 M KNO_3 and 10^{-3} M $AgClO_4$ was disconnected from the electric circuit and illuminated with λ=365 nm light from a 500 W xenon lamp.[1] After photochemical charging by Q_{ch}=*ca.* 6.0 mC, as estimated by a local-cell consideration,[1] the action spectrum of the near-infrared photocurrent was not so different from that obtained by electrochemical charging (Fig. 2). Therefore, the origin of the photocurrent is the same regarding both electrochemical and photochemical chargings.

References

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