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Photoelectrochemical Behavior of Zinc Oxide Sintered Electrode in Aqueous Solution

Yasuhisa Maeda, Takaya Kitagawa, Keisuke Gotoh, Yasumasa Tomita and Kenkichiro Kobayashi
Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Hamamatsu 432-8561, Japan
Fax: 81-053 -478 -1624, e-mail: tymaeda@ipc.shizuoka.ac.jp

Photoelectrochemical behavior of the zinc oxide electrode prepared from sintering of zinc oxide powders at the temperature of 900 – 1200°C was investigated for the purpose of application of this electrode to water purification. Photoanodic fading of dyes (Methylene Blue, Crystal Violet, Congo Red) in aqueous solutions on the zinc oxide electrode was examined. In this case, the photoelectrochemical cell consisted of the zinc oxide photoanode in 0.1 M Na_2SO_4 solution containing 10 μM dye (volume: 100 ml) and graphite cathode in 10 mM $Fe_2(SO_4)_3$ – 0.1 M Na_2SO_4 solution (volume: 100 ml) under light irradiation (wavelength: 365 nm, intensity: 30 mW/cm^2). Although the electrode sintered at 900°C showed a low photocurrent quantum efficiency, 8 %, mainly due to the many boundaries on the surface, 80 % of the initial concentration of Methylene Blue faded after 6 hours irradiation. The electrode sintered at 1200°C showed 80 % of photocurrent quantum efficiency and caused the fading of Methylene Blue with 86 % of initial concentration after 6 h irradiation. The comparison of responses between photoelectrode and photocatalysis was also checked for the sintered zinc oxide samples.
Key words: zinc oxide, sintering, electrode, photoelectrochemistry, dye

1. Introduction

Environmental purification processes by using illuminated semiconductor material such as titanium dioxide have been studied actively. Titanium dioxide is used widely as photocatalyst in the field of air purification, removal of pollution, self-cleaning, anti-bacteria, water purification, and so on[1-3]. Zinc oxide is also expected as photocatalyst material. There are several reports concerning photo-treatment of pollutant in water by zinc oxide photocatalyst[4-7]. Zinc oxide has disadvantage of occurrence of photo-dissolution in water. However, we confirmed the suppression of photo-dissolution of zinc oxide in alkali solution. In the attempt of water purification based on light energy, photoelectrochemical system consisting of semiconductor photoanode and carbon cathode may be suitable for treatment of pollutant because of effective separation of photo-generated hole and electron pair due to the space charge layer at the semiconductor electrode / electrolyte interface. In this system, anodic oxidation and cathodic reduction proceed at the semiconductor and carbon electrodes, respectively.

In the present work, we prepared the zinc oxide electrode from sintering of zinc oxide powders at the temperature of 900–1200°C and investigated photoelectrochemical behavior of this electrode in aqueous solution in order to make clear its utility as a photoanode in the cell for the purpose of water purification.

2. Experimental

The ZnO powder (Wako, weight: 1.6 g) was pressed at the pressure of 2 MPa for 5 minutes and molded to the disk. This was heated at the temperature of 900, 1000, 1100 and 1200°C for 1 hour under air-atmosphere by the electric furnace (Yamato, FP100). These ZnO sintered samples (diameter: 16 mm) connected to a lead wire through the ohmic contact by In/Ga alloy were used as the working electrode. The counter electrode was a graphite sheet (size: 15x20x0.6 mm^3) connected to a lead wire. A light source was 500 W high pressure Hg lamp (Ushio, USH-500D). By using filter (Toshiba, UV-D36C), the main wavelength of irradiation was 365 nm and the intensity was 30 mW/cm^2.

Mott-Schottky plot of the ZnO electrode in electrolytic solution was examined by LCR meter (Hioki, 3520). The photocurrent between working electrode and counter electrode was measured by the ammeter (Hokuto, HM-101) and potentio-galvanostat (Hokuto, HAB-151).

3. Results and Discussion

Figures 1a, b, c and d show the SEM images of the ZnO samples sintered at 900, 1000, 1100 and 1200°C, respectively. The ZnO particles with the size less than 1 μm began to combine each other on the sample heated at 900°C. The combination of the particles proceeded on the sample heated at 1000°C The growth of the particles due to their combination was observed on the sample at 1100°C and the further growth of the particles proceeded on the sample heated at 1200°C.

Figures 2a, b, c and d show the relation between potential and current on the ZnO electrode sintered at 900, 1000, 1100 and 1200°C, respectively, in 0.1 M Na_2SO_4 aqueous solution under irradiation and in the dark. On all the electrodes, anodic current did not flow in the dark. Under irradiation, the photocurrent was

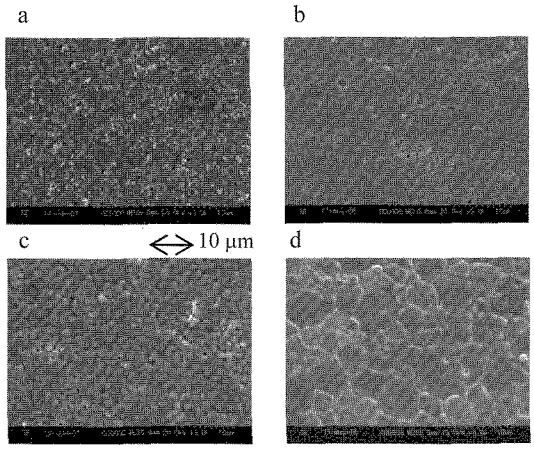

Fig. 1 SEM images of the ZnO samples sintered at different temperatures
a: 900°C b:1000°C c: 1100°C d: 1200°C

observed at the electrode potential more positive than – 0.4 V vs. Ag/AgCl. The photocurrent on the ZnO electrode increased with a rise in sintering temperature. The electrode sintered at 1200°C showed almost saturated photocurrent at the potential more positive than 2.0 V. The values of the photocurrent quantum efficiency at 2.0 V for these ZnO electrodes sintered at 900, 1000, 1100 and 1200°C were 8, 10, 23 and 80 %, respectively, from evaluation of photocurrent value and light intensity. There was a large difference in quantum efficiency between 1200 and 1100°C treated electrodes. As shown in Fig.1c and d, the growth of ZnO particles on the electrode sintered at 1200°C proceeded by far compared with the electrode sintered 1100 °C. This reflects few defects which may act as recombination sites for photogenerated hole and electron on the surface of the electrode sintered at 1200°C. The fact of high quantum efficiency of 80 % and of the saturated photocurrent implies few recombination sites existing on the surface of this electrode.

Figure 3 shows the Mott-Schottky plot for ZnO electrode sintered at 1100 and 1200°C in 0.1 M Na_2SO_4 aqueous solution. The capacitance of semiconductor electrode / electrolyte interface, C is related to electrode potential, E as shown by equation (1).

$$1/C^2 = 2(E - E_{fb})/eN\varepsilon\varepsilon^0 \quad (1)$$

Where E_{fb} is flatband potential, e elementary charge, N carrier density, ε dielectric constant, ε^0 permittivity of free space. According to eq.(1), the linear relation between $1/C^2$ and E could be obtained. The slope of this linear plot, that is Mott-Schottky plot, provides the carrier density and the intersection of this line and E-axis corresponds to flatband potential. The values of N=2.9x10^{17}cm^{-3}, E_{fb}= – 0.40 V and N=2.2x10^{18} cm^{-3} E_{fb}= – 0.22 V were evaluated for the electrodes sintered at 1100 and 1200°C, respectively. The linear relation between $1/C^2$ and E was not recognized for the electrodes sintered at 900 and 1000°C.

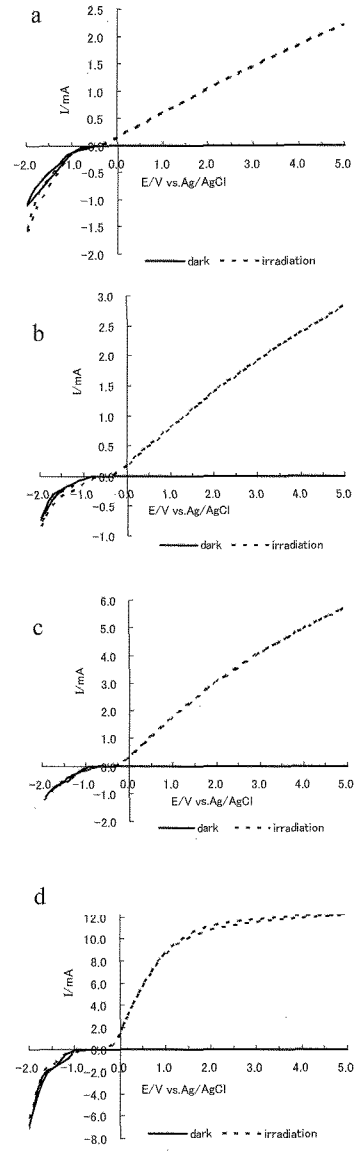

Fig. 2 Potential – current relation on the ZnO electrode sintered at different temperatures in 0.1 M Na_2SO_4 aqueous solution
a: 900°C b:1000°C c: 1100°C d: 1200°C

In order to examine the response of these ZnO electrodes to photo-fading of dyes in aqueous solution, the photoelectrochemical cell consisting of the ZnO photoanode in 0.1 M Na_2SO_4 solution containing 10 μM dye (volume: 100 ml) and graphite cathode in 10 mM $Fe_2(SO_4)_3$ – 0.1 M Na_2SO_4 solution (volume: 100 ml) was used. In this case, two electrolytes were separated through a KCl salt bridge. In the dark, no current flowed in this cell. Under light irradiation to the ZnO electrode, photocurrent was observed without supply of voltage.

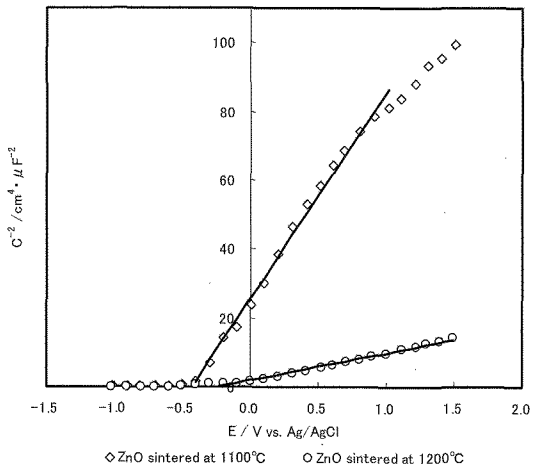

Fig. 3 Mott-Schottky plots of the ZnO electrode sintered at 1100 and 1200°C in 0.1 M Na_2SO_4 aqueous solution

Figures 4a and b show dependence of the absorption spectrum of the solution (pH=7) containing Methylene Blue on irradiation time at the ZnO electrode sintered at 900 and 1200°C, respectively. It was clear that fading of Methylene Blue proceeded with irradiation time on both the electrodes. The linear relation between logarithm of concentration of Methylene Blue existing and irradiation time was recognized. This suggests that photo-fading of Methylene Blue on the ZnO electrode may proceed as first order reaction. Less than 2% of the initial concentration (10 μM) of Methylene faded after 6 hours in the dark. This means few adsorption of Methylene Blue on the surface of the electrode. The light irradiation for 6 hours caused fading of 80 and 87 % of the initial concentration on the electrode sintered at 900 and 1200°C, respectively. The fading of 75 and 74 % of the initial concentration after 6 hours irradiation was observed on the electrode sintered at 1000 and 1100°C, respectively.

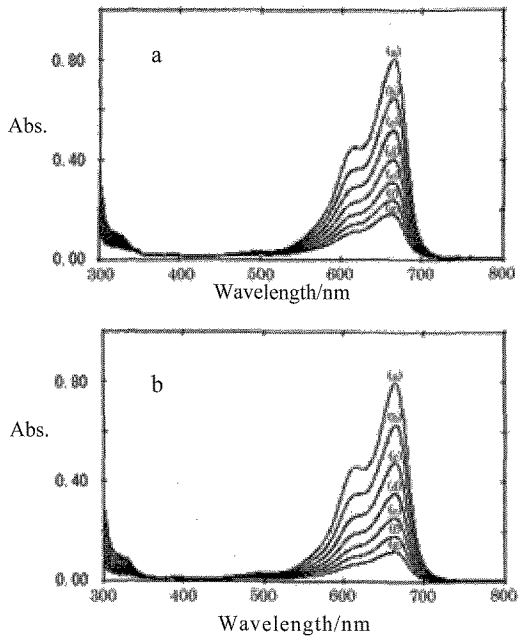

Fig. 4 Dependence of absorption spectrum of Methylene Blue solution (pH=7) on irradiation time using the ZnO sintered at 900°C (a) and 1200°C (b) as photoelectrode
before irradiation (a); after irradiation for 1h (b), 2h (c), 3h (d), 4h (e), 5h (f) and 6h (g)

Figure 5a and b show dependence of the absorption spectrum of the solution (pH=7) containing Methylene Blue on irradiation time at the ZnO sintering samples at 900 and 1200°C, respectively. In this case, the ZnO samples acted as photocatalyst. The fading of 72 and 58 % of the initial concentration after 6 hours irradiation was observed on the samples sintered at 900 and 1200°C, respectively. The sample sintered at 900°C showed higher activity for photo-fading of Methylene Blue compared with the sample sintered at 1200°C as photocatalyst. This may be due to facility for photo-oxidation of Methylene Blue on the surface of the ZnO sintered at 900°C.

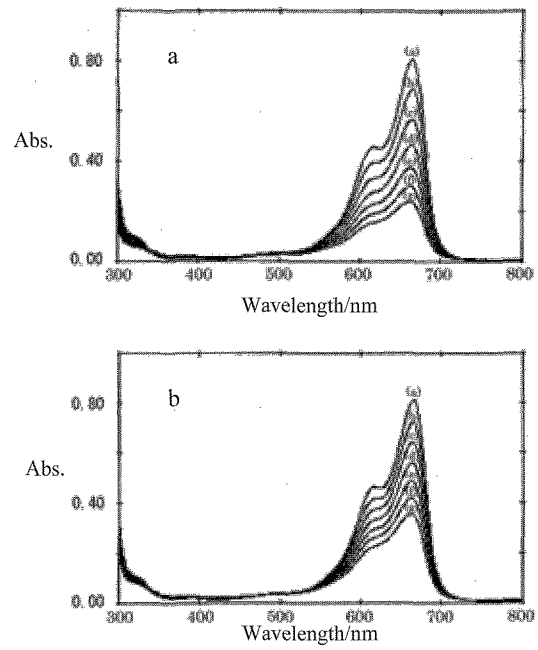

Fig. 5 Dependence of absorption spectrum of Methylene Blue solution (pH=7) on irradiation time using the ZnO sintered at 900°C (a) and 1200°C (b) as photocatalyst
before irradiation (a); after irradiation for 1h (b), 2h (c), 3h (d), 4h (e), 5h (f) and 6h (g)

Figure 6 and Figure 7 show the dependence of absorption spectrum of Crystal Violet solution (pH=7) and Congo Red solution (pH=7), respectively, on irradiation time using the ZnO electrode sintered at 1200°C. The photo-fading of Crystal Violet and Congo Red proceeded with irradiation time. The fading of 87 % for Crystal Violet and of 67 % for Congo Red of the initial concentration was confirmed after 6 hours irradiation.

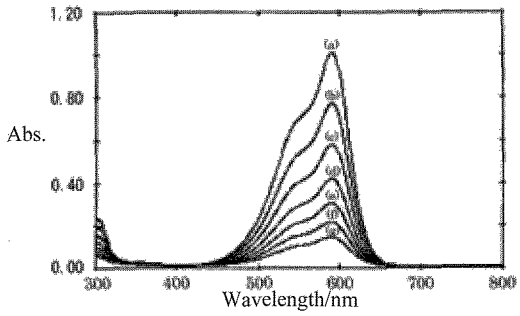

Fig. 6 Dependence of absorption spectrum of Crystal Violet solution (pH=7) on irradiation time using the ZnO sintered at 1200°C as photoelectrode
before irradiation (a); after irradiation for 1h (b), 2h (c), 3h (d), 4h (e), 5h (f) and 6h (g)

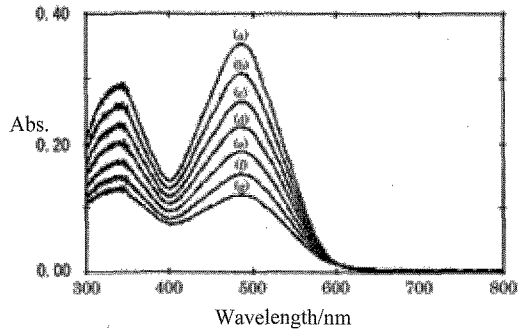

Fig. 7 Dependence of absorption spectrum of Congo Red solution (pH=7) on irradiation time using the ZnO sintered at 1200°C as photoelectrode
before irradiation (a); after irradiation for 1h (b), 2h (c), 3h (d), 4h (e), 5h (f) and 6h (g)

4. Summary

The photoelectrochemical characteristics of the ZnO sintered at 900 - 1200°C was investigated. The ZnO sintered 1200°C showed a high photocurrent quantum efficiency, 80 % and a large carrier density, 2.2×10^{18} cm^{-3}. This electrode responded to photo-fading of dyes in the aqueous solution actively. Although the ZnO sintered at 900°C had a low photocurrent quantum efficiency, 8 %, this showed a high response to photo-fading of dyes. Since the separation of photo-generated hole and electron may occur rapidly on the surface of the sintered ZnO, this is expected to be applied to water purification.

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