

*Short Communication*

## **Enhancement of Photocatalytic Activity of ZnO Thin Films by Electrochemical Reduction**

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Photocatalytic activity of zinc oxide (ZnO) films under UV irradiation was enhanced by electrochemical reduction in an aqueous solution containing phosphoric acid and potassium chloride. The photocatalytic activity of the ZnO films depended on the electrochemical reduction time. The ZnO film with the electrochemical reduction for 20 min exhibited the highest photocatalytic activity for the decomposition of methylene blue (MB). The removal efficiency of MB in the solution was 96.5% after 180 min light irradiation. The photocatalytic activity of the ZnO film with the electrochemical reduction for 20 min was about five times higher than that of the ZnO film without the electrochemical reduction. The enhanced photocatalytic activity of the ZnO film was relatively stable throughout five consecutive cycle experiments. As the electrochemical reduction treatment is performed at room temperature, it is a very simple and effective way to improve the photocatalytic activity of ZnO films.

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**Keywords:** zinc oxide, photocatalyst, electrochemical reduction, metal nanoparticle

### **1. INTRODUCTION**

Zinc oxide (ZnO) is an important oxide semiconductor for optoelectronic devices such as transparent electrodes, surface acoustic wave devices, and thin film transistors [1–5]. ZnO is very versatile because of its non-toxicity and high natural abundance. Many methods including non-vacuum processes are used for the growth of ZnO. High-conductive ZnO thin films are deposited by vacuum processes such as pulsed laser deposition and sputtering [1,2]. ZnO nanowires, nanorods and thin films can be synthesized from aqueous solutions at low temperatures [6–8]. The solution-based growth method is attractive because of its simplicity and cost-effectiveness.

Photocatalytic activity of oxide semiconductors has been focused by many researchers because photocatalysis is an attractive technology for organic wastewater treatment. It is known that nanostructure formation and surface modification enhance the photocatalytic activity of oxide

semiconductors [9–11]. ZnO is one of oxide semiconductors with photocatalytic properties [11–13]. The photocatalytic activity of ZnO is influenced by its composition, defects, and surface structures. Čížek et al. have reported that hydrogen was electrochemically introduced into ZnO crystals [14]. In our previous study, electrical properties of ZnO films were changed by electrochemical reduction and oxidation in an aqueous solution [15]. Sheet resistance of ZnO films was decreased by the electrochemical reduction for 30 s. The electrochemical reduction for a longer period resulted in the formation of defective ZnO layer. Hydrogen and oxygen vacancies are donors in ZnO [16–18]. These defects near surface region may improve charge transfer for photocatalysis because they affect the surface band bending of ZnO [19,20].

There are many studies on ZnO photocatalysts, but it is still a challenge to improve photocatalytic activity of ZnO by using a simple method. It is possible that defects and nanostructures formed by the electrochemical reduction at room temperature improve the photocatalytic activity of ZnO. However, the influence of the electrochemical reduction on the photocatalytic properties of ZnO has not been well studied. In this paper, we discuss the effect of the electrochemical reduction on the photocatalytic activity of ZnO films.

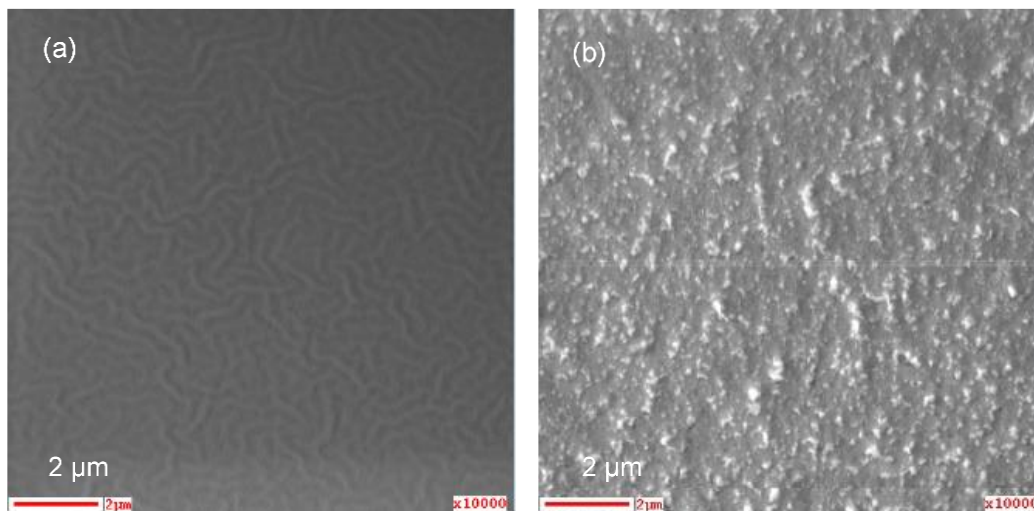
## 2. EXPERIMENTAL

Al-doped ZnO films were deposited on soda lime glass substrates by sol-gel method. The precursor solution for the sol-gel deposition was prepared by mixing zinc acetate dihydrate ( $0.25 \text{ mol L}^{-1}$ ), aluminum nitrate nonahydrate (Al/Zn = 3 at%), and monoethanolamine ( $0.50 \text{ mol L}^{-1}$ ) in ethanol at  $75 \text{ }^\circ\text{C}$ . The precursor solution aged for one day at room temperature was coated on the substrate with a spin coater. The rotation speed and acceleration time were 3000 rpm and 10 s, respectively. After the spin coating, the substrate was dried on a hotplate at  $270 \text{ }^\circ\text{C}$  for 10 min in air. The spin-coating and drying process was repeated 10 times, and subsequently the substrate was annealed in air at  $500 \text{ }^\circ\text{C}$  for 1 h. Thickness of the ZnO film was  $\sim 300 \text{ nm}$ . To increase electrical conductivity, the as-grown ZnO film was annealed in  $\text{H}_2$  at  $400 \text{ }^\circ\text{C}$  for 20 min. The electrochemical reduction treatment was performed at room temperature in an aqueous solution containing phosphoric acid ( $4.9 \times 10^{-5} \text{ mol L}^{-1}$ ) and potassium chloride ( $5.6 \times 10^{-3} \text{ mol L}^{-1}$ ). The ZnO film annealed in  $\text{H}_2$  was used as a cathode and a platinum plate was used as an anode. A constant current of  $0.38 \text{ mA cm}^{-2}$  was applied between the ZnO film and the platinum plate. The treatment time was varied from 0 to 25 min. The sample after the electrochemical reduction was rinsed in deionized water and dried with  $\text{N}_2$  blow. To evaluate the photocatalytic activity, the ZnO film was immersed in 20 ml of methylene blue (MB) aqueous solution in a 50-ml Teflon beaker and irradiated with a high-pressure mercury lamp. The concentration of the MB aqueous solution ( $C_0$ ) was  $2.1 \text{ mg L}^{-1}$ . The MB concentration during the light irradiation ( $C_t$ ) was estimated from the optical transmittance of the MB solution at 664 nm.

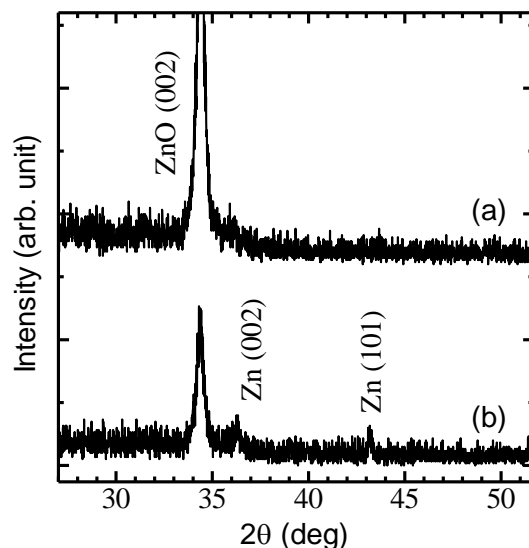
## 3. RESULTS AND DISCUSSION

SEM images of the ZnO films without and with the electrochemical reduction are shown in Fig. 1. The wrinkle pattern on the surface were unintentionally formed during the sol-gel deposition. The

hydrogen annealing performed before the electrochemical reduction had no significant effect on the surface morphology of the ZnO film. The wrinkle pattern was removed, and nanometer-sized particles were formed on the surface by the electrochemical reduction for 20 min.



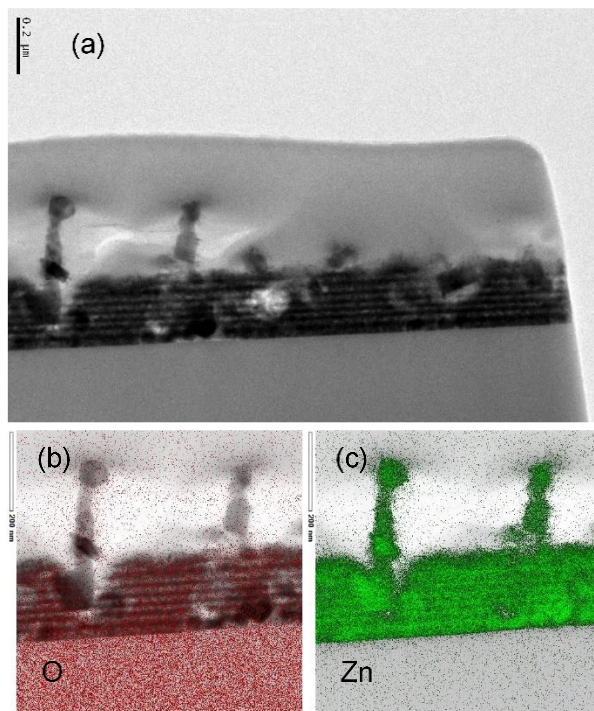
**Figure 1.** SEM images of the ZnO films without (a) and with (b) the electrochemical reduction.



**Figure 2.** XRD patterns of the ZnO films without (a) and with (b) the electrochemical reduction for 20 min.

Figure 2 shows XRD patterns of the ZnO films without and with the electrochemical reduction for 20 min. The ZnO (002) diffraction peak was observed in the XRD patterns. The ZnO films had a *c*-axis preferred orientation perpendicular to the glass substrate. However, the intensity of the ZnO (002) diffraction peak decreased after the electrochemical reduction for 20 min, and the Zn (002) and Zn (101) diffraction peaks appeared in the XRD pattern. It was indicated that Zn is deposited on the sample surface

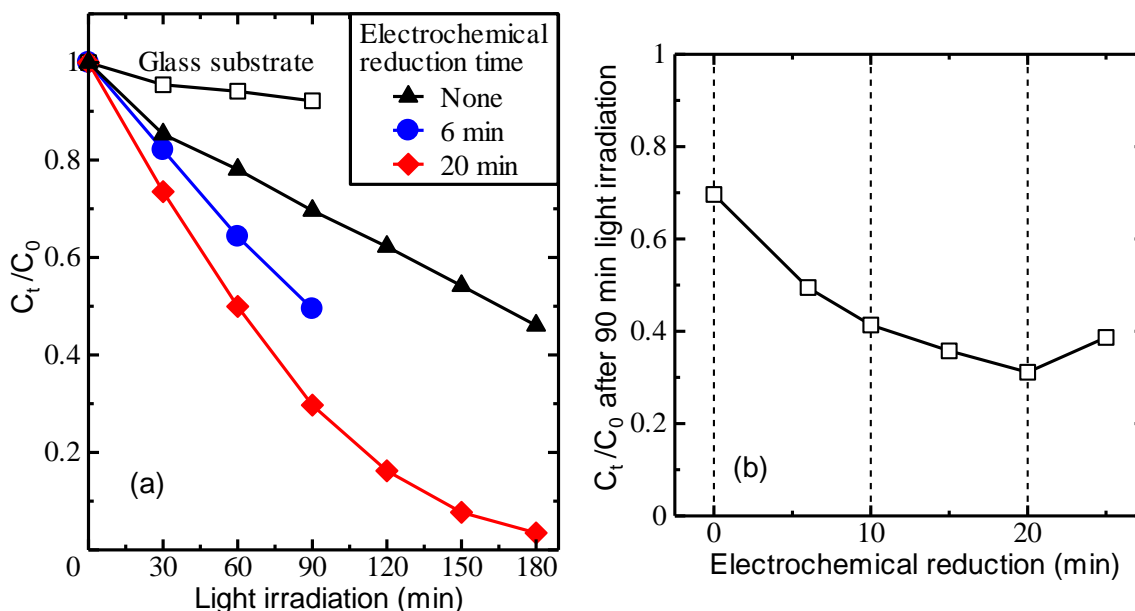
by the electrochemical reduction. The color turned grey and the optical transparency of the ZnO film decreased after the electrochemical reduction.



**Figure 3.** Cross-sectional TEM (a) and EDX images (b, c) of the ZnO film with the electrochemical reduction for 20 min.

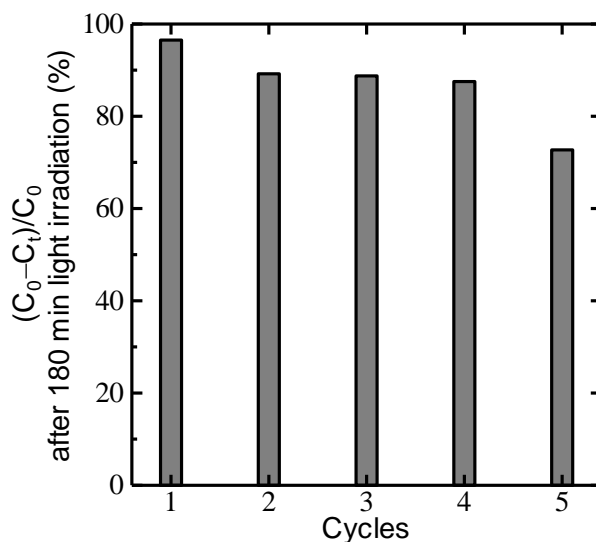
Cross-sectional TEM and EDX images of the ZnO film with the electrochemical reduction for 20 min are shown in Fig. 3. The stripes observed in the TEM image may be due to the repetitive sol-gel deposition. Nanoparticles and nanorods on the sample surface were formed by the electrochemical reduction. As shown in the EDX images, these nanostructures contain much less oxygen than the ZnO film. The surface after the electrochemical reduction was covered with Zn nanoparticles and Zn nanorods. This result is consistent with the XRD patterns in Fig. 2.

The photocatalytic properties of the ZnO films were evaluated by photodegradation of MB aqueous solution. The MB photodegradation ( $C_t/C_0$ ) by the ZnO films with a different electrochemical reduction time is shown in Fig. 4. In Fig. 4(a), the MB photodegradation by the glass substrate without ZnO film is shown as a reference. When the glass substrate was used, the  $C_t/C_0$  slightly decreased with increasing light irradiation time. However, more than 90% of MB ( $C_t/C_0 = 0.92$ ) remained in the solution after 90 min light irradiation. The slight decrease is due to absorption and/or self-photodegradation of MB. The electrochemical reduction improved the photocatalytic activity of the ZnO films. The photocatalytic activity increased with increasing electrochemical reduction time.



**Figure 4.** MB photodegradation ( $C_t/C_0$ ) by the ZnO films with a different electrochemical reduction time; (a)  $C_t/C_0$  versus light irradiation time, and (b)  $C_t/C_0$  after 90 min light irradiation.

The  $C_t/C_0$  for the ZnO film with the electrochemical reduction for 20 min was 0.035 after 180 min light irradiation. 96.5% of MB in the solution was decomposed within 180 min. The photocatalytic activity of the ZnO films was fitted using the pseudo first-order kinetic equation  $\ln(C_t/C_0) = -kt$ . The rate constant  $k$  for the ZnO film with the electrochemical reduction for 20 min was  $0.020 \text{ min}^{-1}$ . The rate constant was about five times larger than that for the ZnO thin film without the electrochemical reduction ( $k = 0.004 \text{ min}^{-1}$ ). The  $C_t/C_0$  for the ZnO films with various electrochemical reduction time is shown in Fig. 4(b). The  $C_t/C_0$  measured after 90 min light irradiation decreased with increasing electrochemical reduction time until 20 min. Further electrochemical reduction did not improve the photocatalytic activity. It has been reported that oxygen vacancies enhance the photocatalytic activity of ZnO under visible light [10,21]. However, both samples without and with the electrochemical reduction had no photocatalytic activity under visible light irradiation ( $\lambda > 400 \text{ nm}$ ), suggesting that oxygen deficient ZnO layer which exhibits the photocatalytic activity under visible light is not synthesized by the electrochemical reduction. On the other hand, Zn nanoparticles and Zn nanorods were formed on the sample surface by the electrochemical reduction. The formation of nanometer-sized metal particles such as Au and Pt is one of effective methods to enhance photocatalytic activities [22–24]. Yan et al. have reported that nanometer-sized Ag ohmic contacts enhance the photocatalytic activity of ZnO [25]. When ZnO is irradiated with UV light with energy greater than its bandgap, electron-hole pairs are generated. The photogenerated electrons migrate to metal contacts acting as an electron sink, which reduces electron-hole pair recombination rate. Consequently, the charge transfer from ZnO to reactants increases. The results in this study indicate that the Zn nanoparticles and Zn nanorods formed by the electrochemical reduction act as an electron sink and improve the photocatalytic activity of the ZnO films.



**Figure 5.** Removal efficiency of MB in the solution  $[(C_0-C_t)/C_0]$  by the reused ZnO film with the electrochemical reduction for 20 min.

Reusability of photocatalysts is important in practical applications. The ZnO film with the electrochemical reduction for 20 min was reused to evaluate the stability of the photocatalytic activity. Figure 5 shows the removal efficiency of MB in the solution  $[(C_0-C_t)/C_0]$  after 180 min light irradiation. The cycle experiments until the fourth cycle were performed within two days. The fifth cycle was performed one month later from the fourth cycle. At the end of each cycle, the sample was rinsed in deionized water and dried with  $N_2$  blow. The  $(C_0-C_t)/C_0$  for the first and second cycles was 96.5% and 89.2%, respectively. Although the removal efficiency decreased during the second cycle, the  $(C_0-C_t)/C_0$  was almost constant between the second and fourth cycles. The photocatalytic activity enhanced by the electrochemical reduction was relatively stable.

#### 4. CONCLUSION

The photocatalytic activity of the sol-gel-derived ZnO films was enhanced by the electrochemical reduction. The ZnO film with the electrochemical reduction for 20 min had the highest photocatalytic activity for MB decomposition. The photocatalytic activity of the ZnO films was fitted using the pseudo first-order kinetic equation  $\ln(C_t/C_0) = -kt$ . The rate constant  $k$  for the ZnO film with the electrochemical reduction for 20 min was about five times larger than that for the ZnO film without the electrochemical reduction. The enhanced photocatalytic activity was relatively stable during five consecutive cycle experiments. The ZnO film photocatalyst had good reusability. The ZnO films showed no photocatalytic activity under visible light irradiation ( $\lambda > 400$  nm). It was indicated that the improvement of the photocatalytic activity by the electrochemical reduction is attributed to the formation of Zn nanoparticles and Zn nanorods. The electrochemical reduction treatment performed at room temperature is a very simple and effective way to improve photocatalytic activity of ZnO films.

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