Microstructure and Photoelectrochemical Characteristics of TiO_2-ZnO Electrodes Prepared by Plasma Spraying Technique†

YE Fuxing*, OHMORI Akira**

Abstract

The photoelectrochemical characteristics of plasma sprayed porous TiO_2, TiO_2-5%ZnO and TiO_2-10%ZnO electrodes in 0.1N NaOH solution were studied through a three-electrode cell system. The microstructure, morphology and composition of the electrodes were analyzed using electron probe surface roughness analyzer (ERA-8800FE), scanning electron microscope (SEM) and X-ray diffraction. The results show that the sprayed electrodes have a porous microstructure, which is affected by the plasma spraying parameters and composition of the powders. The photo-response characteristics of the plasma sprayed electrodes are comparable to that of single crystal TiO_2, but the breakdown voltage is about 0.5V (vs. SCE). The photocurrent density increases with a decrease of donor concentration, which is calculated according to Garner-Bulter model. For the lowest donor concentration of a TiO_2-5%ZnO electrode prepared under an arc current of 600A, the photocurrent density is approximately 0.4mA/cm^2 higher than that of the TiO_2 electrodes under 30mW/cm^2 xenon light irradiation. The photocurrent density increases linearly with light intensity.

KEY WORDS: (Photoelectrochemical characteristic) (Plasma spraying) (TiO_2) (ZnO) (Electrode)

1. Introduction

Since Prof. Fujishima and Honda discovered the photoelectrolysis of water on TiO_2 electrodes in 1972, extensive research have been performed to understand the fundamental principles and improve the electrode (cell) properties of TiO_2, such as light harvesting, light converting components, photocurrent density (Jsc), open circuit voltage (Voc), fill factor (FF), stability and so on [1,2]. For the lower cost of polycrystalline TiO_2, compared with single crystalline TiO_2, polycrystalline n-TiO_2 has been mainly studied as a semiconductor electrode in photoelectrochemical cells[3].There have many techniques for the preparation of the photoelectrode, including wet chemical processing (e.g.: sol-gel, screen printing), vapor processing techniques (e.g.: CVD, PVD) and thermal oxidation of Ti [4]. However, the electrodes prepared by the above methods have many defects, for example, the electrode adhesion strength with the substrate is generally very low, result in an increase in the ohmic resistance and then lower cell power.

To improve the photocurrent density of TiO_2 electrode, one method is to obtain optimal electrical resistivity of the electrode. It is reported that ZnO additive can change the electrical resistivity of TiO_2 for the formation of defects and zinc titanates [5].

Thermal spraying is an economical and versatile fabrication process to produce large surface coatings with unlimited types of materials. The coatings thickness, texture and bonding strength can be controlled easily through spraying parameters, powders and spraying method etc. [3]. Moreover, plasma spray atmospheres are reductive, and it is easy to produce oxygen deficiency in plasma atmospheres. Therefore, in the present study, the TiO_2 and TiO_2-ZnO electrodes were prepared on stainless steel by plasma spraying technique. The microstructure and photoelectrochemical characteristics of the electrodes were analyzed with ERA-8800FE, SEM, X-ray diffraction and a three-electrode cell system equipped with a quartz window.

2. Materials and experimental procedures

2.1. Materials

The variation of photoelectrochemical property with particle size is associated with an increase in the specific area and a corresponding increase of light harvesting. If the size of the feedstock powder is smaller than 10μm, it is difficult to deposit coatings by thermal spraying because of the low speed of the particles. So to satisfy the two demands, the original diameter of the TiO_2 particle is held at 0.2μm, and polyvinyl alcohol is used as a binder for the thermal spraying TiO_2 powder (diameter approximately 30μm). Because the photoelec-

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trochemical property of anatase titanium dioxide is better than that of rutile, anatase TiO_2 was used as feedstock powder. The average size of the TiO_2 powder is 33.7μm. It is reported that ZnO can improve the photoelectrochemical property of the TiO_2 electrode [5]. Therefore, to investigate the influence of ZnO additive, TiO_2-5%ZnO and TiO_2-10%ZnO powders were designed in this study. The average size of TiO_2-ZnO powder is approximately 30μm. The x-ray diffraction patterns of the feedstock powders are illustrated in **Fig.1**. The substrate is stainless steel (JIS SUS316).

2.2 Plasma spraying equipment

A plasma spraying system, whose commercial gun name is Plasma DYNE Gun, has been used to prepare TiO_2, TiO_2-5%ZnO and TiO_2-10%ZnO electrodes. Argon was used as a primary plasma gas and helium was used as the secondary gas. The thermal spraying parameters are illustrated in **Table 1**.

Table 1 Plasma spraying parameters

Ar gas pressure (MPa) /flow (slpm)	0.42/58
He gas pressure (MPa) /flow (slpm)	0.21/9
Arc current (A)	400, 600, 800
Arc voltage (V)	28～30
Spraying distance (mm)	70

2.3 Analysis of the feedstock powders and sprayed electrodes

Electron probe surface roughness analyzer (ERA-8800FE) and scanning electron microscope (SEM) were used to examine the structure characteristics of the feedstock powders and the sprayed electrodes. The phase composition of the feedstock powders and the sprayed electrodes were investigated by X-ray diffraction using Cu-K_α radiation (λ =1.5405Å) with a graphite crystal monochromator (JDX3530, JEOL, Japan).

2.4 Photoelectrochemical characteristics evaluation apparatus and process

The voltammetry was performed in a three-electrode glass cell at room temperature, in which a commercial saturated calomel electrode (SCE) was used as the reference electrode and a platinum plate (30*30mm) as the counter electrode. The electrolyte was 0.1N NaOH solution and deaerated by purging with Ar gas for 30 minutes before the experiments. The photocurrent against potential at each sprayed electrode (working electrode) was measured using a scanning potentiostat and recorded by a personal computer through an AD converter (NR-110, KEYENCE company). The sweep speed of the potential was 2mV/s

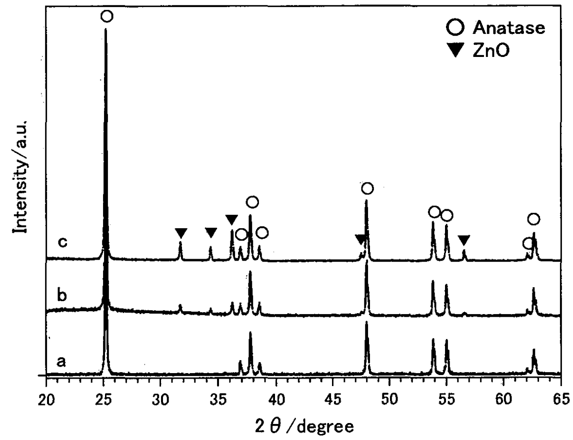

Fig.1. The X-ray diffraction patterns of feedstock powders (a:TiO_2, b:TiO_2-5%ZnO and c:TiO_2-10%ZnO powder).

in every experiment. A 500W xenon lamp was used as light source and the light intensity was measured by a UV radiometer (UVR-2, TOPCON, Tokyo, Japan) with UD-40 or UD-35 detector.

3. Results and Discussion

3.1 The microstructures of the sprayed TiO_2 and TiO_2-ZnO electrodes

Fig.2 shows the typical microstructures of TiO_2, TiO_2-5%ZnO and TiO_2-10%ZnO electrodes prepared by plasma spraying technique under the arc current of 600A. The sprayed electrodes are not very dense, containing many holes. The porosity of the specimens increases with the increasing of ZnO amount. It may result from the volatilization of Zn during the deposition process as clearly shown in **Fig.3**, where the hollow voids remain after the Zn gas is given off.

The density of the TiO_2-5%ZnO electrodes becomes denser with an increase of arc current as shown in **Fig.4** for the much more melted feedstock powder.

The typical X-ray diffraction pattern of plasma sprayed TiO_2-5%ZnO electrodes is illustrated in **Fig.5**. The electrode consists of anatase TiO_2, rutile TiO_2 and $Zn_2Ti_3O_8$ phase. Despite the relative unstability of $Zn_2Ti_3O_8$, the formation of $Zn_2Ti_3O_8$ phase rather than Zn_2TiO_4 is rational for the similarity in structure between anatase and $Zn_2Ti_3O_8$ when the anatase phase of TiO_2 was used in the starting mixture especially in plasma spraying process [6-8].

3.2 Transient photocurrent-time profile of TiO_2 electrode

Fig.6 shows a typical photocurrent-time profile of TiO_2 electrode with hand-chopped light. An anodic photocurrent spike appears immediately after the light is turned on, and then decreases continuously with time until a steady state photocurrent is reach. When the light is turned off, the photocurrent decreases quickly down to

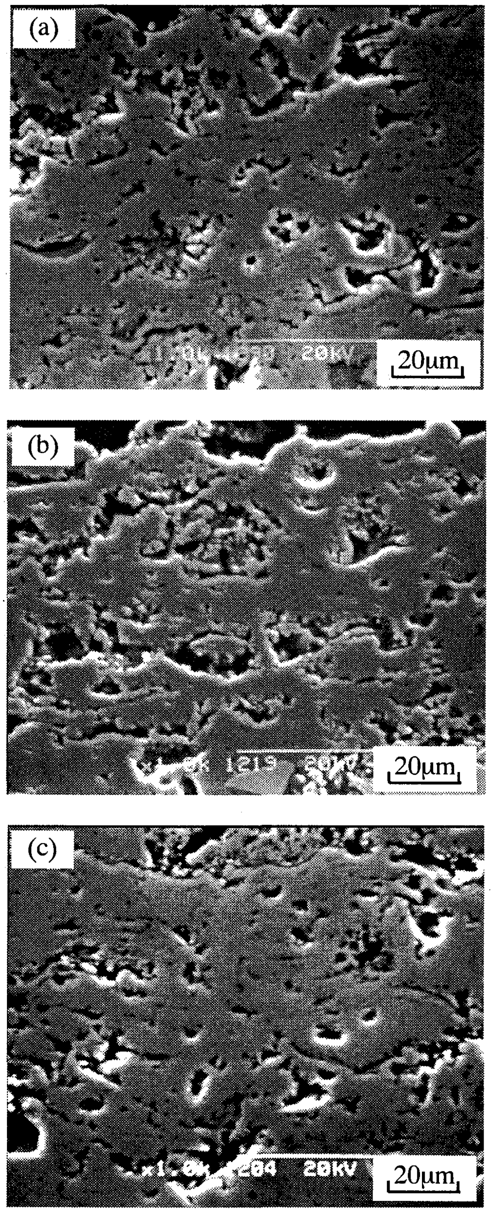

Fig.2. The typical microstructures of plasma sprayed TiO_2 (a), TiO_2-5%ZnO (b) and TiO_2-10%ZnO (c) electrode.

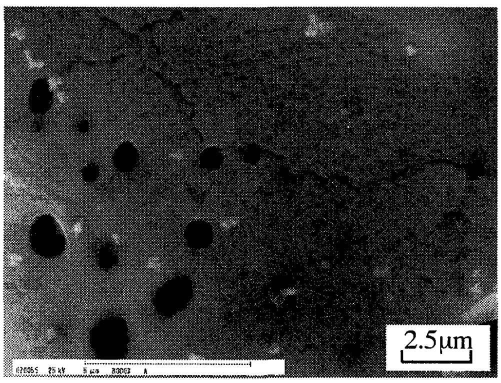

Fig.3. The typical hollow voids of plasma sprayed TiO_2-ZnO electrode.

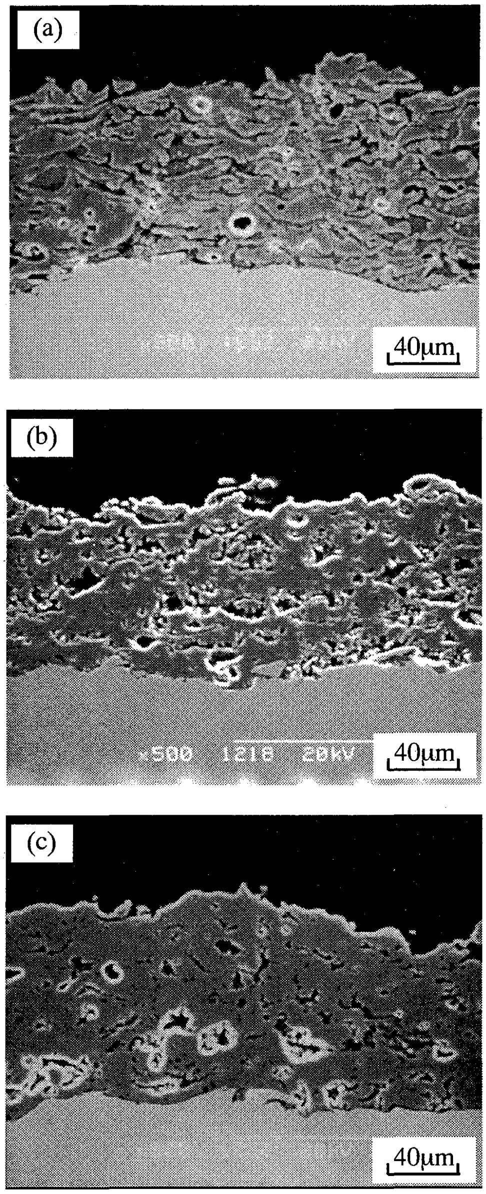

Fig.4. The typical microstructures of the plasma sprayed TiO_2-5%ZnO electrodes under the arc current of 400A (a), 600A(b) and 800A (c).

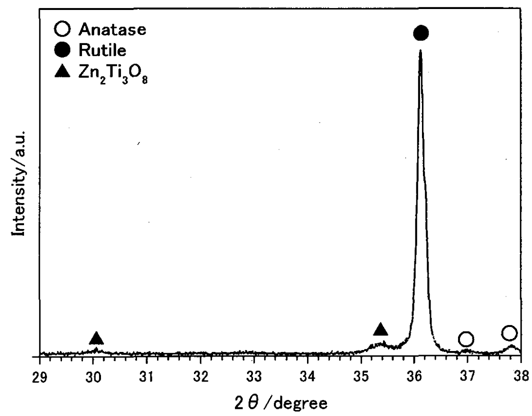

Fig.5. The typical X-ray diffraction pattern of a plasma sprayed TiO_2-5%ZnO electrode.

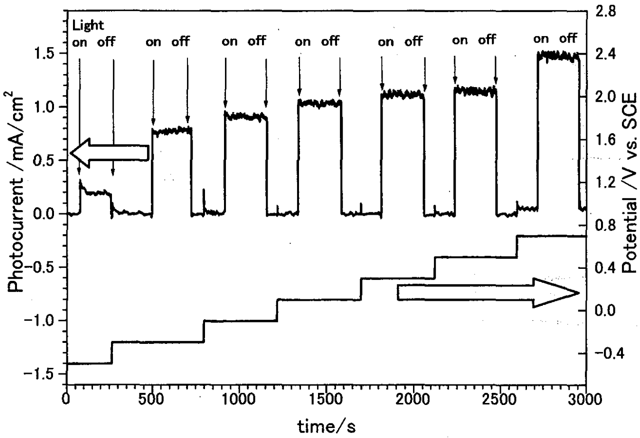

Fig.6. The transient photocurrent-time profile of TiO_2 electrode.

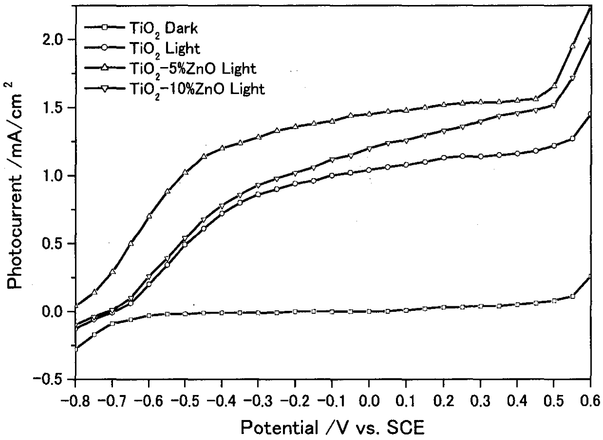

Fig.7. The photocurrent–potential curves of the TiO_2, TiO_2-5%ZnO and TiO_2-10%ZnO electrode prepared under the arc current of 600A.

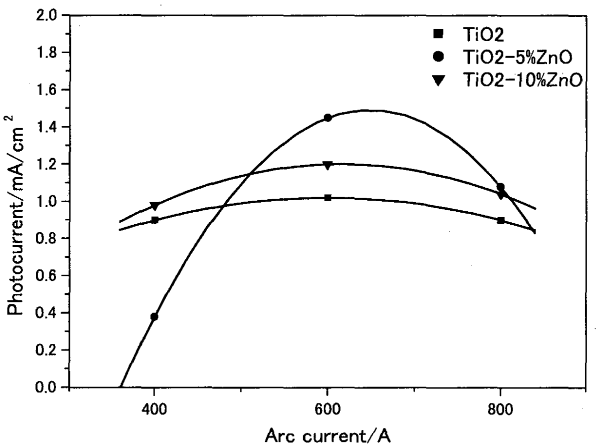

Fig.8. The relationship between photocurrent density and the arc current of TiO_2 (a), TiO_2-5%ZnO (b) and TiO_2-10%ZnO (c) electrode.

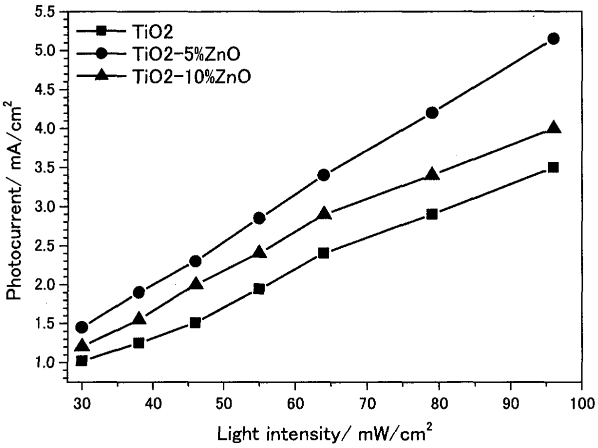

Fig.9. The relation between photocurrent density and light intensity.

zero. The initial anodic photocurrent spike is due to instantaneous photo-induced electron transitions to the conduction band as discussed by Liu [9] and Salvador [10].

3.3 The photoelectrochemical characteristics of the sprayed TiO_2 and TiO_2-ZnO electrodes

Fig.7 illustrates the photocurrent–potential curves of the TiO_2, TiO_2-5%ZnO and TiO_2-10%ZnO electrode prepared under an arc current of 600A. The photo-response characteristics of the sprayed electrodes are comparable to that of single crystal TiO_2, but the breakdown voltage is about 0.5V (vs. SCE), which is similar to the plasma sprayed electrodes prepared by Wang [3]. The photocurrent density of the TiO_2-5%ZnO electrode is higher than that of the TiO_2 and TiO_2-10%ZnO electrodes prepared under the same spraying parameters.

The conductivity of the TiO_2 electrode decreases with the addition of ZnO (unpublished data). It has been reported that the electrode materials for PEC conversion must have optimal conductivity for the efficient movement and lowest recombination of excited hole-electron pairs. The variation of electrode resistivity can be understood in terms of the change in electron concentration induced by the possible defect reactions and the microstructure. Furthermore, certain transition metals diffuse through these channels into lattices because TiO_2 contains interstitial channels in the *c* direction. The diffusing ions have been found to locate preferentially on either the substitutional or interstitial sites [5]. Thus, on the one hand, the increase of resistivity for the TiO_2-5%ZnO electrode can be explained by substitution of Ti (0.68 Å) site with Zn (0.74 Å). As a result, the electron concentration may be reduced as expressed by the following defect equation:

$$ZnO + 2e' + \frac{1}{2}O_2 \rightarrow Zn_{Ti}^{\bullet\bullet} + 2O_o^{\times}$$

On the other hand, the increase of resistivity for the TiO_2-5%ZnO electrode results from the porous microstructure as shown in Fig.2 compared with the TiO_2 electrode. For the relative high resistivity, the

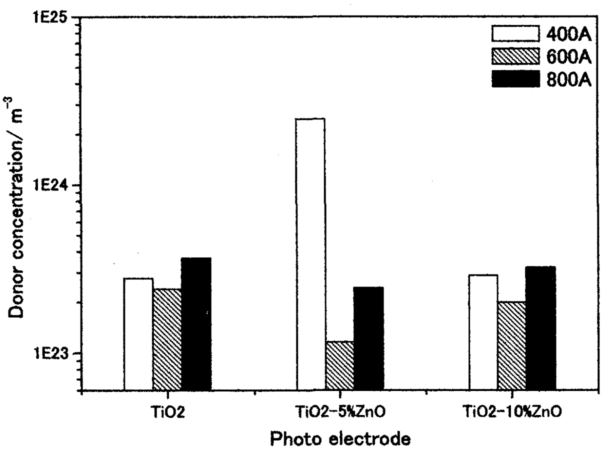

Fig.10. The donor concentration of plasma sprayed TiO_2, TiO_2-5%ZnO and TiO_2-10%ZnO electrode.

recombination speed of hole and electron pairs of TiO_2-5%ZnO electrode may decrease and then increase the photocurrent density. However, the much lower conductivity for the TiO_2-10%ZnO electrode may well increase ohmic loss and then lower the photocurrent density.

The photocurrent density of the electrodes prepared under an arc current of 600A is higher than that under 400A or 800A for the same powder as shown in **Fig.8**, and it increases linearly with the light intensity as shown in **Fig.9**.

3.4 The donor concentration of sprayed electrodes

The semiconductor surface properties are of paramount importance and their determination has received considerable effort. Because the donor concentration is one of the key parameters, it is obtained from the quantum efficiency measurement according to the well-known Gartner-Butler model [11] in this study. Generally, the low donor concentration will benefit to increase the photocurrent density.

According to the Gartner-Butler model, the quantum efficiency is expressed by the following equation

$$J_{SC}^{\ 2} = \frac{2\varepsilon_R\varepsilon_0 e\alpha^2 I_0^{\ 2}}{N_d}(V - V_{FB}) \qquad (1)$$

where J_{SC} is the photocurrent density, I_0 is the photo intensity, α is the optical absorption coefficient, ε_0 is the permittivity of free space, ε_R is the relative dielectric constant, e is the elementary charge, V is the electrode potential, V_{FB} is the flatband potential and N_d is the donor concentration.

The donor concentration of the sprayed electrodes is calculated according to equation (1), and the results are illustrated in **Fig.10**. The donor density of the electrode under the arc current of 600A is lower than that under the arc current of 400A or 800A for the same feedstock powder, and the donor density of TiO_2-5%ZnO electrode prepared under the arc current of 600A is lowest comparing with the other electrodes. These are in good relation with photocurrent density shown in Fig.8. It has been previously mentioned that the photocurrent density increases linearly with the light intensity, which implies the equation (1) is fulfilled, as also reported by P. Salvador [10].

4. Conclusions

In this study, the photoelectrochemical performance of plasma sprayed TiO_2, TiO_2-5%ZnO and TiO_2-10% ZnO electrodes was systematically investigated. The plasma sprayed electrodes have photo-response characteristics and the break down voltage was about 0.5V (vs. SCE). The maximum photocurrent density of the TiO_2-5%ZnO electrode is about 1.45mA/cm^2, which is 0.4mA/cm^2 higher than that of the TiO_2 electrodes under 30mW/cm^2 xenon light irradiation. Furthermore, linear dependence of the photocurrent density with light intensity is obtained under a constant potential. Moreover, the donor concentration (N_d) is in good relation with photocurrent density in this experiment.

References

1) A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, Nature 238 (1972) 37.
2) Amy L. Linsebigler, GuangQuan Lu and John T. Yates Jr, Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results, Chem. Rev. 95 (1995) 735.
3) Rong Wang, Chuck H. Henager Jr, J., Arc-plasma-sprayed rutile anodes for photoelectrolysis of water, Electrochem. Soc. 126 No.1 (1979) 83.
4) F.X. Ye, A. Ohmori, The photocatalytic activity and photo-absorption of plasma sprayed TiO_2-Fe_3O_4 binary oxide coatings, Surf. Coat. Technol., 160 (2002) 62.
5) K. H. Yoon, J. Cho and D. H. Kang, Physical and photoelectrochemical properties of the TiO_2-ZnO system, Mater Res. Bull. 34, No. 9 (1999) 1451.
6) A. I. Sheinkman, F. P. Sheinkman, I. P. Dobrovol skii and S. A. Bolshakova, The solid solution of ZnO in zinc orthortitanate, Inorganic Materials, Vol.13 Issue 3 (1977) 383.
7) A. I. Sheinkman, F. P. Sheinkman, I. P. Dobrovol skii and S. A. Bolshakova, Phase formation sequence in the reaction of zinc oxide with titanium dioxide, Inorganic Materials, Vol.13 Issue 8 (1977) 1171.
8) J. Yang, J. H. Swisher, The phase stability of $Zn_2Ti_3O_8$, Materials Characterization, Vol. 37 Issues 2-3 (1996) 153.
9) C. Liu, Y. Chen., W. Li, Direct observation of elementary steps in charge transfer mediated by surface states on TiO_2 electrode under illumination, Surface Sci. 163 (1985) 383.

10) P. Salvador, Subbandgap photoresponse of n-TiO_2 electrodes: transient photocurrent-time behavior, Surface Sci. 192 (1987) 36.
11) S. E. Lindquist, B. Finnstrom, L. Tegner, Photoelectrochemical properties of polycrystalline TiO_2 thin film electrodes on quartz substrates, J. Electrochem. Soc. 130 No.2 (1983) 351.