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NEW APPROACH FOR GENERATING Cu$_2$O/TiO$_2$ COMPOSITE FILMS FOR SOLAR CELL APPLICATIONS

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Abstract

In this paper, Cu$_2$O was studied as a photon absorber for solar cell applications. Cu$_2$O was deposited on a TiO$_2$ film using the electrochemical deposition (ECD) method. Based on the physical appearance of the samples, the particles of Cu$_2$O seemed to penetrate the TiO$_2$ film and were primarily deposited near the TiO$_2$/substrate interface rather than on the TiO$_2$ film surface. This method could be one way to generate a p-n bulk-heterojunction interface. The film was confirmed to be a Cu$_2$O/TiO$_2$ composite via X-ray diffraction measurements. The top electrode was formed by evaporating indium for I-V characterization, and the fabricated cell showed photovoltaic properties.

Keywords: composite materials, electrodeposition, solar energy materials, thin films.
Introduction

TiO$_2$ is an n-type semiconductor with a wide band-gap energy of 3.2 eV and is known for having photo-catalytic effects [1]. Grätzel et al. developed a type of cell called a dye-sensitized solar cell (DSSC), or a Grätzel cell, and its efficiency can be improved by 11% with the use of ruthenium dye [2]. However, the Grätzel cell has problems with dye desorption, leakage, packaging and long-term stability. Many attempts have been made to improve the cells. One alternative solution is to convert it to a solid-state cell by using a p-type semiconductor as a hole conductor instead of a liquid electrolyte. Recently, many p-type semiconducting materials have been used in an attempt to convert cells to solid-state DSSCs, including Spiro-OMeTAD [3] and copper (I) iodide (CuI) [4-5]. However, contact between the dye monolayer and the p-type material is crucial in solid-state DSSCs. Therefore, previous attempts to resolve these problems have failed because only incomplete filling of the TiO$_2$ pores with a p-type material was achieved, especially when thicker films were used.

One way to overcome the problems with solid-state DSSCs is to use ETA (extremely thin absorber) solar cells or quantum dot (QD) sensitized solar cells, which are conceptually similar to solid-state DSSCs [6-9]. In those solar cells, a small band-gap p-type semiconductor, such as CuInS$_2$, CdTe and SnS replaces the molecular dye in the DSSC and works as a photon absorber in the cells [10-12]. The semiconductor typically covers the n-type semiconductor film, which is usually TiO$_2$. The structure of the ETA and QD solar cells has the advantage of enhanced light harvesting due to surface enlargement and multiple scattering [7-8]. The TiO$_2$/CdTe cells fabricated by Ernst et al. [10] exhibited an open-circuit voltage of 0.67V and a short-circuit current of 8.9mA cm$^2$ under 100 mW cm$^{-2}$ of simulated sunlight. Nanu et al. [11] generated TiO$_2$/CuInS$_2$ solar cells using an atomic layer chemical vapor deposition method (ALCVD) with 4% solar energy efficiency.

Following these previous studies, we considered the use of cuprous oxide (Cu$_2$O) as a p-type solar cell material to be deposited on TiO$_2$ for solar cell applications. In this study, Cu$_2$O was used as a photon absorber. Cu$_2$O, with a direct band-gap of 2.1 eV, is regarded as a suitable material for high-efficiency solar cells [13-14]. McFarland et al. created a Cu$_2$O/TiO$_2$ heterojunction thin film and observed a photoresponse in a photoelectrochemical cell [15]. Li et al. prepared core shell Cu$_2$O/TiO$_2$ solar cell with an efficiency ~0.01%
The combination of Cu₂O and TiO₂ could contribute to efficient photoelectric conversion. In this research, Cu₂O/TiO₂ composite thin films were generated through a combination of electrochemical deposition (ECD) and squeegee methods, and a cell was fabricated by forming metal electrodes on the film. Through ECD, we observed that the particles of Cu₂O penetrated the nanoporous layer of the TiO₂. The structural and optical properties of the films were also characterized, and the photoresponse of the cell was measured.

**Experimental Procedures**

TiO₂ films with a thickness of approximately 16 μm were prepared by the squeegee method using a 0.8 g/mL paste of TiO₂ powder (P25, Aerosol Japan) with 0.5 mL of acetyl acetone. The paste was mixed and blended with 0.4 g of polyethylene glycol and 2.5 mL of triton X for about 5 min. Then, the TiO₂ films were heated and annealed at 100°C and 400°C for 30 min in air. The substrate used was F-doped SnO₂ (FTO) coated glass. The deposition of Cu₂O on the TiO₂/FTO substrate by ECD was accomplished using an aqueous solution containing 0.5 mol/L copper (II) sulfate and 6 mL of lactic acid in 20mL of pure water. The solution pH was adjusted to 12.5 with KOH. Galvanostatic electrochemical deposition on the TiO₂/FTO substrate was performed at a current density of approximately -1 mA/cm², and the deposition time was 10 min unless otherwise stated.

**Results and Discussion**

The physical morphologies of the films are shown in Figures 1 (a), (b) and (c). After the Cu₂O was deposited, the top surface remained white, while the bottom side (the substrate side) turned orange (the color of Cu₂O). Thus, the Cu₂O seemed to penetrate the TiO₂ film and was primarily deposited near the TiO₂/FTO interface rather than on the TiO₂ film surface. This result likely occurred because the Cu₂O gradually filled the porous matrix of TiO₂ from the bottom, as shown in Figure 1 (d). When Cu₂O, was deposited, it is likely that the deposition solution easily penetrated the TiO₂ film. For Cu₂O to deposit on the top surface of the TiO₂ film, the electric current needed to flow through the TiO₂ matrix. However, the TiO₂ particles composing the matrix are resistive. Therefore, it is possible that the current preferentially flowed from the
film/substrate interface into the deposition solution. Thus Cu$_2$O was preferentially deposited near the interface rather than on the top surface.

Figure 2 shows X-ray diffraction patterns for the Cu$_2$O, TiO$_2$ and Cu$_2$O/TiO$_2$ composite films. All of the peaks observed for TiO$_2$ can be attributed to the TiO$_2$ anatase structure, and the peaks observed for Cu$_2$O can be attributed to the Cu$_2$O cubic structure. For the composite film, in addition to the TiO$_2$ peaks, Cu$_2$O peaks were also observed.

Figure 3 shows optical transmission spectra for the TiO$_2$, Cu$_2$O, and Cu$_2$O/TiO$_2$ composite films. The Cu$_2$O film has an absorption edge around 570 nm, which corresponds to its band gap of 2.1 eV. The TiO$_2$ film was porous. Thus, the transmission was low in the visible range due to scattering. The absorption edge was observed near 400 nm. For the composite films, the transmission was minimal for wavelengths shorter than 520 nm due to absorption by the Cu$_2$O.

For the I-V characterization, indium was evaporated as shown in Figure 4 (a). Figure 4 (b) shows the photovoltaic behavior of the Cu$_2$O/TiO$_2$ composite films measured during illumination through the FTO glass substrate. Three samples with different Cu$_2$O deposition times were prepared and measured. The AM1.5 light intensity was maintained at 100 mW/cm$^2$ for all of the measurements. For the 10 min deposition sample, the short-circuit current was 0.0031 mA/cm$^2$, the open-circuit voltage was 0.47 V, and the efficiency was 5x10$^{-4}$ %. Thus, a rectifying p-n junction was formed, with the front surface side acting as an n-type semiconductor and the film/substrate interface side acting as a p-type semiconductor. This arrangement likely occurred because the surface side was primarily comprised of TiO$_2$ and the interface side was primarily comprised of Cu$_2$O, as shown in Figure 2.

A solar cell based on a mixture of n-type and p-type semiconductors is commonly called a blend solar cell or a bulk-heterojunction solar cell. In almost all previous studies on bulk-heterojunction solar cells, the photovoltaic blend film consisted of two organic semiconductors or one organic and one inorganic semiconductor. We have demonstrated that the Cu$_2$O/TiO$_2$ composite film shows photovoltaic behavior, as shown in Figure 4 (c). Therefore, we can regard our composite film as an inorganic-inorganic bulk-heterojunction thin film.

Conclusions
Cu$_2$O films were deposited by ECD on TiO$_2$ films prepared by the squeegee method, and a cell was generated by evaporating In on the film. During I-V characterization, the cell showed electrical rectification and photovoltaic effects. Even though the overall performance of the cell has not yet been optimized, we have demonstrated that an inorganic bulk heterojunction solar cell can be created using a simple approach based on the ECD and squeegee methods.

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References

**Figure 1**: (a) Physical appearance of the TiO$_2$ film, (b) and (c) images of deposited Cu$_2$O on TiO$_2$ from the top and bottom sides view, respectively and (d) model of the Cu$_2$O/TiO$_2$ film structure.

**Figure 2**: X-ray diffraction patterns of (a) Cu$_2$O, (b) TiO$_2$ and (c) Cu$_2$O/TiO$_2$ composite films.

**Figure 3**: Transmission spectra for (a) Cu$_2$O (b) TiO$_2$ and (c) the Cu$_2$O/TiO$_2$ composite films.

**Figure 4**: (a) Position of the electrodes for the I-V measurement, (b) I-V curves for Cu$_2$O/TiO$_2$ composite films with different Cu$_2$O deposition times, (c) photo-response behavior from I-V characterization of the Cu$_2$O/TiO$_2$ composite films under an illumination of 100mW/cm$^2$.
Figure 2

Figure 3
Figure 4