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# Flexible dye-sensitized solar cells by 28 GHz microwave irradiation

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## Abstract

Microwave preparation of $TiO_2$ nanocrystalline electrode for use in dye-sensitized solar cells is examined. A multi-mode microwave heating system operating at a frequency of 28 GHz is used to produce rapid synthesis. Well-sintered $TiO_2$ nanocrystalline thin film is successfully fabricated on transparent conductive PET–ITO electrode. Photoelectron energy conversion efficiency of 2.16% is achieved in an electrode prepared by 28 GHz microwave irradiation at 1.0 kW for 5 min.

*Keywords:* Dye-sensitized solar cell; Microwave; 28 GHz; Nanocrystalline $TiO_2$; Firing

## 1. Introduction

The dye-sensitized solar cell unveiled by [1] has attracted much attention as the next-generation solar cell [1–2]. Remarkably, high quantum efficiency [3] in combination with the expected ease and low cost of manufacturing makes this new technology interesting as an alternative to existent solar cell technologies. Various aspects of dye-sensitized solar cells have therefore been researched, including the sensitized dye, semiconductor particles, electrolyte, electron transfer process and photovoltaic mechanism [4–13].

In spite of these vigorous studies, the assembling of flexible $TiO_2$/dye solar cell is still under investigation [14–19]. Flexible electrodes, like polyethylene terephthalate sheet coated with tin-doped indium oxide (PET–ITO), present lower costs and technological advantages relative to conductive glass electrodes, e.g. lower weight, impact resistance and less form and shape limitations. However, deposition of nanoparticulated $TiO_2$ on PET–ITO is difficult, because the thermal treatment must be limited to 150 °C, decreasing adhesion, electrical contact between the particles and adsorption of the dye [17–19].

To achieve the selective heating of organic–inorganic composite film, microwave processing is an attractive field in modern material science. Various inorganic phases have been synthesized using microwave ovens operating at a frequency of 2.45 GHz [20–24]. This technique was also applied to the preparation of nanosize $TiO_2$ powder with a high degree of crystallinity and monodispersed crystallite sizes [25,26]. Recently, the use of 28 GHz microwaves has been demonstrated to be effective in the synthesis of various inorganic oxides [27–31]. In these cases, reactions proceed rapidly via microwave–material interactions. Here, in this work, a 28 GHz microwave irradiation process for flexible dye-sensitized solar cells is newly proposed.

## 2. Experimental

### 2.1. Preparation of the $TiO_2$ paste

Titanium oxide nanoparticles were prepared by hydrothermal treatment of titanium oxide slurry (TAYCA Corp., TKS-201). This slurry contains titanium oxide particles in a solid/liquid ratio of 32.6 wt.%. Mean particle diameter was measured to be about 6 nm by X-ray diffraction. The dispersing agent of the slurry is hydrochloric acid and the solution pH is about 1.0. The titanium oxide slurry in which the solid/liquid ratio and pH were adjusted to 16.3 wt.% and 1.0 was used as the reactant. The adjusted slurry was put into a stainless steel tube with a Teflon® inner cup. The tube was closed and put in a dry oven at 225 °C for 8 h. The resulting particle size of the titanium oxide colloidal paste was about 30 nm in diameter.

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### 2.2. Cell assembly

To measure photovoltaic properties, the synthesized titanium oxide paste was applied without any additives to FTO, fluorine doped $SnO_2$ coated transparent conductive glass plate having a sheet resistance of $15\,\Omega\,cm^{-2}$. The dimensions of the FTO glass size were 25 mm × 25 mm × 1.1 mm, and titanium oxide paste was applied to a 4 mm × 5 mm rectangular surface region to a thickness of about 60 μm. The titanium oxide film was then heated using the multi-mode microwave heating system operating at a frequency of 28 GHz (Model FMS-10-28, Fuji Dempa Kogyo Co. Ltd., Japan) for 5 min. The titanium oxide electrode was put on an alumina block. These were then placed in the cavity of microwave irradiation equipment. After microwave irradiation, electrodes were then soaked in 0.5 mM $Ru(NCS)_2L_2$·bis-TBA (L = 2,2′bipyridyl-4,4′dicarboxylic acid) ethanol solution for 20 h at room temperature. Finally, the dye-sensitized titanium oxide electrode and counter electrode were located facing each other, and electrolyte solution was introduced into the space between the electrodes to form a solar cell. The counter electrode was Pt (2000 Å) coated FTO glass. Electrolyte solution was prepared by mixing 0.1 M LiI, 0.05 M $I_2$, 0.6 M 4-*tert*-butylpyridine and 0.5 M 2,3-dimethy-propyl-limidazolium iodide into 3-methoxy-propionitrile as a solvent.

In case of film type $TiO_2$ electrode, nanosize $TiO_2$ powder (P-25, Nippon Aerosil Co. Ltd.) was directly applied on the PET–ITO film (OTEC-110, Tobi Co. Ltd., 125 μm, $10\,\Omega\,cm^{-2}$, $T = 80\%$) by special spray painting method about 9 μm in thickness without any polymer additives. The counter electrode was Pt (100 Å) coated PET–ITO film.

### 2.3. Photovoltaic property measurement

Solar cells were evaluated using a 300 W Xe lamp (Hyper Xenon Exciter, Bunkoh Keiki Co. Ltd.) as the light source. A glass filter (HA-50, HOYA) was equipped to filter out IR (over 700 nm) and UV (under 400 nm) spectral regions. Illumination intensity was held constant at $100\,mW\,cm^{-2}$ using a pyranometer (LI-200SB, LI-COR). Photocurrent and voltage data were automatically captured by a PC using 12-bit A–D converter and relayed set of variable resistors. The working area of the titanium oxide electrode was $0.2\,cm^2$.

## 3. Results and discussion

In order to clarify the heat mechanism of $TiO_2$ electrode, as a preliminary experiment, the degree of microwave absorption of various inorganic material powders was evaluated. The temperature–time profiles were measured under microwave irradiation of 1 kW power output from a multi-mode microwave heating system operating at a frequency of 28 GHz. The temperature was measured by conventional stainless steel sheathed thermocouple (87% platinum and 13% Rhodium, Type R).

Fig. 1 shows the temperature–time profile of $SnO_2$, $In_2O_3$, $TiO_2$ and $SiO_2$ powder under 28 GHz microwave irradiation at 1 kW. Both $SnO_2$ and $In_2O_3$ absorb microwaves well, and can be heated rapidly. The temperature reaches at 1200 °C for $SnO_2$ after the irradiation for 4 min. The temperature becomes over 800 °C within 4 min for $In_2O_3$. The $TiO_2$ was found to exhibit moderate coupling to microwaves. The maximum temperature was 200–300 °C. Interestingly, no clear relationship between the particle size (MERCK: 200–300 μm; ST-01: 7 nm; P-25: 21 nm), the specific surface area (MERCK: $<1\,m^2\,g^{-1}$; ST-01: $300\,m^2\,g^{-1}$; P-25: $45\,m^2\,g^{-1}$) and the temperature–time profile could be found. The main constituent of glass electrode, $SiO_2$ (amorphous) is transparent to microwaves because there was no relationship between the microwave irradiation and the temperature increase.

Considering the fact that $SnO_2$ and $In_2O_3$ are non-stoichiometric semiconductors having high electrical conductivity, material–microwave coupling in both compounds possibly correlates with higher concentration of conduction electrons. Increases in the temperature of a material by microwave–material interactions are mostly attributed to induction losses from electric conduction. The $TiO_2$ showed moderate coupling to microwaves because it is stoichiometric semiconductor having both low electrical conductivity and low magnetic induction loss. The absorbed energy $P$ ($W\,m^{-3}$), material–microwave interaction is explained with the generalized energy loss equation as follows:

$$P = 2\pi f \varepsilon_0 \varepsilon_r \tan\delta\, E^2 V_s \Theta$$

where $f$, $\varepsilon$ are the frequency, dielectric constant, $\tan\delta$ stands for the dielectric and magnetic loss factor value. $E$, $V_s$, $\Theta$ are the electric field values inside the sample, volume and shape factor, respectively.

For more practical operation, microwave irradiation for $TiO_2$ nanocrystalline film electrode was examined. The resulting $J$ (photocurrent density) versus (voltage) $V$ curve is shown in Fig. 2. Photovoltaic parameters are also summarized in Table 1.

Photoelectron energy conversion efficiency of 5.51% was achieved using a 9.0 μm thick $TiO_2$ film at 0.7 kW for 5 min. This almost matches the 5.88% of the electrode fabricated by conventional electric furnace heating at 480 °C for 50 min.

Table 1
Photovoltaic properties of a solar cell in different heating method for glass electrodes

| Heating method | $V_{OC}$ (mV) | $J_{SC}$ ($mA\,cm^{-2}$) | FF | $\eta$ (%) |
|---|---|---|---|---|
| Microwave | | | | |
| 0.7 kW, 5 min | 697 | 11.8 | 0.67 | 5.51 |
| Electric furnace | | | | |
| 150 °C, 1200 min | 745 | 7045 | 0.70 | 3.86 |
| 480 °C, 50 min | 752 | 12.6 | 0.62 | 5.88 |

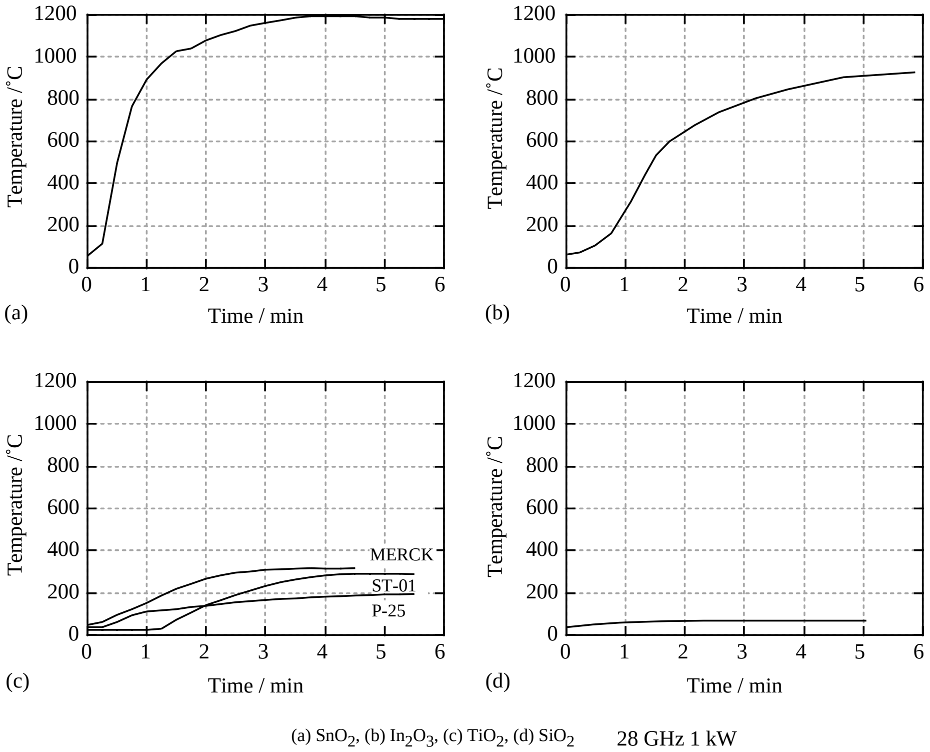

Fig. 1. Temperature as a function of time during 28 GHz, 1 kW microwave irradiation of (a) $SnO_2$; (b) $In_2O_3$; (c) $TiO_2$; (d) $SiO_2$.

The efficiency of 3.86% was also obtained by electric furnace heating at 150 °C for 1200 min. These results indicate that 28 GHz microwave irradiation promotes electrical interconnection between $TiO_2$ nanocrystal particles, comparing favorably with electric furnace heating. It is worth to note that the operating time was less than one-tenth. In contrast, when a microwave oven with 2.45 GHz frequency for various power outputs (Toshiba, ER-A30S1) was used, the $TiO_2$/FTO/glass electrodes cracked easily under more than 0.2 kW irradiation. This may be caused by rapid, inhomogeneous thermal stresses, because the wavelength of 2.45 GHz microwaves of 122 mm is much longer than the 10.7 mm of 28 GHz microwaves. Using a low power output of 0.1 kW at 2.45 GHz, an electrode was fabricated with a conversion efficiency of 0.58%

Finally, this microwave technique was applied to the $TiO_2$ film on the flexible PET–ITO film. The comparison of photoelectron conversion efficiencies in different microwave irradiation is shown in Fig. 3. Photovoltaic parameters are summarized in Table 2.

It can be clearly seen that the efficiency of these all-plastic cells improve by microwave heating from 0.45 to 0.74% at

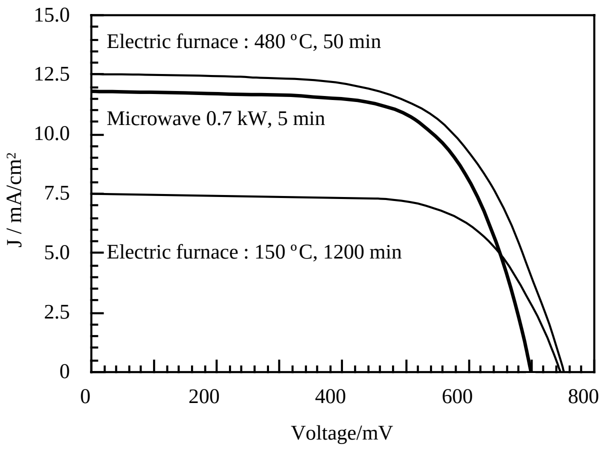

Fig. 2. Comparison of electric furnace heating and 28 GHz microwave irradiation for glass electrodes.

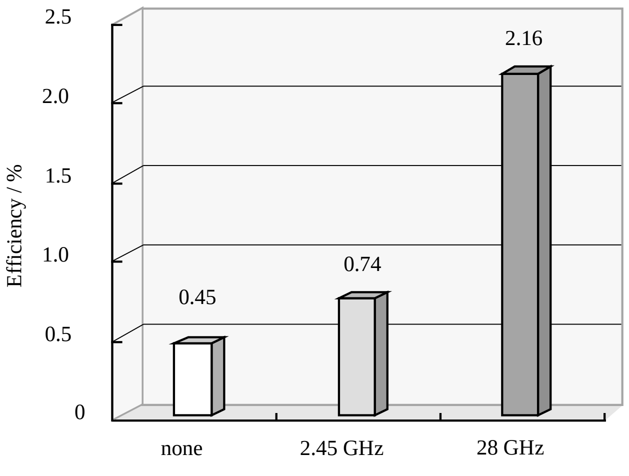

Fig. 3. Comparison of efficiencies in different microwave irradiation at 1 kW for 5 min for PET–ITO electrodes.

Table 2
Photovoltaic properties of a solar cell in different microwave irradiation for PET–ITO electrodes

| Heating condition | $V_{OC}$ (mV) | $J_{SC}$ ( mA cm$^{-2}$) | FF | $\eta$ (%) |
|---|---|---|---|---|
| Non-irradiation (0.148 cm$^2$) | 611 | 1.28 | 0.57 | 0.45 |
| 2.45 GHz (0.142 cm$^2$) | 657 | 1.76 | 0.64 | 0.74 |
| 28 GHz (0.142 cm$^2$) | 685 | 4.91 | 0.64 | 2.16 |

Counter: Pt coated PET–ITO film; measurement: AM 1.5 G, 100 mW cm$^{-2}$.

2.45 GHz, and up to 2.16% at 28 GHz. Relatively, high open circuit voltage of 685 mV at 28 GHz irradiation is considered to the better electrical connectivity of each nanosize $TiO_2$ particles. This well firing resulted higher photoelectron conversion efficiency.

## 4. Conclusion

Well-sintered $TiO_2$ thin film is thus shown to be successfully fabricated on transparent conductive FTO glass electrode in a short time using 28 GHz microwave irradiation. This technique is also applied to the PET–ITO film electrode. Photoelectron energy conversion efficiency of 2.16% is obtained for all-plastic cell prepared by 28 GHz microwave irradiation at 1.0 kW for 5 min.

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