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Preparation and characterization of FTO (fluorine-doped tin oxide) particles using fluorine gas

*Takashi Kimura[1)], Jae-Ho Kim[2)], Susumu Yonezawa[3)] and Masayuki Takashima[4)]

[1), 2), 3), 4)] *Department of Materials Science & Engineering, University of Fukui, Fukui 910-8507, Japan*
[2)] kim@matse.u-fukui.ac.jp

ABSTRACT

Fluorine contents in SnO_2 powder was adjusted using fluorine gas (F_2 gas) to find the optimum contents of F in the FTO (Fluorine-doped Tin Oxide). Also the relationship between fluorine contents and electrical conductivity was investigated. From XPS patterns (F 1s) of fluorinated SnO_2 particles, it proved that the particle surface could be fluorinated using F_2 gas. Comparing with untreated SnO_2, the fluorinated SnO_2 made to improve the dispersion stability. The dispersion stability of it could be sustained in water for 24 h. In addition, the surface fluorination of SnO_2 particles could improve the electrical conductivity (approximately $75Sm^{-1}$) under a fluorine pressure of 66.7 kPa at 200℃ for 1h.

1. INTRODUCTION

Dye-sensitized solar cell (DSSC, DSC) using sunlight as an energy source has attracted attention as a sustainable power generation device. FTO films are used as the material of DSSC, have been the major films in TCO (Transparent Conductive Oxide) films, and formed on a glass using FTO particles which are prepared to make transparent conductive films. Fluorine atoms in FTO attack the oxygen sites in the lattice creating free electrons to promote higher conductivity in the samples [1]. As advantages of FTO, it is lower cost than ITO (Indium-Tin Oxide) which is a kind of TCO because the price of tin is more stable than indium. Moreover, the amounts of resource are more stable [2]. However, there are some problems in difficult to find the optimum contents of F in the FTO films for the high conductivity. The common strategy for forming the FTO films has been reported forming with SPD (Spray Pyrolysis Deposition) using $SnCl_4 \cdot 5H_2O$ dissolved in ethanol and a saturated aqueous solution of NH_4F [3]. SPD is the way to jet the sample solution with a spray on the heated glass and form the transparent conductive films on it by thermal decomposition reaction. Comparing with sputtering or CVD (Chemical Vapor Deposition), SPD has many advantages, for example, the temperature of film formation is lower, the parent material has a higher degree of freedom of selecting, the preparation of components is easier and the speed of film formation is faster at low temperature [2]. In this study, in order to find the optimum contents of F in the FTO, F_2 gas was used as a dopant for SnO_2. Furthermore,

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[1)] Graduate Student
[2),3),4)] Professor

SnO_2 powder was fluorinated using it under various fluorine pressures or temperatures. Also the relationship between F contents and electrical conductivity was investigated.

2. EXPERIMENTAL DETAILS

2.1 Material preparation

Tin dioxide (SnO_2) powders were purchased from Sigma-Aldrich, used as starting materials. For the preparation of FTO particles, at first, SnO_2 powders (2.5g) were fluorinated under a fluorine pressure of 101 kPa at 25℃–250℃ for 1hour using F_2 gas. Next, SnO_2 powders (2.5g) were fluorinated under a fluorine pressure of 13.3–115 kPa at 200℃ for 1h.

2.2 Material characterization

The structure of the fluorinated SnO_2 by temperature conditions was investigated using XRD (X–ray diffraction; XRD–6100, SHIMADZU, Ltd.). The surface composition was investigated using XPS (X–ray photoelectron spectroscopy; JPS–9010MC, JEOL Ltd.). The particle surface was observed using FE-SEM (Field Emission–scanning electron microscopy; ULTRA plus, ZEISS).

The dispersion stability of untreated, fluorinated (25℃, 101kPa, 1h) and fluorinated (200℃, 66.7kPa, 1h) SnO_2 powders was observed using the pure water. Several samples were put into vial containers containing the pure water. After shaking the vial containers, these samples were left for 1 week. Until 1 hour had passed, these samples were observed every 15 minutes, after 1 hour had passed, these samples were observed every 1 day.

2.3 Electrical conductivity measurements

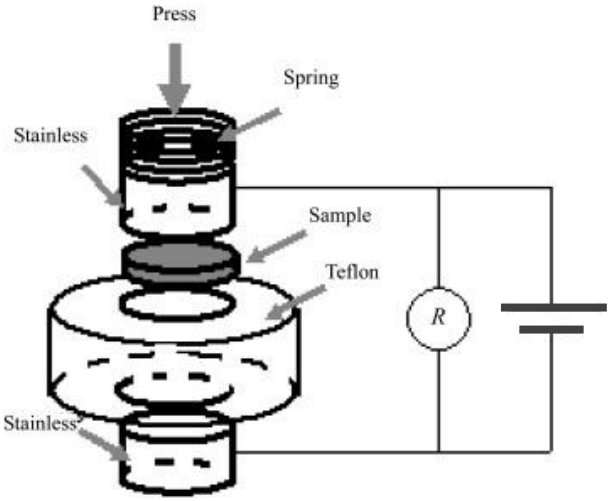

Fig. 1 Schematic illustration of electrical conductivity measurements [4].

The electrical conductivities of untreated and fluorinated SnO_2 particles by temperature conditions and fluorine pressure conditions were measured using the four-terminal dc method with a disk sample (diameter of 10mm) pressed at 3kg/cm^2 as shown in Fig. 1 [4]. The conductivity was calculated by the following equation (1).

$$\sigma = I / RS \quad (1)$$

In this equation, σ is the electrical conductivity (Sm^{-1}), I is the sample thickness (m), R is the resistance (Ω), and S is the sample area (m^2).

From XPS data and the calculated conductivities, better surface fluorine conditions could be found for high conductivity. Therefore, the optimum contents of F in the FTO could be found in this study.

3. RESULTS and DISCUSSION

3.1 Structural analysis

With different temperature (25℃, 100℃, 200℃, 250℃), the XRD patterns of untreated and fluorinated SnO_2 powders are shown in Fig. 2. These fluorine conditions of pressure and time were maintained at 101kPa for 1 hour. In Fig. 2, comparing with the untreated SnO_2, any new peaks and peak shifts were not found for all fluorinated SnO_2. From XRD patterns, internal crystal structure wasn't changed by the fluorination using F_2 gas and didn't depend on temperature conditions (25℃-250℃).

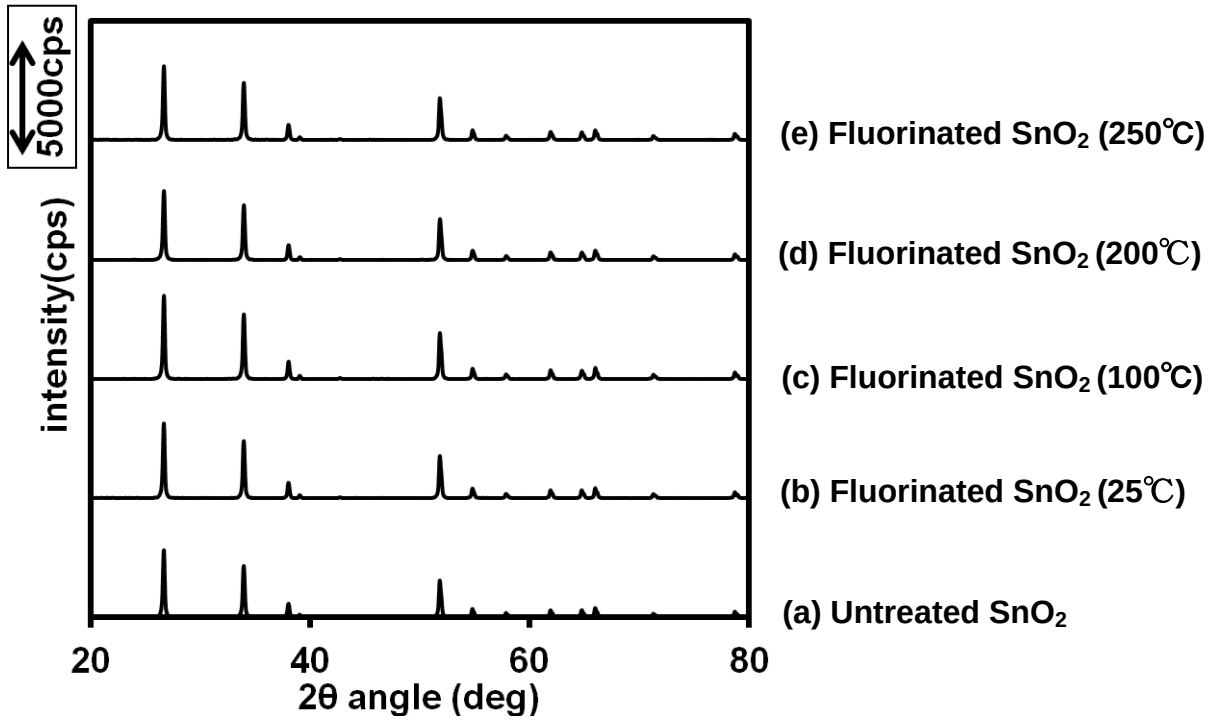

Fig. 2 XRD patterns of fluorinated SnO_2 with different temperature condition.

FE-SEM images of untreated and fluorinated SnO_2 particles are show in Fig. 3. Samples (a)-(e) correspond to the untreated SnO_2 (a), fluorinated SnO_2 at 25℃ (b), at 100℃ (c), at 200℃ (d) and at 250℃ (e) under a fluorine pressure of 101 kPa for 1 hour. These particle sizes obtained from SEM images were less than 200nm. Comparing with the untreated SnO_2, the surface fluorination effects of SnO_2 could not be confirmed in FE-SEM images.

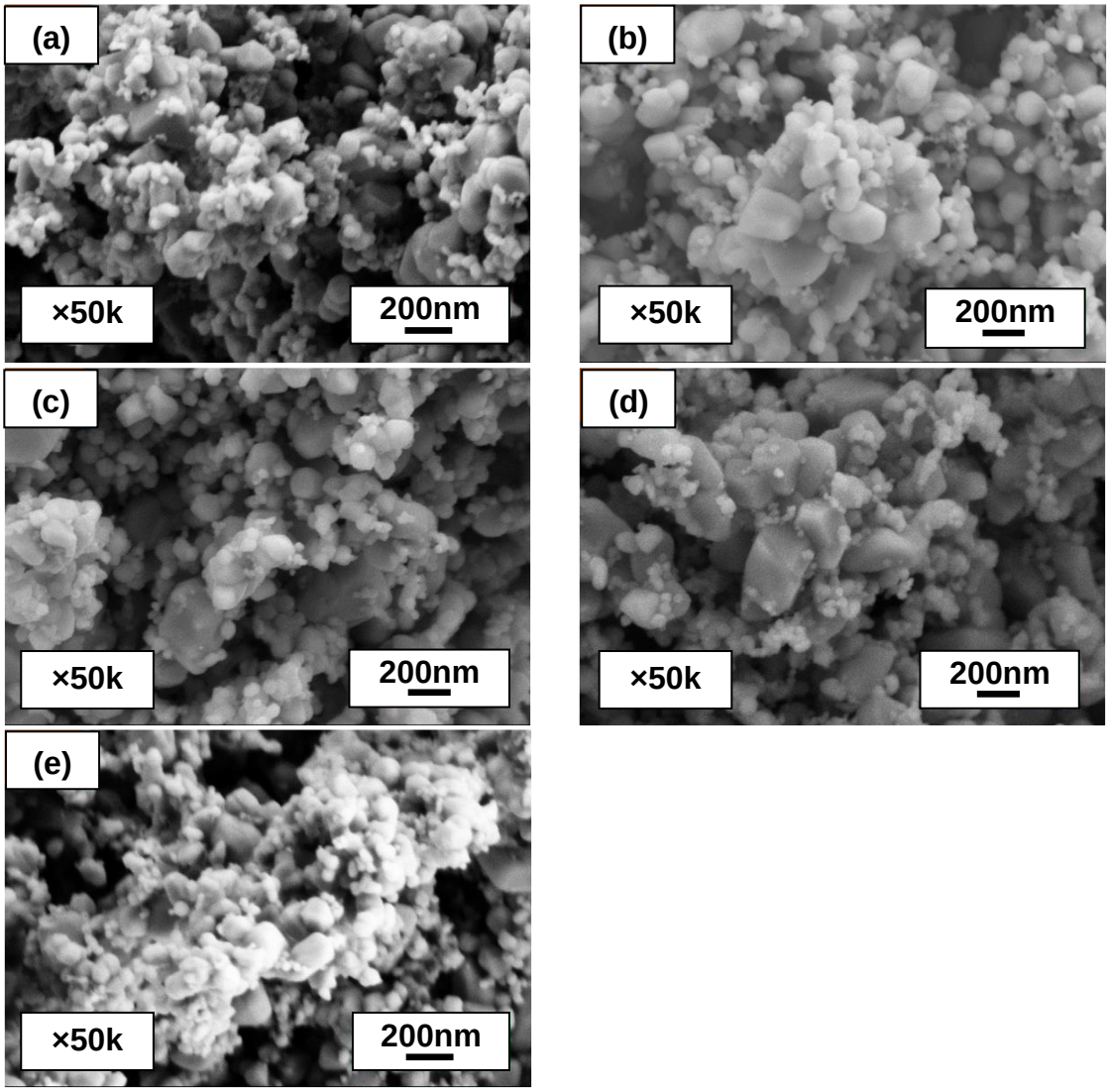

Fig. 3 FE-SEM images of SnO_2 particles prepared with untreated (a), fluorinated at 25℃ (b), at 100℃ (c), at 200℃ (d) and at 250℃ (e).

3.2 Surface composition

Fig. 4 and Fig. 5 show the binding energies of Sn 3d5/2 and F 1s of SnO_2 samples measured by XPS. All binding energies obtained from XPS analysis were calibrated to the C 1s peak at 284.8 eV. XPS spectra of untreated and fluorinated SnO_2 particles with different temperature condition are shown in Fig. 4. These reaction conditions of F_2 pressure and time were maintained at 101kPa for 1 hour. Samples (a)-(e) correspond to the untreated SnO_2 (a), fluorinated SnO_2 at 25℃ (b), at 100℃ (c), at 200℃ (d), and at 250℃ (e). From F 1s spectra (B), comparing with the untreated SnO_2 (a), F 1s peak located at the binding energy (BE) of 683.2 eV was detected in fluorinated samples (b)-(e). As a result, it proved that the particle surface was fluorinated using F_2 gas. Furthermore, From Sn 3d5/2 spectra (A), comparing with the untreated SnO_2 (a), the

binding energy of Sn 3d5/2 of fluorinated SnO_2 (b)-(e) shifted higher. These results seem to be related to the creation of Sn-F bond of $SnO_{2-x}F_{2x}$.

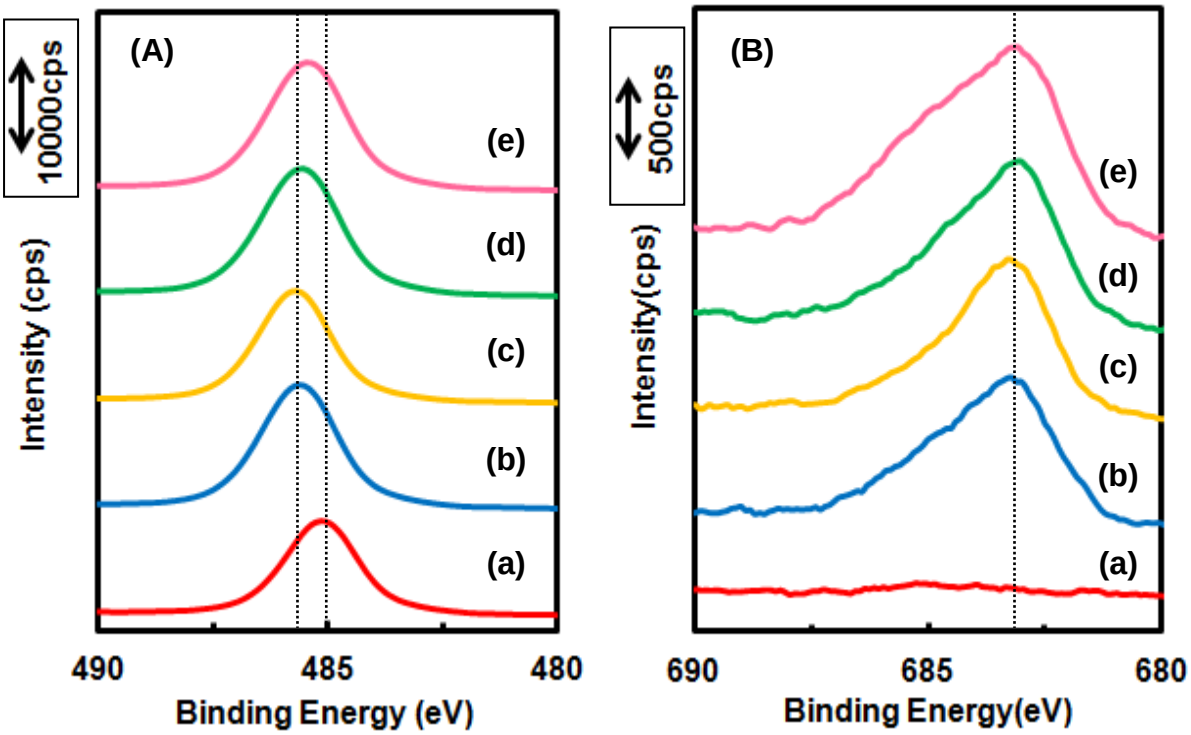

Fig. 4 XPS spectra of untreated and fluorinated SnO_2 with different temperature condition; (A) Sn 3d5/2; (B) F 1S. Samples (a)-(e) correspond to the untreated SnO_2 (a), fluorinated SnO_2 at 25℃ (b), at 100℃ (c), at 200℃ (d), and at 250℃ (e) under a fluorine pressure of 101 kPa for 1 hour.

XPS spectra of untreated and fluorinated SnO_2 with different F_2 pressure are shown in Fig. 5. These reaction conditions of temperature and time were maintained at 200℃ for 1 hour. Samples (a)-(i) correspond to the untreated SnO_2 (a), fluorinated SnO_2 at 13.3kPa (b), at 26.7kPa (c), at 40.0kPa (d), at 53.3kPa (e), at 66.7kPa (f), at 80.0kPa (g), at 101kPa (h) and at 115kPa (i). From Sn 3d5/2 spectra (A), comparing with the untreated SnO_2 (a), the binding energy of Sn 3d5/2 of fluorinated SnO_2 (b)-(i) shifted higher. Furthermore, by different F_2 pressure, the peak shifts varied between 484.9 and 486 eV. These results seem to be related to the different of fluorine contents (x) in $SnO_{2-x}F_{2x}$. From Fig. 5 (A) and Table 1 (3.4 Electrical conductivity measurements), (e), (f), (h) which is x = 0.17, excluding (c) were similar peak shifts. Also, (g), (i) which is x = 0.18 were similar peak shifts.

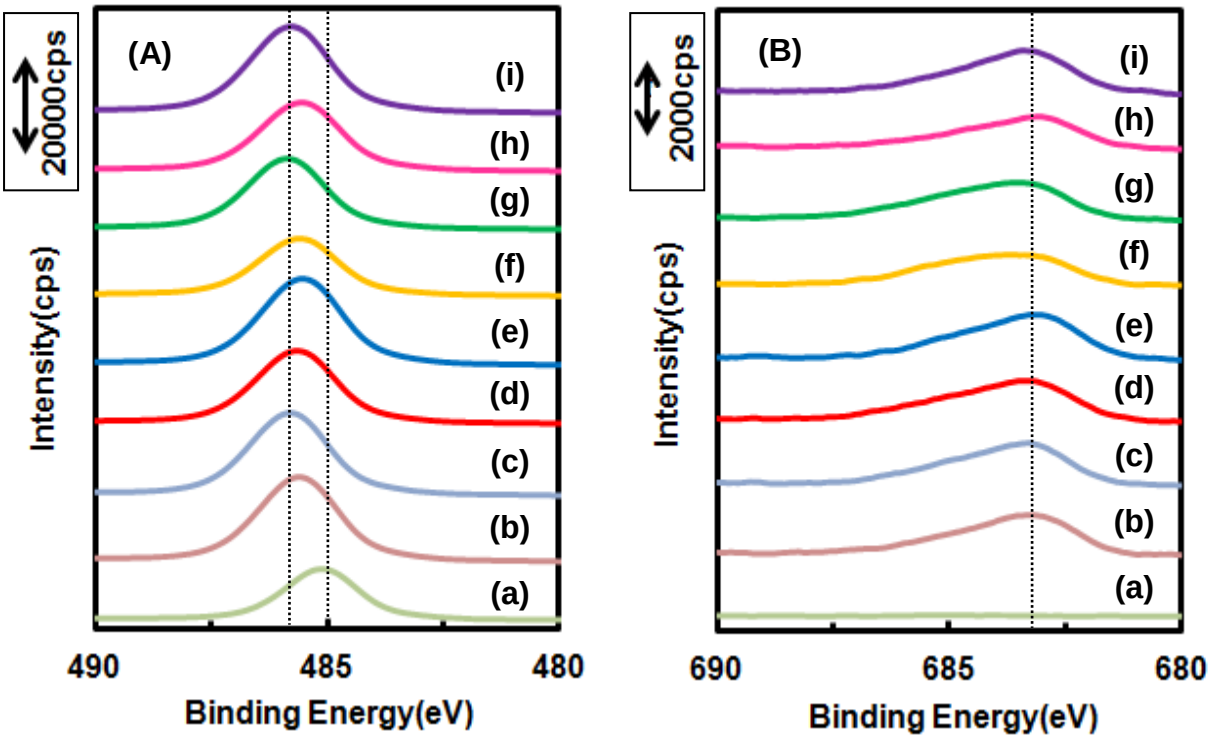

Fig. 5 XPS spectra of untreated and fluorinated SnO_2 with different F_2 pressure; (A) Sn 3d5/2; (B) F 1S. Samples (a)-(i) correspond to the untreated SnO_2 (a), fluorinated SnO_2 at 13.3kPa (b), at 26.7kPa (c), at 40.0kPa (d), at 53.3kPa (e), at 66.7kPa (f), at 80.0kPa (g), at 101kPa (h) and at 115kPa (i) at 200℃ for 1 hour.

3.3 Dispersion stability

Fig. 6 shows the dispersion stability of untreated, fluorinated (25℃, 101kPa, 1h) and fluorinated (200℃, 66.7kPa, 1h) SnO_2 powders in pure water. While the untreated sample (a) started reforming into large agglomerates within 1 hour in water, the dispersion stability of the fluorinated samples (b), (c) could be sustained in water for 1 day. After 1day, the untreated sample completely reformed into large agglomerates, and after 1 week, the fluorinated samples did. The difference of reaction conditions (b), (c) could not be obtained from Fig. 6. From those results, the dispersion stability in water wasn't affected by the reaction conditions with F_2 gas.

	After the addition	1 hour	1 day	1 week
(a)Untreated sample				
(b)Fluorinated sample (25℃ 101kPa 1h)				
(c)Fluorinated sample (200℃ 66.7kPa 1h)				

Fig. 6 Photograph of untreated and fluorinated SnO_2 powders in pure water.

3.4 Electrical conductivity measurements

Sample names, reaction conditions, fluorine contents (x) in $SnO_{2-x}F_{2x}$ and electrical conductivities are summarized in Table 1, in which, fluorinated SnO_2 samples prepared at various reaction conditions with F_2 gas were named as the Fluorinated 1-11 respectively. The fluorine contents in surface region of fluorinated SnO_2 particles were evaluated from the XPS data. The conductivity was calculated by Eq. (1). Comparing with the untreated SnO_2 (Untreated), the fluorinated SnO_2 (Fluorinated 1-11) improved

in the conductivity. Fig. 7 shows the relationship between temperature condition and electrical conductivity in the fluorinated SnO_2 samples. Under F_2 pressure of 101 kPa for 1 hour, the temperature condition of 200℃ (Fluorinated 3) was the highest conductivity. Fig. 8 shows the relationship between F_2 pressure and electrical conductivity in the fluorinated SnO_2 samples. Under fluorine pressures of more than 66.7kPa at 200℃ (Fluorinated 3, 9, 10, 11), the high conductivity (approximately between 65 to 75Sm^{-1}) was proved. The optimum fluorine contents (x) in $SnO_{2-x}F_{2x}$ for the high conductivity seem to be 0.17, however, the high conductivity seems to be related not only the fluorine contents (x) in $SnO_{2-x}F_{2x}$, but also the various reaction conditions.

Table 1. Electrical conductivities of SnO_2 samples prepared at various reaction conditions with F_2 gas.

Sample name	Temperature (℃)	F_2 pressure (kPa)	Time (h)	x in $SnO_{2-x}F_{2x}$	σ (Sm^{-1})
Untreated	**—**	**—**	**—**	**0.00**	**0.144**
Fluorinated 1	**25**	**101**	**1**	**0.14**	**49.5**
Fluorinated 2	**100**	**101**	**1**	**0.18**	**35.7**
Fluorinated 3	**200**	**101**	**1**	**0.17**	**74.3**
Fluorinated 4	**250**	**101**	**1**	**0.18**	**58.9**
Fluorinated 5	**200**	**13.3**	**1**	**0.16**	**4.56**
Fluorinated 6	**200**	**26.7**	**1**	**0.17**	**10.9**
Fluorinated 7	**200**	**40.0**	**1**	**0.19**	**9.16**
Fluorinated 8	**200**	**53.3**	**1**	**0.17**	**47.9**
Fluorinated 9	**200**	**66.7**	**1**	**0.17**	**73.2**
Fluorinated 10	**200**	**80.0**	**1**	**0.18**	**65.3**
Fluorinated 11	**200**	**115**	**1**	**0.18**	**65.2**

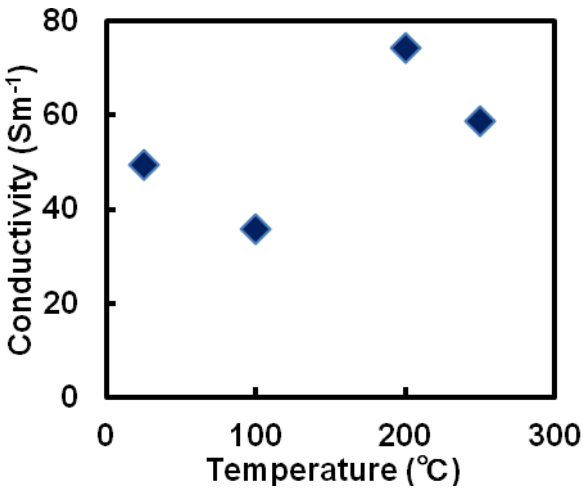

Fig. 7 The relationship between temperature condition and electrical conductivity in the fluorinated SnO_2 samples.

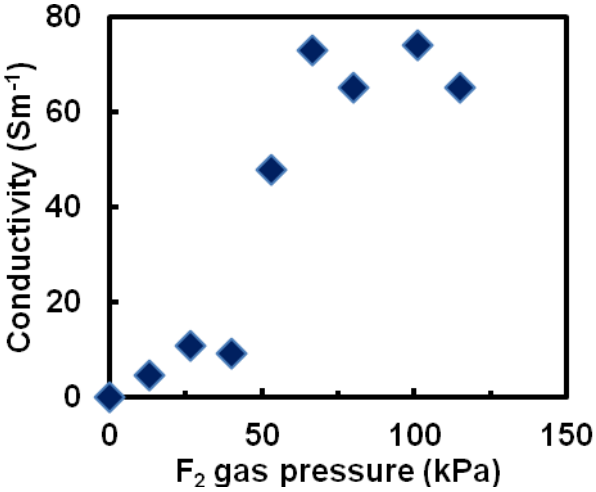

Fig. 8 The relationship between F_2 pressure and electrical conductivity in the fluorinated SnO_2 samples.

4. CONCLISIONS

The surface fluorination of SnO_2 particles using F_2 gas improved electrical conductivity (approximately 75 Sm^{-1}) under fluorine pressure of 66.7 kPa at 200℃ for 1 hour. The optimum fluorine contents (x) in $SnO_{2-x}F_{2x}$ for the high conductivity was 0.17. From XRD and XPS patterns, the surface of SnO_2 particles was fluorinated but internal crystal structure wasn't changed. From FE-SEM images, SnO_2 particle sizes were less than 200nm. Also the surface fluorination of SnO_2 particles improved the dispersion stability in water and could sustain the dispersion stability for 1 day. From these results, the FTO particles using F_2 gas can be useful for FTO films as the material of DSSC.

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