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Use of Salicylic acid as a de-aggregating agent in Dye Sensitized Solar Cells

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Solar cells, being an effective solution for the energy crisis, have been investigated and being developed by researchers from all around the world. So far silicon solar cells have been developed mostly and used widely, with a conversion efficiency around 30%, but the production cost has always been putting limitations on daily use. As a cheaper solution for this, Dye sensitized solar cells (DSC) have attracted much more attention among the research community, yet the best reported power conversion efficiency is still very low as 12%. Many attempts are being taken to improve the efficiency of these cells. The main components of a DSC, namely transparent conducting oxide film, semiconductor thin film, sensitizer, electrolyte and counter electrode should be optimized in order to have the DSC perform well. Among these components, the semiconductor thin film is the most investigated component so far. For better performance, the semiconductor thin film should be porous, well-crystallized and should have inter-connected particle networks. As a better alternative to acetic acid which is used as a de-aggregating agent in TiO_2 film formation process of Dye sensitized Solar Cells (DSC) when the spray pyrolysis deposition method is used, Salicylic acid was used. The cell characteristics, surface morphology and crystallinity of the films were investigated for different amounts of salicylic acid used with. The optimum concentration of Salicylic acid was found to be 0.1M, while that particular cell showed a V_{OC} of 0.77 V, a J_{SC} of 12.19 mA, a fill factor of 0.69 and a conversion efficiency of 6.52%.

Keywords: Dye sensitized solar cells, TiO_2, Salicylic acid, Photovoltaic

1. INTRODUCTION

Dye sensitized solar cells (DSC) have become a promising alternative for fossil fuel, in finding a solution for the energy crisis [1]. But, still the conversion efficiency is insufficient to compete with the conversion efficiency of Silicon solar cells. To improve the efficiency, the four main components of the DSCs, namely the semiconductor substrate, dye, electrolyte and counter electrode, has to be optimized. Among these the role of semiconductor substrate is the most important and most investigated. A lot of efforts have been reported on optimizing the thickness [2], porosity [3], surface area of the electrode [4] etc. In producing a good photoelectrode with well developed pore sites, the TiO_2 particles should be well-dispersed in the initial solution or paste, without coagulation [5]. There are various techniques used to fabricate TiO_2 thin films such as spin coating, doctor blade method sol-gel dip coating, screen printing, spray pyrolysis deposition and hydrothermal method. Among these spray pyrolysis deposition (SPD) method has been identified as a convenient and widely used technique in this purpose. In SPD technique, a TiO_2 colloidal suspension is sprayed onto a substrate heated to150 ºC along with a surfactant like Triton X-100 and a de-aggregating agent like acetic acid which is the most widely used chemical agent used in DSCs in this purpose. For wide application, a less harmful dye is preferred for safety and easy handling. Acetic acid has an acidity (pK_a) of 4.79, boiling point at 118~119ºC and flash point at 40 ºC. Therefore, the use of acetic acid in spray method sometimes may not give what is expected from it, due to evaporating before 150 ºC. Also, it can give various health hazards due to long time exposure to acetic acid vapor. Therefore it is important to find safer and better alternative to acetic acid, without affecting the performance of the DSC.

In this paper, we investigated the influence of Salicylic acid on TiO_2 thin film to be used in DSCs, and suggest that salicylic acid is a good alternative for typically used acetic acid. Salicylic acid was chosen because of its relatively high boiling point (211 ºC) and high flash point (157 ºC) and also being a solid.

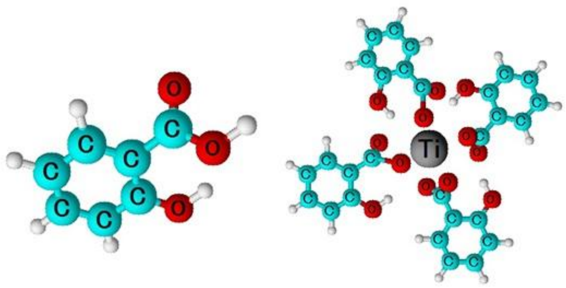

Figure 1. Chemical structure of Salicylic acid (left) and Titanium(IV) salicylate

With salicylic acid, used as a deaggregating agent, the DSCs showed a V_{OC} of 0.77 V, a J_{SC} of 12.19 mA, a fill factor of 0.69 and a conversion efficiency of 6.52%.

2. EXPERIMENTAL

2.1. Fabrication of TiO_2 thin film substrate

0.25 g of Degussa P-25 TiO_2 powder was ground with 0.01M of salicylic acid (SAL1). Next, 20ml of Tayca TiO_2 colloidal suspension was added to the ground powder along with 5 drops of Triton

X-100 and ground well again. The resultant suspension was ultrasonicated for 30 minutes followed by addition of 20 ml of ethanol. The final suspension was sprayed on to the heated FTO glass plates at 150ºC, using the improved atomized spray pyrolysis depositing machine [3]. After spraying, the plates were sintered for one hour at 500ºC. This same procedure was repeated with different amounts of Salicylic acid (0.02M (SAL2), 0.05M (SAL5), 0.1M (SAL10) and 0.2M (SAL20) in a series. For comparison, a separate sample was prepared using 5.5ml of acetic acid instead of salicylic acid, in conventional method.

2.2. Dye sensitization and cell assembly

The sintered TiO_2 substrates were immersed in a 0.3 mM Ruthenium N719 dye solution for 24h. After that, the plates were washed with acetonitrile to wash away the extra dye molecules and sandwiched together with a Pt plate which was used as the counter electrode. The electrolyte used between the sandwiched plates is the conventionally used Iodine based liquid electrolyte.

2.3. Characterization

I-V characteristics of the DSC were measured using the JASCO CEP-25BX solar simulator. IR absorption peaks were determined using the JEOL JIR-WINSPEC50 IR spectrometer. The morphology of the TiO_2 films was investigated using the JEOL JSM-6320F FE-SEM microscope. The crystallinity was checked using the RIGAKU RINT Ultima III X-ray diffractometer. JASCO V-630 UV-Vis spectroscopy was used to determine the adsorbed dye amount.

3. RESULTS AND DISCUSSION

Upon mixing salicylic acid with TiO_2 particles, the color of the solution changed to yellow giving a clear indication of formation of Titanium(IV) salicylate surface complexes [7]. This has also been noted by Tunesi and Anderson [8] and by Dagan and Tomkiewicz [9].

Figure 2 shows the ATR-FTIR spectrum for the TiO2 films prepared with and without salicylic acid. In addition to the observed yellow color, the formation of Titanium(IV) salicylate can be verified by the FTIR peaks at 1722 cm^{-1} and 1454 cm^{-1} which belongs to the C=O stretching vibration and the O-H Bending vibrations of the Carboxylic group in Salicylic acid respectively , at 1600 cm^{-1} which belongs to the C=C stretching vibration of the aromatic ring of salicylic acid, at 1336 cm^{-1} which is the peak for δ(C-OH) bending vibration of the phenolic group of salicylic acid [10,11], at 1239 cm^{-1} which represents the ν(C-OH) stretching vibration of the phenolic group of salicylic acid [10,12,13]**,** at 749 cm^{-1} which is the (C-H) bending (ortho) vibration peak of the aromatic ring of the salicylic acid. Moreover, the peak at 430 cm^{-1} which belongs to the Ti-O-Ti vibration bonds of anatase TiO_2 indicates that Salicylic acid facilitates the formation of Ti-O-Ti network even before annealing.

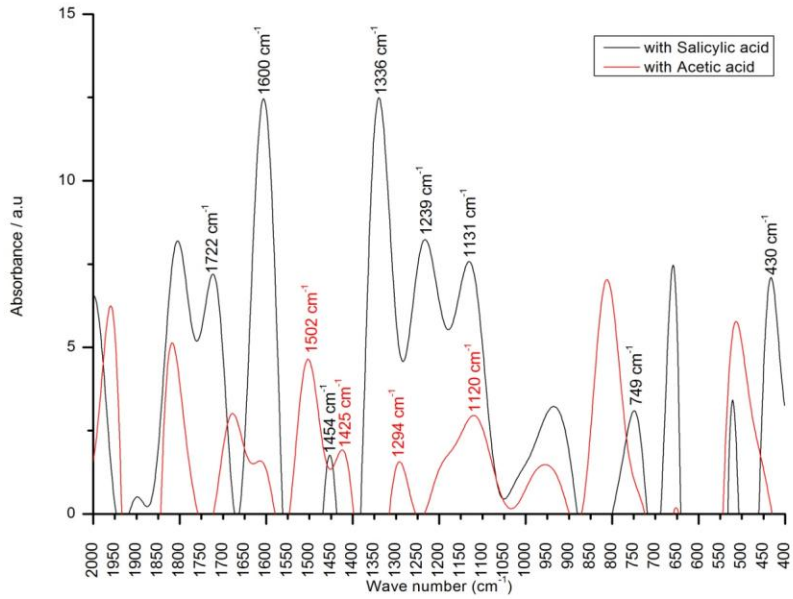

Figure 2. ATR-FTIR spectrum for films prepared with and without Salicylic acid

Peaks at 1425 cm^{-1} and 1294 cm^{-1} can be identified as the O-H bending vibrations and C-O stretching vibrations of the Acetic acid. Ethanol, which was used as the solvent in both cases, is responsible for the peaks at 1131 cm^{-1} and 1120 cm^{-1}.

Figure 3 shows the SEM images of the TiO_2 prepared with different amounts of salicylic acid.

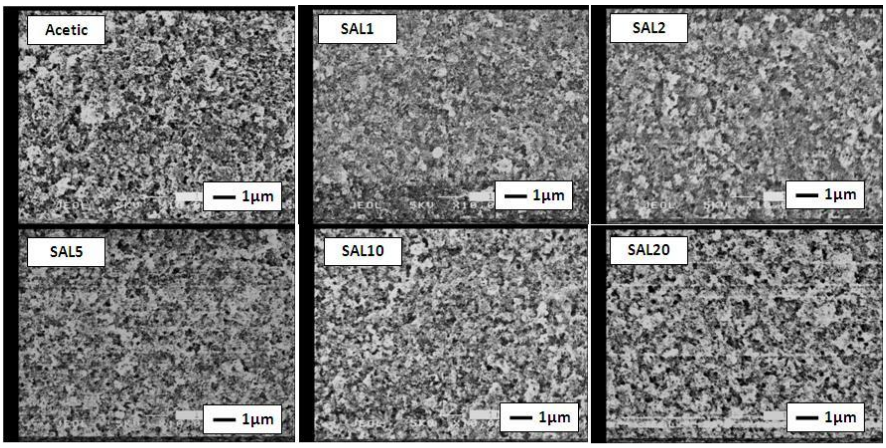

Figure 3. SEM images of TiO_2 films prepared with Salicylic acid.

The SEM images clearly indicate that TiO_2 films are porous and have interconnected TiO_2 networks. Increasing the salicylic acid concentration, the porosity increased. With 0.1M of salicylic acid the surface morphology of the film looked similar to the films prepared with acetic acid. The TiO_2 film has to be porous in order to have more dye molecules adsorbed, but, being too much porous means there is less amount of TiO_2 particles and electron flow from TiO_2 particles to the FTO layer is limited or restricted due to dead-ends in the network.

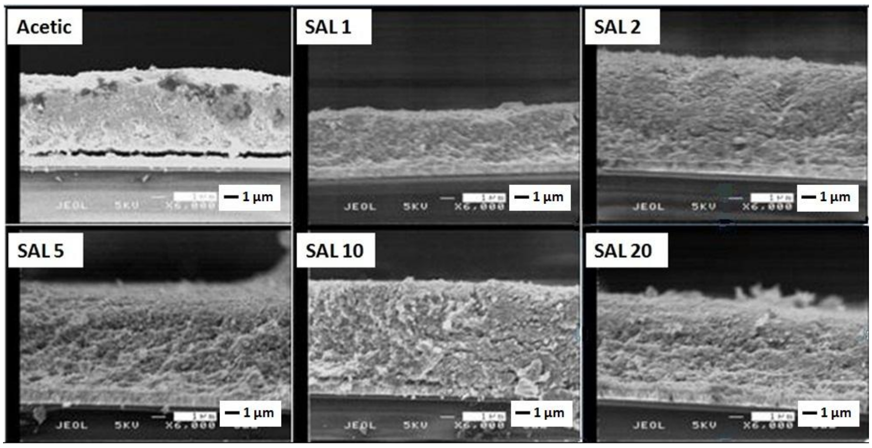

Figure 4. SEM images of cross section of TiO_2 films prepared with Salicylic acid.

The cross sectional images shows in figure 4 also indicates that the films are of thickness about 7 μm, but still very porous except for the SAL1 sample, which is very dense and as a result of that, has a less thickness of about 4 μm.

Figure 5 shows the data for dye adsorption.

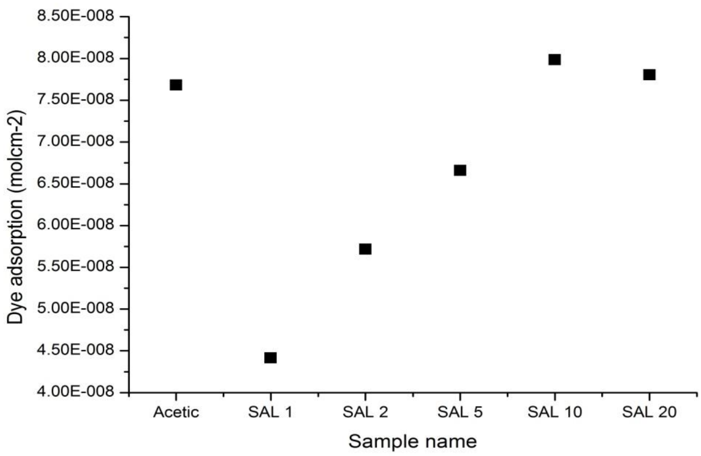

Figure 5. Dye adsorption measurement data

As expected, the adsorbed amount of dye molecules in the TiO_2 films increased with the increase of amount of salicylic acid added. With 0.1M of salicylic acid, the dye adsorption is slightly higher than that of cells made with acetic acid. When the amount of salicylic acid was increased further, the dye adsorption began to drop again because of less number of TiO_2 particles to adsorb on.

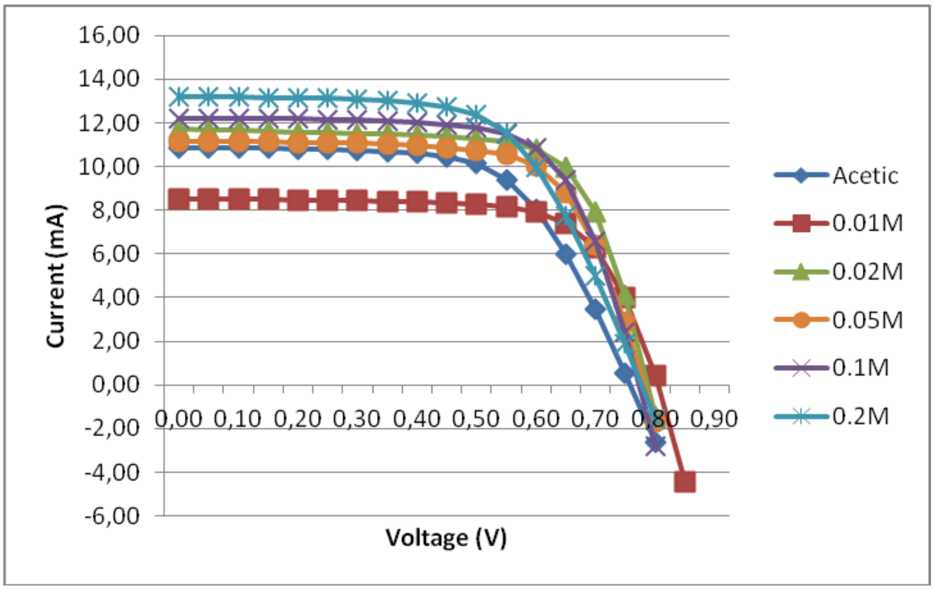

Figure 6. I-V characteristics of the DSCs prepared with Salicylic acid.

Figure 6 shows the I-V characteristics of the samples prepared and table 1 gives the relevant data. It is interesting to notice that all the samples prepared with salicylic acid showed higher V_{OC} than the reference sample made with acetic acid. The sample made with the least amount of salicylic acid showed the highest V_{OC}, but the least short circuit current due to less porous structure comparing with other samples. All other salicylic acid DSC samples showed higher short circuit currents than with acetic acid. Higher the concentration of salicylic acid, higher the short circuit current is. The increase of porosity, resulting in more dye adsorption has caused this enhancement in short circuit current.

Table 1. DSC performances.

	Acetic	0.01M	0.02M	0.05M	0.1M	0.2M
J_{SC} (mA/cm^2)	10.87	8.51	11.73	11.15	12.19	13.18
V_{OC} (V)	0.76	0.80	0.79	0.78	0.77	0.78
FF	0.63	0.70	0.70	0.69	0.69	0.62
EFF (%)	5.17	4.81	6.48	6.02	6.52	6.34
Dye adsorption (molcm^{-2})(x10^{-8})	7.68	4.41	5.71	6.66	7.98	7.80

As witnessed in dye adsorption measurement data, all the salicylic acid DSCs had lower than or almost the same dye adsorption with acetic acid DSC. But, except for the 0.01M salicylic acid DSC, all the others showed better V_{OC}, J_{SC}, fill factors resulting in better efficiencies. That means there should be another factor which enhances the performance even with less amount of dye molecules attached.

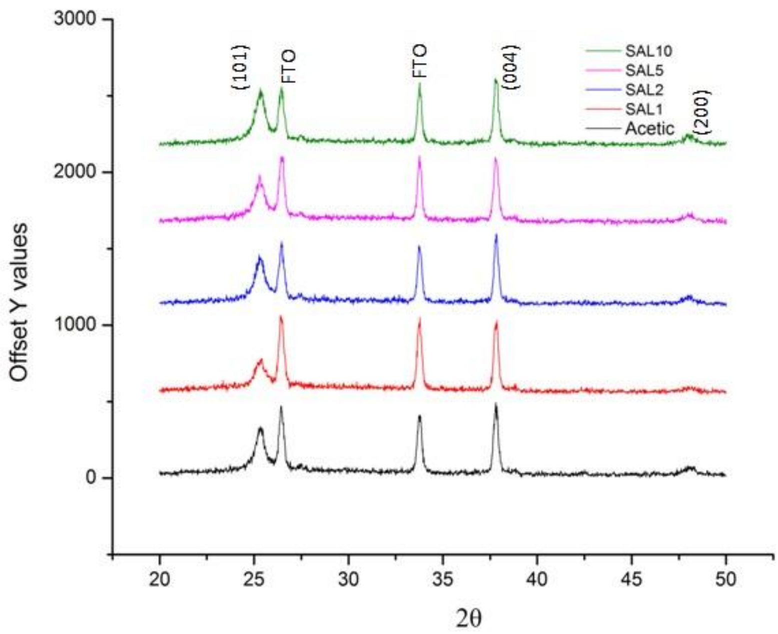

Figure 7. XRD analysis data for the TiO_2 films prepared with salicylic acid

Figure 7 shows the XRD analysis data for the samples prepared with salicylic acid and with acetic acid. It can be seen that the crystal structure of the TiO_2 films obtained is anatase. As predicted, the crystallinity of the TiO_2 film increases with addition of Salicylic acid. Only the SAL1 sample shows a less crystallized structure comparing with the acetic acid TiO_2 film, but, all the others shows better crystallinity comparing with acetic acid sample. Ken-ichi Katsumata et al. suggests that, as the photoexcited electrons are trapped and recombined in defect sites of the TiO_2 film, the crystallinity is one of the most important factors which determines the electron conductivity in the film [14]. That is why the efficiency is low for the SAL1 sample and high for the other samples even with lower dye adsorptions.

The ideal thickness for a TiO_2 film in a DSC is about 15~18 μm. The thickness of the films prepared in this research is around 7μm. Therefore it is suggested that a higher efficiency can be obtained using a thicker TiO_2 film. Ken-ichi Katsumata et al. also suggests that 600 ºC is more suitable for the sintering temperature when TiO_2 films are made of salicilate complexes.

4. CONCLUSION

Salicylic acid was successfully used with TiO_2 to fabricate thin films for DSCs and better conversion efficiencies were obtained comparing with acetic acid. The enhancement of the efficiency was 26%. The optimum concentration of salicylic acid was found to be 0.1M.

References

1. B. O'Regan, M. Gratzel, *Nature*, 353 (1991) 737.

2. M. G. Kang, K. S. Ryu, S. H. Chang, N. G. Park, J. S. Hong, K. Kim, *B. Kor. Chem. Soc.*, 25, 5 (2004) 742.
3. L. Liang, S. Dai, L. Hu, F. Kong, W. Xu, K. Wang, *J. Phys. Chem. B*, 110 (2006) 12404.
4. K. Zhu, N. Kopidakis, N. R. Neale, J. Lagemaat, A. J. Frank, *J. Phys. Chem. B*, 110 (2006) 25174
5. S. Kim, *Appl. Chem*., 12 (2008) 49.
6. H. M. N. Bandara, R. M. G. Rajapakse, K. Murakami, G. R. R. A. Kumara, G. A. Sepalage, *Electrochimi. Acta*, 56, 25 (2011) 9159.
7. A. E. Regazzoni, P. Mandelbaum, M. Matsuyoshi, S. Schiller, S. A. Bilmes, M. A. Blesa, *Langmuir*, 14 (1998) 868.
8. S. Tunesi, M. A. J. Anderson, *Phys. Chem*., 95 (1991) 3399.
9. G. Dagan, M. Tomkiewicz, *J. Phys. Chem*. 97 (1993) 12651.
10. P. Z. Araujo, P. J. Morando, M. A. Blesa, *Langmuir*, 21 (2005) 3470.
11. I. M. Ziegler, F. Billes, *J. Mol. Struc.-Theochem.*, 618 (2002) 259.
12. P. Z. Araujo, C. B. Mendive, L. A. G. Rodenas, P. J. Morando, A. E. Regazzoni, M. A. Blesa, D. Bahnemann, *Colloid. Surface A*, 265 (2005) 73.
13. P. A. Connor, K. D. Dobson, A. J. McQuillan, *Langmuir*, 11, 11 (1995) 4193.
14. K. Kasumata, Y. Ohno, K. Tomita, M. Sakai, A. Nakajima, M. Kakihana, A. Fujishima, N. Matsuhita, K. Okada, *Photochem. Photobiol*, 87 (2011) 988.