Influence of Acetic Acid on the Photovoltaic Performance of Ru(II) Dye Sensitized Nanocrystalline TiO_2 Solar Cells

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Abstract

In the photoelectrode, the important factor to achieve high efficiency of DSSC is weak acid treatment rather than specific regime of heat treatment. Acid treated paste of titanium oxide nano particles enhanced a factor of three higher of the energy conversion efficiency(none (η=2.0%), H_2SO_4(η=1.7%), HCl(η=2.8%), CH_3COOH(η=6.2%) in dye-sensitized solar cells (DSSCs). The effects of the different concentrations were investigated. To anal size the results, the chemical reaction schemes with XPS, scanning electron microscopy, attenuated total reflection Fourier transform infrared spectroscopy, current density-voltage property and power conversion efficiency of the DSSCs were introduced. Acetic acid treatment is advantageous for the adsorption to molecules and enhancement of the photoelectric performance of DSSC.

It was found that DSSC showed better photovoltaic performance when the TiO_2 paste was treated by acids. The acid treatment of TiO_2 electrode provides useful information to understand the mechanism of energy conversion of DSSC.

Introduction

The dye sensitized solar cells (DSSCs) is one of the promising solution to solve the energy problem. In order to improve the photovoltaic performance much efforts have been done, But still, further research is necessary to understand the physics of high energy conversion mechanism clearly and device design with the cost effective materials for commercialization. Titanium dioxide (TiO_2), crystal structures with anatase and rutile type is useful materials; catalytic property, optically transparency(3.2 eV), electron acceptor and/or transport material. The usages are UV protection cosmetics, ecological catalyst, DSSCs and etc. The DSSC working mechanisms have been studied from K. J. Veter in 1952. Swedish Gratzel group has been much contribution in this field introducing porous TiO_2 nano-particles which gives much attachment site of the organic dyes to harvest much of the sun light.[1] The light to electron conversion principles are generally accepted as follows;

$$TiO_2 / dye + hv \Rightarrow TiO_2 / dye \quad (1)$$
$$TiO_2 / Dye \Rightarrow TiO_2 / S^+ + ecb \quad (2)$$
$$TiO_2 / S^+ + ecb \Rightarrow TiO_2 / S \quad (3)$$
$$TiO_2 / S^+ + (3/2)\, I^- \Rightarrow TiO_2 / S + (1/2)\, I_3^- \quad (4)$$
$$(1/2)\, I_3^- + e\,(Pt) \Rightarrow (3/2)\, I^-,\ I_3^- + 2\, ecb \Rightarrow 3\, I^- \quad (5)$$

From these series mechanism, the incident a photon energy (> 387.5 nm) excited one electron in the Highest Occupied Molecular Orbital (HOMO) to the Least Unoccupied Molecular Orbital (LUMO) of the organic dye, and then the separated charge in conduction band of the dye transferred into the chemisorpted taitannia conduction band. The charge diffused to the photoelectrode and moved along with the circuit to the counter electrode. Finally, I^-/I_3^- , the function of redox couples of electrolyte make full cell of photovoltaic circuit. The optimization of device design with new materials and/or architectures have been attempted including electrolyte with redox couple and counter electrode; S. A. Sapp et al reported that cobalt-porpyrine complex ligand introduced as an alternatives of the I^-/I_3^- couple[2]. X. Bofei et al achieved 4% of conversion efficiency using composite electrolyte containing $LiI(Ch_3Oh)_4$-I_2, SiO_2 particle and ionic liquid, triethylamine hydrothiocyanate[3].

The role of photoelectrode is the most important factor to get high efficiency in DSSCs because of the first step of light to electron harvest. So, lots of efforts have been reported to enhance the dispersion and adhesion relating to porosity, dispersion and modification between FTO and TiO_2 particles as a photoelectrode. For example, HNO_3 has been introduced to modify the powder surface of TiO_2. Not yet systematic researches and the novel fabrication method of photoelectrode were reported[4-6].To achieve the unique thickness of nanoporous photoelectrode, the fabrication technique of TiO_2 paste need the well dispersion property without coagulation among TiO_2 powders.

In this paper, our group investigated the influence of acetic acid treatment of photoelectrode with acids (none, H_2SO_4, HCl, CH_3COOH) and various concentrations of the acetic acid (0 ~ 1M) of the photovoltaic performance of DSSC. And suggested the scheme of chemical reaction between acid and TiO_2, as well as verified with XPS, scanning electron microscopy, attenuated total reflection Fourier transform infrared spectroscopy, current density-voltage property and power conversion efficiency of the DSSCs; acid treated TiO_2 photoelectrode/electrolyte with I^-/I_3^-/Pt doped FTO electrode.

Results and discussion

The key point of acid treatment of TiO_2 nano particles was to prevent from coargulating of nano particles and disperse into the paste solution well. In addition to, the good quality of the TiO_2 coating layer make lots of the chemisorptions' site for the dyes.

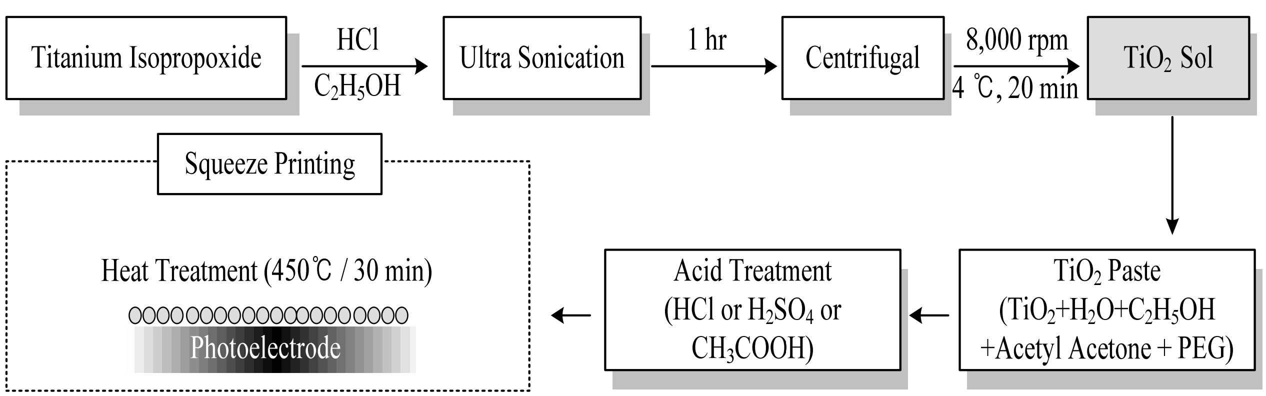

FIG. 1 Flow chart of TiO2 sol synthesis and photoelectrode fabrication process

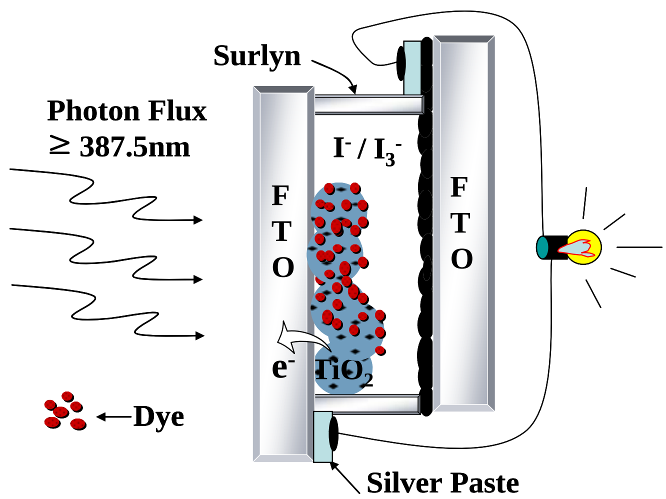

FIG. 2 The device structure of dye sensitized solar cell which is consisted with the photoelectrode, organic dye, electrolyte containing with redox couple and counter electrode.

Eventually, the results showed the enhanced energy conversion efficiency with the reduction of resistance at the interfaces between FTO substrate and TiO_2 nano particles. The proposed reaction mechanism was shown in Fig. 1.

The photocurrent density and potential properties of DSSCs with the 0.5M of acid (CH_3COOH, HCl, H_2SO_4 and none)treated full cell shown in Fig. 2.

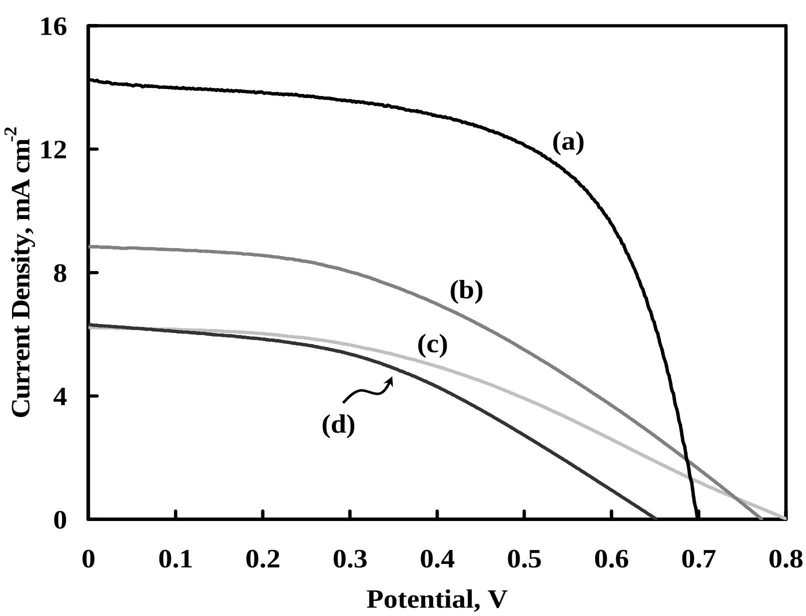

FIG. 3 Photocurrent-photovoltaic (J–V) characteristics of acid treated TiO_2 nano particles of DSSCs (a) CH_3COOH, (b) HCl (c) None acid and (d) H_2SO_4

In Fig. 3, acid treated cells were enhanced of the current density in comparison with normal cell. In case of HCl and CH_3COOH treated cells showed higher current density, 8.8 mA/cm^2 and 14.3 mA/cm^2, and reduced open circuit voltage 0.75V and 0.7V, respectively. CH_3COOH treated cell showed over 300% of conversion efficiency (η 6.2) with the 14.3 mA/cm^2 of short circuit current, 0.7V of open circuit voltage and 0.62 of fill factor in comparison with typical one (none acid; Isc 6.2 mA/cm^2, Voc 0.81V, ff 0.4 and η 2.0%). These phenomena could be conferring that the acid contributed regular arrangement of the photoelectrode by the dispersion of TiO_2 nano particles. This dispersion is one of the factors to make much chemisorption site for the organic dyes.

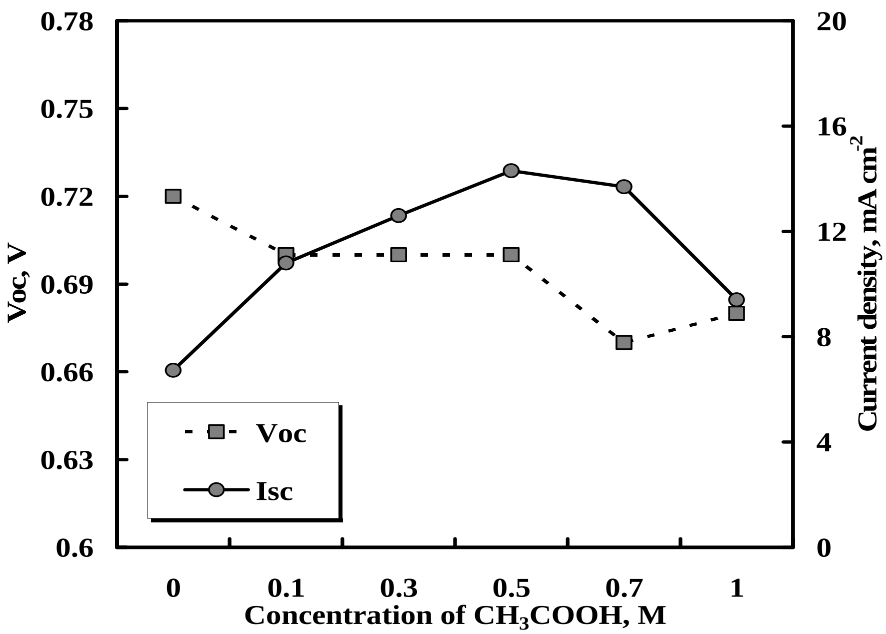

FIG. 4 Current density with the concentration of CH_3COOH (a) open circuit voltage is square symbol, (b) short circuit current is circle symbol

The results of photovoltaic effects with the CH_3COOH treated DSSCs was best among HCl, H_2SO_4 and CH_3COOH. Both the Acetic acid and the hydrochloric acid treated devices showed relatively high conversation efficiency, for the wide application, more safe and easy handle of weak acid is useful. So, CH_3COOH was proper for the purpose of finding out optimal concentration of the acid. The concentration of the acetic acid were varied from 0 to 1M .

The photocurrent-concentration properties were increased till 0.5M(none : 6.3mA/cm^2, 0.1M: 11 mA/cm^2, 0.3M: 13mA/cm^2 and 0.5M: 14.2 mA/cm^2) then, decreased (0.7M: 13.9mA/cm^2 and 1M: 9.8 mA/cm^2) which is shown in Fig 4.

The maximum energy conversion efficiency was achieved at the 0.5M concentration of the acetic acid. The tendency of the current density was increased with the acid concentration. But, the excess acid make over dispersion of TiO_2 nano particles that led to quite well stacking onto the FTO surface and finally well stacked TiO_2 layer make an obstacles to attach of organic dyes, as well as come to a difficult end to pass by redox couples and/or electrolyte, finally, poor efficiency of the devices were achieved from the lack of electron excitation sites. To analysis of the morphology of the samples which examimned using field emission scanning electron microscope (FE-SEM). Figure 5 is the FE-SEM photos of vertical cut of photoelectrode before and after acid treatment.

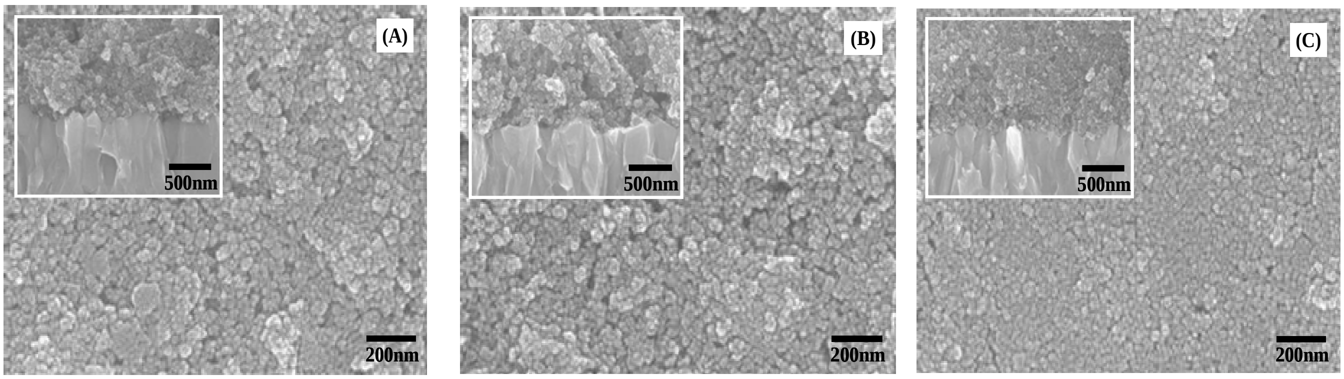

FIG. 5 FE-SEM images of the vertical cut of photoelectrodes with the concentration of acetic acid treated TiO_2 (inlet) and photoelectrode surface images

Fig. 5 (a) and (b) are surface images of the TiO_2 layer before acid treatment, and interface of TiO_2 and FTO is inset. The morphology of no acid treated surface is looks like similar that of Fig. 5 (b) but, Fig. 5 (b) is well developed pore site. Fig. 5 (b) and (c) are 0.5M and 1M concentration of the acid treated surface and interfaces, respectively. In these images, 0.5M concentration has well dispersed with the unit of TiO_2 nano cluster and proper chemisorption sites were achieved among three of samples

With the 1M concentration of the acid treated sample showed the surface with dense unite of particles, therefore, there is less chemisortion sites and difficult to contact inner particle sites. This means the number of chemisorped organic dyes is limited.

0.5M of concentration of the acid treated image shows development of the pores between TiO_2 particles from the surface of the electrode to bottom of the TiO_2 layer. without acid treatment or with excess acid treatment donot well developed the pores site onto the TiO_2 particles.

To enhance the current density in DSSCs first, well development of nano pores between TiO_2 particles for much of the chemisorption of the organic dyes, second, the adhesive property between TiO_2 and FTO substrate to reduce the resistance and get good fill factor and conversion efficiency.

Table 1 The photovoltaic characteristics of the dye sensitized solar cell which was consisted with the Acid (H_2SO_4, HCl, CH_3COOH and none) treated photoelectrode

	Normal Device	**H_2SO_4**	**HCl**	**CH_3COOH**
I_{SC} (mA/cm^2)	6.2	6.3	8.8	14.3
V_{OC} (V)	0.81	0.65	0.75	0.7
FF (%)	40	42	41	62
η (%)	2.0	1.7	2.8	6.2

Conclusion

Maximum efficiency conditions related with the adhesive properties and conversion efficiency were achieved by the variation of the acid and concentrations. In comparison with none acid treated DSSC, the enhancement of conversion efficiency and fill factor were 310% and 230%, respectively. The chemical reaction of the acid and TiO_2 were proposed. An observed, acid introduced into TiO_2 paste, the dispersity of the TiO_2 enhanced to make pore site between TIO_2 particles and well stacked TiO_2 layer one by one. Optimal concentration, 0.5M of acetic acid treated paste enhance the current density and photon to electron conversion efficiency in DSSCs. Acid treated DSSCs were increased current density and fill factor, but open circuit voltage were slightly reduced. In the photoelectrode, the important factor to achieve high efficiency of DSSC is weak acid treatment rather than specific regime of heat treatment. The acid treatment of TiO_2 electrode provides useful information to understand the mechanism of energy conversion of DSSC.

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