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## Effect of large TiO<sub>2</sub> Nanoparticles as Light Scatter in Matrix of Small Nanoparticles to Improve the Efficiency in Dye-Sensitized Solar Cell

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#### 1. Introduction

 $TiO_2$  has been particularly studied for its usefulness as a catalyst [1, 2], as a ceramic microporous membrane [3, 4], as a chemical sensor

#### Abstract

In this study, we investigated the effect of using large  $TiO_2$  nanoparticles in the matrix of small nanoparticles to improve the performance of dye-sensitized solar cells (DSSCs), as light scatter to increase the light harvesting. The mixed powder was deposited by electrophoretic deposition (EPD) on FTO (F-SnO<sub>2</sub> coated glass). It is shown that adding small quantity of larger nanoparticles can enhance the performance of DSSCs. This paper also studies the deferential scanning calorimetry (DSC) of mixed powders to detect the phase transitions, due to the change of weight percentage between large and small nanoparticles.

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for humidity [5-8], as a photocatalytic component [9–11]. It also well known for its remarkable applies in dye-sensitized solar cell (DSSCs) systems [12-14]. Dye-sensitized solar cells based on nanocrystalline mesoporous  $TiO_2$  films have attracted much attention as a potential low-cost

alternative for single-or polycrystalline p-n junction silicon solar cells. Since Grätzel dyesensitized solar cell in 1991 [12], much research has been carried out to the development of DSSCs structures for better efficiency [15-20]. Due to the dye loaded on the surface of oxide and the presence of redox electrolyte in the porous network of oxide layer, the mesoporous oxide layer (typically TiO<sub>2</sub>) is one of the most important parts of the DSSCs structure. Therefore, improvements in the structure of the oxide can enhance the DSSCs efficiency via increase of the electron diffusion, the dye loading on the oxide and decrease the recombination reactions [21-23]. One approach is to improve the light harvesting of the DSSC, for example, by altering the sensitizers or adding scattering layers [24]. The  $TiO_2$  nanoparticles that used in working electrode of DSSCs are very weak scatterers of visible light, resulting in a significant portion of the light shone on the DSSCs transmitting through the TiO<sub>2</sub> film without interacting with the sensitizer. Scattering layers of various structure, including scattering centers and upper scattering layers, have been effectively employed to enhance light harvesting and thus to improve the efficiency of the solar cell [25–29]. According to the Mie theory [30] the particles used for light scattering should have a large size. The results from computer simulation showed the use of larger TiO<sub>2</sub> particles as a scattering center mixed in a TiO<sub>2</sub> matrix containing 20-50 nm particles cause increase of DSSCs efficiency. Therefore, it can increase the light harvesting in the sensitized TiO<sub>2</sub> layer and overall increase the DSSCs efficiency [25].

In the present study, we have investigated the effect of using larger  $TiO_2$  nanoparticles as scattering center in the sensitized  $TiO_2$  layers that prepared by small nanoparticles. The mixed powders have different ratio of small and large  $TiO_2$  nanoparticles. The  $TiO_2$  layers have been deposited by electrophoretic deposition on FTO glasses. We have also studied the phase transition of mixed powder due to the different ratio of  $TiO_2$  structures (rutile and anatase). Finally, the performance of prepared layers has been tested in the dye-sensitized solar cell system.

### 2 Experimental

The TiO<sub>2</sub> nanoparticles (P-25 from Degussa, Germany) nm and (Fluka, Switzerland) with diameter around 50 and 250 nm, respectively, were used to prepared mixture powder. Also, absolute ethanol >99.9%, acetylaceton >99.0%, iodine >99.8 (Merck, Germany), acetone >99.0% (Fluka, Switzerland) and deionized water (produced by SG instrument, Germany) were used to prepare the electrophoretic suspension according to Zaban et al reported [31]. The  $I/I_3$  electrolyte consisted of mixture of 0.05M Iodine, 0.5M lithium iodide >98.0% (Merck, Germany), 0.5M 4-tertbutylpyridine (Sigma-Aldrich, USA) in the acetonitrile (Fluka, switzerland).

The mixture powders were prepared by mixing 2, 5, 7 and 10 ratio of weight percentage of Fluka to P-25 TiO<sub>2</sub> nanoparticles.

The EPD was performed at constant potential (10V) for 20 seconds on the FTO glasses substrate

(Dyesol,  $15\Omega$ /square, Australia). Finally, the prepared micrometer TiO<sub>2</sub> layers were sintered at 500°C for 30 min.

These photo electrodes were immersed in a 0.3 mM N719 dye (RuC<sub>58</sub>H<sub>86</sub>N<sub>8</sub>O<sub>8</sub>S<sub>2</sub>, Dyesol, Australia) in solution tert-butyl alchol (Fluka, Switzerland)/ acetonitrile (50:50 volume ratio) for 24 hours at room temperature. Then, the electrodes were taken out of the dye solution and rinsed in acetonitrile to make a monolayer of the dye molecules on the surface of TiO<sub>2</sub> nanoparticles.

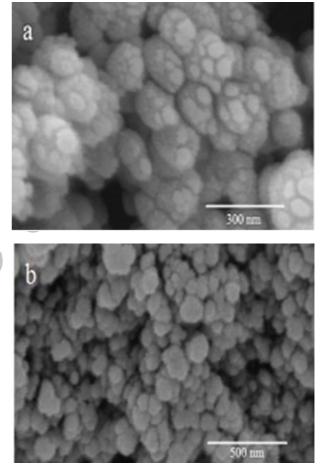
As counter electrode, a platinum electrode was used which had been prepared by chemical deposition of hexachloro-platinic (IV) acid (Riedel-de Haen, Germany) in ethanol solution at 350°C.

A sandwich solar cell was assembled using dyesensitized electrode as the working electrode and a platinum electrode as the counter electrode. The 30  $\mu$ m-thick thermoplastic film was used to separate the electrodes and sealed by heating. The  $\Gamma/\Gamma_3$ electrolyte was injected in the gap between the electrodes through the injecting hole that was previously made in counter electrode.

The TiO<sub>2</sub> nanoparticles were characterized by scanning electron microscopy (SEM, Hitachi S-4160). The phase transitions of prepared powder were measurement by deferential scanning calorimetry (DSC) (NETZSCH DSC 204 F1 Phoenix). The DSSCs performance was estimated under AM 1.5 simulated light (Luzchem) using potantiostat/galvanostat (PGSTAT 100, Autolab, Eco-Chemie).

#### 3. Results and discussion

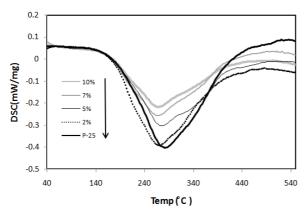
Figure 1 shows the morphological images of  $TiO_2$  nanoparticles which were used to prepared mixture powders with different ratio. As it shown, the surface of Fluka nanoparticles (fig. 1a) is roughish and it can slightly compensate the decrease of dye loading on the surface due to the nanoparticles size increasing.



**Fig. 1.** The SEM images of a) Fluka nanoparticles, b) P-25 nanoparticles

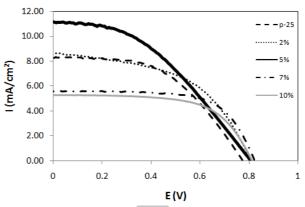
Fig. 2. shows the deferential scanning calorimetry (DSC) results of mixture powders with different ratio of precursor  $TiO_2$  powders. Sience, the pure P-25 powder consist of rutile and anatase structure with 20 and 80 percentage, respectively, adding Fluka powder (just anatase structure) have

been effected on phase transitions. Due to, anatase and rutile structures are metastable and stable, respectively, the peak of DSC curves was shifted to lower temperature and the peak area was decreased with relation to increase of percentage of Fluka powder in the mixed powder.



**Fig 2.** The DSC carves of mixed powder with different weight percentage of large nanoparticles (Fluka particles) comparing to pure P-25

The I-V curves of prepared cells with different amount of mixture between P-25 and Fluka comparing to pure P-25 are shown in the figure 3 and the photovoltaic characteristics are from the carves summarized in Table 1. The results shows that the change of quantity ratio of precursor powders effects on performance of DSSCs fabricated from them. The The short-circuit current density( Jsc) of the sensitized layer was increased with relation to increase of amount of Fluka powder up to 5%, due to increase of light harvesting in the prepared layer by scattering the absorbed light. Since, the dye loading on TiO<sub>2</sub> particles is decreased with relation to decrease of surface, the increase of percentage of Fluka powder more than 5% cause decrease of dye loading and overall decrease of efficiency.



**Fig. 3.** The I-V characteristic carves of DSSCs with different weight percentage of large nanoparticles (Fluka particles) comparing to pure P-25

**Table 1.** The summarize performance of DSSCs withdifferent percentages of large nanoparticles (Flukaparticles).

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sample	I <sub>sc</sub>	V <sub>oc</sub>	Efficiency	FF
	(mA)	(V)	(η)	
p-25	8.34	0.79	3.26	0.48
2 %	8.26	0.80	3.33	0.49
5 %	11.1	0.80	3.70	0.41
7 %	5.62	0.81	3.05	0.67
10 %	5.27	0.80	2.69	0.63

#### 4. Conclusion

We investigated the effect of using larger nanoparticles of  $TiO_2$  in the matrix of small nanoparticles of  $TiO_2$  to increase the scattering and harvesting of light in the  $TiO_2$  layer. The layer with up to 5%wt of large nanoparticles that was used to fabricate DSSCs showed the best efficiency of DSSCs performance.

#### References

[1] X. Z. Li, H. Liu, L. F. Cheng, H. J. Tong, Environ Sci Technol, 17 (2003) 3989.

- [2] S.J. Bu, Z.G. Jin, X.X. Liu, L.R. Yang, Z.J. Cheng, J. Eur. Ceram. Soc. 25 (2005) 673.
- [3] M. Wark, J. Tschirch, O. Bartels, D. Bahnemann, J. Rathousky', Microporous

Mesoporous Mater. 84 (2005) 247.

- [4] M. Nag, P. Basak, S.V. Manorama, Mater. Res. Bull. 42 (2007) 1691.
- [5] T. Van Gestel, C. Vandecasteele, A. Buekenhoudt, C. Dotremont, J. Luyten, R.
- Leysen, B. Van der Bruggen, G. Maes, J. Membr. Sci. 209 (2002) 379.
- [6] U. Aust, S. Benfer, M. Dietze, A. Rost, G. Tomandl, J. Membr. Sci. 281 (2006) 463.
- [7] K. M. Lee, V. Suryanarayanan, K.-C. Ho, Sol. Energy Mater. Sol. Cells 91 (2007)

1416.

- [8] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartulli, J.S. Beck, Nature 359 (1992) 710.
- [9] L.Y. Zheng, M.X. Xu, T.X. Xu, Sens. Actuator B 66 (2000) 28.
- [10] H. Tai, Y. Jiang, G. Xie, J. Yu, X. Chen, Sens. Actuator B: Chem. 125 (2007) 644.
- [11] A.K. Alves, F.A. Berutti, F.J. Clemens, T. Graule, C.P. Bergmann, Materials Research Bulletin 44 (2009) 312.
- [12] B. O'Regan, M. Grätzel, Nature. 353 (1991) 737.
- [13] P. Ball, Nature 377 (1995) 290.
- [14] Z. Ma, S. Brown, S.H. Overbury, S. Dai, Appl. Catal. A: Gen. 327 (2007) 226.
- [15] Chang H, Chen T L, Huang K D, Chien S H and Hung K C, Journal of Alloys and Compounds. 504S (2010) S435.
- [16] Tirosh S, Dittrich T, Ofir A, Grinis L and Zaban A,J. Phys. Chem. B 110 (2006) 16165.
- [17] H.J. Snaith, Adv. Funct. Mater. 20 (2010) 13.
- [18] Kroon J M, Bakker N J, Smit H J P, Liska P, Thampi K R, Wang P, Zakeeruddin S M, Gratzel

M, Hinsch A, Hore S, Wurfel U, Sastrawan R, Durrant J R, Palomares E, Pettersson H, Gruszecki T, Walter J, Skupien K and Tulloch G E, Prog. Photovolt: Res. Appl. 15 (2007) 1.

- [19] Hagfeldt A, Boschloo G, Sun L, Kloo L and Pettersson H, Chem. Rev. 110 (2010) 6595.
- [20] Wang Q, Moser J E and Gratzel M, J. Phys. Chem.B. 109 (2005) 14945.
- [21] H. J. Koo, J. Park, B. Yoo, K. Yoo, K. Kim, N. G. Park, Inorganica Chimica Acta 361 (2008) 677.
- [22] K. Zhu, N. Kopidakis, N. R. Neale, J. van de Lagemaat, A. J. Frank, J. Phys. Chem. B 110 (2006) 25174.
- [23] T. H. Meen, W. Water, W. R. Chen, S. M. Chao, L.W. Ji, C. J. Huang, Journal of Physics and Chemistry of Solids 70 (2009) 472.
- [24] F. Huang, D. Chen, X. Li. Zhang, R. A. Caruso, Y.B. Cheng, Adv. Funct. Mater. 20 (2010) 1301.
- [25] J. Ferber, J. Luther, Sol. Energy Mater. Sol. Cells, 54 (1998) 265.
- [26] Z.-S. Wang, H. Kawauchi, T. Kashima, H. Arakawa, Coord. Chem. Rev. 248 (2004) 1381.
- [27] S. Hore, P. Nitz, C. Vetter, C. Prahl, M. Niggemann, R. Kern, Chem.Commun. 15 (2005) 2011.
- [28] J.-H. Yoon, S.-R. Jang, R. Vittal, J. Lee, K.-J. Kim, J. Photochem. Photobiol. A: Chem. 180 (2006) 184.
- [29] S. Hore, C. Vetter, R. Kern, H. Smit, A. Hinsch, Sol. Energy Mater. Sol. Cells, 90 (2006) 1176.
- [30] H. C. van de Hulst, Light Scattering by Small Particles, Wiley, New York 1957.
- [31] L. Grinis, S. Dor, A. Ofir, A. Zaban, Journal of Photochemistry and Photobiology A: Chemistry 198 (2008) 52.