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RESEARCH ARTICLE

Preparation and Characterisation of Tailored TiO₂ nanoparticles Photoanode for Dye Sensitised Solar Cells

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ABSTRACT: Pure and Al-doped anatase TiO₂ nanoparticles are prepared by an acid tailored sol-gel method and successfully used as a photoanode for dye-sensitized solar cells (DSSCs). The samples were characterized by using powder XRD, FE-SEM with EDX, UV-DRS, and Current-Voltage curve. After Al doping, the conductivity of the TiO₂ increases and it has a positive shift. The energy-conversion efficiency of a cell based on 0.05 mol% Al-doped TiO₂ is significantly better, by about 4.6%, compared to that of a cell based on undoped TiO₂. The synthesized Al-doped TiO₂ material is proven in detail to be a better photoanode material than pure TiO₂ nanoparticles with a simple and versatile way to prepare excellent photoanode materials.

Keywords: Sol-gel, N719 dye, DSSC, Modified Photoanode

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INTRODUCTION

Dye-sensitized solar cells (DSSCs) have attracted much attention because of their low cost, possible fabrications of flexible devices, and relatively efficient devices for the photovoltaic conversion of solar energy [1]. DSSCs containing titanium oxide (TiO₂) thin film electrode often use ruthenium dyes, such as N719 dye [cis-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium (II) bis-tetrabutylammonium], as photosensitizer. Such N719 based DSSCs exhibit relatively high photovoltaic performance and good stability [2]. In order to develop DSSCs with excellent photovoltaic properties, researchers have tried to control the nanostructure and morphology of TiO₂ photo-electrodes [3-6]. Moreover, enhanced dye-sensitized solar cell efficiency would provide enormous economic advantages [7-11]. Recently, nano-sized TiO₂ powders have been used as a working electrode for dye-sensitized solar cells (DSSC) due to higher efficiency than any other metal oxide semiconductor [12].

Kyung Hyun Ko et al. [13] reported Al and Al-W doped TiO₂ nanoparticles for the fabrication of DSSC. Jin Young Kim

[14] reported the photovoltaic performance of various oxide materials shows the electrical charge transfer could be disrupted within the thick dye layers. However in this study, doping elements were designed to substitute the lattice Ti element, not to form a passive layer. Rather, fabricating a cell using combined surface area and charge-transfer enhancement by doping would be a more promising solution. We investigate nano-sized TiO₂ doping to enhance photovoltaic efficiency.

EXPERIMENTAL

Materials

Chemical reagents including titanium isopropoxide, ethanol anhydrous (Sigma -Aldrich), Aluminium nitrate (Loba Chemie) Triton X-100 (Sigma -Aldrich), acetyl acetone (Sigma -Aldrich) polyethylene glycol 600(Merck) and the organic solvent were used as such without further purification. FTO (Flurine doped SnO₂, 10 Ω/sq, Spektron) coated glass substrates were cleaned in isopropyl alcohol, acetone and DI water sequentially by ultrasonic treatment for 20 min each before using. The sensitized dye N-719 [RuL₂(NCS)₂, L = 4,4'-dicarboxylate-2,2'-bipyridine], Plasi-tol and Idolyte TG 50 was from Solaronix SA (Aubonne, Switzerland).

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Preparation of modified TiO₂ powder

The nano -TiO₂ powder was prepared with titanium isopropoxide solution as the raw material. In a typical experiment, (0.01, 0.03, 0.05 mol%) Aluminium nitrate were dissolved in 60 mL of deionized water at room temperature, followed by adding 5 mL of glacial acetic acid to obtain solution A. 14 mL titanium isopropoxide was dissolved in 40 mL of anhydrous ethanol with constant stirring to form solution B. Then, the solution B was added drop-wise into the solution A within 60 min under vigorous stirring. Subsequently, the obtained sol was stirred continuously for 2 h and aged for 48 h at room temperature. As-prepared TiO₂ gels were dried for 10h at 80 °C. The obtained solids were ground and finally calcinated at 450 °C for 2 h (heating rate = 3 °C/min).

Preparation of DSSC

Fluorine doped tin oxide, (FTO, Spektron) was washed with 2-propanol, ethanol, and distilled water several times to remove impurities and then dried. A dye-sensitized solar cell (effective area is 1cm X 1cm) was fabricated according to the following process. TiO₂ paste was prepared with certain proportions of nano- TiO₂ powder with distilled water, acetylacetone (A.R), polyethylene glycol and triton(X-100) in agate mortar [15]. The photo anode was obtained using doctor blade method on the conductive glass and then sintered at 450 °C for 30 min in air. After being cooled, the TiO₂ electrode was immersed into 0.5 mM N719 ethanol solutions for 24 hours at room temperature [16]. Sensitized TiO₂ photo-anode and the Pt coated counter electrode were assembled and the liquid electrolyte solution drop penetrates into the working space and counter electrode via capillary action. The two electrodes were held with a binder clip [17].

Photocurrent -voltage behaviours of the DSSCs

The photocurrent-voltage behaviour of the DSSC with different aluminium doping are characterized by the open-circuit voltage (*V_{oc}*) and the short-circuit current (*I_{sc}*) of each sample measured at *I*=0 mA and *V*=0 V. The maximum voltage (*V_{max}*) and the maximum current (*I_{max}*) were calculated at the maximum power value based on the following equation [18-20].

$$P = I \times V \tag{1}$$

Furthermore, the fill factor (FF) and efficiency (η) are given by the following:

$$FF = \frac{V_{max} \times I_{max}}{V_{oc} \times I_{sc}} \tag{2}$$

$$\eta(\%) = \frac{V_{oc} \times I_{sc} \times FF}{P_{in}} \times 100 \tag{3}$$

RESULTS AND DISCUSSION

Crystal structure and morphology analysis

Fig. 1 shows the XRD patterns of the sample annealed in air at 450 °C. TiO₂ can be assigned to anatase crystal phase according to the standard XRD patterns (JCPDS Patterns No.

21-1272). A clear peak broadening in Al -doped TiO₂, versus that for pure TiO₂, suggested that the Al -doped TiO₂ has a smaller average size than the pure TiO₂. The average grain size was calculated from the (1 0 1) peak of anatase using Scherrer's equation, $d = k\lambda/\beta \cos \theta$, where *k* is the constant (shape factor about 0.9), λ the X-ray wavelength, β the full width at half maximum (FWHM) of the diffraction line, and θ is the diffraction angle. In this case, the average crystallite size of pure,0.01-Al ,0.03-Al and 0.05 Al mol% were 8.62 nm, 8.35 nm, 8.22 nm and 7.75 nm, respectively.

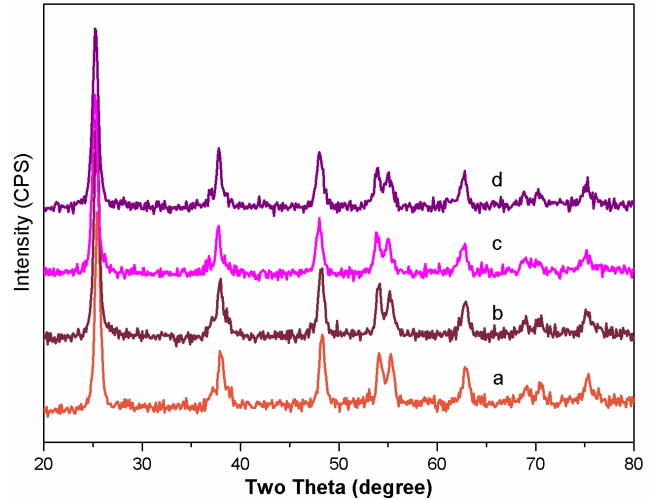


Figure 1. X-ray diffraction patterns of the sample: pure TiO₂ and different Al (0.01, 0.03 and 0.05 mol%) -doped TiO₂.

Figure 2 shows the FE-SEM micrographs of the pure and Al doped TiO₂ nanoparticles. It has been observed that the samples were almost spherical particles for pure TiO₂ nanoparticles whereas for aluminium doped TiO₂, spherical particles with high porous nature were observed which enhancing the photovoltaic performance. Table 1 shows doping ratio results measured by EDX. Aluminium could be doped into TiO₂ lattice successfully by chemical reaction during synthesis. It was found that the doping element did not affect crystalline transformation but it was expected that doping elements would have an affect only on the dye sensitized solar cell photovoltaic properties.

Table 1: The content of synthesized TiO₂ nano-powders

Sample	Element	Weight (%)	Atomic (%)
Pure - TiO ₂	O	30.1	56.32
	Ti	69.9	43.68
Al-TiO ₂ (0.01 mol%)	O	50.18	75.03
	Al	0.22	0.2
Al-TiO ₂ (0.03 mol%)	O	22.43	46.35
	Ti	77.39	53.43
Al-TiO ₂ (0.05 mol%)	O	38.99	65.55
	Al	0.43	0.43
	Ti	60.58	34.02

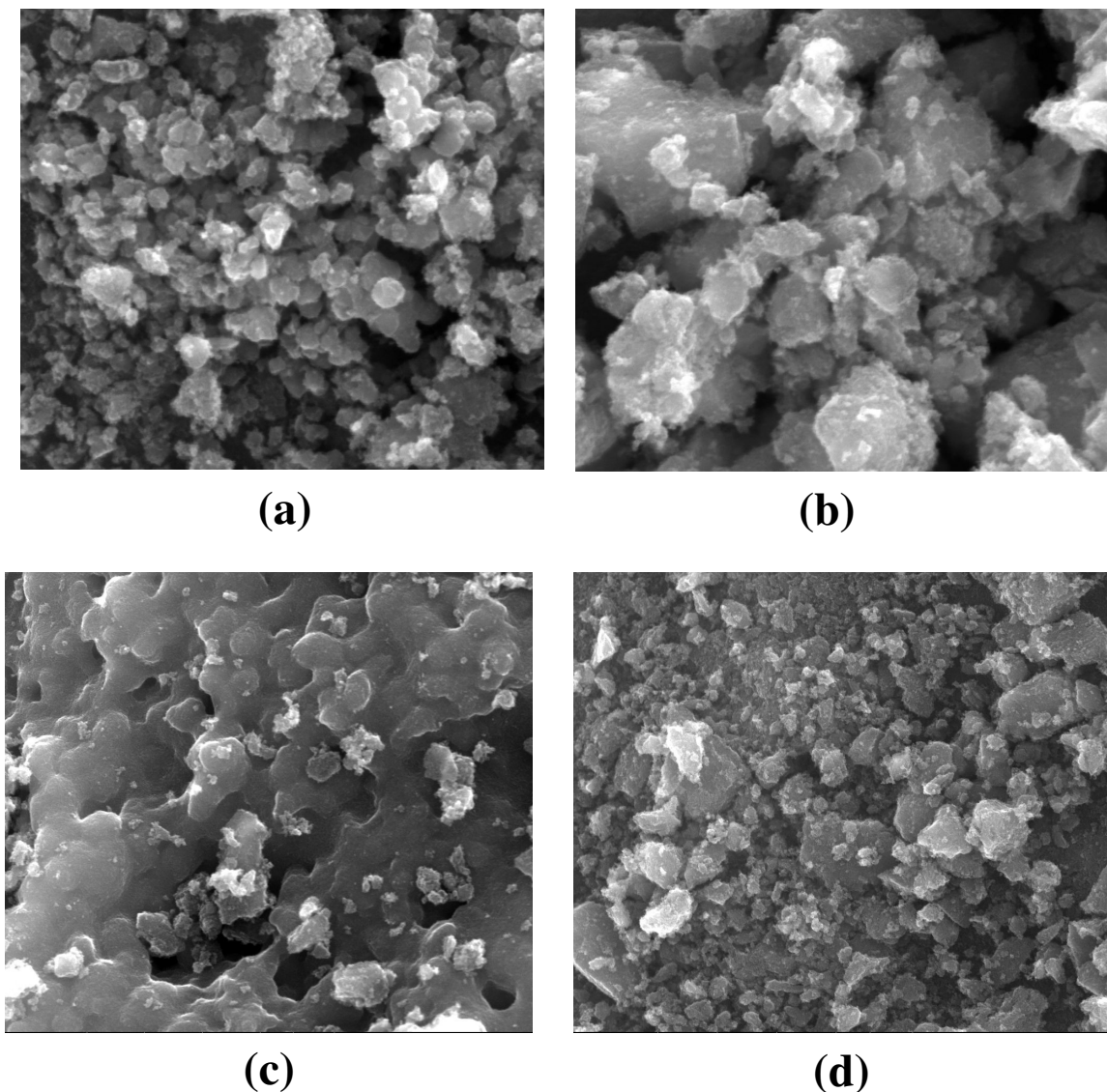


Figure 2. FE-SEM micrographs of TiO₂ - (a) Pure (b) Al-TiO₂(0.01 mol%) (c) Al-TiO₂ (0.03 mol%) (d) Al -TiO₂ (0.05 mol) (— 3μm)

UV-vis spectra analysis

The UV-visible spectra of the Al-TiO₂ nanopowders were obtained to determine the relationship between the solar energy conversion efficiency and spectroscopic property, as shown in Fig.3. It was evident that the absorption of the doped TiO₂ nanoparticle exhibited the largest red shift. The edge of the absorption was extended towards 477 nm. According to the formula $\lambda = 1240/E_g$, the band gap energies of pure TiO₂ and Al - TiO₂ was 3.2 and 2.59 eV respectively. This phenomenon can be ascribed to the quantum size effect, because the addition of Al has significantly decreased the crystal size of TiO₂.

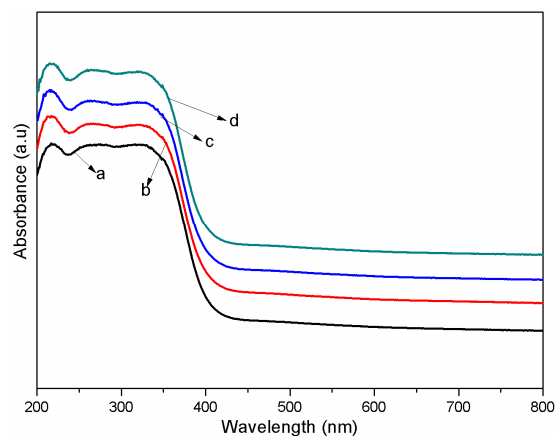


Figure 3. UV-visible spectra of (a) Pure (b) Al-TiO₂(0.01 mol%) (c) Al-TiO₂ (0.03 mol%) (d) Al -TiO₂ (0.05 mol%)

Photovoltaic properties of dye-sensitized solar cells

Fig.4 shows the photovoltaic properties of DSSCs based on different Al-TiO₂ nanopowders as a working electrode. Table 2 summarizes the photovoltaic parameters of N719 dye with pure has 2.33 % and for Al (0.05 mol%) has 5.00% and this is mainly due to the lower energy gap after Al doping. From the I-V characteristics it is noticed that the photoelectric properties were improved using porous TiO₂ nanopowders, which could increase the short circuit current and the open circuit voltage. This is because of the molecular structure and the diffusion rate of redox electrolyte.

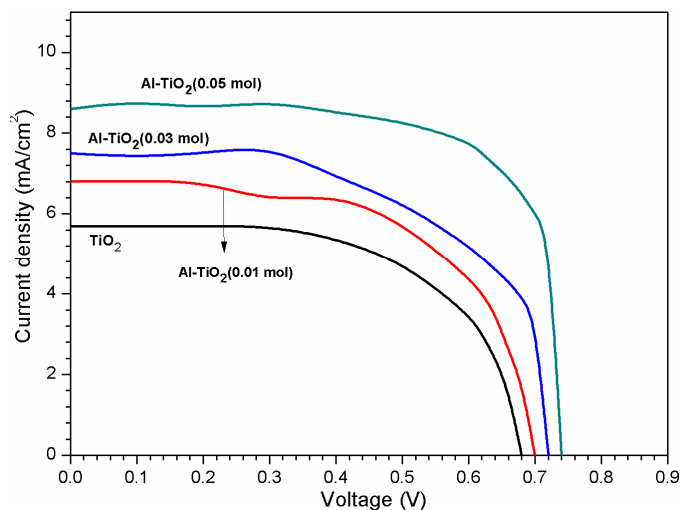


Figure 4. Photovoltaic properties of DSSCs for pure and different Al-TiO₂ nano-powders

Furthermore, the structure is favourable for the separation of electron/hole pairs and the transport of electrons. In addition doping with Al has a good influence on the energy band structure of nano- TiO₂ powders and it is beneficial to the separation and transition of electrons which increases the photoelectrical conversion.

Table 2. The V_{oc} , J_{sc} , FF and η of Dye solar cells

Solar cells	V_{oc} (V)	J_{sc} (mA/cm ²)	Fill Factor (FF)	Efficiency (η in %)
Pure TiO ₂	0.68	5.71	0.601	2.33
Al-TiO ₂ (0.01 mol%)	0.7	6.81	0.503	2.4
Al-TiO ₂ (0.03 mol%)	0.72	7.5	0.54	3.31
Al-TiO ₂ (0.05 mol%)	0.74	8.6	0.786	5

CONCLUSION

Al doped TiO₂ nanopowders were prepared by using an acid tailored sol-gel method to enhance the solar energy conversion efficiency. The XRD analysis shows that the crystalline size of prepared sample is purely in anatase form and from UV analysis the Al doping can narrow the band gap of TiO₂. The 0.05 mol% Al- TiO₂ showed excellent solar

energy conversion efficiency compared to that of pure TiO₂. In 100 mW/cm² simulated sunlight, the performance of the 0.05 mol% Al- TiO₂ was as follows: V_{oc} = 0.74 V, J_{sc} = 8.60 mA/cm², fill factor = 0.786 and energy conversion efficiency (η) is 5.00%. This is probably due to the availability of higher absorption sites, red shift, decreased crystalline size and prevention of electron-hole recombination.

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REFERENCES

- Rong-Ho Lee., Yu-Wei Huang., 2009. Synthesis and Electroluminescence Properties of Novel Hyper-branched Light Emitting Polymers. *Thin Solid Films*, 517, 5903-5908.
- Nazeeruddin, Md,K., Humphry-Baker, R., Liska, P., Gratzel, M., 2003. Investigation of Sensitizer Adsorption and the Influence of Protons on Current and Voltage of a Dye-Sensitized Nanocrystalline TiO₂ Solar Cell. *J. Phys. Chem., B* 107, 8981-8991.
- Uchida, S., Chiba, R., Tomiha, M., Masaki, N., Shirai, M., 2002. Application of Titania Nanotubes to a Dye-sensitized Solar Cell, *Electrochemistry*, 70, 418-420.
- Adachi, M., Murata, Y., Takao, J., Liu, J., Sakamoto, M., Wang, F., 2004. Highly efficient dye-sensitized solar cells with a titania thin-film electrode composed of a network structure of single-crystal-like TiO₂ nanowires made by the oriented attachment mechanism. *J. Am. Chem. Soc.*, 126,14943-14946.
- Jiu, J., Isoda, S., Wang, F., Adachi, M., 2006. Dye-sensitized solar cells based on a single-crystalline TiO₂ nanorod film. *Phys. Chem., B* 110 2087-2092.
- Flores, I.C., de Freitas, J.N., Longo, C., De Paoli, M.A., Winnischofer, H., Nogueira, A.F., 2007. Dye-sensitized solar cells based on TiO₂ nanotubes and a solid-state electrolyte. *J. Photochem. Photobiol. A Chem.* 189 153-160.
- Chappel, S., Chen, S.G., Zaban, A., TiO₂-Coated Nanoporous SnO₂ Electrodes for Dye Sensitized Solar Cells. *Langmuir* 18 (2002) 3336-3342.
- Bedja, I., Kamat, P.V., Hua, X., Lappin, A.G., Hotchandani, S., Photosensitization of Nanocrystalline ZnO Films by Bis (2,2'-bipyridine)(2,2'-bipyridine-4,4'-dicarboxylic acid) ruthenium(II). *Langmuir* 13 (1997) 2398-2403.
- Keis, K., Bauer, C., Boschloo, G., Hagfeldt, A., Westermarck, K., Rensmo, H., Siegbahn, H., Nanostructured ZnO electrodes for dye-sensitized solar cell applications *J. Photochem. Photobiol. Chem.* 148 (2002) 57-64.

- 10.S. Chappel, A. Zaban, Nanoporous SnO₂ electrodes for dye-sensitized solar cells: improved cell performance by the synthesis of 18 nm SnO₂ colloids. *Solar Energy Mater Solar Cells*, 71 (2002) 141-152.
- 11.P. Guo, M.A. Aegerter, RU (II) sensitized Nb₂O₅ solar cell made by the sol-gel process. *Thin Solid Films*, 351 (1999) 290-294.
- 12.M. Gratzel, Dye-sensitized solar cells. *J. Photochem. Photobiol. C* 4 (2003) 145-153.
- 13.Kyung Hyun Ko, Young Cheol Lee, Young Jin Jung, Enhanced efficiency of dye-sensitized TiO₂ solar cells (DSSC) by doping of metal ions. *Journal of Colloid and Interface Science*, 283 (2005) 482-487.
- 14.Jin Young Kim & Sangwook Lee & Jun Hong Noh & Hyun Suk Jung & Kug Sun Hong, Enhanced photovoltaic properties of overlayer-coated nanocrystalline TiO₂ dye-sensitized solar cells (DSSCs). *J. Electroceram.* 23 (2009) 422-425.
- 15.Y. Zhang, N. Cai, Y. Zhao, Influence of Triton X-100 on the Performance of Dye-Sensitized Solar Cell. *Imaging sci. Photochem*, 26(2) (2008) 125-130
- 16.C. D. Yuan, N. CAI, Y. Zhao. The optimization of dye-sensitized solar cell's technology parameters *J. Artif. Crystal*, 38(1) (2009) 53-59.
17. G.P. Smestad, M. Gratzel, Demonstrating electron transfer and nanotechnology: A natural dye-sensitized nanocrystalline energy converter. *J. Chem. Edu.* 75 (1998) 752-756.
- 18.Y. Lee, J. Chae, M. Kang. Comparison of the photovoltaic efficiency on DSSC for nanometer sized TiO₂ using a conventional sol-gel and solvothermal methods *J. Ind. Eng. Chem.* 16 (2010) 609-614.
- 19.J. Wu, G. Xie, J. Lin, Z. Lan, M. Huang, Y. Huang. Enhancing photoelectrical performance of dye-sensitized solar cell by doping with europium-doped yttria rare-earth oxid, *J. Power Sources*, 195 (2010) 6937-6940.
- 20.Z. Tang, J. Wu, Q. Li, Z. Lan, L. Fan, J. Lin, M. Huang. The preparation of poly(glycidyl acrylate)-polypyrrole gel-electrolyte and its application in dye-sensitized solar cells. *Electrochim. Acta*, 55 (2010) 4883-4888.