

Fabrication of Dye Sensitized Solar Cells with a Double Layer Photoanode

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ABSTRACT

Dye sensitized solar cell was fabricated from a double layer photoanode. First, TiO₂ nanoparticles were synthesized by hydrothermal method. These TiO₂ NPs were deposited on FTO glasses by electrophoretic deposition method in applied voltage of 5 V and electrophoretic deposition time of 2.5-10 min. Then TiO₂ hollow spheres were synthesized by sacrificed template method with Carbon Spheres as template and titanium (IV) isopropoxide as precursor. Then these template sacrificed and the hollow structures found. Since the HSs paste was prepared as same method of prepared TiO₂ nanoparticles and this paste was deposited on last layer by doctor blade method. The prepared photoanodes were soaped in N-719 dye after sintering in 500 °C. The dye sensitized solar cells were fabricated with the finalized double layer photoanodes. The best photovoltaic characteristics of the optimized cell were 734 mV, 13.16 mA/cm², 62% and 5.96% for V_{oc}, J_{sc}, F.F. and efficiency respectively.

INTRODUCTION

Dye sensitized solar cell is one of the attractive scopes in recent decade because of low cost materials and high efficiency operation. The photoelectrode of the DSSC fabricate from TiO₂ nanostructures commonly. There are many approaches for the DSSC's photoelectrode such as doctor blade method [1-4], screen printing [1, 5, 6], drop-casting [7, 8], spin-coating [9, 10], spray coating [11, 12], chemical vapour deposition [13], chemical bath deposition [14], hydrothermal method [15-18] and electrophoretic deposition (EPD). Although screen printing and doctor blade was used for the TiO₂ nanostructure deposition in last years, the EPD method has attracted special attention because of its simple and low cost deposition

aspects.

Nevertheless, the main problem with this method is related to the cracks, which could be created during the solvent evaporation [19-26]. Different approaches have been applied to decrease the density of the cracks on the surface of the photoanode layers. Application of some binders in TiO₂ sol [27], multistep electrophoretic deposition with intermediate heating [28-30], application of mechanical pressure after deposition and controlling the temperature and atmosphere of the layers during the drying stage [31, 32] are some of the reported solutions.

Many approaches were applied for increasing of DSSC efficiency [33-35]. One of these approaches is the use of scattering layer on the TiO₂ NPs layer. These Scattering particles increase the light length and then increase the efficiency of converting photons into elect-

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ricity. In this research, the TiO₂ NPs were synthesized by hydrothermal method. After that this NPs were dispersed in Isopropanol and then the cyclic EPD was applied for deposition of NPs on FTO glass. The compact photoelectrode was sintered. The TiO₂ hollow spheres were synthesized by sacrificed template method and the TiO₂ HSs paste was prepared according to the literature [1-4]. The TiO₂ HSs paste was deposited on the last prepared photoelectrode by Doctor Blade method. The finalized prepared photoelectrode was sintered and used in DSSCs. The best photovoltaic characteristics of the optimized cell were 734 mV, 13.16 mA/cm², 62% and 5.96% for V_{oc}, J_{sc}, F.F. and efficiency respectively.

MATERIALS AND METHODS

Synthesis of TiO₂ nanoparticles (NPs)

TiO₂ NPs were synthesized by hydrothermal method [36]. Briefly, 0.325 mole Acetic acid were added to 0.325 mole Titanium (IV) isopropoxide and then was mixed for 15 min. The obtained solution was added into 49 g water slowly when the water stirred rapidly. The mixed solution was refluxed after addition of 0.65 mL Nitric acid. The gel solution was transferred to Teflon-lined autoclave at 230°C for 12 h. The synthesized TiO₂ NPs were washed with ethanol by centrifuge for 5 times.

Synthesis of TiO₂ Hollow Spheres (HSs)

First Carbon spheres with different sizes were synthesized by a hydrothermal method [37]. Briefly, an aqueous solution of glucose with different concentrations of 0.5 M, 1.0 M and 1.5 M was prepared in the first step. Then it was transferred to a 100 ml Teflon-lined autoclave and heated at 180 °C for 8 h. The dark-brown precipitate was centrifuged and washed with ethanol and DI water for several times. Finally, the carbon spheres were dried at 75 °C for 5 h. TiO₂ Hollow Spheres were prepared by liquid phase deposition (LPD) of TiO₂ on the surface of the carbon sphere templates. 0.2 g of the as-prepared carbon spheres was added to 20 ml ethanol solution and dispersed. Then 0.002 mol of Titanium tetraisopropoxide (TTIP) was added to this solution. The mixture was stirred at room temperature for 24 h for the LPD process. The C/TiO₂ precipitate was centrifuged and washed with ethanol and DI water and dried at 40 °C for 10 h. Finally, the precipitate was heated at 450 °C to remove the carbon templates and form the pure TiO₂ structures. The synthesized HS from basic aqueous glucose

solution of 0.5, 1 and 1.5 M was called HSa, HSb and HSd respectively.

Fabrication of DSSC

The photoanode of DSSC was prepared from double layer TiO₂ structure. First the active layer of TiO₂ NPs were deposited by electrophoretic method [38]. For this purpose, the synthesized TiO₂ NPs were dissolved in isopropanol with concentration of 10 g/l and mixed overnight. The electrophoretic deposition was applied. The applied voltage and EPD time were set on 5 V and 2.5, 5, 7.5 and 10 min respectively. A nomination rule was applied for the photoelectrode deposited in different EPD time and voltages. For example, V5T10 demonstrates a layer, which is prepared at EPD voltage of 5 V and EPD time of 10 min. The deposited layer was sintered and then HS layer was deposited on NP layer by Doctor Blade method. The obtained photoanodes were heated at 500 °C again. finally the photoanodes were soaked in dye (N-719) solution for sensitization. After about 20 hours the photoanodes were applied and other stages of cells preparation i.e. fabrication of platinum counter electrode, cell assembly, electrolyte injection and sealing were performed.

The characteristics of the photoanode and fabricated cells were measured using SEM, optical spectroscopy and I-V measurement analyses. SEM images were taken using a T-Scan System. The X-ray diffraction pattern was also recorded with Cu K α radiation by a Philips Xpert-pro system. Optical spectroscopy was performed by a Mecasys Optizen spectrophotometer, I-V measurements were done using 30V Autolab potentiostat system.

RESULTS AND DISCUSSION

Fig. 1 demonstrated the X-ray diffraction (XRD) pattern of TiO₂ NP and TiO₂ HS. As seen peaks located at 2 θ of 25.3°, 37.8°, 48°, 54°, 55.2°, 62.7°, 68.9°, 70.3° and 75.3° belong to the (101), (004), (220), (105), (211), (204), (116), (220) and (215) planes of the anatase phase TiO₂, respectively.

The X-ray diffraction (XRD) demonstrates that the phase of carbon spheres is amorphous (Fig. 2). Two peaks at 2 θ of 22 ° and 43° can be seen for Carbon Spheres with around 320 nm diameters. These two peaks are assigned to (002) and (101) planes of carbon materials.

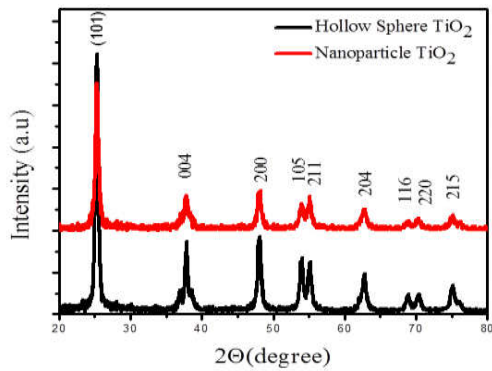


Fig. 1. X-ray diffraction pattern of the hydrothermally grown TiO_2 nanoparticles and Hollow sphere TiO_2

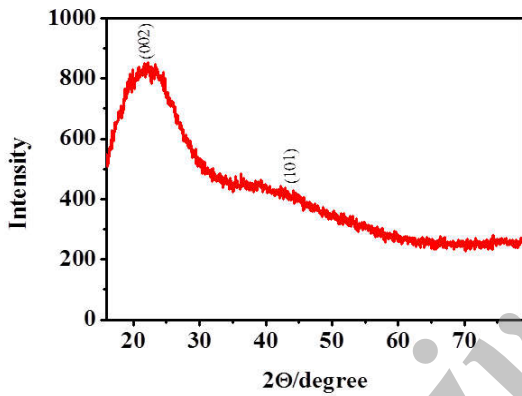


Fig. 2. X-ray diffraction pattern of the synthesized carbon spheres nanoparticle

Carbon spheres with different sizes were synthesized by hydrothermal method. Fig. 3 demonstrates the SEM images of three sizes of prepared Carbon spheres at different concentrations of the glucose solution. According to the results, the carbon structures are well-spherical while their average size is increased with the glucose concentration. It could be seen that the dominant sizes of carbon spheres are about 230 nm, 320 nm and 435 nm for the glucose concentration of 0.5 M, 1.0 M and 1.5 M, respectively

The carbon templates were dispersed in ethanol and LPD process. Then the thin layer of TiO_2 was supposed to form on the surface of the carbon spheres. Finally, the carbon cores were sacrificed by performing a calcination process to get submicron-scale TiO_2 hollow spheres.

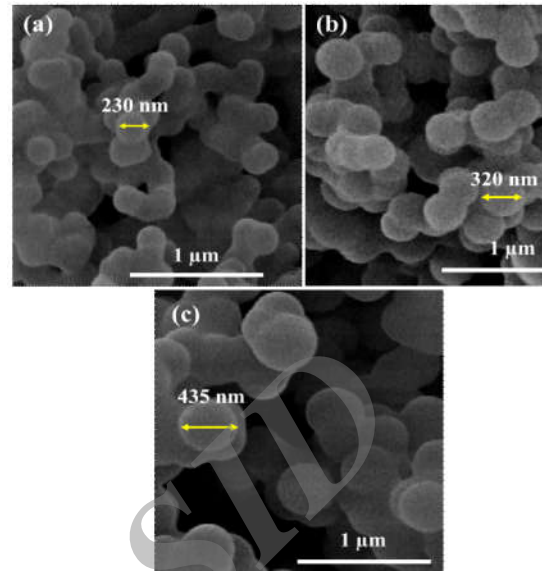


Fig. 3. SEM images of Carbon Spheres prepared with glucose concentration of 0.5 M (a), 1 M (b) and 1.5 M (c)

Fig. 4 shows the SEM images of the TiO_2 Hollow Spheres by using these carbon spheres templates in 24 h LPD time. According to the Figure. 4(a), 4(b) and 4(c) the external diameters of the TiO_2 hollow spheres formed in LPD time of 24 h is about 260 nm, 435 nm and 520-600 nm respectively. As shows the spherical and hole of these TiO_2 Hollow Spheres are formed. The SEM image of hydrothermally grown TiO_2 nanocrystals was shown in figure. 4(d).

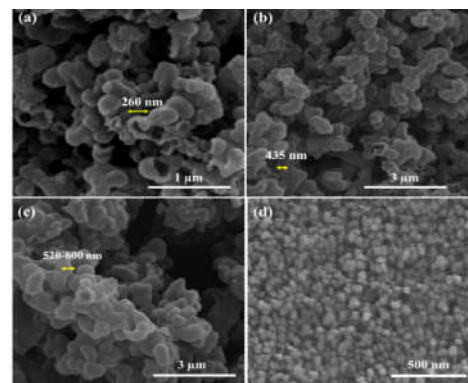


Fig. 4. SEM images of TiO_2 Hollow Spheres on the surface of Carbon spheres templates with 230 nm diameter (a), 320 nm diameter (b), 435 nm diameter (c) and SEM image of hydrothermally grown TiO_2 nanocrystals (d)

Fig. 5 demonstrate the cross SEM image of the nanocrystalline TiO_2 sub-layer prepared and TiO_2 Hollow Spheres as scattering top layer. According to this image the thickness of NPs layer was about $7\ \mu\text{m}$ and the thickness of TiO_2 HSs layer was about $2\ \mu\text{m}$. The optical transmittance of the prepared photoelectrodes was shown in fig. 6. The transmittance of zero was observed for the photoelectrode with scattering layers of HSa, Hsb and HSc. The effective scattering of the HS layers resulted the zero value for the double layer photoelectrodes.

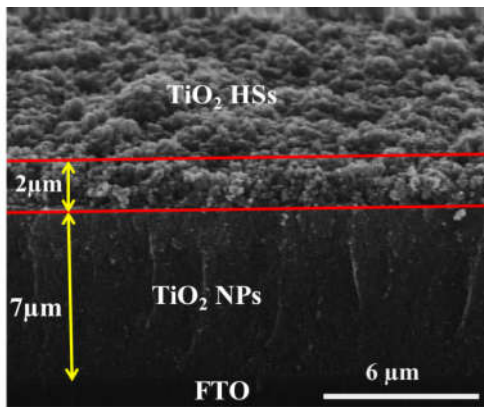


Fig.5. Cross SEM image of a TiO_2 Hollow Spheres layer (with thickness of $2\ \mu\text{m}$) on the TiO_2 NPs layer (with thickness of $7\ \mu\text{m}$)

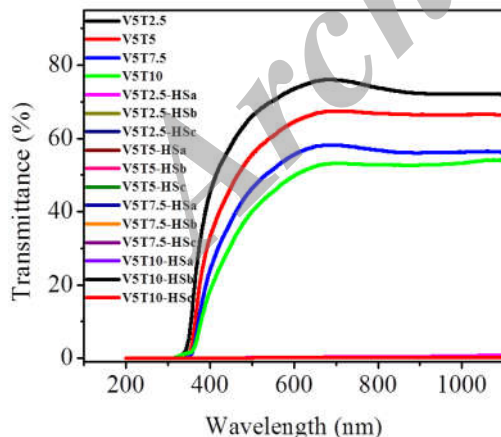


Fig. 6. Transmissions of the V5T2.5, V5T5, V5T7.5 and V5T10 and double layer photoanodes of V5T2.5-HSa, V5T2.5-HSb, V5T2.5-HSc, V5T5-HSa, V5T5-HSb, V5T5-HSc, V5T7.5-HSa, V5T7.5-HSb, V5T7.5-HSc, V5T10-HSa, V5T10-HSb, V5T10-HSc

Fig. 7 demonstrate the absorbance of the dye N719 solution which is fully desorbed from the surface of the different photoanodes. According to the result there are two adsorption peaks located at $380\ \text{nm}$ and $510\ \text{nm}$. It could be deduced that the dye adsorption of photoanodes with scatterers is higher than photoanodes without scattering layer because of higher surface area. However the dye adsorption of photoanodes with scattering layer decreased by increasing the diameter of TiO_2 Hollow sphere because of lower surface area.

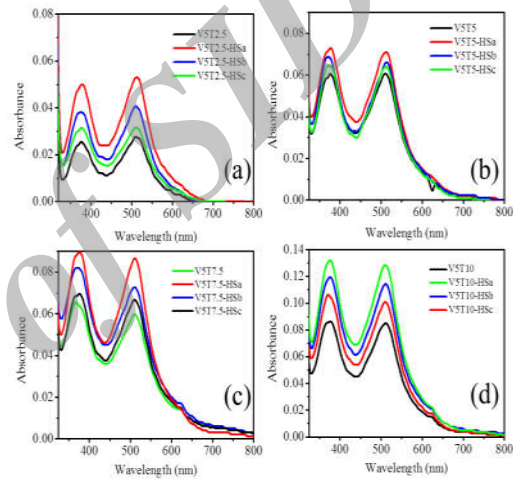


Fig. 7. Dye adsorptions of V5T2.5, V5T2.5-HSa, V5T2.5-HSb, V5T2.5-HSc (a), V5T5, V5T5-HSa, V5T5-HSb, V5T5-HSc (b), V5T7.5, V5T7.5-HSa, V5T7.5-HSb, V5T7.5-HSc (c), V5T10, V5T10-HSa, V5T10-HSb, V5T10-HSc (d)

The fabricated dye sensitized solar cells were characterized under standard irradiation of AM 1.5 condition. The I-V characteristic curves of the cells made of different photoanodes are displayed in Fig. 8. The detailed photovoltaic aspects of these cells were listed in Table 1. As seen the photocurrent efficiency was increased by use of scattering layer in the photoanode. It is due to higher light path of incident photon.

The best efficiency is obtained for the cell fabricated with V5T7.5-HSb photoanode. There are several parameters including thickness, dye loading, adhesion of deposited layer to substrate (FTO) and light scattering which seriously affect the cell efficiency. It seems that these parameters are optimized in DSSC

with V5T7.5-HSb photoanode. Here the maximum efficiency of the cells with photoanodes prepared by electrophoretic method is about 6%.

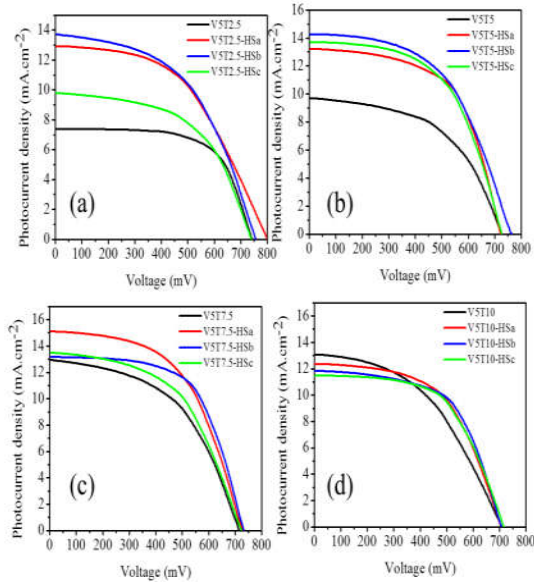


Fig. 8. I-V curves of DSSCs with V5T5, V5T10, V5T15 and V5T20 photoanodes V5T2.5, V5T2.5-HSa, V5T2.5-HSb, V5T2.5-HSc (a), V5T5, V5T5-HSa, V5T5-HSb, V5T5-HSc (b), V5T7.5, V5T7.5-HSa, V5T7.5-HSb, V5T7.5-HSc (c), V5T10, V5T10-HSa, V5T10-HSb, V5T10-HSc (d) photoanodes.

Table 1. Photovoltaic aspects of fabricated DSSCs

Sample	V _{OC} (mv)	J _{sc} (mA)	FF	η (%)
V5T2.5	745	7.35	0.67	3.69
V5T2.5-HSa	802	12.95	0.49	5.15
V5T2.5-HSb	758	13.72	0.5	5.23
V5T2.5-HSc	741	9.8	0.54	3.88
V5T5	725	9.45	0.53	3.68
V5T5-Has	725	13.23	0.59	5.69
V5T5-HSb	765	14.28	0.53	5.76
V5T5-HSc	728	13.72	0.56	5.6
V5T7.5	716	12.95	0.5	4.65
V5T7.5-Has	728	15.12	0.54	5.9
V5T7.5-HSb	734	13.16	0.62	5.96
V5T7.5-HSc	725	13.51	0.52	5.1
V5T10	710	13.09	0.45	4.25
V5T10-Has	710	12.39	0.55	4.84
V5T10-HSb	710	11.83	0.59	4.92
V5T10-HSc	716	11.48	0.58	4.78

CONCLUSION

The electrophoretic deposition method was used for preparation of active layer of TiO₂ nanoparticles (NPs). The scattering layer of hollow spheres with different sizes were deposited on last active layer and the prepared photoelectrode was used in dye sensitized solar cell. The DSSCs with double layers photoanodes shows higher efficiency than DSSCs with single active layer photoanodes. The best conversion efficiency was related to V5T7.5-HSb. The photovoltaic characteristics of the optimized cell were 734 mV, 13.16 mA/cm², 62% and 5.96% for V_{oc}, J_{sc}, F.F. and efficiency respectively. This DSSC shows 28% increase in efficiency than DSSC with V5T7.5 photoanode.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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