

1D and 0D Advantage Materials Application on TCO Surface On Dye Sensitized Solar Cells

[Halil İbrahim YAVUZ¹]

Abstract—Semiconductor metal oxide nanowires (SCMONWs) are favorable materials for various quantum devices which have one dimensional interaction and huge surface-to-volume ratio. Growth of these nanowires is commonly performed using expensive techniques requiring high vacuum and high temperature conditions, which also consume some hazardous raw materials. However, the sol-gel technique employed in this study is used primarily for the fabrication of materials including metal oxides beginning from a wet chemical solution, where low temperatures and non-vacuum conditions are utilized. Indium tin oxide (ITO) is generally used as a transparent conducting oxide for solar cells and LCD, touch screens applications. In this work, indium tin oxide (ITO) nanoparticles, nanowires and thin films are prepared on glass substrates by sol-gel technique and used for the production of nano-crystalline dye-sensitized solar cells (nc-DSSC), which are a relatively new class of low-cost thin film solar cells. Structural, topographical and chemical analyses were performed using XRD, SEM and EDS. SEM analysis confirm the presence of 15 nm thick and 500 nm long nanowires obtained 24h treatment ITO. The transparency of the ITO films is analyzed using UV spectrometer. 24h treatment of ITO nanowires in nc-DSSCs causes an improvement of 83 % in the power converted efficiency and 30 % indecent photo current efficiency with respect to pure TiO₂ based dye sensitized solar cells

Keywords—Solar cells, Dye sensitized solar cell, Advantage materials, nanotechnology, nanomaterials, energy

I. Introduction

After the introduction in 1991, dye-sensitized solar cells (DSSC) have attracted great interest due to their large potential applications as a cheap alternative candidate to replace conventional silicon-based p-n junction solar cells. The key points of highly efficient dye sensitized solar cell production depends on light harvesting, charge generation and charge transport in photoelectrode components. The photoelectrode is composed of a photogenerator nanoporous oxide thick film and a highly transparent conducting oxide (TCO) thin film. Most of research has been reported about working principle, problems and solution on photovoltaic generation on DSSCs. Nevertheless, important parameters of light conversion efficiency which are light transmittance, charge collection, and charge extraction to the external circuit take place on TCO, it has been barely researched. A lot of widely used transparent conductor and commercially TCOs has been used of DSSC applications such as FTO (F:SnO₂), ITO (In:SnO₂), ATO (Sn:SbO₂), and AZO (Al:ZnO).

Indium tin oxide (ITO, tin-doped indium oxide) is a nanocomposite solid-solution of In₂O₃ and SnO₂ in 10:1 ratio. ITO which is an advanced ceramic material can be applied to numerous optoelectronic devices due to its excellent

properties of high conductivity and high transparency and it is colorless to visible light in thin film layers while in bulk form it is yellowish to grey. The high electrical conductivity is originated from Sn dopants which create a conducting carrier-oxygen vacancy at the matrix (In₂O₃).

Although ITO which is barely expensive than other choice, still best performance on highly transparency and lowest resistivity. There are fairly two problems using ITO on DSSC applications. One of them is production cost of ITO can be solved by sol-gel processing which is one of the cheap attractive solution based technique. The second problem is interaction between maximize the interface area between the transparent conductive indium tin oxide (ITO)-coated glass electrode and the photo anodic TiO₂ layer. For this purpose several work has been focused on about the interface area has been developed using 1D nanostructure of ITO nanowires to obtain an electrode with a high interface area. To produce highly efficient the interfacial area between ITO- TiO₂ h, Cross like 1-D nanostructure of ITO is needed. Before this report there is no advantage report presenting in literature. ITO nanowires can be produced using several methods such as laser ablation, electrospinning, electro deposition, and sputtering.

In this work, indium tin oxide (ITO) nanoparticles, nanowires and thin films have been realized on glass substrates by sol-gel technique and these were used for the production of nano-crystalline dye-sensitized solar cells (nc-DSSC), which are a relatively new class of low cost thin film solar cells.

ITO film produced by sol-gel method showed enhanced optical characteristics an electrical conductivity after annealing, ITO nanowire modification helps to increase interaction between the interface area between the transparent conductive indium tin oxide (ITO)-coated glass electrode and the photo anodic TiO₂ layer, and charge transport properties.

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II. Experimental

A. Synthesis of ITO gel

In(NO₃)₅ (Aldrich Chemical Co.) and SnCl₄ (Aldrich Chemical Co.) were mixed with a solution of ultra-pure water, acetic acid (HA) (Merck Chemical Co.) and polyethylene glycol (PG) in a 250 ml flux at 80 °C. Different solvent concentrations and their effect on the gel formation are shown in figure 1. In the light of the observed data, Increase of water would increase the hydrolysis rate and hence decrease the gel time. On the contrary, when water was in excess, the gel time increased slightly. The water addition adverse effect on reaction rate. As a result H₂O/PG = 10 and PG/HA= 4 concentrations were best performance of reaction time, therefore they has been selected for the synthesis of ITO gel.

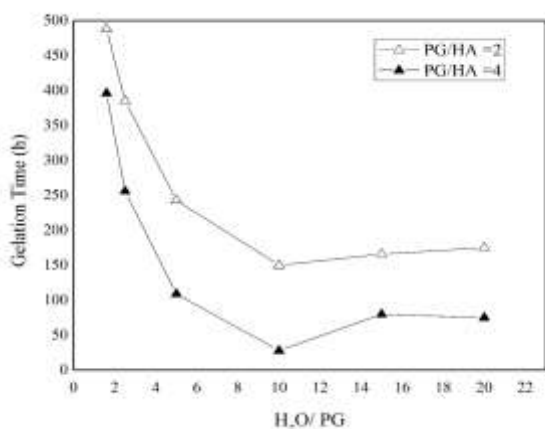


Figure 1. The results for the gel formation as a function of H₂O /PG for two HA/PG weight ratios.

B. Synthesis of ITO film, nanopowders, nanowires and TiO₂ nanopowders

The glass substrates were sonicated in distilled water, acetone and isopropanol mixture (1:1:1 volume ratio) for 15 min. Then, they were cleaned in a detergent solution for 10 min, and then dipped in isopropanol-HCN mixture (5:1) for 35 min in an ultrasonic homogenizer. All substrates were rinsed with distilled water and alcohol for three times, and then dried under air flow. The glass surfaces were coated by ITO gel using spin coating technique at 900 rpm 4 s and 2750 rpm at 30 sec. Following deposition, the ITO films were dried 20- 30 min at 20 oC and annealed at 400 oC for 2 h.

C. Synthesis of ITO nanopowders, nanowires and TiO₂ nanopowders

In order to obtained better and faster ITO nanowire, nucleation step is needed. The nucleation step depends on agglomerated nano particles (seed). To produce the suitable

seed particles, the gels were dried at 40 °C for 2 h and 60 °C for 2 h and then annealed at 400 °C for 2 h ITO nano powders (ITO pw) were obtained. The Figure 2 represents FE-SEM images of ITO pw which is average particles size 10-20nm.

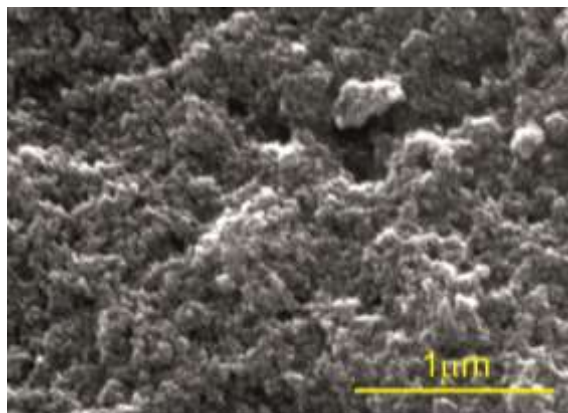


Figure.2 SEM micrograph of ITO nano powders obtained by sol-gel method.

D. Synthesis of ITO film nanowires

ITO nanowires (ITO nw) were obtained by seeding ITO nanopowders on ITO thin films and keeping them in a solution of 1 mM 10:1 In(NO₃)₅ (Aldrich Chemical Co.) and SnCl₄ (Aldrich Chemical Co.) for 24h 12h, 6h by two steps as seen in Figure 3a and Figure 3b.

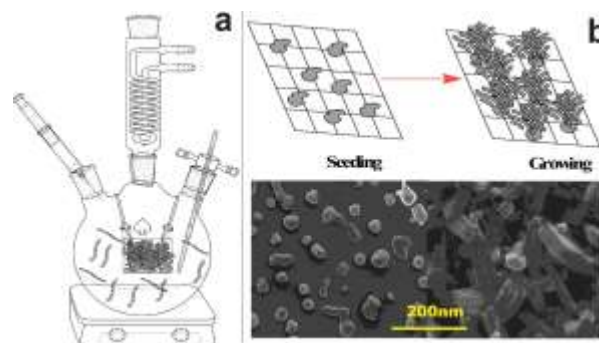


Figure 3. (a) Schematic reaction vessel for the production of ITO nanowires. (b) Schematic of nanowire growth steps.

150 mg ITO nanopowders and 8 ml ethanol were mixed, crushed, and grinded using an agate mortar. After grinding, mixture was transferred to a Teflon beaker adding some ethanol by completing to volume of 50 ml. Then, 0.5 ml HNO₃ was added to the solution in order to prevent agglomeration of these particles. Finally, the solution was mixed with a magnetic strip and sonicated with an ultrasonic horn (with cycles of 3 s work, 3 s rest). This ITO seeding solution was applied on ITO coated glass substrates by spin coater two times at 2000 rpm and final annealing was done at 400 oC for 30 minutes. Seeding step is crucial for nucleation of ITO nanowire. ITO seeded substrates can be seen in the SEM micrograph of Figure 3b.

The annealed ITO seeded substrates were placed in a reaction vessel perpendicular to the vessel bottom (Figure 1.a). Then 1 mM 10:1 In(NO₃)₅ and SnCl₄ solution were added until the substrate was completely covered. The nanowires were obtained by hydrothermal treatment in the solution at 85 oC for 24 h. (Figure 2). The nanowire length and homogeny distribution was found to increase with time of growth step, Figure 2 However, on the negative side, the angle of substrate is most important parameter. Only nanowire formation was obtain sample has in 90O angle to base of reaction weasel. The figure 4.a and 4.b represent to ITO nanowires obtained by hydrothermal treatment at 85 oC for 24 h.

E. Synthesis of TiO₂ nanopowders

TiO₂ nano powders were synthesized through a sol-gel method using tetraisopropyl orthotitanate (Aldrich Chemical Co.), isopropanol alcohol, ethylene glycol, polyethylene glycol (monolaurate) and acetic acid (HA) (Aldrich Chemical Co.) [28]. After adding a few droplets of water, a very soft white-blue colored gel was obtained and this gel was homogenized in two steps. The first step is mechanical homogenization by TiCl₄ treated SS316 blender (Daihan homogenizer). The final homogenization is ultrasonic homogenization by a titanium probe (Bandelin Sonoplus HD 2070) using 3 cycles, of %75 power for 2 min. Then, the gel was dried at 70 °C in a rotary evaporator at 100 mbar. Finally, the glass-like dried gel was transferred to a crucible and annealed at 550 °C for 2 h yielding nanoparticles of TiO₂. The surface area of TiO₂ was determined 64 m²/g by The Brunauer–Emmett–Teller (BET) method. The value of BET is higher than commercial P25 (BET 56 m²/g). The higher surface helps to photoanode absorb more dye.

F. Fabrication of the nanocomposite ITO-TiO₂ dye-sensitized solar cell

ITO glasses were treated by TiCl₄ solution at 30 minutes due to protection of recombination caused liquid electrolyte touch the ITO surface. The dye-sensitized TiO₂ electrodes were prepared from the TiO₂ paste synthesized by sol-gel method and coated on ITO film and ITO nanowires by Doctor Blade technique. The transparent counter Pt electrode was assembled into a sandwich type cell. The electrolyte, which was prepared from the solution of 10:1:5 lithium iodide, iodide and 4-tert-butylpyridine in acetonitrile, was injected into the interspaces between the photoanode and the counter electrode and the two electrodes were brought together using Surlyn (25 μm) frames and laminated at 120 °C. The active cell area was 0.25 cm².

III. Results and Discussion

A. ITO Films

To determine best sol-gel based ITO for DSSC applications, different cycle (Times) coated sample has been analyzed. UV/Visible/near IR (UV-NIR) spectra were taken

using a Perkin-Elmer Fourier transform Lambda 950 UV/vis spectrometer over a wavelength range of 330 to 2500 nm in both transmission n and reflection modes. The transmission spectra background was taken against an air background and substrate absorbance. UV-NIR transparency spectra analyses (figure 4.a.) of different cycle (times) ITO coated glass substrates were carried out, which indicates that the transparency of 5 Cycle times ITO (5T) coated glass substrates has showed best performance. The transparency of 5T between 330-1000 nm was average 80% and ~85% transmission at 550 nm. Due to ITO direct band gap started to absorb bellow the 400nm wavelength, the transmission falls rapidly. Transmission approaches zero while wavelength close the 330nm. Included in Figures 4.b is plot of reflectivity spectra, the 3T film also showed ~33% reflectivity in the infrared at 2500 nm in air. The transparency for 3T and 10T decreased slightly to ~70% and ~60%. The sheet resistance analyses of ITO thin films, which were carried out on Keithley analyzer system using a mercury probe, are given in Table 1.

Table 1	Sheet resistance analysis of ITO coated glasses.
Sample	R Calculated
3 T ITO	485 Ω.sq ⁻¹
5 T ITO	204 Ω.sq ⁻¹
10 T ITO	668 Ω.sq ⁻¹

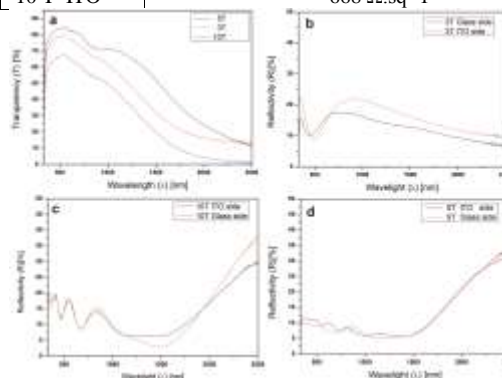


Figure 4. (a). Transmittance analysis of 3 times ITO coated (3T), 5 times ITO coated (5T), and 10 times ITO coated (10T) glass substrates. Reflectivity analysis of 3T (b), 5T (c) and 10T (d).

The band gap of the ITO films can be calculated from the transmission data in the lower wavelength region. By extrapolating the linear portion of the $(\alpha h\nu)^2$ vs photon energy $E(ev)$ graph gives the direct band gap of the sample.

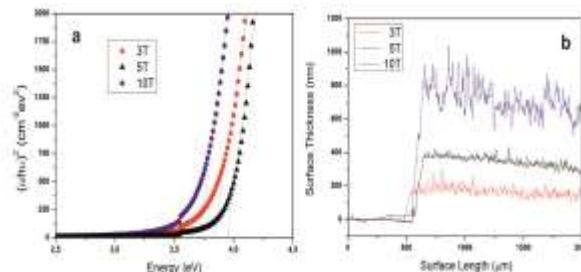


Figure 5.a. linear portion of the $(\alpha h\nu)^2$ vs photon energy $E(ev)$ graph of 3T, 5T and 10T ITO coated glass substrates. **b.**

surface profilometer results of 3T, 5T and 10T ITO coated glass substrates.

Figure 5.a. is the plot of $(h\nu\alpha)^2$ vs photon energy $E(eV)$ from which the direct optical band gap is calculated. The optical band gap (E_g) for 300nm ITO film is 3.94 eV. The results of 5T of E_{gap} close the literature (%10 tin doped In2O5 thin film 3.93 eV, which was produced by spatter). But on the 3T and 10T 3,80eV and 3,70 eV direct band gap, it was higher the literature. Therefore 5T sample was used as transparent conductive glass on DSSC application, on following experiments which is illustrated DSSCs continue whit 5T samples. After decide the 5T sample used as a transparent conductive glass on DSSC application. A computer-controlled Keithley 2400 source meter with 300 W AM 1.5 simulated sunlight (2X2 beam, w/6258 lamp) was employed to obtain the current density-voltage (J-V) characteristics. The active areas of all of the ITO-TiO₂ DSSCs were 0.25 cm². The results of the current density-voltage (J-V) curves are given below in Table 4 and J-V characteristic curves are shown in Figure 8.

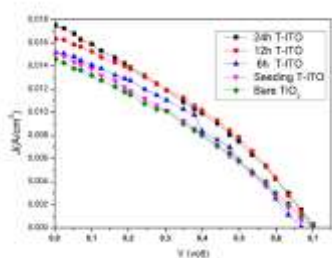


Figure 6. Current density-voltage characteristics of ITO nanowire and TiO₂ nano powder composite dye sensitized solar cells.

On the table 2 shows that short circuit current density, J_{sc} increases with ITO treatment time increases, due to improvement in contact surface of ITO- TiO₂. The best improvement is found 175 mA in 24h T-ITO. Seeding of ITO and 6h T-ITO has nearly same J_{sc} . After ITO nanowires treatment under before coated TiO₂ matrix, ITO nanowires help the electrons to reach to the electrode surfaces causing an increase in the efficiency. That is why we observe higher efficiency than pure TiO₂ structures. There is not much differences between 24 and 48 hours treatment. Therefore 24 hours ITO nanowire treatment enough to get higher efficiency on the TiO₂ matrix, during the production of DSSC doctor blade technique. ITO nanowires reach the maximum effect on the photovoltaic conversion on ITO substrate after 24 hours treatment.

Table 2				
Efficiency analysis of ITO nanowire and TiO ₂ nano powder composite dye sensitized solar cells.				
Sample	Fill Factor (%)	J_{sc} (mA/cm ²)	V_{oc} (Volt)	Efficiency (%)
24 T-ITO	40.46	17,50	0,710	3.26
12 T-ITO	39.21	16.25	0,705	3.21

6 T-ITO	33.77	15.26	0,701	2.41
Seeding ITO	32.04	15.21	0,670	1.74
Bare TiO ₂	31.90	14.50	0,660	1.78

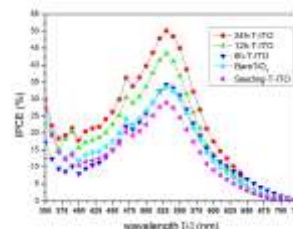


Figure 7. IPCE spectra of DSSCs based on Bare TiO₂ and 24 h T-ITO sample.

On The IPCE curve (figure7), the photosensitization of the TiO₂ electrodes in the visible region is clearly observed. 540 nm peak is much higher than 460 nm therefore, 540nm peak is more effect in light absorption around 540 nm. There are no differences between 6h T-ITO and bare TiO₂. It is due to the light absorption of the ITO when the light is incident from the ITO substrates. However %59 improvement has been observed total IPCE.

EIS technique has been widely employed to investigate the kinetics of electrochemical and photo electrochemical process occurring in DSSCs, super capacitor and lithium cell. The impedance spectra of 24h T-ITO, 6h T-ITO and Bare TiO₂ synthesis by sol-gel method were given figure 9. The experiments were under illumination whit ranging from 0.1Hz ro 100 kHz at V_{oc} with values 710mV for 24h ITO and715 mV for 12hT-ITO and 701 mV for 6h T-ITO 670 mV for seeding ITO and 660mV for Bare TiO₂. On the Nyquist plots of EIS spectra, two semicircles were observed. On the light of resources on the EIS model analysis in the DSSC, values of important EIS parameters (R_{ct} and R_w) were calculated by Zsimpwin software. The calculated EIS data given in table 3.

Table 3	The calculated EIS data					
Samples	R_s (Ω)	R_{ct} (Ω)	C_1	R_w (Ω)	C_3	τ_e (ms)
Bare TiO ₂	28	87	5.60 E-05	174	2.80 E-05	0.47
Seeding T- ITO	23	305.	1.60 E-04	84	3.27 E-05	0.37
6h T-ITO	27	86	5.60 E-05	145	4.00 E-04	2
12h T- ITO	35	171	2.60 E-04	84	5.60 E-05	2
24h T- ITO	23	49	4.06 E-09	134	1.32E-04	20

According to table 3, 24h T-ITO system give the best performance among the all cells. It has low R_w and R_{ct} resistance values, lower R_w means that, 24h T-ITO system showed the most efficient charge transfer process at dye coated TiO₂ layer / treated ITO layer or dye coated TiO₂ / redox electrolyte interface on this work. Lowest R_{ct} means

that 24h T-ITO system was exhibited higher electron flow process between Pt counter electrolytes / redox electrolyte interfaces.

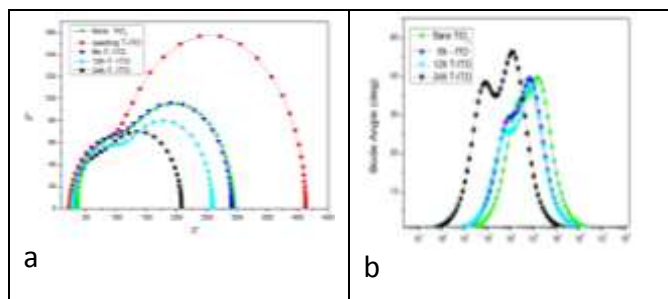


Figure 8. a. Nyquist plots of EIS data comparison of cells
 b. Bode plots of comparison of cells

On the bode phase plot of EIS spectra, as shown figure 10, Frequency of charge transfer process at different interfaces produced by sol gel method were shown in frequency versus θ (angle). The characteristic low frequency peaks (f_{max}) are located 1050 Hz for bare TiO_2 and 220Hz for 6h T-ITO and 25 Hz for 24h T-ITO. The most important parameter affecting the efficiency of electron life time for recombination at DSSC can be calculated from bode plot characteristic peak from f_{max} value equation of ($\tau=1/2\pi f_{max}$).

IV. Conclusion

Semiconductor metal oxide nanowires (SCMONWs), favorable materials for various quantum devices which have 1 D interaction and huge surface-volume ratio, were synthesized by a novel technique. Indium tin oxide (ITO) is primarily used as a transparent conducting oxide for solar cells and LCD applications. The sol-gel technique can be an alternative production method for one dimensional materials. In this work, we successfully produced ITO nano powders, nanowires and films on glass substrates (TCO) using sol-gel technique. ITO nanowire treatment between the conductive transparent ITO film and TiO_2 matrix improved photovoltaic efficiency. This efficiency increase due to decrease the serial resistance parts and increase the shunt resistance. Higher shunt resistance enable to higher I_{sc} , and higher fill factor, better IPCE. And also EIS measurements said that diffusion length and recombination time increase whit increase ITO treatment time. The finally highly efficient transport and improve dye sensitized solar cell and maximum performance of Sol-gel based DSSC has been obtained by ITO NW treatment.

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