Fabrication Dye Sensitized Solar Cells by Using Natural Dye Beet Root (Beta Vulgaris) as Photosensitizer and Nano Electrodes

Amir .F .Dawood AL-Niaimi[1], AbdulKareem .M.Ali.ALsamarai[2] and Zianab. I.Sadq[3]

[1,3]Chemistry department - College of science - Diyala University

[2] Chemistry department - College of science- Baghdad University

[1]Dr.amer960@sciences.uodiyala.edu.iq

[2]samuraee2000@hotmail.com

Received 5 December 2016 Accepted 23 February 2017

Abstract

In this study different types of Dye Sensitized Solar Cells (DSSCs) were fabricated using two kinds of titania (TiO_2) semiconductors as photo anodes and four kinds of counter electrodes, sensitized natural dye Beta vulgaris (beetroot) dye (Betalin). And the electrolyte (I^-/I_3^-). TiO_2 semiconductors includes; Nano sized powder (deposited on Indium doped Tin oxide (ITO) glass) and anodized nanotubes template on titanium foil. The counter electrodes include; platinum, electropolymerized polyaniline (PANI), polythiophene (PTh) and polypyrrole (PPY) (also all deposited on ITO glass). The surface structure of prepared photo anodes and counter electrodes were analysis by AFM, SEM,XRD and FTIR. The absorption spectra of natural dye was investigated by UV-Visible spectroscopy which showed absorbed light at 479 nm and 536 nm. The efficiency of prepared DSSCs were estimated through I-V characterization, the fall factors (ff) and electrical conversion efficiencies (η %) were measured using potentiostat. The efficiencies of all DSSCs follow the order ;

ITO/Pt – Ti/TNTs > ITO/Pt – ITO/TiO_2 > ITO/PANI – Ti/TNTs > ITO/PPY – Ti/TNTs > ITO/PTh – Ti/TNTs > ITO/PTh – ITO/TiO_2 > ITO/PANI – ITO/TiO_2 > ITO/PPY – ITO/TiO_2.

The best efficiencies were achieved using Ti/ TNTs and ITO/TiO_2 as anode and ITO / Pt as cathode they were 1.38% and 0.56% respectively.

Key words : Dyes sensitized solar cells, titanium nanotubes. Nano polyaniline, Nano polypyrrole, Nano polythiophene, natural dyes.

تصنيع خلايا شمسية ذات صبغات متحسسة باستعمال صبغة الشمندر الطبيعية كمحفز ضوئي واقطاب نانوية

عامر فاضل داود النعيمي[1] ، عبد الكريم محمد علي السامرائي[2] و زينب اسماعيل صادق[3]

[1,3]قسم الكيمياء - كلية العلوم - جامعة ديالى
[2] قسم الكيمياء - كلية العلوم - جامعة بغداد

الخلاصة

في هذه الدراسة تم تصنيع عدة انواع من الخلايا الشمسية المحفزة بالصبغة باستخدام نوعين من اشباه موصلات التيتانيا (TiO_2) كأنودات ضوئية واربع انواع من الاقطاب الموصلة (الكاثودات) . والمحلول الالكتروليتي هو (I^-/I_3^-). اشباه الموصلات (TiO_2) تتضمن : دقائق TiO_2 النانوية (مطلية على زجاج الانديوم المشوب بأوكسيد القصدير ITO) وانابيب التيتانيوم النانوية المحضرة بطريقة الطلاء على ورق التيتانيوم. الاقطاب الموصلة تتضمن : البلاتين، متعدد الانلين(PANI)، متعدد الثايوفين(PTh) ومتعدد البايرول(PPY) المتبلمرة كهربائيا (ايضا متموقعة على زجاج ITO). الصبغة الطبيعية المستخدمة هي صبغة الشمندر (البيتالين). التركيب السطحي للانودات الضوئية والاقطاب الموصلة تم تحليلها بعدة تقنيات تتضمن الـ AFM و الـ SEM والـ XRD وكذلك الـ FTIR. اطياف الامتصاص للصبغة الطبيعية تم تشخيصها بمطيافية UV-Visible والتي تبين بأن صبغة الشمندر تمتص الضوء عند 479nm و 536nm. تم تخمين كفاءة الـ DSSCs من خلال تشخيص I-V، عامل الملئ (ff) و كفاءات التحويل (%η) تم قياسها باستخدام المجهاد الساكن. تم تعيين كفاءات جميع الـ DSSCs كالتالي :

ITO/Pt – Ti/TNTs > ITO/Pt – ITO/TiO_2 > ITO/PANI – Ti/TNTs > ITO/PPY – Ti/TNTs > ITO/PTh – Ti/TNTs > ITO/PTh – ITO/TiO_2 > ITO/PANI – ITO/TiO_2 > ITO/PPY – ITO/TiO_2.

Fabrication Dye Sensitized Solar Cells by Using Natural Dye Beet Root (Beta Vulgaris) as Photosensitizer and Nano Electrodes

Amir .F .Dawood AL-Niaimi, AbdulKareem .M.Ali.ALsamarai and Zianab. I.Sadq

و 1.38% ككاثود وكانت ITO/Pt كأنود و ITO/TiO_2 و Ti/TNTsتم الحصول على اعلى الكفاءات باستخدام على التوالي.0.56%

الكلمات المفتاحية: خلايا شمسية ذات صبغات متحسسة، انبوب التيتانيوم النانوي ،بوليمر الانيلين النانوي ، ،بوليمر البايرول النانوي ، بوليمر الثايوفين النانوي، اصباغ طبيعية

Introduction

Dye-sensitized solar cells (DSSCs) is promising to global energy and environmental problems because its clean ,low cost, easy preparation, good durability and high conversion efficiency[1-5]. DSSCs were first proposed by Grätzel et al [3] it is the third generation photovoltaic device for low cost conversion of solar energy into electrical energy. The principle of operation of DSSCs is based on sensitization of a wide band- gap metal oxide semiconductor to the visible light region by an adsorbed molecular dye ,when the metal oxide semiconductor is immersed in the dye, a monolayer of the dye is anchored onto its surface. Excitation of dye by sun light and the photo generated charges are separated at the interface between the dye and metal oxide. Nano metal oxide semiconducting used in the fabrication of DSSCs[6] due to the large surface area they offer for dye anchoring [7].The charge transport is highly affected by the crystalline quality of metal oxide ,therefore it is important to reduce the charge traps in the films to speed up charge transport[8].

The ideal dye should strong absorb all light below a threshold wavelength of about 920 nm(broad range of wavelength and high molar extinction coefficient) ,strong binding to the semiconductor oxide surface (it carry attachment groups usually carboxylate or phosphonate, energy levels at the proper positions (LUMO high enough in energy for efficient electron injection and HOMO low enough for efficient regeneration). Stability over many years of exposure to sunlight, simple and reproducible and purification ,low cost, small reorganization energy for excited and ground state electron transfer to minimize energy losses [9].

In the attempt to find dyes satisfying these requirements, a large number of different molecules have been synthesized and characterized of new families of organic dyes and of metal complexes .The most efficient dye is found to be Ru (II) and Os(II) [10,11].These complexes have good absorption ,long excited lifetime, and highly efficient metal-to-ligand charge transfer. The disadvantages of these complexes are high cost and sophisticated preparation techniques. Therefore, alternative organic dyes such as nature dyes have been studied intensively .The main features of natural dyes are their availability, environmental friendly and low cost.In this work ,natural dye was extracted from beetroot and characterized by UV-VIS absorption spectrum. Different types of DSSCs were fabricated using two kinds of titania (TiO_2) semiconductors as photo anodes and four kinds of counter electrodes, and the electrolyte (I^-/I_3^-) are the same. TiO_2 semiconductors includes; Nano sized powder (deposited on ITO glass) and anodized nanotubes template on titanium foil. The counter electrodes include; platinum, electropolymerized polyaniline(PANI), polythiophene (PTh) and polypyrrole(PPY) (also all deposited on ITO glass).

Experimental (Materials and instruments)

All chemicals used were of the highest purity available. Different types of instruments and apparatus were used in this work. Potentiostat (Miab 200 with software, Bank Eleikronik,Germany,2000) used for electro polymerization and I-V evaluation for DSSC, Avometer digital Taiwan origin for measurement of voltage ,current and resistance. Xenon lamp 100Watt Japan for I-V characterization, power supply GW Instek,PSP-603 .UV-Vis spectroscopy 160 V Shimadzu Japan ,FT-IR spectrophotometer 8400 maximum resolution 0.5cm^{-1} Shimadzu Japan .Atomic force microscope (AFM) 220V ,Resolution 0.26 nm lateral 0.1 nm vertical Advanced Inc.USA for imaging of insulated surface, structure at atomic resolution. Scanning electron microscope (SEM) 0.5-20 KV Hitachi FE-SEM model S-4160,Japan for microscopic imaging of the surface structure.

Cleaning of ITO and Ti foil :Indium doped Tin Oxide (ITO) glasses (2x 2)cm^2 and Ti foil were cleaned by sonicate 8 mints with distilled water and 8 mints with ethanol and dried by heat gun.

Fabrication of TiO_2 Nano particles photo anode; 1gm of TiO_2 Nano powder (assay 99,9%MTI,USA) was treaded with few drops of (0.1M) HNO_3 to give a viscous paste. The paste was applied on a conductive side of cleaned ITO glass which determined by avometer via the doctor blade method [12]. It then annealed in furnace at 400°C for 2 hours, the annealed TiO_2 Paste is cooled down to room temperature gradually and then soaked into a nature dye solution 3 hr and washed with ethanol after soaking.

Fabrication of TiO_2 Nano tube photo anode (TNT): Cleaned Titanium foil with thickness 0.25mm was used for anodic growth of (TNT). The anodization reaction was carried out in two electrode electrochemical cell Ti foil which served as the anode –working electrode and Pt electrode as the counter electrode . The anodization electrode preparation from 0.4 wt% NH_4F and 3vol % deionized water first mixed for 5 mints in order to dissolve NH_4F .The volume was completed with ethylene glycol then stirred by magnetic stirrer for 30 mints. The anodization process was operated under a constant potential of 60 V for 1 hr at room temperature ,after anodization the Ti foil was washed carefully first with deionized water and second with ethanol to remove the surface residual electrolyte in the Nano tube arrays and dried by heat gun and annealed at 400°C for 1 hr in order to transform the TNT from amorphous to anatase phase. The TNT electrode was doped into dye 3 hr and again wased carefully with distilled water then dried by heat gun

Fabrication of Pt counter electrode: Few drops of solution (H_2PtCI_6) (44098ppm) on the was applied on a conductive side of cleaned ITO glass which determined by avometer by using few drops of zahi wasd solution and dried by heat gun and annealed at 450°C for 2 hr then washed carefully with distilled water and ethanol then dried by heat gun .

Fabrication of polyaniline (PANI) counter electrode: The aniline polymerization was occurred with electrochemical method ,using two electrodes (ITO glass as working electrode and Pt as counter electrode) under a constant potential of 12 V for 5 mints at room temperature at the same method and conditions prepared polypyrrol and polythiophene. The polyaniline was prepared by mixing 0.3 M of aniline with 1M H_2SO_4 for 30 mints using magnetic stirrer then washed with deionized water and with ethanol and dried .The poly thiphene was prepared by mixing 0.1M thiophene with 0.5M sodium perchlorates .The polypyrrol prepared by mixing 0.1M of pyrrol with 0.25M oxalic acid.

Preparation of cell electrolyte: The cell electrolyte composed by dissolving(0.5M) of KI and (0.05 M) of I_2 in Ethylene Glycol to obtain an (I^- / I_3^-) ions which served as acceptor and donor for electrons through an oxidation reduction reaction with anode and counter electrode.

Dye extraction: The dye was prepared by extraction the juice from the small pieces of clean beet root by electric mixer and the resulting extracts were filtered to remove any solid residue and were used for sensitization. Solution were protected from direct light and stored in the refrigerator.

Assembling the dye sensitive solar cells (DSSCs) : The cell assembly was performed by adding a few drops of (I^-/ I_3^-)electrolyte on the photo anode and fix both electrodes (anode and counter) facing each other using a clips binder .The space between two electrodes was obtained by using two sides scotch as a spacer.

Evaluation of the fabricated DSSCs: The evaluation system for DSSCs equipment's [light source (Xe lamp) ,cables, potentiostat] connect solar cell with potentiostat using cables ,shine the light ,control the voltage value through potentiostat which give a table and diagram for I – V characterization. The I-V curves were measured at 100 m W/cm^2 irradiations using Xe lamp.

Results and Discussions

The absorption characteristic is a very important property in DSSCs as it directly reflects the optical transition probability[13] .Figure(1) exhibit the UV-VIS absorption spectrum of dye which show that absorbed light in the region visible and s how two peaks at 479 nm and 536 nm.

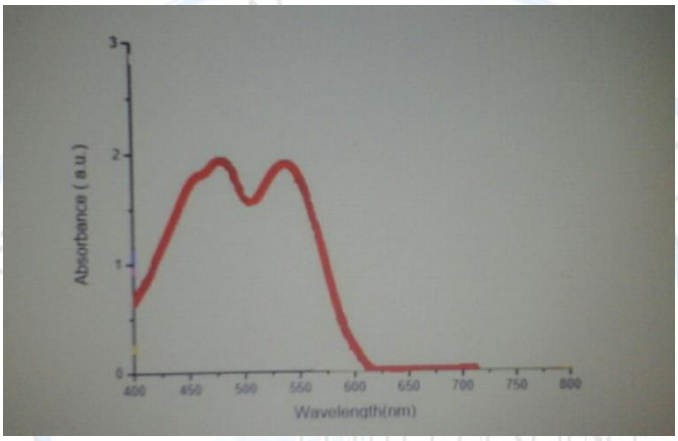


Figure (1) The absorption spectrum of beet root dye

The FT-IR of PANI shown in figure (2) ,the spectrum show a typical infrared spectrum of the PANI ,the main absorption peaks was at 3468cm^{-1} it is possible assign asymmetric stretching vibration of NH_2. The N-H stretching in benzoid –NH- benzoid (B-NH-B) ,the broad band at 3310cm^{-1} to hydrogen bonded NH and 3178 cm^{-1} to terminal quinoid =NH(Q= NH) .The 2943 cm^{-1} represented C-H stretching region. The absorption peak observed at 1647.21 cm^{-1} was attributed to C=C stretching in atomic nuclei .Absorption bands at 1477.4 cm^{-1} evidenced to C=N stretching in aromatic compounds .Absorption bands at 1300-1200 which confirms the C-N stretching of primary aromatic amines. The 1141 cm^{-1} band is vibrational mode of (B^+-NH =Q) and (B^+ =NH –Q) which is formed in doping reaction ,this band is very intense and broad which may be attributed to an existence of positive charges [13].The absorption peak at 1546.91 cm^{-1} assigned to quinoid structure does not reveal any significant changes for all polymer samples, that concludes that the polymers were prepared using di and tri basic acids .It has been

Fabrication Dye Sensitized Solar Cells by Using Natural Dye Beet Root (Beta Vulgaris) as Photosensitizer and Nano Electrodes

Amir .F .Dawood AL-Niaimi, AbdulKareem .M.Ali.ALsamarai and Zianab. I.Sadq

reported that H_2SO_4 may interact with PANI by donating either hydrogen sulfate $(HSO_4)^-$ or sulfate $(SO_4)^{-2}$ anions as dopant anions .Many authors agreed that $(HSO_4)^-$ dopant anions are present in PANI / H_2SO_4[14,15].

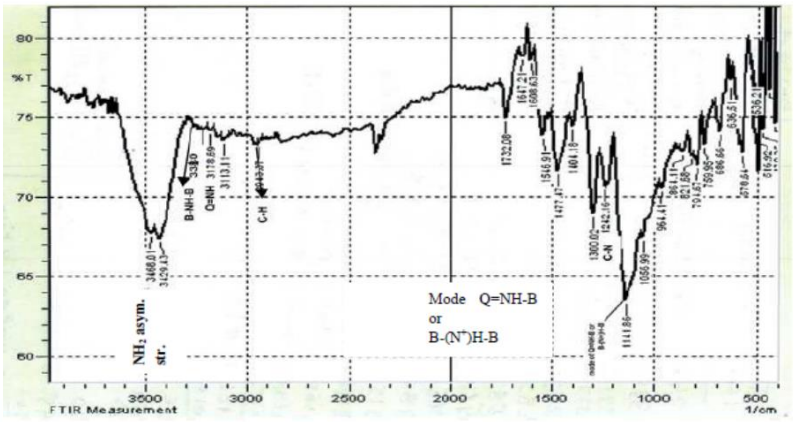


Figure (2) FT-IR spectrum of electro polymerized PANI electrode

Figure (3) shows FT-IR of PTh , the main absorption peaks at (629.1 ,1085,1631, 3416.6 cm^{-1}) were attributed to bands C-S, ,C-C, C=C and C-H in poly thiophene respectively.

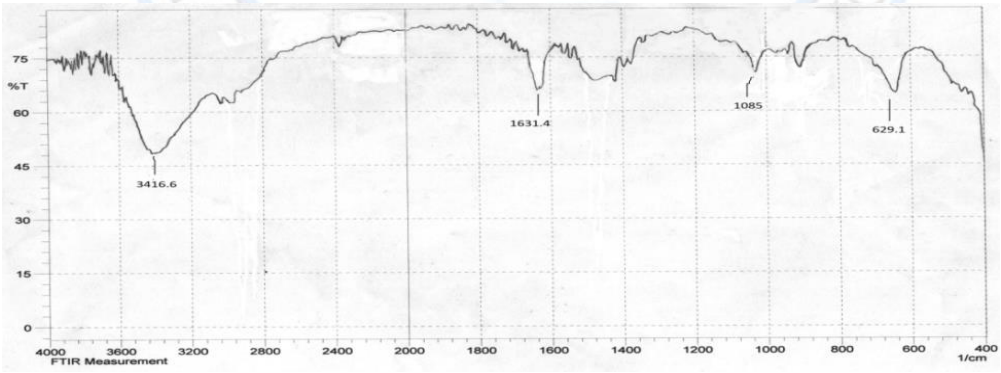


Figure (3) FT-IR spectrum of electro polymerized PTh electrode

Figure (4) shows the FTIR spectra of polypyrrole .The peaks at 811 cm^{-1} ,920 cm^{-1} are attributed to C-H wagging (16-18).The characteristic peaks at 1558 cm^{-1} and 1487cm-1 correspond to the C=C stretching, whereas peaks at 1686 cm-1 and 1315 cm^{-1} represent to respectively C=N and

C-N bonds (19) .The small peaks at 3522cm^{-1} , 3415cm^{-1} is assigned presence of N-H stretching vibrations.

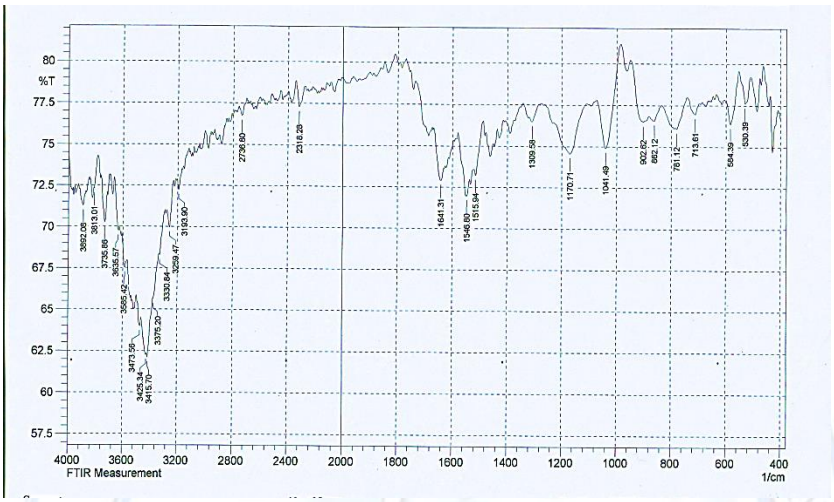


Figure (4) FT-IR spectrum of electro polymerized PPY electrode

XRD Measurement of TiO_2 and TNT Electrodes

The electrodes (TNT and TiO_2) were studied by XRD techniques to identify the crystalline phases .Fig (5) shows XRD spectra of TiO_2 Nano tube and TiO_2 revealed the titania with Rutile phase. TNT in Anatase phase with high crystalline .

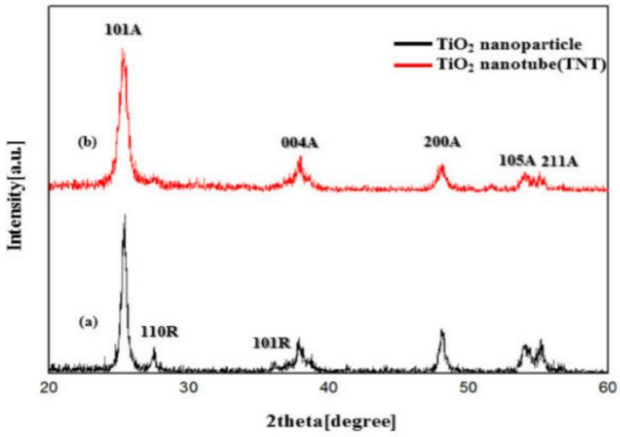


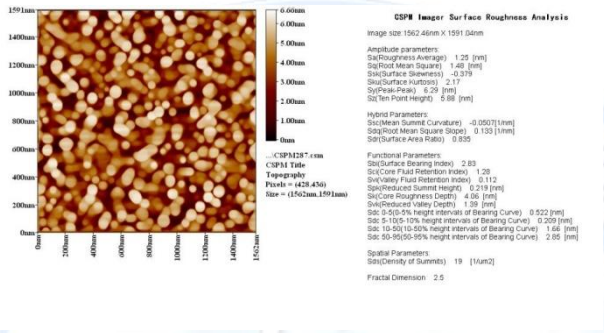
Figure (5) XRD pattern of TNT prepared via anodizing and TiO_2 Nanoparticles

Fabrication Dye Sensitized Solar Cells by Using Natural Dye Beet Root (Beta Vulgaris) as Photosensitizer and Nano Electrodes

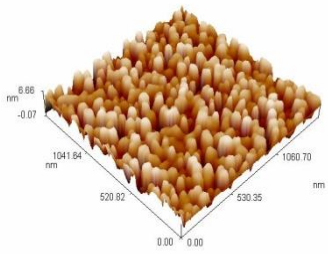
Amir .F .Dawood AL-Niaimi, AbdulKareem .M.Ali.ALsamarai and Zianab. I.Sadq

AFM of TiO_2 electrode :AFM Measurement

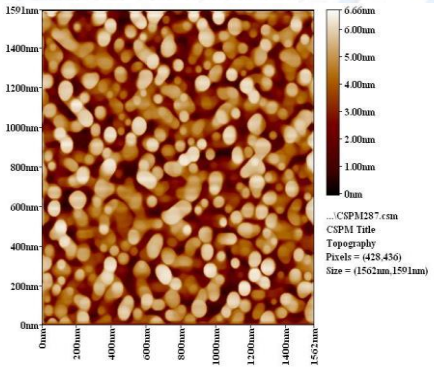
Images of AFM 2D and 3D for TiO_2 electrode (TiO_2 paste on ITO glass) and the average particle distribution 54 nm as show in fig(6).



A



C



B

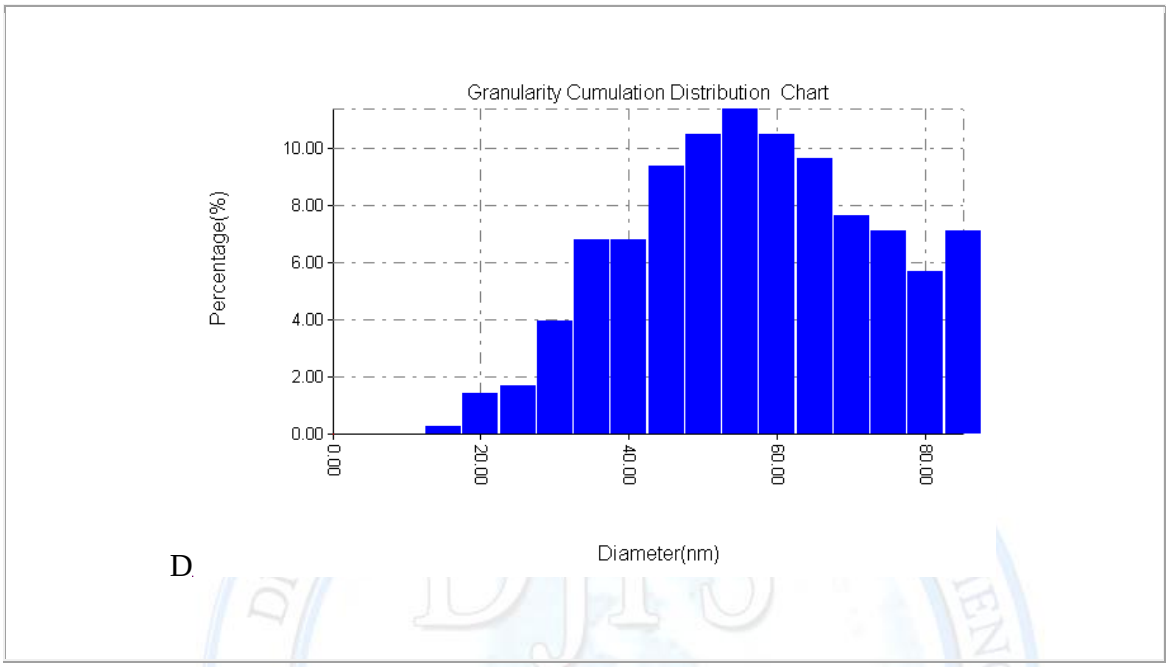
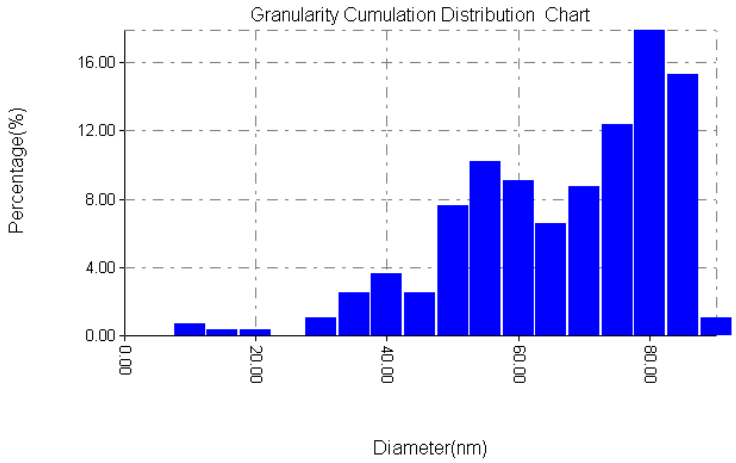


Figure (6) :A – Image of AFM roughness report, B and C ,images of AFM 2D and 3D for TiO_2 electrode (TiO_2 paste on ITO glass) D-Particle size distribution

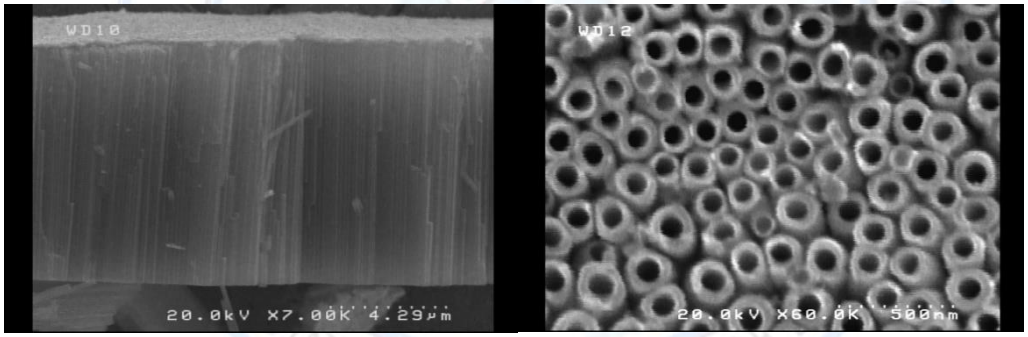
AFM and SEM of TNT

The prepared TNT was subjected to AFM and SEM examination as shown in figures (7) and (8) respectively ,the measurements of the tube parameters (length, diameter, wall thickness)were conducted on SEM images using (Imager J) software they revealed the length 5 micrometer, the tube diameter around 64 nm while the wall thickness about 30 nm. Somehow similar results achieved using AFM images and highly accurate cell dimensions measured as

show in fig(7) for 2D and 3D views and roughness report Particle size distribution .



Figure(7) Particle size distribution of TNT prepared



B **A**

Figure (8) SEM Measurement **A-Top view ,B-Side view of TNT prepared by anodizing method ,with anodizing potential of 60V for 1 hr.**

From the 2D and 3D AFM images and AFM roughness reports for PPy ,PANI,Pt and PTh electrodes the particles size distribution as shown in figures (9-12) respectively.

Avg. Diameter:94.79 nm	**<=10% Diameter:75.00 nm**
<=50% Diameter:90.00 nm	**<=90% Diameter:115.00 nm**

Fabrication Dye Sensitized Solar Cells by Using Natural Dye Beet Root (Beta Vulgaris) as Photosensitizer and Nano Electrodes

Amir .F .Dawood AL-Niaimi, AbdulKareem .M.Ali.ALsamarai and Zianab. I.Sadq

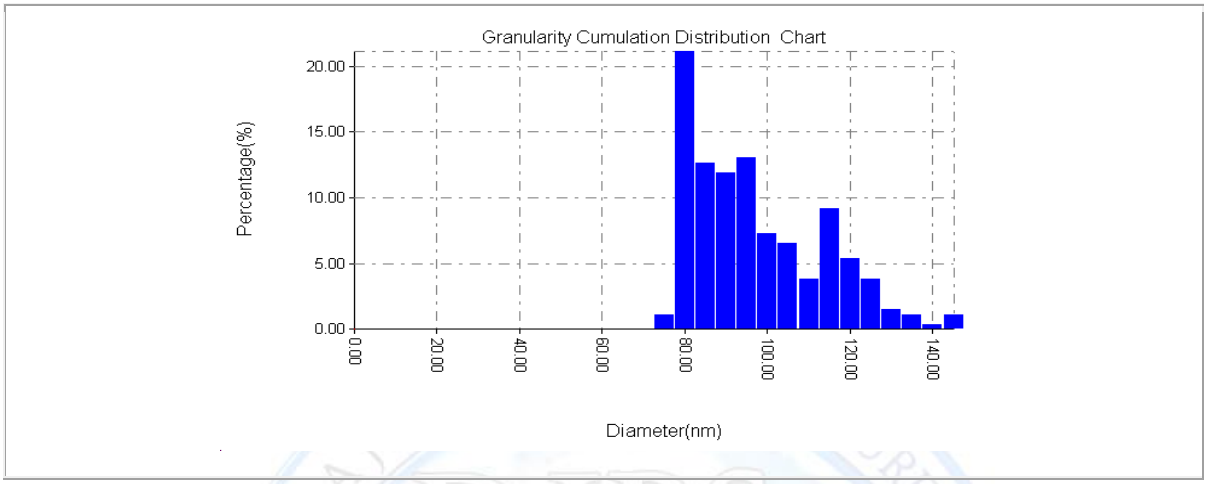


Figure (9) Particle size distribution of ppy

Avg. Diameter:98.76 nm	**<=10% Diameter:50.00 nm**
<=50% Diameter:90.00 nm	**<=90% Diameter:150.00 nm**

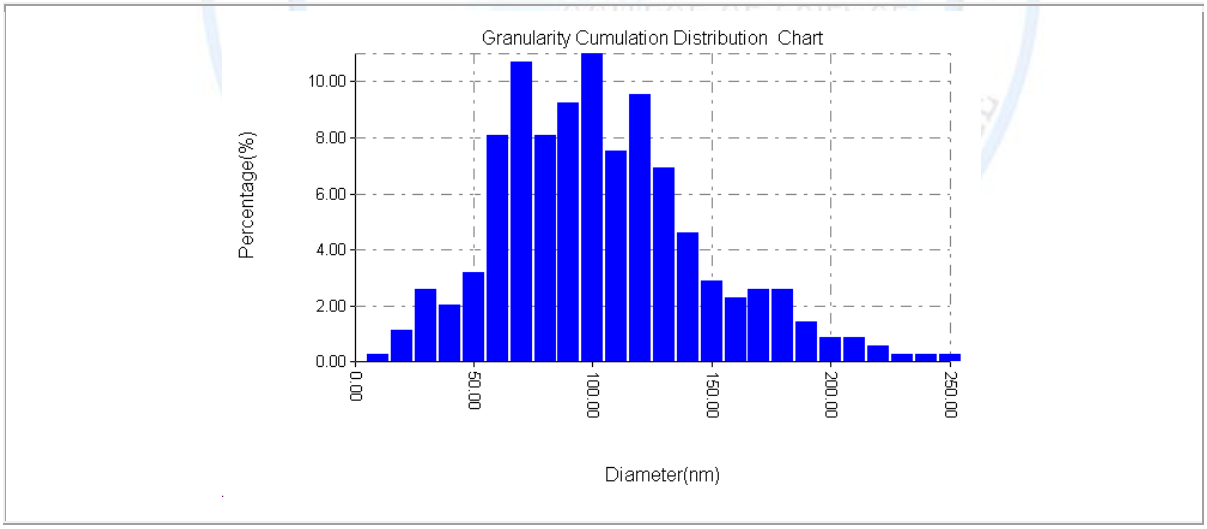


Figure (10) Particle size distribution of PANI electrode

Avg. Diameter:72.28 nm	**<=10% Diameter:30.00 nm**
<=50% Diameter:70.00 nm	**<=90% Diameter:105.00 nm**

Fabrication Dye Sensitized Solar Cells by Using Natural Dye Beet Root (Beta Vulgaris) as Photosensitizer and Nano Electrodes

Amir .F .Dawood AL-Niaimi, AbdulKareem .M.Ali.ALsamarai and Zianab. I.Sadq

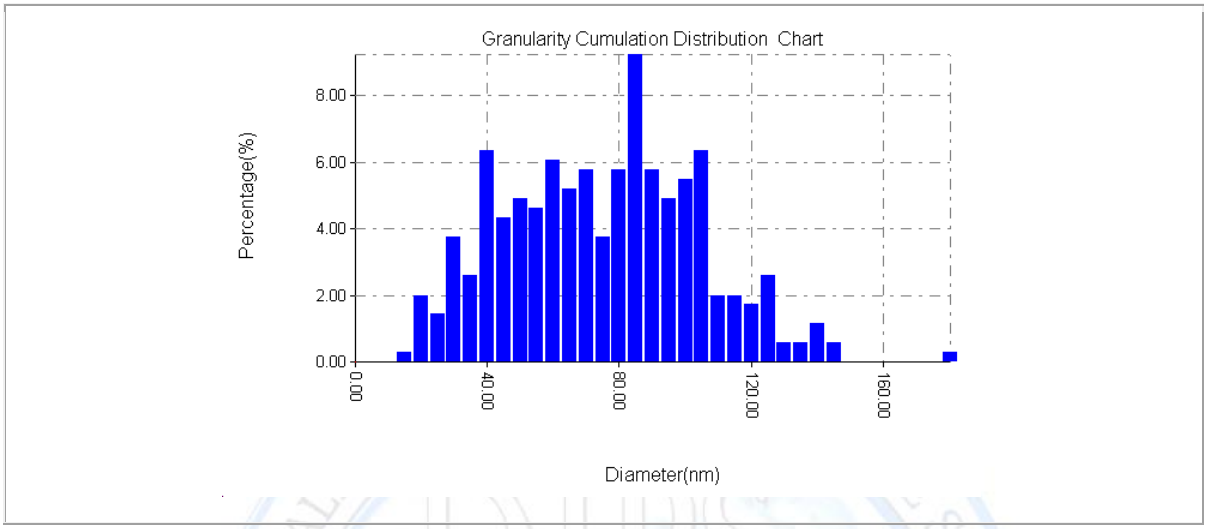


Figure (11) Particle size distribution of Pt electrode

Avg. Diameter:68.04 nm	**<=10% Diameter:40.00 nm**
<=50% Diameter:65.00 nm	**<=90% Diameter:90.00 nm**

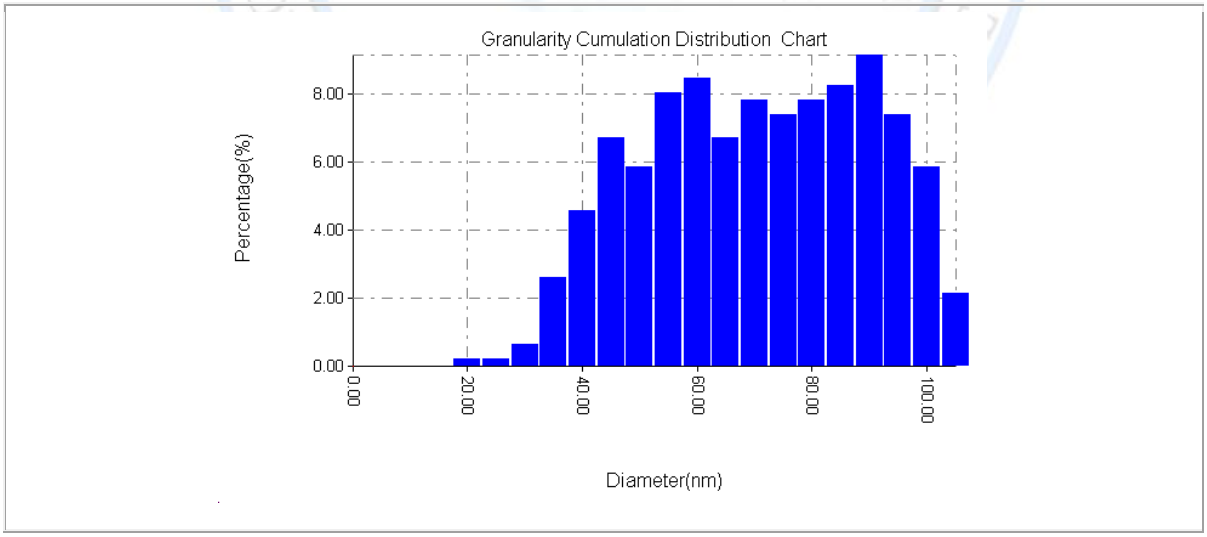


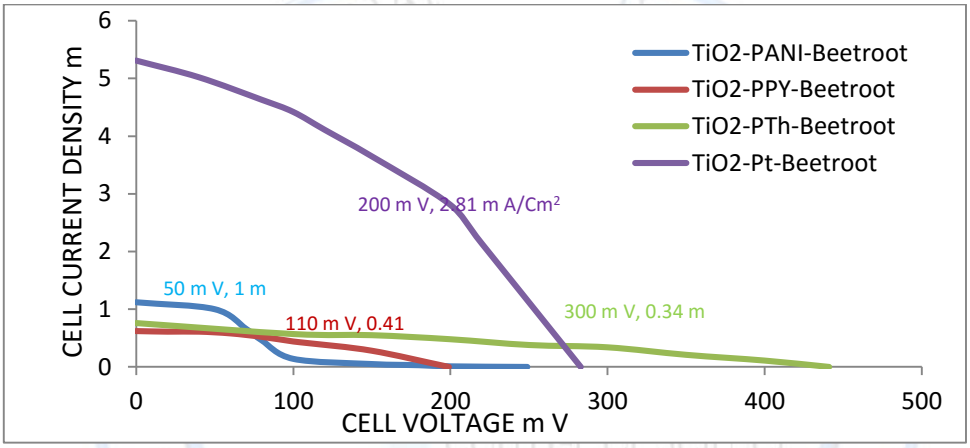
Figure (12) Particle size distribution of PTh electrode.

Fabrication Dye Sensitized Solar Cells by Using Natural Dye Beet Root (Beta Vulgaris) as Photosensitizer and Nano Electrodes

Amir .F .Dawood AL-Niaimi, AbdulKareem .M.Ali.ALsamarai and Zianab. I.Sadq

Characterization of Assembled DSSCs

All types of the assembled DSSCs were subjected to I-V characterization by fast scan with two electrodes potentiostat to evaluate all parameters of each them ; current short circuit (Isc) ,voltage of open circuit (Voc) ,maximum cell power (Pmax),the full factor (ff) and conversion efficiency (ɳ) were estimated .Figures (13 and 14) show the I-V curves of all assembled DSSCs and they reflect the effect of cathode materials on the performance of the assembled DSSCs.



Figure(13) I –V tests of the four assembled DSSCs from TiO_2/ITO glass as anode and different catalyzed cathodes with beetroot dye

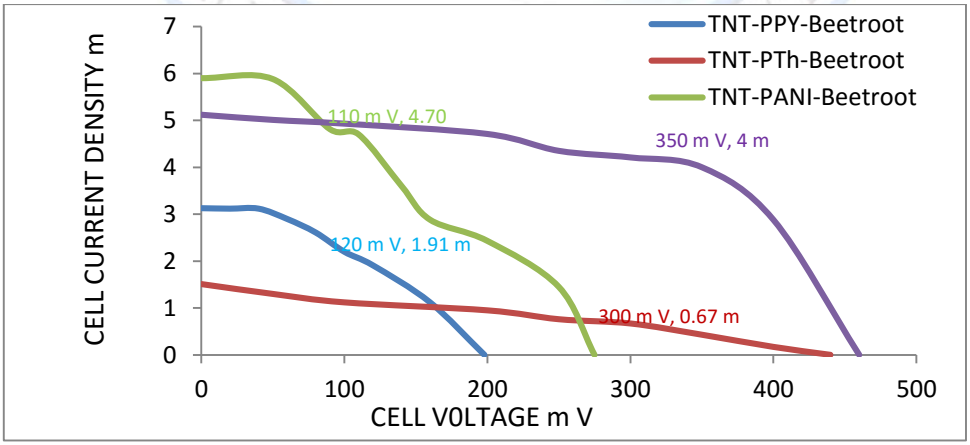


Fig (14) I-V tests of the four assembled DSSCs from TNT/ITO glass as anode and different catalyzed cathodes with beet root dye.

The cell parameters ; Isc ,Voc, I_{max} and V_{max} were estimated from the above I-V curves ,while the full (ff) and the cell efficiency were calculated using the following equations. % $\eta = (Isc \times Voc \times ff / P_{in}) \times 100\%$ Where $ff = I_{max} \times V_{max} / Isc \times Voc$

The efficiencies of all cells follow the order.

ITO/Pt – Ti/TNTs > ITO/Pt – ITO/TiO_2 > ITO/PANI – Ti/TNTs > ITO/PPY – Ti/TNTs > ITO/PTh – Ti/TNTs > ITO/PTh – ITO/TiO_2 > ITO/PANI – ITO/TiO_2 > ITO/PPY – ITO/TiO_2.

The best efficiencies were achieved using(Ti/TNT as anode and ITO/Pt as cathode), (ITO/TiO_2as anode and ITO/Pt as cathode) and(Ti/TNT as anode and ITO/PANI as cathode) ,showing 1.38% ,0.56% and 0.51% respectively. Using the ITO/PANI as counter electrode gave very comparative substitute to the ITO/Pt which is more expensive and difficult to control the number of layers of Pt which may led to weaken the transparency of the ITO/glass, in addition to that the PANI has a beautiful appearance. The effectiveness of using nanostructure materials ,PANI,TiO_2 NP and monolayers of Pt in making the anodes or the cathodes are very clear and always gives efficiencies.

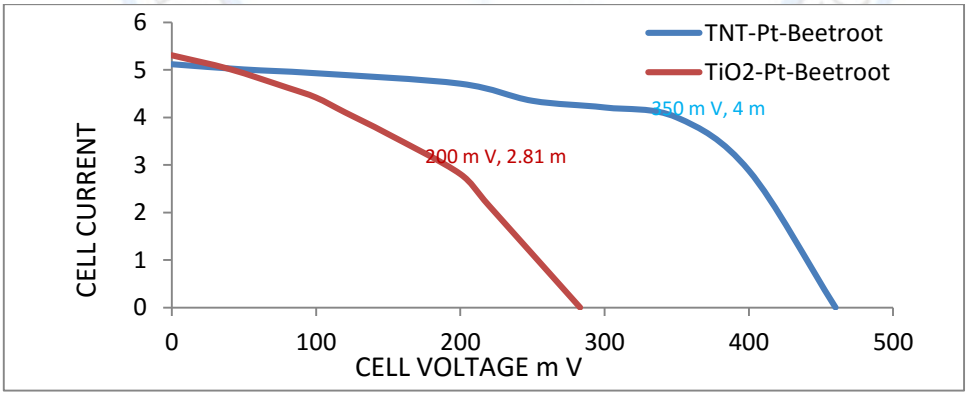


Fig 15 : I-V tests of the two assembled DSSCs from TNT/Ti glass TiO_2/ITO as anode and Pt/ITO catalyzed cathodes with beet root dye.

Fig 15 explain the effect of type of anode materials play the major role in making the DSSC ,a wide difference in the values of the cells efficiencies was noticed.

References

1. Grätzel,M.Photoelectrochemicalcells.Nature., 2001,414, 338 - 344.
2. Wang.P.et al. A stable quasi-solid-state dye-sensitized solar cell with an amphiphilic ruthenium sensitizer and polymer gel electrolyte. Nat. Mater., 2003,2,402-407.
3. O'Regan,B& Grätzel , M.A low- cost, high-efficiency solar cell based on dye –sensitized colloidal TiO2 films. Nature., 1991, 353,737-740.
4. Wu.J. et al. An all-solid-state dye-sensitized solar cell-based poly (N-alkyl-4-vinyl-pyridine iodide)electrolyte with efficiency of 5.64%.J.Am.Chem.Soc. 2008,130,11568-11569.
5. Wu.J .et al. Bifacial dye-sensitized solar cells: A strategy to enhance overall efficiency based on transparent polyaniline electrode .Scientific Reports, 2014, 1-7,.
6. H.Chen et al," Dye sensitized solar cells combining ZnO Nanotip arrays and nonliquid gel electrolytes ," Minerals metals &materials so-ciety, Journal of electronic materials . ,2009,Vol .38,pp.1612- 1617.
7. M.K.Nazeeruddin et al ,J. Am. Chem. Soc., ,1993,Vol.115,pp.6382-6387.
8. M.Law et al, Nat. Mater., 2005,Vol.4,pp.455.
9. M. Grätzel, Dye –sensitized solar cells ,Journal of Photochemistry and Photobiology C:Photochemistry Reviews , 2003,4,145-153.
10. P.Wang et al ,"High molar extinction coefficient sensitizer for stable dye- sensitized solar cells ,"J. Am. Chem. Soc., ,2005,Vol.127,pp.808-809.
11. S. Altobello et al ,"Sensitization of nanocrystalline TiO2 with black absorbers based on Os and Ru polypyridine complexes ,"J. Am. Chem. Soc., 2005, Vol 127,pp.15342- 15343.
12. E.M.Genies and M.Lapkowski,polyaniline films , electrochemical redox mechanisms .Synthetic metals . ,(1988), 24,61-68.
13. J. Vivekanandan et al ,Synthesis characterization and conductivity study of polyaniline prepared by chemical oxidative and electrochemical methods ,.Arch.Appl.SCi.Res., 2011,3(6),147-153.

14. A.Elsanousi et al ,Highly ordered TiO2 Nanotubes and their application to dye sensitized solar cells, Journal of applied and industrial sciences, ,2013,1(1) : 39-42.

15. N.A.Hassan, MSc thesis, Fabrication and study of the efficiency of Dye sensitive solar cells DSSCs using Nano materials, College of Science ,University Bagdad,2014..

16. Manik A.Chougle et al," Synthesis and characterization of polypyrrole (PPY)Thin films," Soft Nanoscience letters ,2011,1,6-10.

17. H.J.Kharat et al ," Synthesis of polypyrrole film s for the Development of Ammonia sensor", Polymers for Advanced Technologies,2007 ,Vol.18,No.5,pp.397-402.

18. B.Tian and G.Zerbi,"Journal of Chemical Physics",2006,Vol.92,No.6,pp.3886-3891.

19. K.Arora et al ," Application of Electrochemically prepared Polypyrrole –Polyvinyl sulphonate films to DNA Biosensor", Biosensors and Bioelectronics ,2006,Vol.21,No.9,1777-1783.