Morphological effect of composite TiO₂ nanorod-TiO₂ nanoparticle/PEDOT:PSS electrodes on triiodide reduction

T. Balkan^{1,2}, A. S. Sarac^{1,2,3*}

¹Department of Chemistry, Istanbul Technical University, Maslak, 34469 Istanbul, Turkey

²Department of Polymer Science and Technology, Istanbul Technical University, Maslak, 34469 Istanbul, Turkey

³Department of Nanoscience and Nanoengineering, Istanbul Technical University, Maslak 34469 Istanbul, Turkey

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Abstract. Composite electrodes consisting of TiO₂ nanoparticles (NPs)-TiO₂ nanorods (NRs) and poly (3,4-ethylene-dioxythiophene)-polystyrene sulfonate (PEDOT:PSS) were prepared on a conductive glass substrate. The presence of TiO₂ in the composite structure was proved by X-ray diffraction (XRD) Raman and FTIR-ATR measurements. The surface morphologies of TiO₂ NP-PEDOT:PSS, TiO₂ NR-PEDOT:PSS and TiO₂ NP-TiO₂ NR-PEDOT:PSS electrodes were characterized by scanning electron microscopy (SEM). According to the cyclic voltammetry measurement (CV), the electrocatalytic activity of composite electrodes on the reduction of triiodide improved after TiO₂ addition compared with pristine PEDOT:PSS and platinum (Pt) electrodes. Electrochemical impedance spectroscopy (EIS) showed that the charge transfer resistance (R_{ct}) strongly depends on the morphologies (ratio between TiO₂ NP and TiO₂ NR) of the composite electrodes. It was found that R_{ct} decreased by increasing the amount of TiO₂ nanorod in the whole mixture of TiO₂ nanoparticles and PEDOT:PSS.

Keywords: nanomaterials, TiO₂ nanorod, PEDOT:PSS, nanocomposites, EIS

1. Introduction

Among various solar cells, dye sensitized solar cells have attracted considerable attention because of their simple fabrication, low fabrication costs and high conversion efficiency [1, 2]. A typical dye sensitized solar cell (DSSC) comprises the dye sensitized nano crystalline TiO₂ photo anode, redox electrolyte and a counter electrode with a catalytic layer deposited on a conductive glass substrate such as fluorine tin oxide (FTO) [3]. The main tasks of counter electrode in DSSC are to collect electrons from the external circuit, transfer them back to the redox electrolyte, and catalyze the reduction of triiodide ions into iodide ions [4]. Therefore, counter-electrode materials should possess high electrical conductivity and a superior electrocatalytic activity [5]. Platinum (Pt) film has been widely used in DSSC so far as a counter electrode, due to its high conductivity and catalytic activ-

ity for the reduction of triiodide (I_3^-) ions. However, its practical application will be limited by its high cost, rare source and corrosion of Pt in the presence of I_3^-/I^- redox couple [6]. Therefore, it is necessary to develop efficient platinum-free counter electrodes for DSSC. In order to reduce the production cost of DSSC, alternative counter electrodes are produced by using such as carbon materials [7–9], metal compounds [10–13] and conductive polymers [14–17]. One of the most known conductive polymers, PEDOT:PSS has been developed as a low cost alternative counter electrode which has many unique properties such as high conductivity, high stability and good catalytic activity for I_3^- reduction [18]. However, PEDOT:PSS electrodes exhibit a poor fill factor and generate lower cell efficiency than pristine Pt electrodes. One way to solve this problem, other materials are combined with PEDOT:PSS in order to increase the surface

*Corresponding author, e-mail: sarac@itu.edu.tr
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area of the film and also the catalytic activity. For example, Maiaugree *et al.* [17] incorporated TiO₂ nanoparticles having different diameters into PEDOT:PSS. They investigated the diameter effect of TiO₂ nanoparticles on DSSC efficiency. They obtained the highest efficiency by using a mixture of large TiO₂ nanoparticles (30 wt%) and small TiO₂ nanoparticles (70 wt%). Sudhagar *et al.* [19] enhanced PEDOT:PSS based on DSSC efficiency by adding cobalt sulfide (CoS) to polymer. The efficiency was improved from 3.8 to 5.4% after incorporation of CoS nanoparticles. Zhao *et al.* [20] fabricated TiO₂-PEDOT:PSS/PEDOT:PSS/glass electrodes which allow Pt and FTO free counter electrodes. According to these articles, it is obvious that by mixing nanoparticles into PEDOT:PSS, surface area of the polymer can be enlarged. And it is known that small particles provide high electrocatalytic activity owing to the large surface area, but they also provide lower electron transport efficiency owing to the abundant grain boundaries and defects [21]. In particular, nanorods (NRs) are believed to have exceptional electron transport properties and have been considered as an alternative to nanoparticles (NPs) [22].

Therefore, in the present work, we report a newly designed counter electrode comprised of TiO₂ nanomaterials (nanoparticles, nanorods and their mixture) incorporated into PEDOT:PSS in order to understand the influence the morphologies of TiO₂. Hence, single ratio between TiO₂ and PEDOT:PSS was chosen to figure out how the performance of electrodes change depends on only morphologies of TiO₂ instead of TiO₂-PEDOT:PSS ratio. TiO₂ was selected because it is non-toxic and inexpensive. The effect of incorporating TiO₂ nanorod and TiO₂ nanoparticles at several ratios upon film structure was investigated. The electrocatalytic activities and impedance properties of electrodes were analyzed by using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements. Results showed that electrochemical properties of the electrodes can be manipulated by governing morphologies of TiO₂ nanomaterials.

2. Experimental

2.1. Preparation of TiO₂ nanorods

First TiO₂ nanofibers were produced by using electrospinning technique according to our previous study [23]. Afterwards, these nanofibers were broken mechanically by ball milling method in order to ob-

tain TiO₂ nanorods (diameter: 153±37 nm, length: 390±160 nm).

2.2. Preparation of TiO₂-PEDOT:PSS and Pt electrodes

Two different TiO₂ forms (nanorod and nanoparticle) were used for preparing four TiO₂ compositions on the basis of weight percentage: 1) 100% TiO₂ NPs (<25 nm, Sigma-Aldrich, USA)-0% TiO₂ NRs, 2) 75% TiO₂ NPs-25% TiO₂ NRs, 3) 50% TiO₂ NPs-50% TiO₂ NRs, 4) 0% TiO₂ NPs-100% TiO₂ NRs. These electrodes were labelled as NR0, NR25, NR50 and NR100, respectively. In a typical procedure, a paste of PEDOT:PSS (PEDOT:PSS) (Sigma-Aldrich, 1.3 wt% dispersion, USA) and TiO₂ was prepared by mixing 0.16 g TiO₂ in 0.4 mL PEDOT:PSS. Then, TiO₂ was dispersed ultrasonically for 20 minutes. Further, the solution was kept under stirring for 1–2 hour to get homogenous composite solution. Composite TiO₂-PEDOT:PSS pastes were coated onto a FTO (Teknoma, Turkey, $R_s < 10 \Omega/\text{cm}^2$) using a glass rod and dried at 85 °C. Thickness of films was measured ≈20 μm except NR100 (≈30 μm) by Mitutoyo Digimatic Outside Micrometer (MDC-25SB, Japan). For a comparison, platinum electrode was prepared by spray coating from 0.01 M chloroplatinic acid hydrate (H₂PtCl₆·xH₂O) (Sigma-Aldrich, USA) solution in isopropanol (Merck, Germany) and subsequently by sintering at 450 °C for 30 min. In addition, the drop casting technique has been used to deposit pristine the PEDOT:PSS film.

2.3. Characterization

X-ray diffraction spectrometer (Bruker™ D8 X-Ray Diffractometer, Germany) was employed to characterize the crystalline structure of TiO₂/PEDOT:PSS composite electrodes. FTIR measurements of composite films were performed using Perkin-Elmer (USA) FTIR-ATR system. Raman measurements were carried out by using Thermo DXR Raman (Massachusetts, USA) with wavelength 780 and 532 nm. The morphologies of the counter electrodes were evaluated by field emission scanning electron microscopy (SEM, FEI-QUANTA FEG 450, USA). The conductivity measurements were performed with the four-point probe technique at the room temperature. A Lucas Labs four-point probe resistivity stand (S-302-4) with a Signatone four-point probe head (SP4-40-085-TFS) was used to make electrical contact with the pellet. Constant current (microamperes) was ap-

plied between external probes using a Keithley 2400 (Ohio, USA) programmable current source, while the resulting voltage was measured between two central probes with a Keithley 2000 multimeter. The film catalytic activity towards to I_3^-/I^- redox couple was measured by cyclic voltammetry (CV) in a three compartment cell at a scan rate of 20 mV/s in 10 mM lithium iodide (LiI), 1 mM iodine (I_2) and 0.1 M lithium perchlorate ($LiClO_4$) in acetonitrile (ACN) solution (Gamry REF 600, USA). TiO_2 -PEDOT:PSS/FTO electrodes as working, a platinum wire as counter and a silver wire as a pseudo reference electrode were used. Surface area of the composite films was measured by Costech Instruments Sorptometer (USA) 1042. The electro-active polymer area was investigated by CV in 5 mM Ferrocene and 0.1 M sodium perchlorate ($NaClO_4$)–ACN solution in a three compartment cell at a scan rate of 25, 50, 100, 150, 200 and 250 mV/s. Electrochemical impedance spectra (Gamry REF 600, USA) were measured by using a symmetric sandwich-type configuration to understand the charge transfer process at the interface between the electrolyte and the counter electrode frequency varied from 0.01 Hz to 100 kHz with an AC amplitude 10 mV. For EIS measurement, a solution which contained 0.5 M LiI, 0.05 M I_2 and 0.5 M 4-tert-Butylpyridine (TBP) in ACN was prepared. Spectra were analyzed by using ZSimp Win version 3.1 software.

3. Results and discussion

3.1. Spectroscopic characterization

FTIR spectra of both pristine PEDOT:PSS and TiO_2 -PEDOT:PSS composite films were shown in Figure 1. It can be seen that the FTIR spectrum of pristine PEDOT:PSS exhibits characteristic peaks at around 1185, 1079 cm^{-1} which may be assigned to C–O–C bond. Peak at 1036 cm^{-1} belongs to O–S–O vibration of sulfonic acid group of PEDOT:PSS. For the composite films in which TiO_2 were dispersed in PEDOT:PSS, the characteristic peaks of PEDOT:PSS can be seen for all samples. Moreover, increasing in absorbance between 900–500 cm^{-1} was obtained after the incorporation of TiO_2 which may belongs to Ti–O and O–Ti–O bonds vibration [24].

Figure 2 shows Raman spectra of PEDOT:PSS and PEDOT:PSS- TiO_2 composite electrodes. It can be seen that all composite samples possess crystal structure of anatase after TiO_2 incorporation. The characteristic peaks were observed at 150, 396, 510

Figure 1. FTIR spectrum of pristine PEDOT:PSS film and composite films

Figure 2. Raman spectrum of a) composite films, b) pristine PEDOT:PSS

and 630 cm^{-1} [3]. As expected, these peaks didn't appear for pure PEDOT:PSS. In addition, the band at 1425 cm^{-1} , which belongs to the stretching vibration of $C_\alpha = C_\beta$ on the five member ring of PEDOT were obtained for all composite samples and PEDOT:PSS [25].

Crystal structure of PEDOT:PSS and TiO_2 -PEDOT:PSS powders were determined by XRD and exhibited in Figure 3. Only one broad peak at around 26° was observed for the PEDOT:PSS powder which was related to its poor crystalline structure and this peak was shifted to 30° after combined with TiO_2 may be due to weak physical interaction between TiO_2 and PEDOT:PSS. In contrast, XRD patterns of TiO_2 NP, TiO_2 NR and all TiO_2 -PEDOT:PSS composite powders exhibited same strong diffraction peaks. These peaks can be assigned to the (101), (004), (200), (105), (211), (204) and (215) crystallographic planes of tetragonal anatase phase TiO_2 [26, 27]. Rutile phase wasn't observed in the composites. Moreover, no major effect of PEDOT:PSS on TiO_2 crystal structure was obtained. Interestingly, decreasing in peak intensity at 25° was obtained with increasing amount of TiO_2 NR (NR100) in the composite powders. This is because during the ball milling process nanofibers were distorted in order to produce

nanorods. Hence peak intensity decreased depends on TiO_2 nanorods ratio. XRD, Raman and FTIR measurements verified presence of TiO_2 nanostructures in the composite films.

3.2. Morphological and surface area analysis

Figure 4 shows the low and high magnification SEM images of TiO_2 -PEDOT:PSS composite films on FTO substrates. It was seen that the surface of NR0 is very rough (agglomerated) and porous which is good for catalytic reduction of I_3^- in comparison to PEDOT:PSS and NR100 composite films. PEDOT:PSS film has very smooth surface. The surface roughness of composite films was also found to vary with TiO_2 NRs to TiO_2 NPs ratio. According to high magnification images, composite films with decreased TiO_2 nanoparticles loading showed less cracks in the films. As known, film thickness affects the film active area, film catalytic activity and film impedance. Therefore, the film thickness of composite electrodes were determined with using SEM cross-section images (Figure 5) and micrometer. Image J program was used to measure the film thickness. Micrographs were taken from 3–4 different regions and the average thickness were calculated and listed in Table 1. As can be seen in Table 1, the average film thicknesses of NR0, NR25 and NR50 were found to be almost same and NR100 showed higher film thickness for both methods. It was expected because of the dimension of TiO_2 NRs. In addition, it was noted that the film thicknesses were found to be higher by micrometer as compared to cross-section methods. We believe that results obtained from micrometer measurements were more reliable than cross-section measurements because it was a direct method. Surface area measurements (BET) of composite films were compatible with SEM images. Table 1 represents surface area results of pure PEDOT:PSS, pure TiO_2 NPs, pure TiO_2 NRs and composite films. The surface area decreases with increasing TiO_2

Figure 3. XRD patterns of PEDOT:PSS, TiO_2 NP, TiO_2 NR and TiO_2 -PEDOT:PSS powders (a). High magnification of PEDOT:PSS, TiO_2 NP, TiO_2 NR diffractions (b).

Table 1. Surface area and thickness of PEDOT:PSS, TiO_2 NPs, TiO_2 NRs and composite electrodes

Sample name	Surface area [m^2/g]	Average thickness by SEM [μm]	Average thickness by micrometer [μm]
TiO_2 NP	50.95	–	–
TiO_2 NR	21.59	–	–
NR0	50.08	4.0	19
NR25	–	4.1	21
NR50	36.71	3.5	22
NR100	19.03	7.0	30
PEDOT:PSS	0.13 [28]	6.7	5

Figure 4. SEM images of PEDOT:PSS and composite electrodes, a) NR0, b) NR25, c) NR50, d) NR100, e) NR0 (high magnified), f) PEDOT:PSS

NRs loading. The surface area of NR0 was almost the same as pure TiO_2 NPs sample. The same relation was found for NR100 and TiO_2 NRs samples which means

that there is no contribution of PEDOT:PSS due to its low surface area ($0.13 \text{ m}^2/\text{g}$) to the surface areas of composite films. These results show that these TiO_2

Figure 5. Cross-section view of PEDOT:PSS and composite electrodes, a) NR0, b) NR25, c) NR50, d) NR100, e) PEDOT:PSS

nanorods or nanoparticles dispersed in PEDOT:PSS, forming a network structure, are beneficial for electron conduction [20].

3.3. Electrochemical analysis of composite electrodes

Figure 6a–6e exhibits the current density versus applied voltage of the PEDOT:PSS and composite electrodes at different scan rates in the ferrocene solution. It can be seen that current density increases with scanning rate. The current density (I_p) coming from these graphs versus the square root of the scanning rate ($v^{1/2}$) curves and their fits of the PEDOT: PSS and

composite films were shown in Figure 6f. All curves obeyed the Randles-Sevcik equation (Equation (1)):

$$I_p = 2.69 \cdot 10^5 n^{3/2} A D^{1/2} C v^{1/2} \quad (1)$$

where n is the electron number, A is the surface area [cm^2], D is the diffusion coefficient [cm^2/s] and C is the concentration [mol/cm^3]. The linearship between I_p and $v^{1/2}$ indicates the diffusion limitation of the redox reaction on the electrodes. This phenomenon shows the adsorption of ferrocene species is little affected by the redox reaction at the PEDOT:PSS and PEDOT:PSS-TiO₂ electrodes surface under these

Figure 6. CV curves of PEDOT:PSS (a) and composite films (b–e) at different scan rates in the ferrocene solution. Curves and fitting curves of current density of ferrocene versus the square root of scan rate for all samples (f).

conditions and this also suggest that no specific interaction between Fc/Fc^+ redox couple and PEDOT:PSS, PEDOT:PSS- TiO_2 electrodes [29]. During measurements, same polymer and same solution medium were used therefore n , C and D values in the Randles-Sevcik equation should be the same. This assumes that TiO_2 doesn't undergo oxidation and reduction with ferrocene. Thus, the slope of the curves relates only to the film electro-active area [17]. The slopes of the curves were found 3.02 (PEDOT:PSS), 10.1 (NR0), 7.96 (NR25), 8.48 (NR50), 9.05 (NR100), re-

spectively. The slope values of composite films were found to be higher than that of the pure PEDOT:PSS film. The increase in the slope values of composite films supports the enlargement of their electro-active areas. Interestingly, according to BET measurements, the surface area of NR0 is two times higher than that of NR100 but they have almost the same slope values which are related to the electro-active surface area. The reason for this distinction is that the BET measurement, performed in the gas phase, determines area based on specific chemically reactive sur-

Table 2. Conductivity values of PEDOT:PSS and composite electrodes

	PEDOT:PSS	NR0	NR25	NR50	NR100
Conductivity [S/cm]	$1.09 \cdot 10^{-3}$	$2.91 \cdot 10^{-4}$	$3.63 \cdot 10^{-4}$	$1.75 \cdot 10^{-4}$	$1.01 \cdot 10^{-4}$

face states. The electrochemical method determines the area which the ferrocene ions can reach and where the electron transfer is a facile process [30]. It is also known that one dimensional nanostructures such as nanorods improve the electron transport process therefore electro-active area of NR100 may be almost the same as NR0 [31]. The electrical conductivity of the composite electrodes can be used to understand this situation (Table 2). As can be shown in Table 2, the conductivity of PEDOT:PSS (10^{-3} S/cm) decreased 10 times after combination with TiO_2 nanostructures as expected. Although NR100 showed smallest values, similar conductivity (10^{-4} S/cm) values were obtained for all composite electrodes. These results can be another explanation why all composite electrodes have similar electro-active area.

CV graphs of the PEDOT:PSS, TiO_2 -PEDOT:PSS composite counter electrodes and the Pt electrode towards to I_3^-/I^- redox couple were presented in Figure 7. Except PEDOT:PSS, the Pt and TiO_2 -PEDOT:PSS composite electrodes showed two pairs of similar redox peaks. The left reduction peaks labelled as $\oplus$ are vital for its operation in DSSC and are associated with the reduction of triiodide ($\text{I}_3^- + 2\text{e}^- \rightarrow 3\text{I}^-$). The right peaks labelled $\star$ correspond to $3\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}_3^-$ and are unimportant for the performance of DSSC [32]. The main task of the counter electrodes in DSSC is to catalyse the reduction of I_3^- to I^- so the characteristic of the left pair are our focus [6, 14]. The TiO_2 based counter electrodes exhibited higher peak current density than Pt and PEDOT:PSS counter electrodes which suggests a faster reaction rate of I_3^- reduction on the TiO_2 -PEDOT:PSS composite films, thus a higher electro-catalytic activity of TiO_2 -PEDOT:PSS counter electrodes. In addition, comparing the reduction peak positions, the pure PEDOT:PSS counter electrode has higher reduction voltages (≈ 0.8 V) than the TiO_2 -PEDOT:PSS and Pt counter electrodes (≈ 0.67 V). Decreasing in reduction peak potential after TiO_2 addition into the PEDOT:PSS depends on enlargement of the film active area or lower film resistance [17]. In order to optimize the electrocatalytic preformances of conductive polymers based counter electrodes, their specific areas and conductivity are maximized [33]. Adding TiO_2 into

the PEDOT:PSS provides larger specific surface areas with more exposed active sites for enhancing catalytic activity of composite electrodes [33]. These results were supported with BET and electro-active measurements as expected. Compare to pure PEDOT:PSS, all composite electrodes showed higher surface area. The influence of the contents of TiO_2 NRs on the catalytic activity of TiO_2 -PEDOT:PSS counter electrodes also were shown in Figure 7. NR100 showed highest current density (not very much) compare to another counter electrodes but actually almost same current densities were obtained with increasing of TiO_2 NRs contents. The current densities of composite electrodes varied between 1.5–2 mA/cm^2 . These results correspond with the works by Shi and Ho who obtained similar current densities (1–3 mA/cm^2) with using acid treated PEDOT:PSS-rGO (reduced graphene oxide) and PEDOT:PSS- TiS_2 electrodes under comparable conditions [34–36]. As explained above, although NR0 has highest surface area according to BET measurement, all composited counter electrodes have almost same electro-active surface area. It is obvious that electro-active area is more relevant parameter than surface area, therefore no too much differences were obtained for reduction current density of I_3^- .

In order to understand the electrochemical characteristics of PEDOT:PSS and TiO_2 -PEDOT:PSS composite electrodes, EIS measurements were carried out. For measurement, the symmetrical TiO_2 -PEDOT:

Figure 7. CV curves of Pt, PEDOT:PSS and TiO_2 -PEDOT:PSS composite electrodes according to I_3^-/I^- redox couple. Symbol $\oplus$ relates with I_3^-/I^- reduction reaction and symbol $\star$ relates with I_2/I_3^- .

PSS/ I_3^-/I^- /TiO₂-PEDOT:PSS were made by assembling two identical TiO₂-PEDOT:PSS (or PEDOT:PSS) on each side. Normally, these electrodes were separated by using hot melt spacer or Surlyn film but in this measurement distance between two symmetrical electrodes was kept constant (1 cm). This cell configuration can be used in order to eliminate the influence of the photoanode [37, 38]. Figure 8 shows the Nyquist plots of PEDOT:PSS (Figure 8a) and TiO₂ based composite electrodes (Figure 8b). Compared to the literature, similar plots were observed [6, 39]. In order to characterize the Nyquist plots, they have been fitted with the equivalent circuit model (Figure 8c) and the results with percentage errors were summarized in Table 3. R_s is the high frequency intercept on the real axis shows series resistance and R_{ct} is the charge transfer resistance at the counter electrode/electrolyte interface for I_3^-/I^- reaction [40]. R_s and R_{ct} describe the resistance of the substrate and the catalytic activity of the electrodes for reducing I_3^- ions, respectively. The R_{ct} values of TiO₂-PEDOT:PSS composite electrodes ($\approx 3\text{--}5\ \Omega$) were lower than pristine PEDOT:PSS electrode (109 Ω) which indicates less over potential for an electron transferring from the TiO₂-PEDOT:PSS electrodes to electrolyte. More-

over, the R_{ct} values decreased with TiO₂ nanorod incorporation as seen in Table 2, probably due to better electron transport properties of nanorods compared to nanoparticles. Besides the charge transfer resistance, the series resistance of the counter electrode (R_s) is another important parameter which affects fill factor of the DSSC. High series resistance causes low fill factor. Interestingly, we found that NR100 has the lowest sheet resistance and the other composite electrodes have similar values which indicated that TiO₂-PEDOT:PSS electrodes has prominent conductivity. The EIS analyses explained why NR100 sample showed (not too much) higher current density for reducing of I_3^- .

4. Conclusions

TiO₂-PEDOT:PSS nanocomposite electrodes with different morphologies were successfully prepared on FTO glass. We found that the catalytic activity of PEDOT:PSS film was significantly improved after adding TiO₂ nanoparticles/nanorods. Although NR0 has the highest electro-active area, NR100 exhibited almost same (a little higher) catalytic activity for reduction of I_3^- . Moreover, we found that R_{ct} values strongly depends on TiO₂ nanorods content into the

Table 3. The fitted EIS parameters of symmetrical cells

	PEDOT:PSS	NR0	NR25	NR50	NR100
R_s [Ω]	54.76 $\pm$ 0.61%	59.08 $\pm$ 0.26%	55.71 $\pm$ 0.19%	55.34 $\pm$ 0.19%	53.09 $\pm$ 0.38%
R_{ct} [Ω]	108.80 $\pm$ 0.81%	5.67 $\pm$ 3.5%	4.43 $\pm$ 3.03%	3.27 $\pm$ 4.12%	3.24 $\pm$ 7.32%
Chi Squ. (10^{-5})	0.54	2.00	1.90	1.80	1.80

Figure 8. Nyquist plots of the symmetrical cell of PEDOT:PSS (a) and composite electrodes (b). The equivalent circuit model was used to fit experimental datas at the highest frequency (c).

composites and it was decreased by increasing TiO₂ nanorods content. Hence, NR100 electrode exhibited lowest R_{ct} and R_s values. In addition, these results showed that both electro-active area and electron transport properties of a material have a great impact on design of the counter electrodes for DSSC application.

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