

Graphene/polyaniline nanocomposite as platinum-free counter electrode material for dye-sensitized solar cell: its fabrication and photovoltaic performance

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Abstract

In this study, it was aimed to produce graphene/polyaniline nanocomposite thin films as counter electrode materials by PECVD system and to determine the photovoltaic performances of these counter electrodes in dye-sensitized solar cells (DSSCs). Graphene/polyaniline counter electrode (GPCE) material was produced in two different steps. Firstly, a single-layer and multilayer graphene thin films were produced on the fluorine-doped tinoxide (FTO) substrates. Then, polyaniline (PANI) thin films were grown on each graphene thin films using plasma polymerization technique, and eventually the production of the graphene/PANI nanocomposite was completed. The fabricated graphene/PANI nanocomposites were used in place of platinum (Pt)-counter electrode which is widely used in DSSCs and the photovoltaic performance of these counter electrodes was investigated. The DSSCs consisted of titanium dioxide (TiO₂) nanotube photoanode, N719 dye, iodolyte liquid electrolyte, and graphene/PANI nanocomposite counter electrode. I–V measurements were carried out in order to calculated photoconversion efficiency (PCE) and it was found that the these efficiency of GPCEs changed between 0.56 and 1.36% according to the number of graphene layers. The photovoltaic performance of DSSC, consisting of TiO₂ nanotube photoanode and Pt-counter electrode was 1.1%.

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1 Introduction

Recently, dye-sensitized solar cells (DSSCs) have attracted attention due to their low-costs [1] and relatively acceptable efficiency compared to conventional solar cells [2-4]. DSSCs are composed of an electrically conductive oxide layer, a photoanode, an electrolyte, and a counter electrode that catalyzes the electrolyte. DSSCs have a lower cell efficiency (about 10.4%) compared to other solar cells, but are also considered more favorable in terms of production cost [5]. In recent years, many studies have been conducted on photoanodes and counter electrodes, which are among the main components of DSSCs, and have an important role in solar cell efficiency [6-10]. In particular, the current costs of the Pt electrode, which are widely used as a counter electrode in DSSCs, necessitated the development of alternative electrode materials. The most important aim of the studies on alternative counter electrode production is not only to increase solar cell efficiency, but also to develop low-cost material compared to the conventional counter electrode. Nowadays, many new generation materials have been developed for the alternative counter electrode.

Polymers [11–16], metal and polymer nanocomposites [17], and recently carbon-based materials [6, 18-25] are used as alternative counter electrodes [26]. Hong et al. [6] produced graphene/PEDOT-PSS composites as an alternative to Pt counter electrodes using spin coating technique on indium tin oxide (ITO) substrates and reported the photoconversion efficiency of the device obtained by adapting these composites to DSSC. The power conversion efficiency of this composite electrode material with optical transmittance of 80% was calculated to be 4.5%, and the power conversion efficiency of DSSC device produced using platinum counter electrode under the same experimental conditions was measured as 6.3%. Zhang et al.[8] developed carbonbased vertically oriented (3D) graphene nanosheet instead of the counter electrode material traditionally used for DSSC applications. They reported that the 3D graphene counter electrode provided a significant improvement in the photovoltaic performance of the DSSC device. The power conversion efficiency of DSSC produced by using TiO₂ nanotube as photoanode material and 3D graphene as the counter electrode has been determined as 6.81%. In particular, 3D graphene, an allotrope of carbon, has been great interest due to its large surface area, great electrical conductivity and excellent electrocatalytic properties [27–31]. Therefore, it is guite natural that graphene is considered an alternative material for the counter electrodes of DSSCs. Graphene and its nanocomposites, which are produced electrochemically, are still not at the desired performance as counter electrodes. The graphene-based counter electrode material has high electrical conductivity but has no high degree of electrocatalytic activity with the electrolyte. High catalytic activity can be achieved by functionalizing the graphene using polymer with some functional groups that are compatible with the electrolyte. Other studies in the literature have also reported the importance of the possible alternative counter electrode material of graphene/polymer nanocomposites [32, 33]. It is also understood from these studies that the polymer is in good agreement with the electrolyte due to its functional groups. In this study, it is aimed to produce nanocomposite counter electrodes by obtaining graphene nanosheet with high charge transfer rate, and PANI thin films with high electrocatalytic activity with iodide which is used as an electrolyte. Moreover, it is aimed to determine the effect of numbers of graphene layers on power efficiency of nanocomposite produced. Graphene nanosheet with various number of layers was produced on copper (Cu) metal catalyst using chemical vapor deposition (CVD) technique. On the other hand, PANI thin films were grown on top of the graphene nanosheet with the various number of layers by the help of the plasma polymerization technique.

2 Materials and method

2.1 Materials

Plasma-enhanced chemical vapor deposition (PECVD) system, which is used in graphene growth process, was established by Nanovak company. Gases such as CH_4 , H_2 , and Ar were used as precursor gases in the graphene growth process. Acetone, propanol, and ethanol were used to remove both the impurities on the Cu foil surfaces and any polymeric residues in the graphene transfer process, and these alcohols were commercially purchased from Sigma-Aldrich. The copper foils used as the substrate were 25 micron thickness and 99.8% purity, and were available from Alfa-Aesar company.

2.2 Graphene (Gr) growth mechanism

The PECVD system presented in Fig. 1 is a system that can be calibrated for both graphene synthesis and polymer production. In this system, polymerization can be done using plasma-enhanced CVD, and graphene production can be made only by activating the CVD part. In other words, two different methods can be applied with the same device. When plasma is active, polymerization process can be done using the PECVD, and graphene production can also be made only but activating the CVD part. In the other words, two different medhods can be applied by using this system. When the radio frequency (RF) power is active, polymerisation processis carried out using the PECVD technique, and it is not active, graphene thin film can be chemically obtained by CVD technique. Graphene growth mechanism can be summarized as follows: First, the annealing process of the Cu foils used as metal catalysts was performed. These foils were placed in the sample holder compartment of the system and the system was vacuumed with the help of the vacuum pump station. For all experiments, the vacuum was set to 10^{-1} mTorr. When the pressure of the vacuum chamber has reached this pressure, H₂ and Ar gases were precisely sent to the vacuum environment by using gas flow



Fig. 1 Schematic diagram of PECVD system [34]

control units, and the temperature of the vacuum environment was increased from room temperature to 1000 °C using the heater for about 30 min. The annealing of Cu foils process was carried out at this temperature for about 30 min. After the annealing process, while the temperature value was maintained, CH_4 , H_2 , and Ar gases were sent to the vacuum chamber with the help of gas flow control units. The flow rates of CH₄, H₂ and Ar gases were 7 standart cubic centimeters per minute (sccm), 20 sccm, and 10 sccm, respectively, and the growth process was continued for 30 min. After growth process, gas flow of CH₄ were immediately terminated and the temperature of the vacuum environment was rapidly cooled down room temperature. Other samples were also produced similarly, provided that these parameters were the same, such as gas flow rates, growth temperature, and coating time. The number of graphene layers was determined using Raman analysis, and samples that have been confirmed to consist of a single-layer or multi (five) layers, were coded as Gr1 and Gr5, respectively. Others were excluded from this study.

2.3 Transfer process of graphene nanosheets (GNs)

The transfer of GNs to FTO substrates was carried out in two steps, also as stated in our previous study [35]. Firstly, 0.1 M FeCl₃ solution was prepared to remove Cu, then etching was carried out in this solution for about 12 h. After the etching, the graphene thin film was removed from these solution using metal backing material and immersed in distilled water for rinsing. The GNs that were kept in deionized (DI) water for about 10 min were placed on the FTO substrates.

2.4 Production of Graphene/Polyaniline (Gr/PANI) nanocomposites

The plasma polymerization technique was used to produce polymer thin films on FTO/graphene [36–40]. The aniline used as monomer was gradually leaked into the vacuum

environment of the system by means of sensitive valves. After that, polymer deposition process was carried out at room temperature, 15 min of coating time, 20 W RF power and totally 500 mTorr growth pressure by these technique. Since the number of graphene layers was intended to influence the cell efficiency, polymer functionalisation (Gr/PANI nanocomposite) was simultaneously performed both Gr1 and Gr5 films using the above-mentioned coating parameters. Thus, it was aimed to optimize the effect of the polymer on the photoconversion efficiency. As a result, Gr1/PANI and Gr5/PANI nanocomposite production were completed after plasma polymerization process.

2.5 Fabrication of TiO₂ nanotube arrays

TiO₂ thin films with one-dimensional morphological structure were obtained by electrochemical method on Titanium foils (0.25 mm thickness, 99.7% purity from Sigma-Aldrich), as described in Ref. [41]. Titanium foils were cut to dimensions of 1.5×2.5 cm and cleaned by wet cleaning process in acetone, isopropyl alcohol (IPA) and DI water with ultrasonic bath for 30 min, respectively, and then dried with nitrogen gas. Titanium foils and Pt mesh were respectively used as a custom-made electrochemical and cell was filled with an electrolyte solution (ethylene glycol, 0.4% wt NH₄F and 5% wt DI water). For each TiO_2 thin film, an anodization voltage of 40 V was applied for 2 h. After electrochemical growth, as-grown TiO₂ film was cleaned in methanol with an ultrasonic bath to remove the chemical residuals and then dried with nitrogen gas. Later, to convert from amorphous phase to anatase phase, as-grown TiO₂ nanotube arrays were annealed at 450 °C for 1 h in air ambient. The mechanism of formation of TiO₂ nanotube arrays grown by anodic oxidation method is detailed in previous studies [41–43] (Fig. 2).

The formation of TiO_2 nanotube arrays starts with the electrolysis of water, which reaction can be expressed as:



$$2\mathrm{H}_2\mathrm{O} \to \mathrm{O}_2 + 4e + 4\mathrm{H}^+ \tag{1}$$

Then, electrochemical oxidation on the Titanium substrate forms an oxide film due to the external electric field, also referred to as the barrier layer, which is expressed as following chemical Eqs. (2):

$$Ti + O_2 \rightarrow TiO_2$$
 (2)

Even if the oxide film becomes thicker, pits form on the surface of the film as a result of chemical dissolution caused by F^- ions in the electrolyte:

$$\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow \text{TiF}_6^{2-} + 2\text{H}_2\text{O}$$
 (3)

After a while, the chemical etching process becomes more dominant than the chemical dissolution, and as a result, the pits on the oxide film deepen, leading to the formation of a uniformly and orderly structure.

$$Ti^{4+} + 6F^- \to TiF_6^{2-}$$
 (4)

Finally, an equilibrium state between the chemical dissolution and the electrochemical etching process occurs and does not continue to increase the length of the nanotubes.

2.6 Fabrication of DSSCs

To obtain the photoanodes, TiO₂ nanotube arrays on Titanium foils were soaked in 0.5 mM ethanol solution of Ruthenium (Ru) based N719 dye (Sigma-Aldrich) for a period of 12 h. Gr (untreated single-layer graphene), Gr1/PANI and Gr5/PANI nanostructures grown on the FTO substrates were used as alternative to Pt used as traditionally counter electrode material for DSSC applications. DSSCs were assembled by placing a Surlyn sealant (~60 µm, Solaronix, active cell area 0.196 cm²) between photoanode and counter electrode. Finally, a commercial I_3^-/I^- liquid electrolyte (Solaronix, Hi-30) was injected between the electrodes [41]. A schematic diagram of DSSC cells are presented in Fig. 3.



Fig. 3 DSSC configuration

3 Results and discussion

3.1 Structural properties of TiO₂ nanotube arrays

Structural properties and phase identification of TiO₂ nanotube arrays obtained on Titanium foil by anodization method were investigated using XRD measurements. Figure 4a shows the X-ray diffraction of the annealed TiO₂ nanotube arrays grown under anodization voltage of 40 V for 2 h. From Fig. 4, the diffraction peaks were determined at $2\theta = 25.3^{\circ}$, 37.9° , 38.3° , 48.0° , 53.9° , 55.0° , 62.6° , and 68.8°, corresponding to (101), (004), (112), (200), (105), (211), (204), and (116) crystal planes of polycrystalline anatase phase of TiO₂ respectively. These results are in good agreement with standard data (JCPDS No. 03-065-5714) and from data literature [41, 44]. However, two very small peaks at $2\theta = 27.4^{\circ}$ and 36.2° belonging to rutile phase of TiO_2 were observed, corresponding to planes (110) and (101), respectively (JCPDS No. 01-086-0148). Normally, by annealing, the as-grown TiO₂ nanotube arrays are largely converted from amorphous to anatase phase [41, 45]. The Anatase phase exhibits better photocatalytic properties and more efficiency in photovoltaic devices than the rutile phase [46]. Also, the diffraction peaks observed at about 35.1°, 38.4°, 40.1°, 53.0°, and 62.9° derived from the Ti substrate were indexed as (100), (002), (101), (102), and (110), respectively (JCPDS No. 03-065-3362).

3.2 Morphological properties of TiO₂ nanotube arrays

Figure 4b–d show the SEM images of the top view and cross-section of TiO_2 nanotube arrays obtained under anodization voltage of 40 V for 2 h. As can be seen in this figure (Fig. 4d), TiO_2 film showed highly ordered and uniform nanotubes with an average inner and outer diameter of 90.3 nm and 121.5 nm, respectively. Also, the average length of nanotubes was measured as around 3.6 µm from the cross-sectional SEM image (Fig. 4c). In this study, the morphological properties of the TiO₂ nanotube arrays grown by anodization method are in good agreement with the previous studies in the literature [42, 44, 47–51]

3.3 Raman analyses of GNs

Structural properties of GNs grown on Cu foils used as metal catalysts by CVD technique were determined by Raman spectroscopy. It is generally represented by 3 basic peaks, D, G, and 2D peaks in the Raman spectrum of graphene. The Raman spectra of GNs are presented in Fig. 5. This spectrum shows that the above-mentioned peaks of the thin films produced are different from each



Fig. 4 a XRD patterns of TiO_2 nanotube arrays derived at 40 V anodization voltage. **b** SEM image of TiO_2 nanotube arrays. **c** Cross-section image for determination of lengths of TiO_2 nanotube arrays. **d** SEM image for determination of radius of TiO_2 nanotube arrays



Fig. 5 Raman spectra of the GNs

other. This difference is due to the intensity and wavelength of the peaks. It is known that the graphene being single-layer or multilayer is determined by the ratio of the intensity of these peaks to each other [52–54]. If the intensity ratio of 2D peak to G peak $(I_{2D}/I_G \text{ is } 2 \text{ or more})$, the structure is stated to be single-layer. The lack of the defect-related D peak and the $-I_{2D}/I_G$ intensity ratio of ~3 indicates that a high-quality and single-layer graphene (SLG) was obtained [55]. As this ratio decreases, the number of layers tends to increase. It was found that the I_{2D}/I_G intensity ratio of the Gr1-coded sample was greater than 2, and thus it was found that this sample was single-layer. Similarly, intensity ratios of Gr2-, Gr3-, Gr4-, and Gr5coded graphene samples were found to be 1.5, 1.2, 0.9, and 0.6, respectively. Therefore, these thin films are believed to be 2 and more layered.

3.4 UV-Vis analyses of GNs

The transmittance spectra of GNs obtained by UV–Visible analyses were given in Fig. 6. The transmittance of these GNs was compared for a wavelength of 550 nm. These values were found to be in the range of 97.6–86.6%. Optical transmittance of those having single-layer of graphene thin films is known as 97.6% in the literature [56]. As the number of layers increases, the optical transmittance of the



Fig. 6 Transmittance spectra of GNs

films linearly decreases. Each layer increase corresponds to a decrease of 2.4% in the optical transmittance of these films. Thus, films having single-layer and multilayer were used and the effect of this number of layers on the cell efficiency of the obtained counter electrode material was investigated. The optical transmittance of the multilayer samsple, encoded as Gr5, was about 86.6%.

3.5 Chemical and morphological analyses of PANI film

The chemical and morphological properties of the PANI thin films grown on FTO/graphene nanolayers using plasma polymerization technique were examined by FTIR and AFM. The FTIR spectrum is presented in Fig. 7. This



Fig. 7 FTIR spectra of aniline and PANI film

spectrum presents both the aniline used as the monomer and the spectra of the PANI film derived from this monomer. The FTIR spectrum confirmed by the presence of N-H stretching at about 3540 cm⁻¹, C-H stretching at 2920 cm⁻¹, N-H bending at 1320 cm⁻¹, and C-C bending at 1275 cm⁻¹ of the PANI film. Apart from these functional groups, only functional groups detected in the fingerprint region of the monomer material could not be detected in the spectra of PANI films. This situation was attributed to the presence of RF power applied between the electrodes during the polymerization process. The surface morphological properties of the PANI film such as average roughness (R_a) and maximum peak height (R_{max}), were determined by AFM and were given in Fig. 8 with UV-Vis spectra. These AFM analyses confirm that thin films have a homogeneous and non-porous structure. Ra and Rmax were 0.19 nm and 1.80 nm, respectively. The very homogeneous and smooth surface of the produced polymer film facilitates electrolyte compatibility with the counter electrode, but non-porous morphology causes low surface area, which is not very desirable for DSSC applications.

3.6 Photovoltaic parameters of graphene-based counter electrodes

Production of DSSC was completed using TiO_2 nanotube photoanode, N719 dye, commercial Γ_3/Γ electrolyte solution and untreated Gr, Gr1/PANI, and Gr5/PANI, respectively, as electrode material. Pt-counter electrode was compared with Gr-based electrodes produced as alternative electrode materials in our study [41]. For DSSCs, the photovoltaic performance of untreated Gr, Gr1/PANI, and Gr5/PANI



Fig.8 a Transmittance spectra of Gr/PANI films determined using UV–Vis spectroscopy. b AFM analysis for morphological properties of PANI film



Fig.9 J–V curves of untreated Gr, Gr1/PANI, and Gr5/PANI electrode-based DSSCs $% \left({{{\rm{DSSCs}}}} \right) = {{\rm{TOSCs}}} \right)$

 Table 1
 Photoconversion efficiency parameters of DSSCs based on counter electrodes derived from graphene-based composites

Sample	Jsc (mA/cm ²)	Voc (V)	FF (%)	η (%)
Gr	0.45	0.59	27	0.03
Gr1/PANI	7.94	0.73	46	1.36
Gr5/PANI	2.77	0.72	28	0.56
Pt [41]	4.60	0.44	53	1.10

counter electrodes is measured by determining the J-V characteristic curve. In this study, illumination was carried out on the counter electrode side. The J-V curves determined for each electrode are presented in Fig. 9 and discussed in detail. The photovoltaic performance of the Gr-based electrode was relatively poor compared to others graphene-based electrodes and the Pt electrode in this study. Although the open circuit voltage (Voc) values of all electrode materials appear to be close to each other on the J-V graph, the photovoltaic performance of the Gr electrode is relatively poor due to the low electrocatalitic activity sites. Furthermore, the short-circuit current density (Jsc) value of the Gr-based electrode material is very low. But efficiencies of Gr/PANI composite electrodes varied considerably. The Gr1/PANI counter electrode have Jsc of 7.94 mA/cm², Voc of 0.730 V, fill factor (FF) of 46% and the PCE of 1.36%. These values of Gr5/PANI electrode material were 2.77 mA/cm², 0.720 V, 28% and 0.56%, respectively. The PCE value (η) of the reference electrode, Pt, was determined as 1.1 in previous studies [41] (Table 1).

The PCE values (η) of the Gr/PANI nanocomposite electrodes were found to be significant increase in efficiency compared to the Pt electrode. However, the η value of the

pure Gr electrode is too low to compare with the Pt electrode. When its electrochemical catalytic activity is compared to that of Gr-based composites, it is understood that the functionalization owing to polymerization process is a more important factor than the number of graphene layers. As shown in Fig. 9, the Voc and Jsc values of the Gr1/PANI electrode correspond to η value, which is relatively similar to Pt electrode due to its low FF value, although much better than these values of the reference electrode. Furthermore, the relatively low these value of the Gr electrode is attributed to the low surface area and charge transfer mechanism of this electrode. The functionalization of the Gr surface with PANI comparetively enhanced this low surface area problem and resulted in higher Jsc for the same Voc. Likewise, for Gr/PANI electrodes, some functional groups of PANI have better catalysis with the electrolyte. As a result, the electron transfer of the electrode improves. However, in the study for the reference electrode, similarly the nanotube radius for TiO₂ nanotube was determined to be approximately 98 nm for an anodization voltage (40 V). In addition, the length of the nanotube is 4.6 μ m. Although similar TiO₂ nanotube photoanode was used for DSSC manufactured for the reference electrode, the diameter and length of these TiO_2 nanotubes also had a significant contribution to the η . Because the larger diameter and length of the nanotube, the active area of the dye attached to or adhered to these nanotubes increases, and hence the number of injected electrons increases. The diameters and lengths of TiO₂ nanotubes used in our study were 90.3 nm and 3.2 µm, respectively. Precisely calibration of the diameters and lengths of these TiO₂ nanotubes is an important factor for comparing the η values of the graphene/PANI nanocomposite electrode and the Pt electrode. Although the nanotube diameters and lengths of the TiO₂ nanotubes used in this study were smaller than those used for the Pt electrode, it still showed very good cell efficiency. When this nanotube optimization is achieved, we believe that the η value of our graphenebased electrode will be even better. The better cell efficiency of the Gr1/PANI nanocomposite electrode compared to the Gr5/PANI can be explained as follows: The opaque TiO_2 nanotubes produced by the anodization technique make it difficult for the sunlight on these photoanodes to stimulate the dye molecules. Thus, in this process, the light has to penetrate the DSSC via the counter electrode. In this case, the optical transmittance of the counter electrode on which the light falls, plays an important role. The high optical transmittance of the electrode makes it easier for the light falling on the FTO to pass through the counter electrode to stimulate the dye molecules. That is, it is natura for the Gr1/ PANI-coded counter electrode to provide better efficiency than Gr5/PANI-coded. However, the fact that the PCE of the untreated Gr counter electrode, which is still single-layer, is much lower than that of other composite electrodes, is not

attributable to the number of layers but to the functional groups of the polymer. Because the number of layers of the electrode with Gr code is set to 1. The number of layers of graphene is not only a sufficient factor, but it also needs to have a good catalytic activity with the electrolyte. Therefore, polymer-based counter electrodes offer better efficiency due to their functional groups compared to untreated Gr counter electrode. Electrochemical Impedance Spectroscopy (EIS) was used to compare the electrochemical catalytic activities of the alternative counter electrodes to the Pt electrode. EIS measurements were performed under sunlight illumination (100 mW/cm²) with AM 1.5 filter and 10 mV AC signal over the frequency range from 10 mHz to 100 kHz. Figure 10 shows Nyquist plots of untreated Gr, Gr1/PANI, and Gr5/PANI electrodes and an equivalent circuit model of the produced DSSCs (inset to Fig. 10). In these graphs, the first and second semicircles generally correspond to the charge transfer resistances at the counter electrode (Rct₁) and TiO₂/ dye/electrolyte (Rct₂), respectively.

As can be seen from the Fig. 10, charge transfer resistance of the untreated Gr (only single-layer) is quite high. This situation is due to the fact that although the untreated Gr has a very high in-plane charge transfer, the basal plane substantially restricts the charge transfer between the electrolyte and itself. Furthermore, its sharp atomic edges and perfect crystal structure are insufficient for the number of electrocatalytic active sites required for the reduction reactions of I_3^-/I^- [57–59]. However, the charge transfer resistances of the Gr5/PANI and Gr1/PANI counter electrodes are significantly reduced compared to untreated Gr counter electrode. Due to the synergistic effect resulting from the functionalization of CVD-grown graphene, charge transfer mobility and electrocatalytic activity have been enhanced for I_3^{-}/I^{-} reduction [60]. The catalytic activity of the material can be improved due to generally oxygen-containing functional groups (-COOH, OH-, etc.), specific large surface area and more active defective sites for triiodide reduction [60]. However, the charge transfer resistance of the Gr1/PANI is higher than that of the Pt electrode. Although the Jsc and PCE of the Gr1/PANI are higher than those of the Pt electrode, its charge transfer resistance is higher than that of the Pt electrode. That is, the electron transfer frequency for the Pt electrode/electrolyte interface (high frequency band) is higher than that of the Gr1/PANI electrode (medium frequency band). However, the current density in total for the Gr1/PANI electrode may be higher than of the Pt electrode, since the dense and smooth morphology of the Pt film limits the penetration and diffusion of iodide and triode ions into the depths [61]. The functionalized graphene-based counter electrode has been found to have higher cell efficiency than the conventional Pt electrode, and this is considered an important step for future research of graphene-based counter electrodes. It is possible to further increase the cell efficiency of the alternative counter electrode produced in this study. Namely, by synthesizing 3D graphene instead of 2D graphene, we can both increase the surface area and develop an alternative material with low charge transfer resistance. However, it should be noted that there is a negative effect regarding photoanode as well, in DSSC applications, photoanode material is generally used as a transparent window, but we used electrochemically produced TiO₂ nanotubes from titanium foil that we produced in this study. Therefore, this optically non-transparent photoanode material has significantly restricted our study because it makes it imperative

Fig. 10 Nyquist plots of untreated Gr, and Gr/PANI counter electrode-based DSSCs and equivalent circuit model (inset)



that sunlight is dropped over the counter electrode material. In future studies, it can be aimed to calculate the cell efficiency of graphene-based counter electrodes by producing optically transparent photoanode. We believe that if such a study is carried out, much higher cell efficiencies can be achieved as a result. Similarly, the improvement of the diameter and length of TiO_2 nanotubes electrochemically produced within the scope of this study can again contribute to cell efficiency by increasing the concentration of dye molecules.

4 Conclusion

In this study, untreated Gr and polymer functionalized Gr/ PANI nanocomposites materials were produced in DSSC as an alternative to Pt electrode. The PCE of 1.1% detected in the DSSC using conventional electrode material was compared to that of untreated Gr and polymer functionalized-Gr electrodes. The PCE of polymer functionalized graphene electrode materials were found to be higher cell efficiency that of untreated Gr, and reasonably improves the charge transfer resintances. Additionally, photovoltaic performance of DSSC with Gr1/PANI counter electrode was better that of Gr5/PANI. Although the nanotube radii and lengths of the TiO₂ nanotubes used in this study were approximately smaller than those used for the Pt reference electrode, it indicated a better PCE value for that of Gr1/ PANI nanocomposite. The photoconversion efficiency for untreated Gr, Gr1/PANI, and Gr5/PANI was 0.03, 1.36, and 0.56, respectively. These results proved that the PANI functionalized Gr electrodes could be an alternative to Pt electrode. It was also understood that polymer functionalized process as well as the number of graphene layers had an important role on the photovoltaic performans of DSSC.

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