

SYNTHESIS AND CHARACTERIZATION OF GOLD NANOPARTICLES DECORATED POLY(3,4-ETHYLENEDIOXYTHIOPHENE) ON GRAPHENE FOR PROSPECTIVE CATHODE CATALYST IN FUEL CELLS

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Abstract: Gold nanoparticles decorated poly(3,4-ethylenedioxythiophene) doped on reduced graphene oxide (AuNPs/PEDOT/rGO) was synthesized and characterized as an efficient cathode catalyst in fuel cells. This electrocatalyst was then deposited on the glassy carbon electrode by drop casting technique as a modified cathode electrode. Then, the composition, structural determination and morphology of electrocatalyst were characterized using Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). FTIR spectrum showed the PEDOT is successfully doped on rGO sheet from the formation of C-O-C stretching of ethylene dioxy group, C-S stretching of thiophene ring and C=C stretching belongs to quinodial structure. Meanwhile, the XRD pattern revealed peak Au (111), Au(200), Au(220), Au(311), Au(222) and C(002), signifying the formation of Au on PEDOT/rGO sheets. These results reflect that the formation of AuNPs and PEDOT on rGO was successfully synthesized. The electrochemical behavior of modified electrode was carried out using cyclic voltammetry (CV) technique and electrochemical impedance spectroscopy (EIS) in 1.0 M KCl with reference 5.0 mM $K_4[Fe(CN)_6]$ redox system. The CV result demonstrated that AuNPs/PEDOT/rGO/GCE has a highest peak current (0.18 mA) and smaller peak separation (59 mV) compared to other modified electrodes, represent that AuNPs/PEDOT/rGO/GCE is controlled by electron transfer and good reversibility of electrode process. EIS result reflects that AuNPs/PEDOT/rGO/GCE has a smaller charge transfer resistance (4Ω) indicating the electrode has a good electron transfer. Thus, AuNPs/PEDOT/rGO composite has a potential as a new cathode catalyst to replace a commercial Pt electrode for fuel cell in order to eliminate the pollution from burning of fossil fuel.

KEYWORDS: graphene materials, electrocatalyst, glassy carbon electrode, modified electrode, fuel cells.

Introduction

Over the past few years, the increasing demand in clean and sustainable energy receives a great attention on the development of energy storage and green technology. Energy storage has been widely used in many applications and technologies, where it can be stored in electrical, chemical and kinetic media (Chai & Isa, 2017). Fuel cells (FCs) are expected to become a clean technology that has an ability to produce electricity and heat without produce any combustion. However, one of the biggest challenges in developing of FCs is the stability and high cost of platinum (Pt) electrocatalyst at cathode electrode. Recent works have been focused on the development of new electrocatalyst to replace Pt-based electrode (Alexeyeva & Tammeveski, 2008; Jeong *et al.*,

2012; Choe *et al.*, 2015; Felix *et al.*, 2016).

Graphene-based electrodes are recently attracted as a new electrode materials that widely used in electrochemical application due to its unique properties such as high chemical and thermal stability, high conductivity, high surface area and excellent electron properties (Jiang *et al.*, 2012; Chen *et al.*, 2014; Wang *et al.*, 2014; Şanlı *et al.*, 2016). The chemical oxidation of graphene to graphene oxide (GO) with an existence of large oxygen-functional group such as hydroxyl and epoxy group is a one of most promising way to produce electrical conducting materials in a large-scale production of materials (Zuo *et al.*, 2016).

Extensive studies have been made on the hybridization of metal nanoparticles with

graphene. The attachment of metal nanoparticles on the graphene sheets is considered as a way to enhanced catalytic activity of electrocatalyst (Shervedani & Amini, 2014). Until now, gold nanoparticles (AuNPs) gained attention as useful materials in an electrochemical application. AuNPs is one of stable metals that exhibit excellent catalytic activity toward CO oxidation, methanol oxidation and reduction of oxygen in FCs (Granmayeh *et al.*, 2011). In other hands, gold in the form of nanoparticles has a specific surface area that makes it suitable for use in catalytic reactions (Steven *et al.*, 2016).

In order to avoid the agglomeration of metallic particles on graphene sheets, conducting polymers (CPs) has been regarded as a matrix to dispersed metal nanoparticles which provide sufficient surface area that increase stability of metal nanoparticles in modification of electrode (Jiang *et al.*, 2012). Poly(3,4-ethylenedioxythiophene) (PEDOT) is a one of the best CPs due to its interesting properties including high stability, good conductivity, excellent capacitive behavior and high stability than most other CPs (Groenendaal *et al.*, 2000). Furthermore, it exhibits not only as a good conducting material but also as a good adhesion with other materials that has a great compatibility to form new electrocatalyst with a metal and carbons (Dinesh & Saraswathi, 2016).

In this paper, AuNPs decorated PEDOT functionalized rGO (AuNPs/PEDOT/rGO) as a novel electrocatalyst for cathode electrode in FCs has been successfully fabricated by facile chemical process. The electrochemical behavior of AuNPs/PEDOT/rGO on glassy carbon electrode (GCE) has been demonstrated by cyclic voltammetry (CV) technique and electrochemical impedance spectroscopy (EIS).

Materials and Methods

Chemical and Materials

Graphite powder, chloroauric acid (HAuCl_4), 3,4-ethylenedioxythiophene (EDOT) monomer and sodium borohydride (NaBH_4) were all purchased from Sigma Aldrich, USA, were used as the oxidant and reductant. Ethanol

(95%), potassium ferrocyanide ($\text{K}_4[\text{Fe}(\text{CN})_6]$) and potassium chloride (KCl) were supplied by Hamburg, German while alumina powder was obtained from Bendosen. All the chemicals used were of analytical grade obtained from local commercial suppliers.

Instruments

The physical characteristics of the composites were determined using Scanning Electron Microscopy (SEM, JEOL JSM 6360LA) at the operational voltage of 5 kV, Fourier Transform Infrared Spectroscopy (FTIR, Perkin Elmer Spectrum 1000) in the spectral range of $3500 \text{ cm}^{-1} - 500 \text{ cm}^{-1}$) and X-Ray Diffractometer (XRD, Rigaku MiniFlex II) over a range of 2θ values from 3° to 80° .

Electrochemical measurements were carried out using Potentiostat/Galvanostat Autolab PGSTAT302N complete with the NOVA 1.10 software using three-electrode system. Glassy carbon electrode (BASi, 3.0 mm diameter) modified with or without composite as a working electrode, Ag/AgCl (3.0 M KCl) as a reference electrode and platinum wire was an auxiliary electrode. Electrochemical impedance spectroscopy (EIS) experiments were performed by using Autolab FRA32M controlled fitness of NOVA 1.10 software with the frequency range of 1-10,000 Hz and direct potential set 0.20 V.

Preparation of AuNPs/PEDOT/rGO Composite

GO was synthesized from graphite powder according to modified Hummers method (Hummers & Offeman, 1958). For the preparation of AuNPs/PEDOT/rGO composite, 61.9 μL of EDOT monomer in 25 mL of ethanol solution was mixed into 350 mL of HAuCl_4 under rapid stirring. The mixture was left under stirring for 4 hours at room temperature. Then, 25 mL of GO solution (0.5 mg/mL) was poured into the mixture solution. The Au/PEDOT/GO solution was dispersed by sonication for 2 hours. After that, 27.5 mL of 0.16 M NaBH_4 was slowly added into the mixture solution under rapid stirring. The mixture was kept stirring

for 6 hours. During the process, the AuNPs and GO were reduced to form AuNPs and rGO, simultaneously. Finally, the mixture was washed with ethanol and deionized water repeatedly by centrifugation, and then the resulting product was dried at 60 °C for 12 hours. The product was dispersed in deionized water for the later use. As a comparison, the rGO and PEDOT/rGO were prepared under same condition.

Preparation of Modified Electrode

A bare glassy carbon electrode (GCE) is pre-polished with alumina powder slurry, then rinsed with ethanol, acetone and deionized water for 10 minutes, respectively. GO, rGO, PEDOT/rGO and AuNPs/PEDOT/rGO suspension were prepared by dissolving it in deionized water (1 mg/mL) and were sonicated for 30 minutes until it is homogenous. Then, 10 μ L of each suspension was drop casted on the surface of GCE and allowed it to dry at room temperature. Prior to use, the modified electrode was carefully rinsed with deionized water after each experiment. All the experiment was carried out at room temperature.

Results and Discussion

Fourier Transform Infrared (FTIR) Analysis

FTIR analysis was employed to determine the bonding interaction and vibrational modes in every functional group present before and after

hybridization of synthesized composite. The FTIR spectrum of composites is shown in Figure 1. From the Figure 1a, the GO spectra shows a peak at 1064 cm^{-1} which is attributed to the C-O bond, confirming graphite was successfully oxidize to GO. The peak at 1622 cm^{-1} is assigned to the C=C stretching of alkyne group. While the broad peak at 3390 cm^{-1} shows the formation of O-H stretching contributed by adsorption of water in GO sheets. The characteristic peak at 1717 cm^{-1} corresponding to the C=O stretching of carbonyl and carboxylic acid group. Meanwhile, rGO spectra in Figure 1b shows the decreasing of intensity for O-H stretching, C=O stretching and C-O stretching, indicating the GO was successfully reduced to rGO (Konios *et al.*, 2014).

For the FTIR spectrum of PEDOT/rGO (Figure 1c), the vibrational bond at 1504 cm^{-1} and 1330 cm^{-1} were due to the formation of C=C and C-C of the quinodial structure of thiophene ring, respectively. The absorption peak at 1199 cm^{-1} and 1087 cm^{-1} are assigned to the C-O-C stretching in the ethylene dioxy group. The C-S bond in thiophene ring is appeared at the spectrum of 839 cm^{-1} and 691 cm^{-1} . The series of spectrum reveal that PEDOT/rGO was also successfully synthesized. In the case of AuNPs/PEDOT/rGO (Figure 1d), there is no peak presence for the formation of AuNPs but the intensity of the peak is increased due to the doping of AuNPs on PEDOT/rGO sheets (Mao *et al.*, 2017; Sharma *et al.*, 2018).

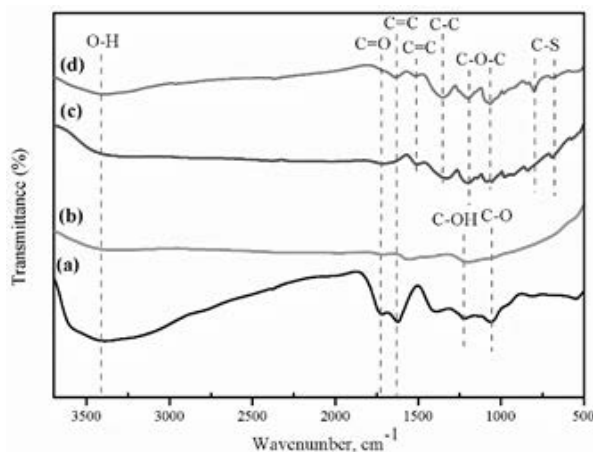


Figure 1: FTIR spectra measured from (a) GO; (b) rGO; (c) PEDOT/rGO and (d) AuNPs/PEDOT/rGO electrocatalyst.

X-ray Diffraction

XRD analysis is used to determine the phase structure of composite growth on GO sheet. As can be seen in Figure 2a, the XRD pattern of GO showed a diffraction peak (001) at $2\theta = 10.52^\circ$ reveals the formation oxygen functional group intercalate in the layer of graphite. The second very broad peak appear at $2\theta = 21.19^\circ$ due to incomplete oxidation of graphite. However, the XRD pattern of rGO showed a broad diffraction peak at $2\theta = 23.0^\circ$ due to the removal of oxygen functional group from GO. There is very weak diffraction peak at $2\theta = 42.83^\circ$ due to the incomplete oxidation of GO. The value of interlayer spacing is obtained from Bragg's law (equation 1):

$$d = \frac{\lambda}{2 \sin \theta} \quad (1)$$

where λ is the wavelength of $\text{CuK}\alpha$ radiation ($\lambda = 1.54\text{\AA}$) and θ is the Bragg's angle complementary to the analyzed peak. The value of interlayer

spacing for rGO (0.386 nm) is much lower compared to GO (0.839 nm). It can be seen that the decreasing of interlayer spacing value due to the removal of oxygen functional group and restoration and conjugation of sp^2 domain on rGO sheets (Cao *et al.*, 2015; Kondratowicz *et al.*, 2015). Furthermore, the characteristic peak of PEDOT is only appear with a broad and diffused reflection peak at $2\theta = 20^\circ\sim 30^\circ$ due to the amorphous structure of polymeric material (Alvi *et al.*, 2011; Mao *et al.*, 2017). This result reveals the presence of PEDOT on rGO sheets. The XRD pattern of AuNPs/PEDOT/rGO in Figure 2(b) shows the 2θ peak appears at 38.05° , 44.17° , 64.52° , 77.30° and 81.84° , which correspond to the reflection planes of Au (111), Au (200), Au (220), Au (311) and Au (222), respectively. It is proved that metallic gold appears in AuNPs/PEDOT/rGO sheets. Besides, a broad diffraction peaks in the range of $18.0^\circ - 27.0^\circ$ is belongs to C (002) from PEDOT and rGO (Liu *et al.*, 2016).

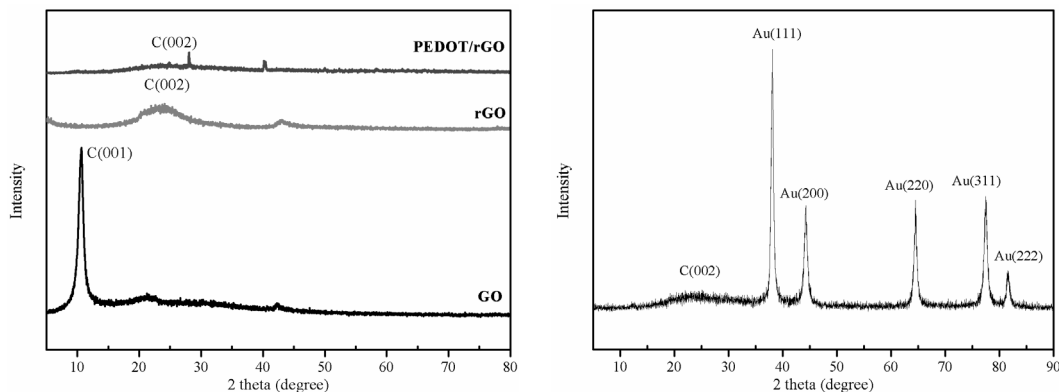


Figure 2: XRD pattern of (a) GO, rGO and PEDOT/rGO and (b) AuNPs/PEDOT/rGO.

Scanning Electron Microscopy (SEM)

The surface morphology of modified composite was determined by SEM. The SEM image in Figure 3a shows a wrinkled surface of GO structure. After treated with NaBH_4 as a reductant, the surface of rGO (Figure 3b) becomes a smooth-like structure. It can be seen for PEDOT/rGO (Figure 3c); the surface of composite is crumpled flakes, suggesting PEDOT polymer matrix is covered on rGO

surface. Clearly, this image shows the open structure of PEDOT/rGO permitting a transfer of electron on the surface of composite (Mao *et al.*, 2017). Surface morphology observation for AuNPs/PEDOT/rGO (Figure 3d) composite generally shows AuNPs/PEDOT particles is agglomerated with rGO sheets. From the image, it is suggested the surface of rGO sheets can provide a sufficient attachment sites for AuNPs/PEDOT particles where it can increase dispersity of composite.

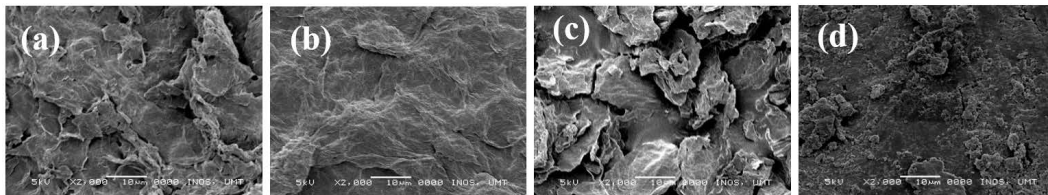


Figure 3: SEM image of (a) GO, rGO and PEDOT/rGO; (b) AuNPs/PEDOT/rGO.

Cyclic Voltammetry (CV) technique

The behaviour of modified electrode was observed by CV technique in 5.0 mM of $K_4[Fe(CN)_6]$ solution containing 1.0 M KCl. Generally, the redox couple of $[Fe(CN)_6]^{3-/4-}$ was chosen as a marker to determine electron transfer of modified electrode due to the sensitivity of GCE surface toward $[Fe(CN)_6]^{3-/4-}$. As shown in Figure 4(a), a pair of well-defined redox peak was found in all cyclic voltammogram of modified electrode which is corresponding to redox reaction of $[Fe(CN)_6]^{3-/4-}$ ion. Clearly, peak current (I_p) of GO/GCE, rGO/GCE and PEDOT/

rGO modified electrode increase gradually and smaller peak separations (ΔE_p) as compared to the bare GCE. However, AuNPs/PEDOT/rGO/GCE modified electrode show the highest I_p . The results suggest that this modified electrode has a high surface area where it provides sufficient reaction site for enhance rate of electron transfer as supported by SEM image. In addition, ΔE_p of AuNPs/PEDOT/rGO modified electrode shows a lower value of 59 mV than that for bare GCE (149 mV), indicating that rapid electron transfer between electrode surface and electrolyte as well as excellent reversibility (Jiang *et al.*, 2012).

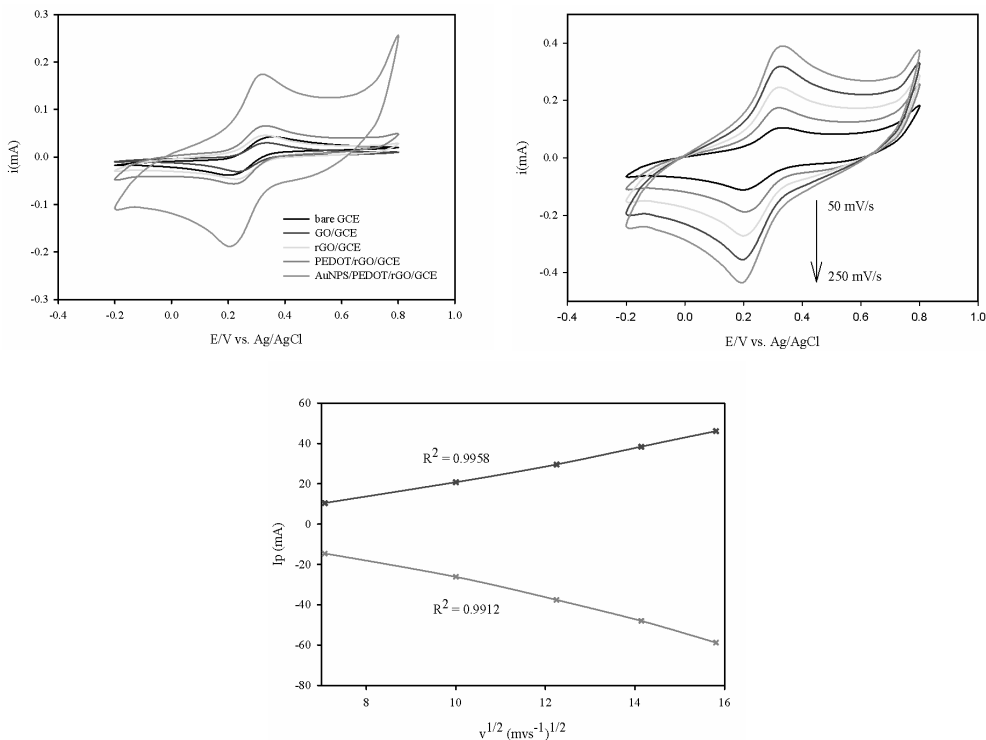


Figure 4: (a) Cyclic voltammogram of modified electrode at scan rate of 100 mVs⁻¹; (b) effect of scan rate on AuNPs/PEDOT/rGO/GCE in the range of 50 mVs⁻¹ – 250 mVs⁻¹ and (c) plot of the anodic and cathodic peak current vs. the square root of the scan rate. (Electrolyte: 5.0 mM of $K_4[Fe(CN)_6]$ in 1.0 M KCl solution).

Table 1: The relationship between peak current and square root of scan rate for modified electrode.

Modified electrode	v	v ^{1/2}	Peak current (µA)		R ² I _{pa} vs v ^{1/2}	R ² I _{pc} vs v ^{1/2}	E _{pa} (mV)	E _{pc} (mV)	ΔE
			I _{pa}	I _{pc}					
Bare GCE	50	7.07	25.48	23.68	0.9978	0.9967	350	200	150
	100	10.00	35.00	33.00					
	150	12.25	41.70	40.00					
	200	14.14	46.80	45.00					
	250	15.81	51.20	49.00					
GO/GCE	50	7.07	14.10	14.00	0.9974	0.9941	350	250	100
	100	10.00	23.20	22.00					
	150	12.25	32.90	32.00					
	200	14.14	39.60	38.00					
	250	15.81	45.90	44.00					
rGO/GCE	50	7.07	17.70	17.00	0.9874	0.9997	350	250	100
	100	10.00	30.40	30.00					
	150	12.25	37.40	40.00					
	200	14.14	46.20	49.00					
	250	15.81	47.10	57.00					
PEDOT/rGO/GCE	50	7.07	28.40	29.00	0.9962	0.9960	350	200	150
	100	10.00	42.60	40.00					
	150	12.25	55.10	50.00					
	200	14.14	66.40	56.00					
	250	15.81	77.50	65.00					
AuNPs/PEDOT/rGO/GCE	50	7.07	52.40	73.00	0.9958	0.9912	300	200	100
	100	10.00	104.00	131.00					
	150	12.25	148.86	168.81					
	200	14.14	192.00	188.00					
	250	15.81	230.68	294.05					

To further investigate behaviour of AuNPs/PEDOT/rGO modified electrode, the effect of I_p toward different scan rates also examined (Figure 4 (b)). The result obtained show that the redox peak current is increase linearly with the square root of scan rate (Figure 4 (c)), which indicates that redox reaction is controlled by the diffusion of [Fe(CN)₆]^{3-/4-} towards electrode surface. It can be concluded that the [Fe(CN)₆]^{3-/4-} reaction is only related to the rate of diffusion process from electrolyte to the AuNPs/PEDOT/rGO/GCE surface electrode. Furthermore, the peak separation remain at the same value shows a perfect reversibility of electrode (Yusoff *et al.*, 2013). Table 1 shows the relationship between

peak current and square root of scan rate. It can conclude that the value of peak current is increase as the scan rate increase for all modified electrode, reveals the increasing of rate of electron transfer.

Electrochemical impedance spectroscopy (EIS)

EIS is a powerful tool to determine charge transport property of surface electrode, which it can evaluate rate of electron transfer, electrode impedance, charge-transfer resistance (R_{ct}) and double layer capacitance (Tehrani & Ghani, 2012). The typical impedance spectrum is presented by Nyquist plot, which it consist of

semicircle part at higher frequency representing to the electron transfer between electrolyte and electrode surface (R_{ct}) and linear portion (Warburg Impedance (Z_w)) reflecting to diffusion-limited process (Liu *et al.*, 2016). Figure 5 represent Nyquist plot of all modified in $[\text{Fe}(\text{CN})_6]^{3-/4-}$ aqueous solution. Specifically, the R_{ct} is decreased as the composite loaded on GCE indicating all modified electrode could facilitate electron transfer between $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and electrode surface (Guo *et al.*, 2009). From

Nyquist plot, the R_{ct} value of modified electrode is decreased in order of bare GCE (297Ω) > GO/GCE (51Ω) > rGO/GCE (33Ω) > PEDOT/rGO/GCE (24Ω) > AuNPs/PEDOT/rGO/GCE (4Ω). Among them, AuNPs/PEDOT/rGO/GCE modified electrode showed a small depressed semicircle at high frequencies and a nearly straight line at low frequencies, reflecting that AuNPs/PEDOT/rGO/GCE has a better electron transfer kinetic and good conductivity (Yusoff *et al.*, 2014).

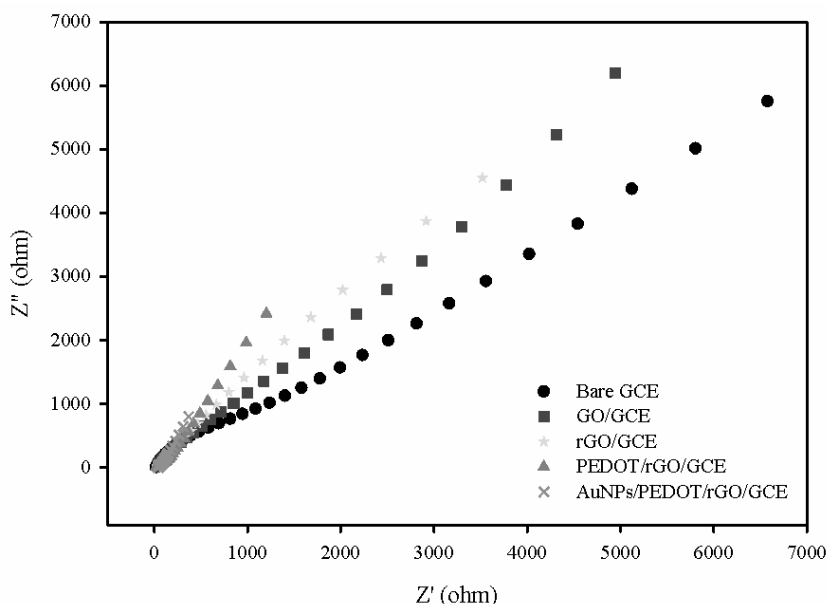


Figure 5: Nyquist plot obtained for modified electrode in 5.0 mM of $\text{K}_4[\text{Fe}(\text{CN})_6]$ and 1.0 M KCl solution at 0.2 V.

Conclusion

Herein, AuNPs/PEDOT/rGO composite is prepared by facile chemical method as an electrocatalyst for cathode electrode in FCs. The physical properties exhibited that AuNPs was successfully agglomerated and attached on PEDOT/rGO surface. AuNPs/PEDOT/rGO modified electrode performed a higher catalytic activity toward $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox reaction than other GO, rGO and PEDOT/rGO modified electrode. The reason could be explained as the intermolecular charge transfer between rGO and PEDOT with the presence of AuNPs. Therefore, AuNPs/PEDOT/rGO composite can

be considered as an alternative cathode catalyst, which it can use for further application in electroanalysis of FCs.

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