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Platinum nanoparticles involved on nitrogen and sulfur-doped nanomaterial as fuel cell electrode

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Abstract A fuel cell is an electrochemical cell that converts a source fuel into an electrical current. It generates electricity inside a cell through reactions between a fuel and an oxidant, triggered in the presence of an electrolyte. Fuel cells have been attracting more and more attention in recent decades due to high-energy demands, fossil fuel depletions, and environmental pollution throughout world. In this study, a facile and cost-effective catalysts have been developed on platinum nanoparticles (PtNPs) supported on nitrogen and sulfur-doped nanomaterial (PtNPs-NS). The successful synthesis of nanomaterials and the prepared glassy carbon electrode (GCE) surfaces were confirmed by transmission electron microscope (TEM), X-ray photo electron spectroscopy, cyclic voltammetry and electrochemical impedance spectroscopy. According to TEM images, the average particle sizes of PtNPs were found to be approximately 20–25 nm. The effective surface areas of NS/GCE and PtNPs-NS/GCE were calculated to be 105 and 518 cm^2/mg, respectively. The PtNPs-NS/GCE also exhibited a higher peak current for methanol oxidation than those of comparable GCE and NS/GCE, providing evidence for its higher electro-catalytic activity.

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1 Introduction

Fuel cells can generate energy from various fuels and they are recently significant method in terms of electricity production. Especially, direct-methanol fuel cells (DMFCs) are proton-exchange fuel cell in which methanol is used as the fuel [1, 2]. The important advantage of these fuel cells is the simplicity of transport of methanol. Methanol as fuel has several advantages such as transport and storage. DMFCs have been used for the production of energy for the several years [3, 4]. A sulfuric acid or perchloric acid as supporting electrolyte is uses in the DMFCs owing to removing of the CO_2 during the electrochemical progress. The reaction of methanol oxidation in an acidic medium can be presented as below [5, 6]:

$$(\text{Anode})\ CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad E^\circ = 0.043\,V\ (SHE)$$

$$(\text{Cathode})\ 3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \quad E^\circ = 1.229\,V\ (SHE)$$

$$(\text{The all electrochemical reaction}):$$

$$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O \quad E^\circ = 1.186\,V\ (SHE)$$

Especially, various nanomaterials and nanoparticles based on electrodes can been utilized for the development of energy, sensor and catalytic effect. The chemically modified electrodes in electrochemistry have been interesting research area in recent years. These electrodes are often prepared by modification of carbon or metal substrates to produce a new electrode to carry out specified reactions or processes. Modification of conductive substrates is also an important objective in material science and molecular electronics, as well as in various sensors applications [7–9].

Platinum nanoparticles are key components in the advancement of future energy technologies. In the substitution of fossil-fuels by renewable energy resources, nanometersized particles play a key role for synthesizing energy vectors from varying and heterogeneous biomass feedstocks. They are extensively used in reformers for the production of hydrogen from solid [10, 11].

It was determined that the compounds that contain the derivatives of 4,5-dihydro-1*H*-1,2,4-triazol-5-one have biological activities [12]. Besides in a recent study in vitro antimicrobial activities of some of these compounds were studied [13].

In the present report, the preparation and characterization of PtNPs-NS nanomaterial were performed. After that, glassy carbon electrode (GCE) surfaces were modified with PtNPs-NS nanocomposite by using infrared heat lamp. The developed surfaces were characterized by EIS, CV and chronoamperometry (CA) measurements. After the characterizations of the glassy carbon surfaces, their effects in fuel cell applications were investigated.

2 Experimental

2.1 Materials

All chemicals that used in the experiments were reagent grade and were used as received following; Chloroplatinic acid (H_2PtCl_6, Sigma-Aldrich, USA), isopropyl alcohol (IPA, Sigma-Aldrich, USA), methanol (Merck, Germany), HPLC grade acetonitrile (MeCN, Sigma-Aldrich, USA), $NaBH_4$ (Merck, Germany), perchloric acid ($HClO_4$, Sigma-Aldrich, USA), and other chemicals were reagent grade quality and were used as received.

2.2 Instrumentation

All electrochemical experiments (CV and CA) were performed using out IviumStat (U.S) equipped with C3 cell stand. Electrochemical impedance spectroscopic experiments were carried out with a Gamry Reference 600 workstation equipped with a PCI4/300 potentiostat in conjunction with EIS 300 software. Modified electrodes were characterized in 1.0 mM ferrocyanide/1.0 mM ferricyanide ($[Fe(CN)_6]^{3-/4-}$) redox couple via EIS methods. EIS data were measured at 100 kHz to 0.1 Hz at 10 mV wave amplitude and at an electrode potential of 0.160 V, the formal potential of $[Fe(CN)_6]^{3-/4-}$ redox couple. XPS analysis were performed on a PHI 5000 Versa Probe (F ULVAC-PHI, Inc., Japan/USA) model with monochromatized Al Ka radiation (1486.6 eV) as an X-ray anode operated at 50 W. To prepare the samples, one drop of the prepared nanocomposites were placed on clear glass and then dried in air.

Melting point was determined in open glass capillary using a Stuart melting point SMP30 apparatus and is uncorrected. The IR spectra were obtained on an ALPHA-P BRUKER FT-IR spectrometer. 1H and 13C NMR spectra were recorded in deuterated dimethyl sulfoxide with TMS as internal standard using a Varian spectrometer at 400 and 100 MHz, respectively.

2.3 General procedure for the synthesis of compound 5 (NS) (for platinum nanoparticles involved on nitrogen and sulfur-doped nanomaterial)

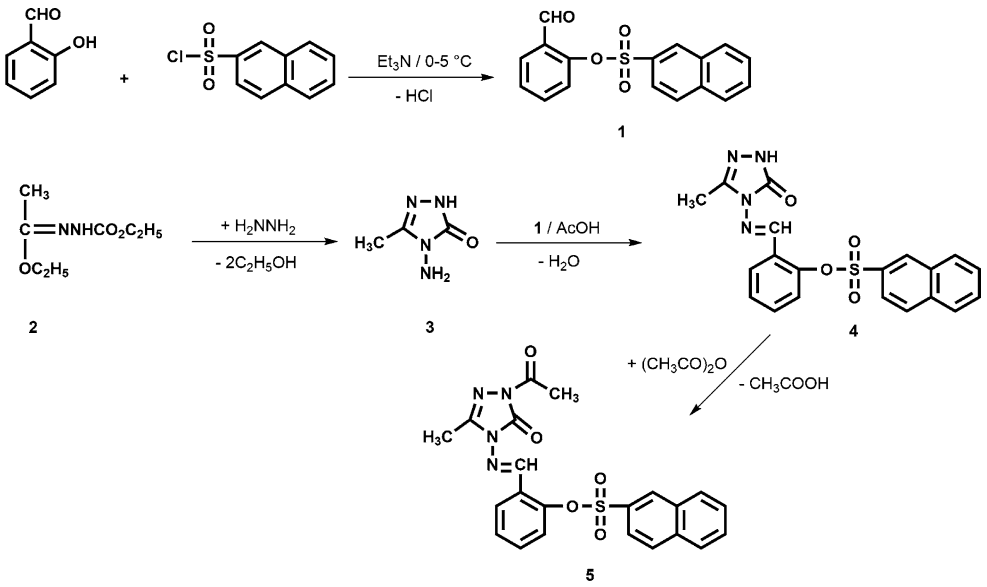
3-Methyl-4-[2-(2-naphthylsulfonyloxy)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-one (4) (4.08 g, 0.01 mol) was refluxed with acetic anhydride (20 mL) for 0.5 h. After addition of absolute ethanol (100 mL), the mixture was refluxed for 0.5 h. more. Evaporation of the resulting solution at 40–45 °C in vacuo and several recrystallizations of the residue from ethanol gave pure compound 5 (1-acetyl-3-methyl-4-[2-(2-naphthylsulfonyloxy)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-one) as colourless crystals (Scheme 1).

Yield: 3.33 g (74 %); mp: 176 °C; IR (KBr, υ, cm^{-1}): 1733, 1718 (C=O), 1601 (C=N), 1373 and 1181 (SO_2), 753 (1,2-disubstituted benzenoid ring); 1H NMR (400 MHz, DMSO-d6): δ 2.03 (s, 3H, CH3), 2.51 (s, 3H, $COCH_3$), 7.39 (d, 1H, Ar–H, J = 8.40 Hz), 7.48 (t, 1H, Ar–H, J = 7.60 Hz), 7.61–7.68 (m, 3H, Ar–H), 7.73 (t, 1H, Ar–H, J = 8.00 Hz), 7.82 (d, 1H, Ar–H, J = 8.00 Hz), 8.02 (d, 1H, Ar–H, J = 8.00 Hz), 8.12 (d, 1H, Ar–H, J = 8.80 Hz), 8.15 (d, 1H, Ar–H, J = 8.40 Hz), 8.61 (s, 1H, Ar–H), 9.38 (s, 1H, N=CH); 13C NMR (100 MHz, DMSO-d6): δ 10.76 (CH_3), 23.44 ($COCH_3$), 122.43, 124.01, 126.65, 126.72, 127.66, 127.96, 128.24, 129.39, 129.92, 130.22, 130.42, 130.66, 131.42, 133.28, 135.18, 146.13 (arom-C), 147.28 (triazole C3), 147.43 (N=CH), 148.11 (triazole C5), 165.76 ($COCH_3$); UV λ_{max} (ε): 282 (22.734), 242 (31.433) nm; Anal. Calcd. for $C_{22}H_{18}N_4O_5S$ (450.47): C, 58.66; H, 4.03; N, 12.44; S, 7.12. Found: C, 58.68; H, 4.34; N, 12.46; S, 6.99.

2.4 Preparation of PtNPs-NS nanohybrid

PtNPs were prepared by mixing 200 μL of 0.1 M K_2PtCl_4 solution with 10 mg $NaBH_4$ solution. The solutions were kept in ultra-sonicated bath for 60 min [14]. After that, 1 mg/mL of PtNPs solution was mixed with the 0.1 mg/mL of NS solution at a 1:1 volume ratio. Finally, the mixture was sonicated to generate a homogeneous mixture (PtNPs-NS). The mixture was then kept undisturbed under ambient condition for 24 h.

Scheme 1 Synthesis route of compound 5



2.5 Procedure for the electrode preparation

GCE was cleaned and prepared by polishing it to a mirror-like finish with fine wet emery paper (grain size 4000). The electrodes were polished successively in 0.1 and 0.05 μm alumina slurries (Baikowski Int. Corp., U.S) on microcloth pads (Buehler, Lake Bluff, IL, U.S). The electrodes were sonicated first in ultrapure water two times and in 50:50 (v/v) IPA + MeCN solution purified over activated carbon. After removal of trace alumina from the surface by rinsing with water and a brief cleaning in an ultrasonic bath (Bandelin RK 100, Germany) with water and then with IPA + MeCN mixture purified over the activated carbon, they were rinsed with MeCN to remove any physisorbed or unreacted materials from the electrode surface [15]. After that, the catalyst inks were prepared by dispersing 1 mg of catalyst (NS and PtNPs-NS) into 1 mL of ethanol via 20 min agitation. 15 μL of NS and PtNPs-NS suspensions was dropped onto the clean GCE surfaces. Then, the solvent was evaporated by an infrared lamp.

2.6 Electrochemical measurements

Electrocatalytic oxidation of 0.5 mol/L methanol on bare GCE, NS/GCE and PtNPs-NS/GCE was performed in 0.1 mol/L $HClO_4$ by cyclic voltammetry (CV) between 0.0 and +1.2 V. The Ag/AgCl and Pt wire electrodes were utilized as reference and counter electrode, respectively.

3 Results and discussion

3.1 Characterization of nanomaterial

The morphology of the platinum nanoparticles involved on nitrogen and sulfur-doped nanomaterial was investigated by using the JEOL 2100 HRTEM with an accelerating voltage of 200 keV. A drop of sample solution was deposited on a polymeric grid at room temperature under an argon gas stream. Figure 1 confirms that the PtNPs have been seen as dark dots with a mean diameter of 20 to 25 nm on NS sheets.

Figure 2 shows narrow region XPS spectra of PtNPs-NS nanocomposite. As seen in Fig. 2; C1s, N1s, and S2p peaks confirmed the formation of nanocomposite. The peaks at

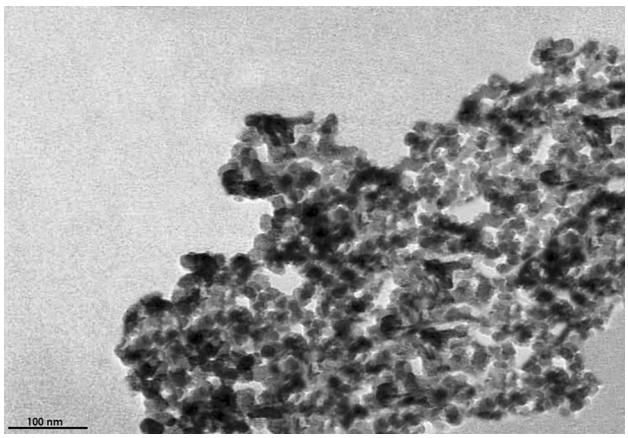


Fig. 1 TEM image of PtNPs-NS nanocomposite

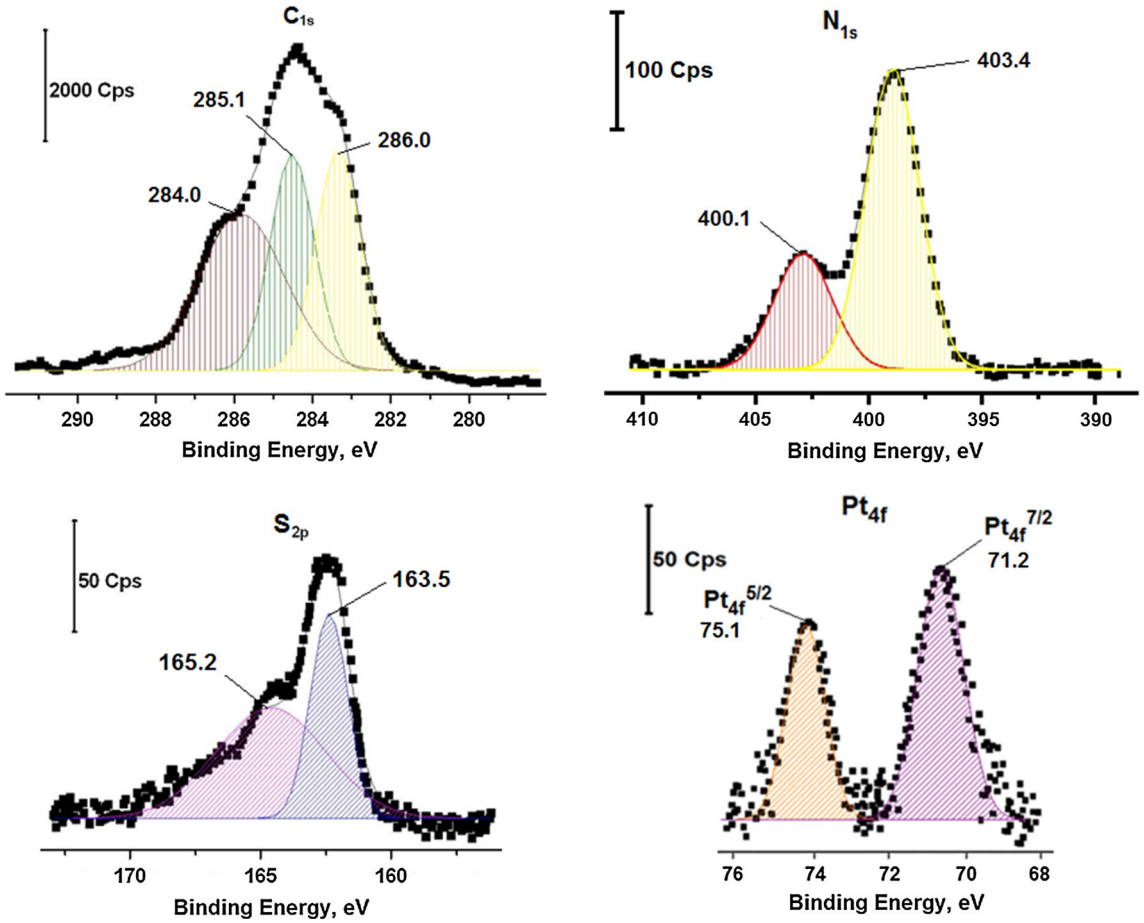


Fig. 2 The narrow region XPS of C1s, N1s, S2p, Pt4f of PtNPs-NS nanocomposite

284.0, 285.1 and 286.0 eV were related to C–C/C=C, C=O and C–N of C1s, respectively. The peak at 400.1 eV in the N1s narrow region spectrum was corresponded to C–N groups in the PtNPs-NS nanocomposite. The peak at 403.4 eV was corresponded to the N–H group in unreacted molecules. The doublet 4f5/2 and 4f7/2 signals of Pt4f region appeared at 75.1 and 71.2 eV, respectively, indicated the presence of PtNPs in the nanocomposite.

3.2 Characterizations of modified glassy carbon electrodes by EIS

Figure 3 shows the impedance plot (Nyquist diagram) of bare GCE, NS/GCE and PtNPs-NS/GCE. The EIS graph (Fig. 3) demonstrated that the value of charge transfer resistance (R_{ct}) of bare GCE was calculated as 230 O for $[Fe(CN)_6]^{3-/4-}$ redox couple solution. When the bare GCE was modified with NS, the value of R_{ct} was lower (175 O). Because of the lower value, we can say that the NS facilitated the rate of electron transfer between surface and solution. When the surface was modified with PtNPs, the value of R_{ct} of PtNPs-NS/GCE was lower than that of NS/GCE. According to the lower values of R_{ct}, PtNPs-NS facilitated the rate of electron transfer in comparison to only NS film. Thus, the addition of PtNPs shows the more increase of catalytic activity, indicating the more active property of the PtNPs-NS film.

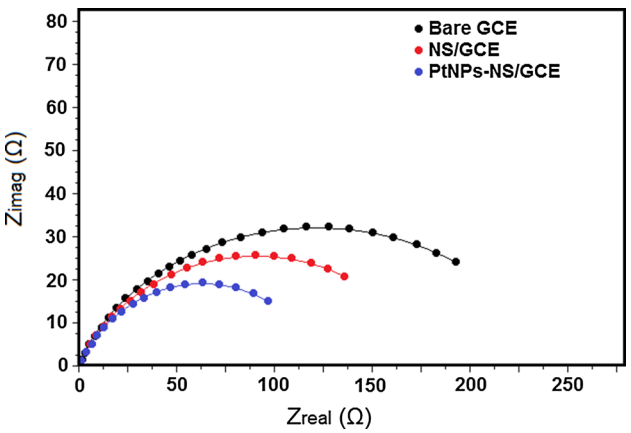


Fig. 3 Fitting of impedance spectrum for 1.0 mM $[Fe(CN)_6]^{3-/4-}$ (1:1) in 0.1 M KCl at bare GCE; NS/GCE and PtNPs-NS/GCE. Frequency range is 100,000–0.1 Hz with 10 mV wave amplitude at a formal potential of 0.160 V

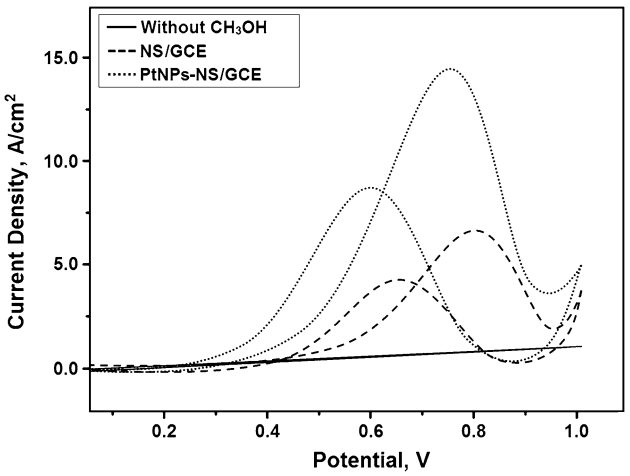


Fig. 4 Cyclic voltammograms of 0.5 mol/L methanol in 0.1 mol/L $HClO_4$ at bare GCE, NS/GCE and PtNPs-NS/GCE

The ESA of different modified electrodes was obtained by CV with 1.0 mM $[Fe(CN)_6]^{3-}$ solution containing 0.1 M KCl as a probe at different scan rates according to the equation: $i_p = 2.69 \times 10^5 An^{3/2}D^{1/2}Cv^{1/2}$, where i_p refers to the peak current and A is the electrode area (cm^2). For 1.0 mM $[Fe(CN)_6]^{3-}$, n = 1, D = 7.6×10^{-6} cm^2/s (0.1 M KCl), C is the concentration of $[Fe(CN)_6]^{3-}$, v is the scan rate. The ESA of NS/GCE and PtNPs-NS/GCE were calculated from the slope of the i_p versus $v^{1/2}$ plot to be 211, and 648 cm^2/mg, respectively. These results show that the electrochemical surface area of the PtNPs-NS/GCE is 3.07 times higher than those of NS/GCE. The high activity was explained by the small size of PtNPs.

The electrocatalytic activities of the modified electrodes were also evaluated for 0.5 M methanol by CV in 0.1 mol/L $HClO_4$ at 50 mV/s (Fig. 4). In the case of the PtNPs-NS/GCE, a current peak of 14.3 ± 0.08 A/cm^2 was observed during a forward anodic scan (If) at a potential of 0.75 V, while the reverse scan (Ib) showed a current peak of 7.38 ± 0.04 A/cm^2 at 0.60 V. The efficiencies of the PtNPs-NS/GCE and NS/GCE on methanol oxidation were given in Table 1. The forward peak of PtNPs-NS/GCE was 2.27 times higher than those of NS/GCE. In addition, a control experiment of the PtNPs-NS/GCE in the electrolyte without methanol was completed (black curve of Fig. 4). According to the black curve, during the forward anodic scan and the reverse scan, no current peak was seen. Thus, the important activity enhancement in methanol oxidation is attributed to high active surface of PtNPs.

In addition, since the anodic peak in the backward scan was related to the removal of CO accumulated on the catalyst surface during the forward scan, the ratio of If/Ib (the ratio of the forward and backward anodic peak current densities) can be used to evaluate the CO tolerance of catalysts [16]. A higher If/Ib ratio indicates the more effective removal of poisoning CO species on catalyst surface. The If/Ib ratio of PtNPs-NS/GCE was 1.94, higher than the 1.70 for the NS/GCE. These electrochemical results reveal that the PtNPs-NS/GCE catalyst has better CO-poisoning tolerance and high electrocatalytic activity toward methanol oxidation.

Table 1 Comparison of methanol oxidation on modified electrodes in this study (scan rate: 50 mV/s) (n = 6)

Electrode	If (A/cm^2)	E (V)	Ib (A/cm^2)	E (V)	If/Ib
PtNPs-NS/GCE	14.3 ± 0.08	0.75	7.38 ± 0.04	0.60	1.94
NS/GCE	6.3 ± 0.04	0.80	3.7 ± 0.01	0.65	1.70

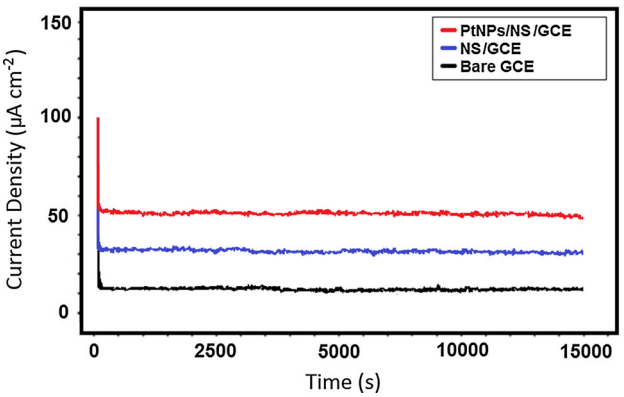


Fig. 5 Chronoamperometry results of 0.5 mol/L methanol in 0.1 mol L $HClO_4$ at bare GCE, NS/GCE and PtNPs-NS/GCE

The chronoamperometry measurements were carried out to investigate the electrochemical performances of the prepared electrodes at 0.7 V in the presence of methanol. As shown in Fig. 5, all electrodes present current decay before steady current status is attained. The decay is possibly attributed to the fact that once the methanol oxidation reaction begins, some incomplete oxidation products adsorb on the catalyst surface and poison it towards further methanol oxidation, which can also been observed in other studies.

In the steady-state region, the current density of methanol oxidation on the PtNPs-NS/GCE is highest than that of methanol oxidation on the other electrodes. This indicates that the PtNPs-NS/GCE is a stable and poisoning-tolerance electrocatalyst for methanol oxidation.

4 Conclusions

A new and cost-effective catalysts based on platinum nanoparticles was fabricated as a working electrode that can be used in fuel cell applications. The catalysts were successfully prepared and modified on GCE surfaces in the

present study. The PtNPs-NS/GCE catalyst was characterized by using TEM, CV and XPS results. According to the results of EIS and CV, the prepared nanocomposite based on platinum nanoparticles showed catalytic activity towards methanol as the fuel. Especially, the PtNPs-NS/GCE catalyst provides an opportunity to prepare a promising electrode with a large active surface area of 648 cm^2/mg.

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