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Electrocatalytic determination of free glycerol in biodiesel at nano nickel modified graphite electrode

ABSTRACT

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For the first time this study reported the success of using nanocrystalline hexagonal close-packed (hcp) nickel (Ni) modified composite graphite (CG) electrode (hcp-nano Ni/CG) for the electrocatalytic oxidation of glycerol in alkaline medium (0.1 M KOH). The hcp-nano Ni/CG electrode had an improve response and specificity on the electrocatalytic oxidation of glycerol over the bare CG. The electrocatalysis was the result of the formation of NiOOH during the oxidation process. The process was influenced by scan rate and concentration of glycerol. A linear relationship of concentration with current was obtained over concentration range of 0.5 – 12.0 mM glycerol with limit of detection (S/N = 3) at 0.033 mM glycerol. The hcp nano Ni modified CG electrode was applied for direct determination of free glycerol in biodiesel samples. As a glycerol sensor the hcp nano Ni modified CG is quite stable.

Keywords: *Biodiesel; Electrocatalytic oxidation; Glycerol; Hexagonal close-packed; Nickel nanocrystals.*

INTRODUCTION

As fossil fuel and other energy sources often available in limited amount it is important to find renewable alternatives like biodiesel (mono alkyl esters). Biodiesel with long chain fatty acids is generated from vegetable oils and animal fats with by-product called glycerol (the simplest triol) [1,2]. The glycerol with its high energy density and less toxic compared to methanol can be electrochemically oxidized. The electro-oxidation of glycerol on direct alcohol fuel cells (DAFCs) has attracted increasing attention from both energy and environmental fraternities in recent years [3,4]. The electrocatalytic oxidation of glycerol on electrodes like palladium (Pd) [1,3,4] and platinum (Pt) [2,5,6] have been investigated. However, many efforts have been undertaken to reduce the cost in production of DAFCs with the usage of less expensive electrodes like Ni but with high catalytic activity [7-11].

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The catalytic behavior of Ni towards alcohols has been investigated since the early 1970s [8]. The catalytic oxidation of alcohols are, generally, more facile in the alkaline medium [9,10] in which Ni has demonstrated long-term stability [9]. The catalytic activity is attributed to anodic polarization of the highly valence oxy-hydroxide species of Ni i.e. β and γ -NiOOH which act as strong oxidizing agents for alcohols [8,11].

The use of Ni nanoparticles (NPs) (size 350 nm) with catalytic properties for the electro-oxidation of glycerol in alkaline media has been reported [8]. Ni NPs normally crystallizes as face centered cubic (fcc) [11,12]. But recently, the chemically synthesized metastable hcp Ni NPs (size ~ 200 nm) has been utilized for glycerol oxidation [12]. Previously our laboratory has succeeded in carrying out the electrosynthesis of hcp Ni (size ~ 10 nm) on CG electrode via high scan rate voltammetry technique [11]. It is the most recent report on the electrochemical synthesis of hcp Ni after the first one by Wright and co-worker in 1965 [13]. Additionally, the electrosynthesized hcp Ni nanocrystal has been used for the electro-oxidation of methanol in alkaline medium [9].

The analysis of glycerol in biodiesel, pharmaceutical, clinical diagnosis and food industries are significant [2,5,14,15]. Several methods such as chromatographic [16], photometric [17] and amperometric [14,15] have been used to analyse glycerol in biodiesel. However, to the best of our knowledge there has never been any report thus far on the usage of hcp nano Ni modified CG being used for the analysis of glycerol via its electro-oxidation in alkaline media. This paper intends to report on the application of hcp nano Ni modified CG electrode (hcp-nano Ni/CG) in electrocatalyzing the oxidation of glycerol and its application for direct determination of free glycerol in biodiesel samples.

EXPERIMENTAL

Reagents and Apparatus

All reagents (AR grade) were purchased from Fluka Chemie, Switzerland without further purification. Biodiesel (B100) samples prepared from the waste cooking oil were obtained from the

Bioenergy Research Institute of Tarbiat Modarres University in Iran.

All solutions were freshly prepared with doubly distilled water (18.2 M Ω cm) from Milli-Q plus (Millipore, USA).

The electrochemical studies were performed using the electrochemical workstation BAS Epsilon E2 (Bioanalytical System, USA). A three compartment electrochemical cell was used with an Ag/AgCl (3M KCl) as reference electrode, a Pt wire as counter electrode and either a bare CG (98 % C and 2 % clay) (Unicorn, Australia), 1.8 mm o.d. or hcp nano Ni modified CG as working electrode.

Procedures

The hcp-nano Ni (particle size of 9.7 ± 2.3 nm) modified CG was prepared under optimal conditions as reported [11]. Briefly, the CG was immersed into the N₂ purged Ni plating solution (5.0 mM NiCl₂·6H₂O and 1.0 M NH₄Cl (pH 6)) for 15 min. The initial potential (high overpotential) of -1500 mV and final potential (low overpotential) of -500 mV were applied for a short period (154 ms scan⁻¹) at scan rate of 6500 mV s⁻¹ and deposition time 120 s for the deposition of Ni. The Ni/CG was, then, rinsed with distilled water and dried in desiccators prior to further investigations. The cyclic voltammetry was used to study the electrocatalytic properties of the hcp-nano Ni/CG electrode and the electro-oxidation of glycerol in solution mixture of aqueous 3.0 mM glycerol and 0.1 M KOH (pH 12) at applied potential of 0 – 800 mV and scan rate 50 mV s⁻¹. Experiments were performed at 25 ± 5 °C. All potentials were measured against the Ag/AgCl (sat. KCl).

In order to obtain a glycerol-free biodiesel sample, approximately 50mL of the biodiesel were transferred to a separatory funnel until the aqueous phase became clear. The organic phases were then drained and placed in a distilling flask at 105 °C for 2 h, to ensure total elimination of the residual water. The absence of free glycerol in the treated biodiesel sample was confirmed by gas chromatography (GC).

RESULTS AND DISCUSSION

Surface morphology and XRD analysis of the hcp-nano Ni/CG modified electrode

The scanning electron microscopic (SEM) image of the hcp-nano Ni/CG prepared under optimal conditions is shown in Figure 1. The size distribution and monodispersity of the hcp Ni nanocrystals are improved at this condition as semi bright grey of Ni nanocrystals are quite regular in shape, homogeneously dispersed on CG substrate electrode.

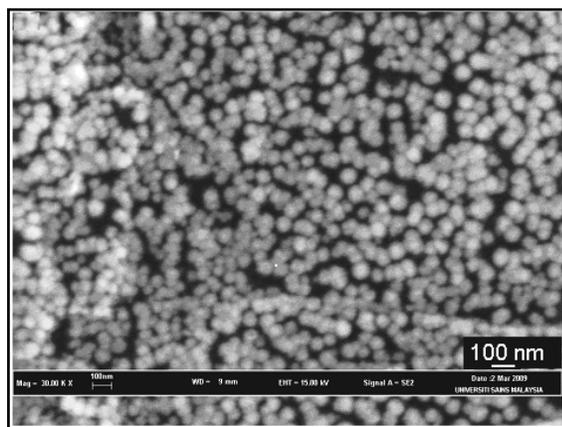


Fig. 1. SEM of Ni nanocrystals obtained at optimal conditions.

The XRD pattern of the nanocrystalline Ni on CG electrode prepared at optimum condition has been reported [11]. The most prominent reflections are assigned to Miller Indices of hcp Ni [11-13]. Some other characterizations of the hcp-nano Ni/CG such as transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) analysis have been also previously reported [11].

Electrochemical oxidation of glycerol on hcp-nano Ni/CG modified electrode

Figure 2 represents typical steady-state CVs in the applied potential of 0-800 mV in 0.1 M KOH. Figure 2a shows the CVs of bare CG in alkaline medium with and without glycerol. A small increase in current is observed when glycerol is presence (curve b), which could be due to the CG substrate electrode has oxidized glycerol. In the absence of glycerol (curve c in Figure 2b) the hcp-nano Ni/CG modified electrode shows a reversible

system at anodic peak potential (E_{pa}) 530 mV and cathodic peak potential (E_{pc}) 400 mV. This is attributed to the β -Ni(OH)₂/ β -NiOOH couple. The anodic oxidation of Ni in alkaline media has been reported [8,9] to have two or more steps.

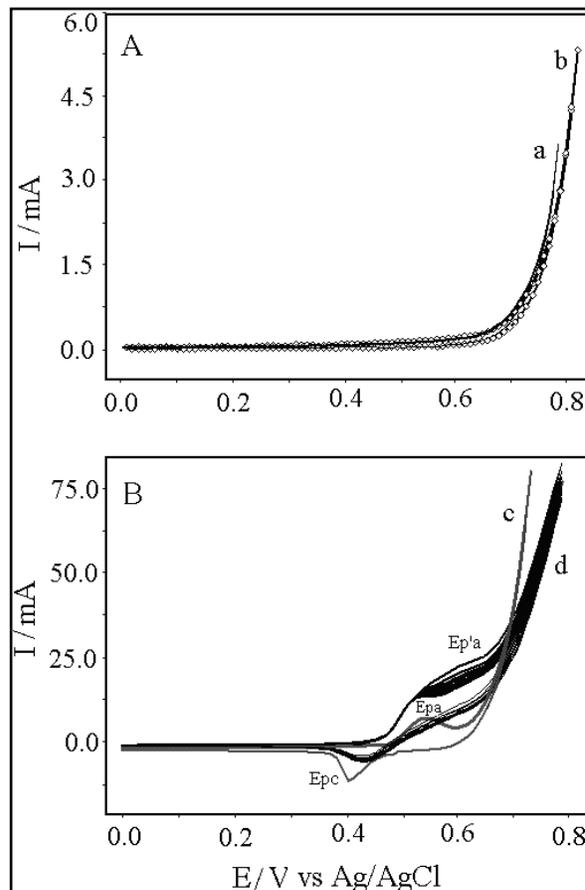


Fig. 2. (A) CVs of bare CG electrodes in (a) the supporting electrolyte (0.1 M KOH) and (b) in the presence of 3.0 mM glycerol, (B) overlay of 10 successive CVs of hcp-nano Ni/CG electrode in 0.1 M KOH (c) and in the presence of 3.0 mM glycerol (d). Scan rate 50 mV s⁻¹.

The first step is the oxidation of Ni to a highly hydrated Ni, α -Ni(OH)₂ at lower potentials close to the hydrogen equilibrium potential. It is worth noted that during the anodic potential scan, different types of Ni hydroxide (intermediate species) may be formed [18]. However, the α -form species, with time and increasing potentials, could transform into less hydrated and more stable phase β -Ni(OH)₂ which then passivate the Ni surface [9,18,19]. Due to stability of β -Ni(OH)₂, the redox waves are not usually observed for Ni(II)/Ni(0) couple, thus the β -form of Ni hydroxide accumulates on the surface. The second step and at more positive applied potentials Ni could be

oxidized to β -NiOOH. The kinetic of redox reactions for Ni oxide species at hcp-nano Ni/CG modified electrode is determined from the relationship of the anodic peak currents against the square roots of scan rate ($10\text{-}400\text{ mV s}^{-1}$) (Figure 3). The obtained linear plot corresponds to a diffusion-controlled process for the transformation of Ni(OH)₂ to NiOOH. Such behavior of Ni modified electrodes has been reported elsewhere [9,20]. With the addition of 3.0 mM glycerol to KOH solution a remarkable change of voltammetric response is observed. Figure 2b (curve d) represents a strong electrocatalytic activity of the hcp-nano Ni/CG modified electrode towards the oxidation of glycerol. As can be seen, a new and broadened anodic peak (Ep'a) appeared at 630 mV with a significantly large anodic peak current (Ipa), while no peak is observed in similar conditions for glycerol oxidation at bare CG electrode (curve b in Figure 2a).

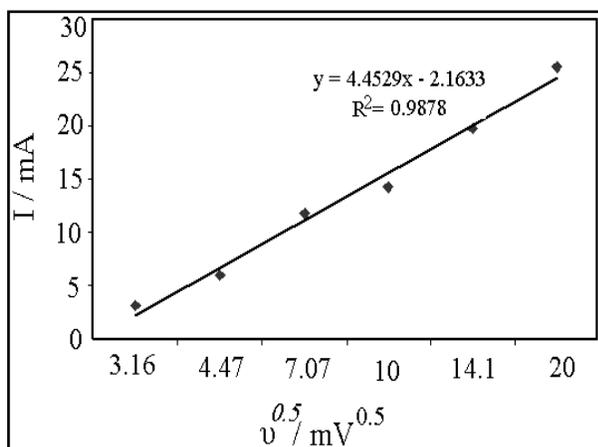
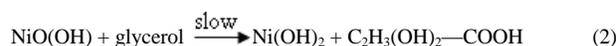
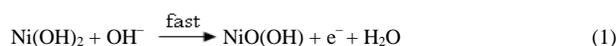


Fig. 3. The dependency of anodic peak current to the square root of scan rate in 0.1 M KOH.

Therefore, the Ep'a can be attributed to the oxidation of glycerol by Ni(III) oxyhydroxide generated at potentials more positive than 530 mV for Ni²⁺/Ni³⁺ transition at hcp-nanoNi modified CG electrode in the absence of glycerol (curve c in Figure 2b). The Epc at 430 mV in curve d is, however, decreased. This is due to consumption of NiOOH species during oxidation of glycerol [9,15]. It is also noticeable that oxygen evolution occurs at more positive potentials when glycerol is present in solution. This may be explained by the great affinity of high-valence Ni species intermediate,

e.g. NiOOH, to glycerol adsorption than to OH⁻ [9,10]. The result clearly shows that there is an interaction between the glycerol and the catalytic sites on the modified CG electrode. Hence, the β -Ni(OH)₂/ β -NiOOH couple has acted as an efficient electron transfer mediator for the oxidation of glycerol [9,21]. It is, then, suggested that in the potential region used the two processes (i) electro-oxidation of glycerol and (ii) electro-generation of NiOOH have merged into one process which continue concomitantly with oxygen evolution. Nonetheless, glycerol is not oxidized until β -Ni(OH)₂ undergoes oxidation (see equation (1) to (3));



This indicates that the rate limiting step for glycerol oxidation at the hcp-nano Ni/CG modified electrode is actually, the reaction between the glycerol and NiOOH [9,22].

Effect of scan rate on the catalytic currents

The effect of scan rate on the electrocatalytic oxidation of glycerol on hcp-nano Ni/CG modified electrode is investigated further. This may provide information on electron transfer kinetics. Figure 4a shows the CVs of the electrode prepared in optimum condition at various scan rates when immersed in a solution containing 3.0 mM glycerol and 0.1 M KOH. It is observed that with increasing scan rate, especially, at 100 mV s⁻¹ and higher the redox peaks have shifted. It could be that at higher scan rates changes in reaction kinetic between Ni³⁺ and glycerol have taken place. The gradual increase in Ipc on increasing scan rate could also be attributed to incapability of glycerol in reducing all the available higher valence Ni species on the passive surface layer [23]. Therefore, the remaining Ni³⁺ species are reduced under the cathodic condition producing the corresponding cathodic peaks. Hence, the higher the scan rate the greater the cathodic peak current would be. Therefore, at 50 mV s⁻¹ and higher, the reaction time for glycerol oxidation process will not be sufficient and the electron transfer rate between the

glycerol and NiOOH is relatively slower than the rate between NiOOH and β -Ni(OH)₂ [24,25]. Thus, the heterogeneous oxidation of glycerol on hcp-nanoNi/CG is not a rapid reaction as this involves the rate-determining step reaction of high valence Ni on the CG with the adsorbed glycerol. Additionally, the linear dependency of the anodic peak current on the square root of the scan rate indicates the oxidation of glycerol is a diffusion-controlled process (Figure 4b, inset). However, in a more moderate scan rate, e.g. 50 mV s⁻¹, seemingly, the rate of electron transfer appears more consistent.

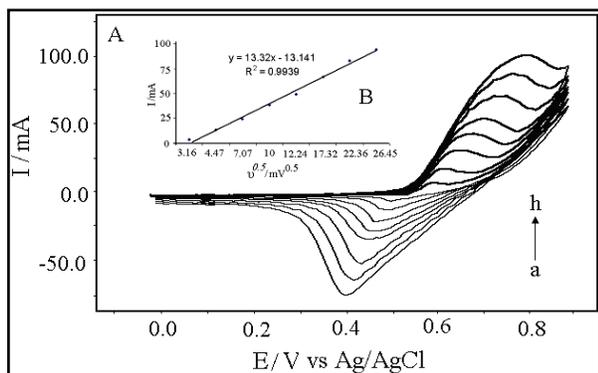


Fig. 4. (A) CVs response of hcp-nano Ni/CG electrode in 3.0 mM glycerol, at the following scan rates: (a)10; (b) 20; (c) 50; (d) 100; (e) 150; (f) 300; (g) 500; and (h) 700 mV s⁻¹, (B) the dependency of anodic peak current to the square root of scan rate.

Calibration curve of glycerol

The differential pulse voltammetry (DPV) is a very sensitive method with better current resolution than the CV. It is then used for preparation of calibration curve in the analysis of glycerol. Figure 5a shows the typical DPV curves for different concentrations of glycerol in alkaline media at the hcp-nano Ni/CG electrode. The I_{pa} increases proportionally with glycerol in the concentration range of 0.5 mM (46.04 mgL⁻¹) to 12.0 mM (1.105 gL⁻¹). The dependence of the I_{pa} on the concentration of glycerol is shown in Figure 5b (inset). From the analysis of linear segment of the plot, the lower limit of detection (LOD) of glycerol is in the order of 0.033 mM (3.038 mgL⁻¹) at a signal-to-noise ratio (S/N) equal to 3. A linear equation of I_{pa} (mA) = 2.6804×C (mM) +17.55, with linear correlation coefficient, $r = 0.9933$ have been obtained in the above range of concentrations.

Determination of free glycerol in biodiesel

The hcp-nano Ni/CG electrode is investigated for the measurement of free glycerol in biodiesel sample prepared as described in Section 2.2.

Three glycerol-free B100 biodiesel samples (2.0 g, weighed with a precision of 0.1mg) were transferred to three screw-cap test tubes. To these samples, a glycerol standard solution (10, 20 and 100 μ L respectively, from 1.0 gL⁻¹) were added and the resulting sample were vortex-mixed for homogenization. The obtained concentrations are shown in Table 1. The average percentage of recovery of the spiked samples is 106.4 %. The results demonstrate the efficiency of the modified electrode in the determination of free glycerol in biodiesel samples.

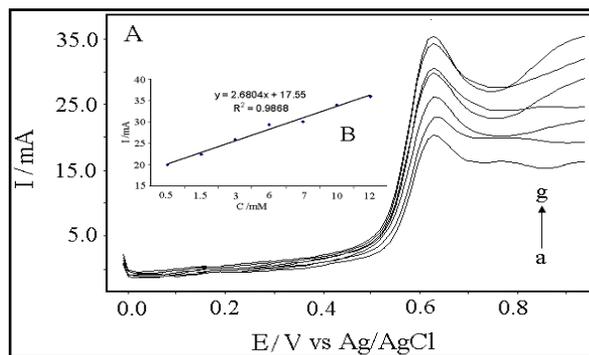


Fig. 5. (A) Typical differential pulse voltammogram of various concentrations (a to g): 0.5, 1.5, 3.0, 6.0, 7.0, 10.0 and 12.0 mM glycerol in 0.1M KOH at hcp-nano Ni/CG electrode. (B) The corresponding calibration plot (inset) at pulse amplitude 50 mV and potential step 10 mV.

Table 1. Determination of free glycerol in biodiesel samples containing a known concentration of glycerol.

Free glycerol	Expected concentration mgL ⁻¹	Obtained concentration mgL ⁻¹	Recovery (%)
Sample 1	5.0	5.3 ± 0.1	106
Sample 2	10.0	10.7 ± 0.3	107
Sample 3	50.0	53.1 ± 0.9	106.2

Operational and storage stabilities of the modified electrode

The operational and storage stabilities of the hcp-nano Ni/CG electrode for glycerol oxidation have been studied. The operational stability shows only < 8% decrease in electro-oxidation capacity when it is subjected at optimum condition, around 400 cycles and after five months of continuous used. The decrease is assumed to have been caused by poisoning of the electrode surface via oxidative intermediates, various impurities formed and accumulated either from electrolyte or from surrounding atmosphere [26]. In order to keep long-term storage stability the modified electrode has to be kept in alkaline solution at 4°C when not in use.

CONCLUSIONS

The nanocrystalline Ni with hcp structure and dispersed homogeneously on a CG electrode, i.e. hcp-nano Ni/CG electrode, has displayed good electrocatalytic activity on the oxidation of glycerol in 0.1 M KOH. This oxidation proceeds alongside the formation of passive film β -Ni(OH)₂. The catalytic effect depends on the concentration of glycerol and scan rate. At low glycerol concentration the oxidation process is diffusion-controlled. Increasing the scan rate decreases the reaction between glycerol and the NiOOH. This study indicates that the hcp-nano Ni/CG electrode is useful in (i) as glycerol sensor in the determination of free glycerol in biodiesel samples and (ii) as anode in DAFCs.

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