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Short Communication

Fabrication of Electrical Conductive NiCu– Carbon Nanocomposite for Direct Ethanol Fuel Cells

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Bimetallic nanostructures are an interesting class of materials for numerous application fields due to their special characterization. In this study, NiCu carbon nanofibers nanocomposite (NiCuCNFs) were investigated as electrocatalyst for ethanol (EtOH) oxidation. nanocomposite were synthesized from calcination of electrospun sol-gel consisted of nickel acetate tetrahydrate (NiAc), copper acetate monohydrate (CuAc), and poly vinyl alcohol (PVA) in the presence of Ar/H_2 gas at 700^oC for 1h. The NFs appeared to have good electrical conductivity and electrocatalytic activity for ethanol oxidation, at the current density ~ 100 mA/Cm^2 and onset potential ~ 350 vs. Ag/AgCl. These enhanced properties are due to the influence synergistic of the bimetallic alloy and thin graphite layer.

Keywords: Nanoalloy; Carbon Nanofibers; Electrospinning; Fuel Cells; Ethanol.

1. INTRODUCTION

Direct alcohol fuel cells (DAFCs) are promising energy devices. Among of them, direct ethanol fuel cells are better ones due to their lower toxicity and higher energy density. Ethanol is easily

produced as a source of renewable energy from agricultural bioprocesses. Furthermore, ethanol when compared with methanol is a better choice for fuel cells [1-3]. An important factor in DAFCs is the selection of electrocatalyst. Precious metal and bimetal nanostructures (e.g. Pt and PtRu) are believed to be higher efficiency electocatalysts in the fuel cells. However, their higher cost constrains them for wider applications. Also, a real critical problem facing the Platnium-based electrocatalysts is a poison accumulated due to the adsorption of CO or CHO species [4-6]. Recently, bimetallic transition metal nanostructures have received much research attention due to their synergistic effects: their low cost, and unique physicochemical property. They differ from their monometallic counterparts in composition, structure, and properties. These differences led to several exhilarating opportunities for applications in various technologically important fields such as transportation industry [7, 8]. Accordingly, nickel-based materials have high surface oxidation properties that make them the best candidates for electrocatalysis [4, 9-11]. Among the based materials, copper has been used in electrooxidation of alcohols and other organic compounds [12, 13]. Thus Ni and Cu composites are able to enhance electrooxidation on DAFCs [13, 14]. However, nude NiCu nanocomposite cause corrosion problem during ethanol electrooxidation. Covering the bimetallic NiCu nanocomposite with chemically stable materials (carbon) might be a good idea to increase corrosion resistance. In addition carbon, nanomaterials can achieve better electrical conductivity and adsorption capacity for enhancing NiCu nanocomposite chemical stability. Carbon when compared with different nanomaterials can improve contact between ethanol and catalyst. Nanofibers (NFs) have a high axial ratio that provides effortless electrons transfer. This is considered the most important factor in the electrocatalysts [4, 15-17]. Electrospinning is a commonly used technique in the preparation of organic and inorganic NFs [18-20]. In this study, synthesized NiCu nanocomposite-decorated on Carbon nanofibers was prepared via an electrospinning technique. The prepared nanocomposite was introduced as economical catalyst for electrocatalytic oxidation of ethanol with better electric conductivity and electrocatalytic activity.

2. MATERIALS AND METHOD

2.1. Materials and preparation

Aqueous solution consisting of 20 wt% CuAc and 80 wt% NiAc was dissolved in 5 g deionized water. The solution was stirred at 323 K until as obtained a clear solution. Then, the solution was added to 15 gm PVA solution (10 wt%) (M_{wt} =85000-124000 g/mol). Stirring was continuous in oil bath at 50 ^{o}C for 5hr. The prepared sol-gel was electrospun, using a DC power supply, at 20 KV. The formed mats were vacuum dried at 323 K for 24 h. Finally, the dried mats were calcined in an inert atmosphere (Ar/H_2) at 700^{o}C for 1h.

2.2. NFs Characterization

Field-emission scanning electron microscope (FESEM, Hitachi S-7400, Japan) was used to observe the morphology of the nanocomposite. The microscope was a transmission electron

microscope (TEM) (JEOL Ltd., Japan) equipped with EDX for the investigation of the crystallinity of nanocomposite. X-ray diffraction technique with Cu Kα (λ=1.54056 Å) (Rigaku Co., Japan) was used to determine the crystallinity structure of nanocomposite. The catalytic activity of introduced nanocomposite was achieved by using an electrochemical cell with three-electrode system. The synthesized nanocomposite, platinum wire, and Ag/AgCl were used as working electrode, counter electrode, and reference electrode, respectively. The catalytic activity was measured using the cyclic voltammetry test (CV) in 1 M KOH solution. The sweep potential ranged from 0 to 0.8 V. 2 mg from nanocomposite powder was mixed with 20 µL Nafion solution (5 wt%) and 400 µL isopropanol. 15 µL from the prepared slurry was poured on the glassy carbon electrode (GCE). Electrode was dried at 80 ^{o}C for 30 min.

3. RESULTS AND DISCUSSION

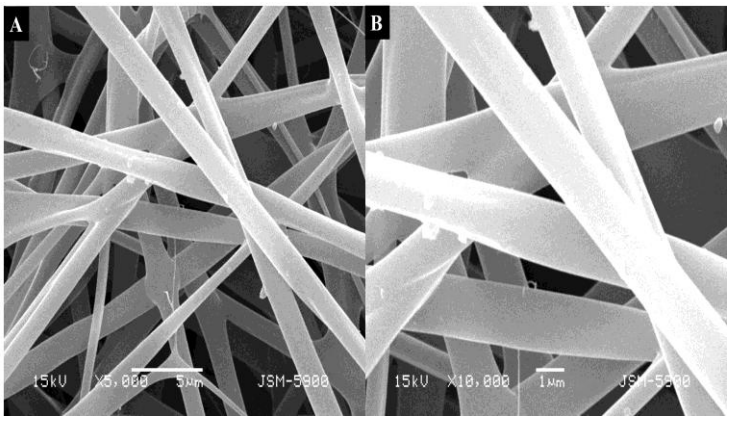

Figure 1. SEM images of the obtained powder after the calcination process.

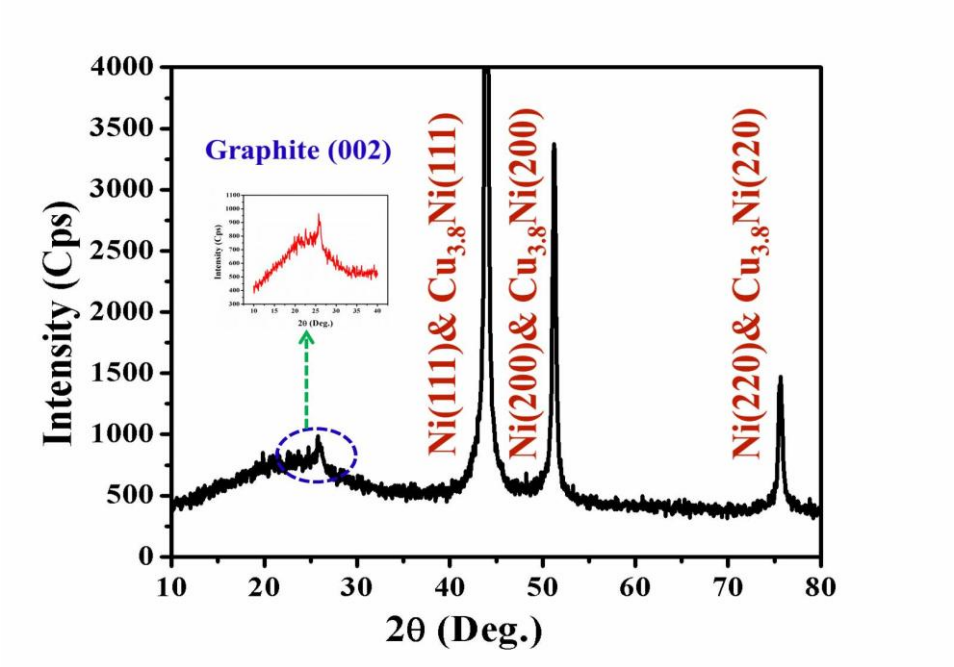

Figure 2. XRD analysis of the obtained powder after the sintering process.

The FE-SEM images of the calcined mats are shown in Figure 1A and B. As shown in the figure, good nanofibrous morphology was obtained.

XRD analysis of the synthesized nanocomposite is shown in Fig. 2 indicating the diffraction peaks at 2θ~ 43.9°, 51.0°, and 75.5°. These peaks match with that of the Ni-Cu alloy. Moreover, graphite peak appeared at 2θ~26°.

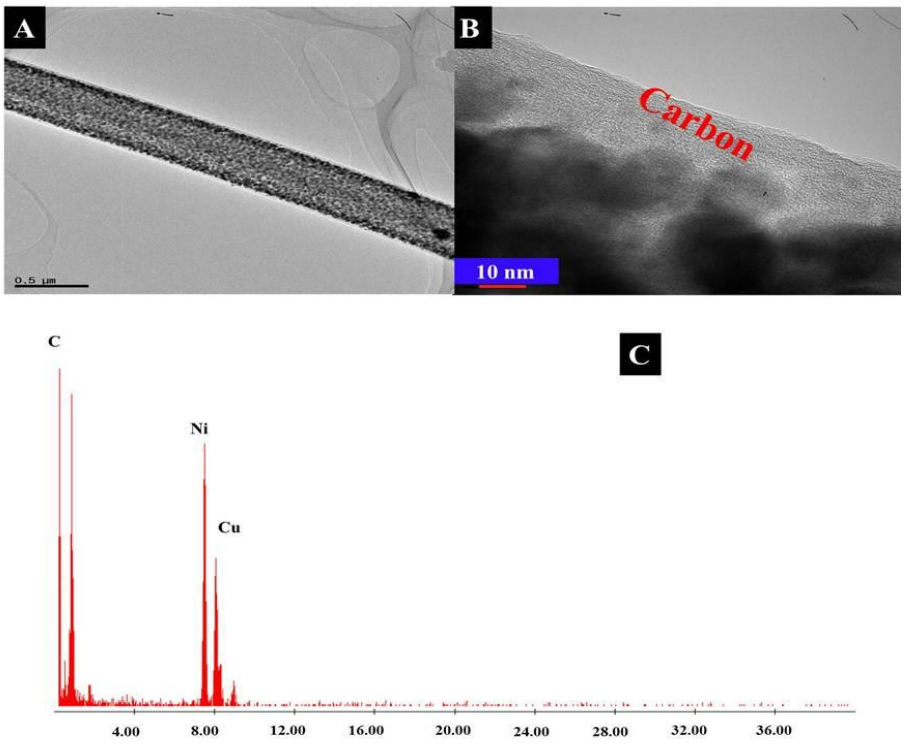

Figure 3. Normal TEM image (Panel A), HR-TEM image (Panel B), and Elemental-EDX analysis (Panel C) of the calcined nanofiber.

Fig. 3A shows TEM image of the obtained powder, where the bimetallic NiCu NFs were covered by a thin graphite layer. HR-TEM image in panel B showed the sheathing of bimetallic NiCu nanocomposite in a shell by graphite-like carbon. Furthermore, TEM-EDX analysis in Panel C confirmed the presence of Ni, Cu, and C only. It is noteworthy mentioning that the graphite layer could be protecting NiCu nanocomposite during vigorous reactions. The graphite has a high electrical conductivity and adsorption affinity enhancing the electrocatalytic activity by the fast ethanol adsorption.

Accordingly, a good electrical conductivity was obtained as shown in Fig. 4. The figure displays the IV plots for a thin film by the prepared material on the silicon substrate. The previous phenomena considers an most important factor for the electrocatalytic activity of materials. Pure copper and nickel were used as effective catalysts in electro-oxidation of alcohols and some organics. However, copper does not undergo redox processes in the potential range of nickel's but only enhance the electrocatalytic activity of nickel in alcohol oxidation depending on the thermodynamic data [13].

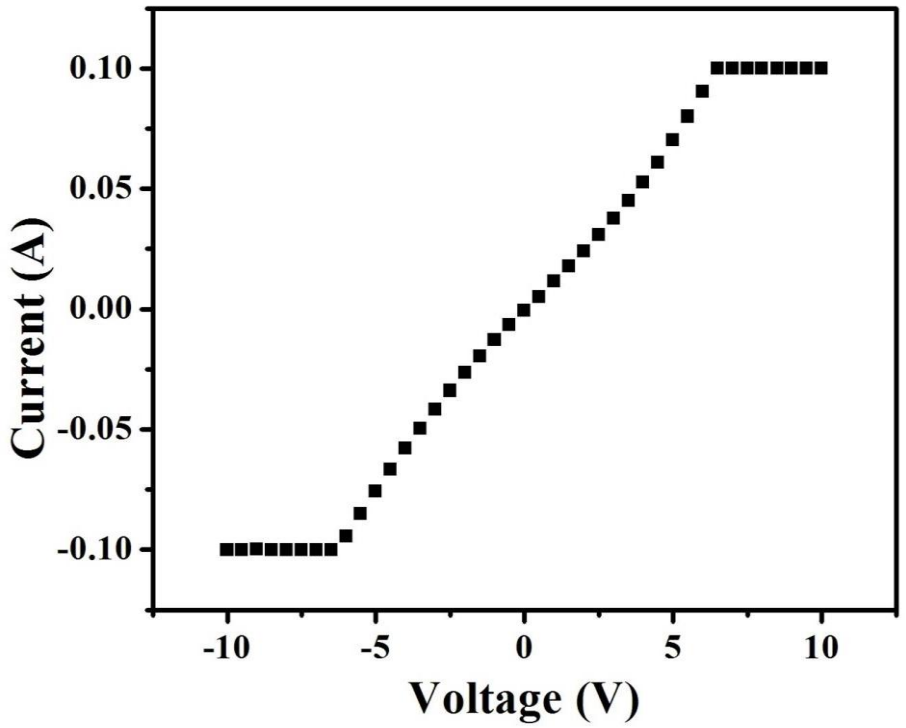

Figure 4. Electrical conductivity measurement for the synthesized NFs.

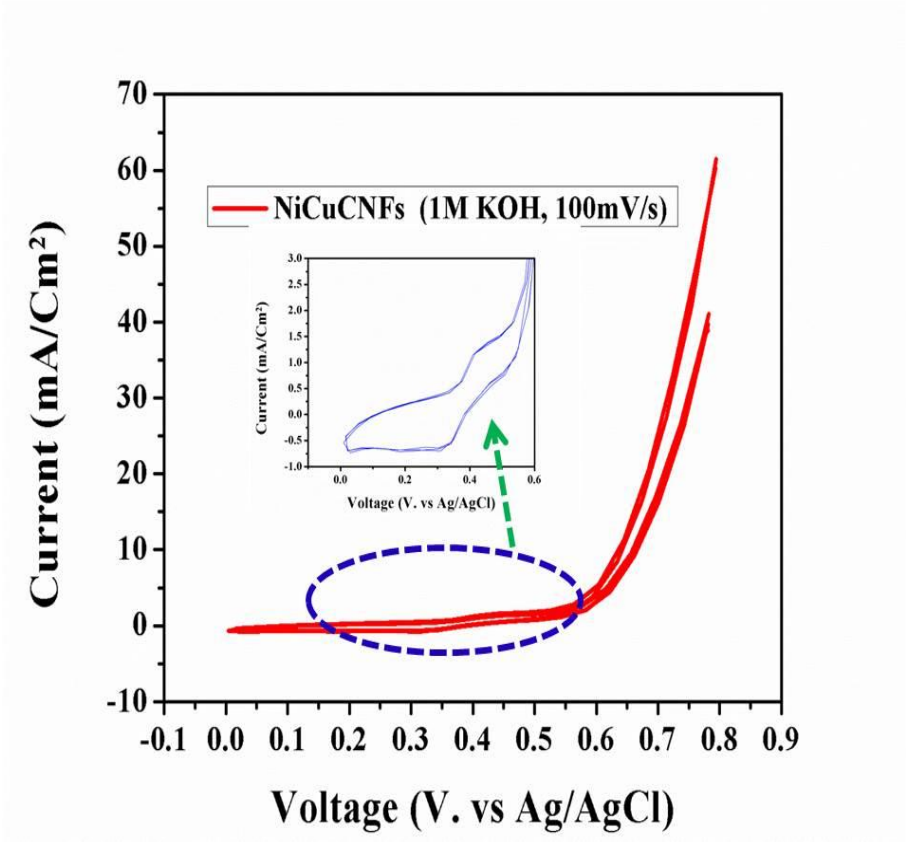

Figure 5. Cyclic voltammograms for activation the introduced NFs.

Fig. 5 displays CV behaviors of prepared NFs in 1M KOH solution. The potential was varied from 800 mV to -200 mV; where the current density was increased from cycle one to cycle ten. Polarization began at a potential scanning 100 mV/s. This attributed to the formation of an active NiOOH layer on the catalyst surface that distinct the Ni-based material. This layer created on the surface was used to initiate electrochemical activity. Moreover, the inset in the figure stated a wide scale for the marked area. Accordingly, two redox peaks appeared in the positive potential side at 430 mV and 320 mV [4, 13], assigning to the oxidation of Ni(II)/Ni(III) in accordance with the following reaction:

$$Ni(OH)_2 + OH^- \longleftrightarrow NiOOH + H_2O + e^- \quad (1)$$

In general, the process of alcohol electro-oxidation depends on the adsorption of the reactants and intermediate compounds. Then successive dissociation steps carry out [15].

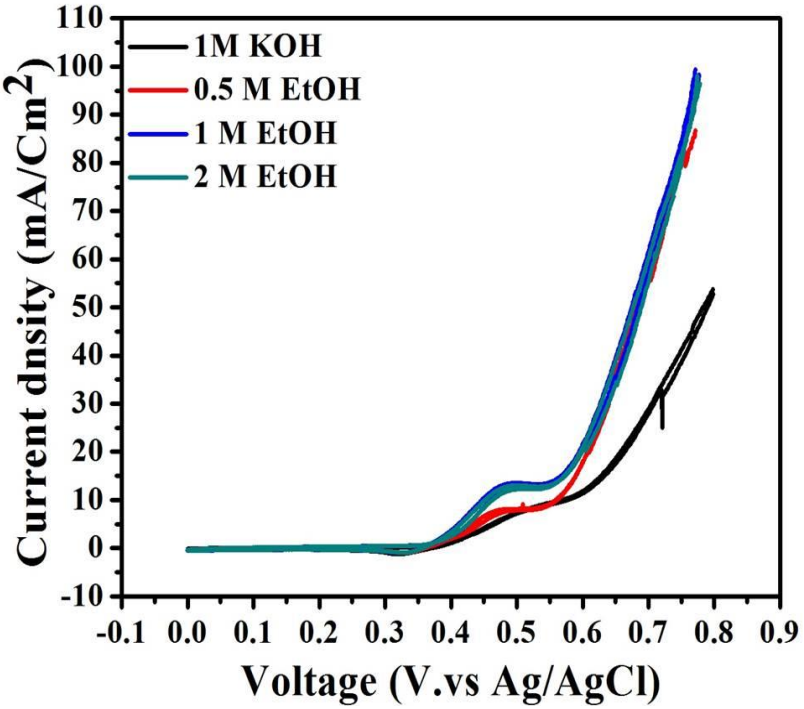

Figure 6. Cyclic voltammograms in the presence of different concentration from ethanol.

Fig. 6 indicates the effect of EtOH concentration on the current density for the synthesized nanocomposite at the potentials between 800 mV to -200 mV with scan rate 50 mV/s and at 25^0C. As shown in the figure, mostly there is no change in current density with increasing ethanol concentration. It is worth mentioning that, increase in EtOH concentration more than 2 M revealed low current densities. Thus it can be denoted that 2 M is the ideal concentration. To study the efficiency of the prepared nanocomposite the onset potential values were used. The magnitude of the negative value indicates lower over potential and higher activity. As shown in Fig. 6, The nanocomposite showed a low onset potential ~ 570 vs.NHE.

The obtained higher electrocatalytic activity of nanocomposite is due to the following; First, copper enhances the electrocatalytic activity of nickel in ethanol oxidation by filling the Ni d-band vacancies by Cu electrons that inhibit volume expansion of Ni^{2+} phase during methanol oxidation in alkaline media [13]. Second, thin graphite shell enveloping NiCu nanofibers (Fig. 2A) is able to enhance the chemical and corrosion resistance of NiCu nanofibers in alkaline media under high oxidizing conditions, and increase adsorption of ethanol molecules on the surface of nanofibers. Finally, the higher performance obtained for the nanofibrous morphology may be attributed to the effect of the one dimensional features that facilitate the electrons transfer through the electrocatalyst.

4. CONCLUSION

Bimetallic NiCu NFs enveloped in thin graphite layer were prepared by the electrospinning technique. Introduced NFs appeared to have higher electrical conductivity and excellent ethano electrooxidation. A current density ~ 100 mA/Cm^2 and onset potential ~ 350 vs. Ag/AgCl were obtained. Overall, the present study introduced Bimetallic NiCu NFs enveloped in thin graphite layer as an effective and low cost electrocatalyst.

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