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RESEARCH PAPER

Core–Shell Titanium Dioxide /Carbon Nanofibers Decorated Nickel Nanoparticles as Supports for Electrocatalytic Oxidation of Ethanol

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ABSTRACT

In this work, a new method for ethanol oxidation based on core–shell titanium dioxide / carbon nanofibers (TiO_2@C NFs), TiO_2 as a core and carbon as a shell, decorated Ni nanoparticles (NiNPs) is presented. TiO_2@C NFs were prepared by mixing the electrospinning technique and hydrothermal method. Nickel nanoparticles were electrodeposed on the surface of TiO_2@C NFs denoted as TiO_2@C- Ni. The catalyst was characterized by SEM and electrochemical methods. Performance of ethanol oxidation was investigated in aqueous NaOH solutions by chronoamperometry and cyclic voltammetry. The electrochemical measurements showed that this electrode is effective and has good electrocatalytic activity for ethanol oxidation and the structures of nanofibers have important effect on the electrooxidation of ethanol. The synergy between Ni, carbon shell and TiO_2 support, boost ethanol oxidation on TiO_2@C- Ni.

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INTRODUCTION

Recently alcohol fuel cells has been increased consideration because of their environmental friendliness, high energy conversion efficiency and low emissions [1,2]. Many effort have been made to improve the electro-oxidation performance of alcohols such as methanol, ethanol and propanol [3]. Ethanol is known as an ideal material for fuel cells due to its high energy density, low toxicity, large production from renewable sources and transportation [4], but several main restrictions exist in the practical usage of ethanol in the field of fuel cells, such as low electro-oxidation activities, high cost of noble metal based catalysts, and so on [5,6]. Hence for reduce the cost of catalysts, Pt-free materials such as Pd have been studied [7,8].

As successor for valuable metals, non-noble metals, nickel and nickel compounds are noteworthy because of their low cost, electrochemical stability, resistance to poisoning, and high catalytic activity for electro-oxidation of ethanol. The catalysts for ethanol oxidation is more energetic in alkaline medium than acid medium [9–12]. In alkaline solutions nickel converted to Ni $(OH)_2$ and the Ni^{2+}/Ni^{3+} redox show high catalytic activity for oxidation of some small organic compounds [13,14]. Nickel is an impressive and inexpensive catalyst for oxidation of small organic compounds including carbohydrates [15,16], methanol [17,18] and ethanol [19–24]. For example, nickel redox, Ni $(OH)_2$/NiOOH, formed on the nickel surface display high catalytic activity for oxidation of ethanol in alkaline media. Because of

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the low electrical conduction of these changed and accumulation of small Ni nanoparticles limited their electrocatalytic performance [25,26]. To solve the problems, Ni nanocrystals were dispersed and fixed on a solid support, usually using carbon materials as the matrix [27–29]. The electrocatalytic performance of the nanocomposites will be improved due to the highly conductive matrix, structural properties and fixation of Ni nanocrystals.

Graphite nanofiber (GNF) [30], carbon nanotubes (CNT) [31–34], carbon nanohorns [35] and carbon nanocoils [36] applied as carbon support for fuel cell usage. TiO_2–carbon materials have been considered as catalyst support materials in fuel cell electrode [37].The nanostructured titania (TiO_2) has usage in drug transfer, filters, solar cells, and biosensors because of its high specific surface area, chemical stability and biocompatibility [38–40]. Electrospinning is a simple technique, and used for many years to process polymer, metal oxides materials into one-dimensional (1D) structural fibers such as TiO_2 nanofiber [41].

TiO_2 doping with transition metals ions such as V, Co, or Fe has been a popular method for modifing the photocatalytic performance of the catalyst [42–44]. However, some problems remain unresolved, for example, doped materials have thermal instability, an increase in the carrier-recombination probability, and photocorrosion [45]. Non-metal (B, F, N, C etc.) doping has been proved to be more prosperous [27,46–49] particularly, in the manner of carbon doping, the C element is infiltrating to the lattice of TiO_2 replacing a lattice O atom and form O–Ti–C species.

To the best of our knowledge, no study has been published so far reporting the electroanalytical applications of TiO_2@C-Ni. We generate TiO_2@C NFs mixing the electrospinning technique (for TiO_2 NFs) and hydrothermal approach (for carbon layer). In this method glucose used as a carbon source and fibrous TiO_2@C core–shell nanocomposites as electro-catalyst supports for NiNPs. It's a new catalyst that use in ethanol oxidation application based on these reasons. First, Ni nanoparticles, when well dispersed and with good particle size, show good catalytic activity for ethanol electro-oxidation due to ability of Ni to adsorb OH^- ions to formation of Ni $(OH)_2$. Second, the high electric conductivity of carbon boosts current collection. Third, a 1D TiO_2 NFs provides accessibility for active species and catalysts and enhances the effective mass transfer of reactants. Also, the use of Ni causes reduces in catalyst cost.

MATERIALS AND METHODS

The electrochemical measurements were done with a Zive lab potentiostat/galvanostat. A three-electrode system was used, where a glassy carbon (GC) electrode was used as the working electrode, a platinum wire as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. An electrospinning device, FANAVARAN NANO-MEGHYAS Model: ES1000 with controllable feeding rate and DC voltage range of 5 kV to 30 kV was used to formation nanofiber.

TiO_2@C nanofibers were synthesized in our laboratory which their synthesis explained here. Acetic acid, titanium tetraisopropoxide (TTIP), polyvinylpyrrolidone (PVP), ethanol, glucose, NaOH were analytical grade from Merck (Darmstadt, Germany).

Preparation of TiO_2 NFs

Firstly, 0.38 g poly (vinyl pyrrolidone) powder (PVP, Mw = 1300000) was added to a mixture of 9 mL absolute ethanol and 2.4 mL acetic acid in a bottle. The solution was stirred for 2 h to provide a homogeneous solution. Then 360 µL Ti $(OC_4H_9)_4$ was added to the solution, the mixture was stirred for 3 h to make precursor solution. The above solutions were drawn into a syringe that was connected to the 15 kV voltage and distance between the needle tip and collector was 15 cm. The as-collected nanofibers were calcined and remained for 2 h at 550 ºC to form TiO_2 NFs.

Preparation of TiO_2@C NFs

TiO_2@C NFs were prepared by hydrothermal method. It was explained as follows: glucose (0.6 g) and TiO_2 NFs (15 mg) were put into a teflon-lined stainless steel autoclave of 25 mL capacity which including 20 mL deionized water to make glucose solution with the concentration of 30 g L^{-1}. After powerful stirring for 10 min, the mixture was then stirred to form a milk like suspension, and hydrothermally treated at 180 ºC for 4 h. After reaction, the autoclave was cooled in air, and the suspensions were isolated by filtration, washed with water several times and dried in oven at 80 ºC for 4 h.

Preparation of the electrode

In these work, Ni nanoparticles were synthesized by electrochemical method [50].To reach the best position in the preparation of TiO_2@C- Ni / GC electrode, at first, the surface of GC electrode was polished on a polishing cloth with 0.05 mm alumina powder and then was washed with deionized water. GC electrode was created with Ni nanoparticle and TiO_2 @C nanofiber in two steps:

First, about 2.0 mg of TiO_2 @C nanofibers were dispersed in 0.45 mL ethanol, 0.45 mL water and 100 µL nafion an ultrasound bath for 30 min then a volume of 3.0 µL of the suspension was applied directly on a GC electrode surface and dried in air, then the potentiostatic deposition of nickel nanoparticle on the TiO_2@C- Ni / GC electrode from an aqueous solution of 60 mM Ni^{+2} by controlled potential coulometry (CPC) applying a constant potential electrolysis at -0.6 V for 60 seconds was used, preparation of TiO_2-Ni/GC electrode is same as the mentioned electrode.

RESULTS AND DISCUSSION

Characterization of TiO_2@C- Ni

The morphologies of the TiO_2 nanofibers, TiO_2@C nanofibers, TiO_2 NFs-Ni and TiO_2@C NFs-Ni have been investigated by scanning electron microscopy (SEM) (Fig. 1) and X-Ray diffraction (XRD) patterns (Fig. 2).

SEM image shows that the lengths of these nanofibers were about several micrometers and the surface of TiO_2 nanofibers was clear Fig 1A. After done hydrothermal, the nanofibrous morphology shown in Fig. 1B remained unchanged and the surface morphology of TiO_2@C NFs catalysts was found to be uniform and porous surface, TiO_2 nanocrystals encapsulated in carbon matrices. The TiO_2 nanofibers can be seen as an intermediate yield in the preparation of TiO_2@ carbon nanofibers. Fig 1C shows SEM image of TiO_2@C- Ni that decorated with carbon matrices and Ni nanoparticles, NiNPs existing on the surface of TiO_2@C. Fig 1D shows SEM image of TiO_2 (NF) that decorated with Ni nanoparticles, it can be seen NiNPs existing on the surface TiO_2 nanofiber.

The X-ray diffraction (XRD) patterns of the TiO_2 NFs,TiO_2@C NFs, TiO_2 NFs-Ni and TiO_2@C NF-Ni are shown in Fig. 2. As observed in Fig. 2, TiO_2 NFs show six reflection peaks appeared at 2Θ = 25.4

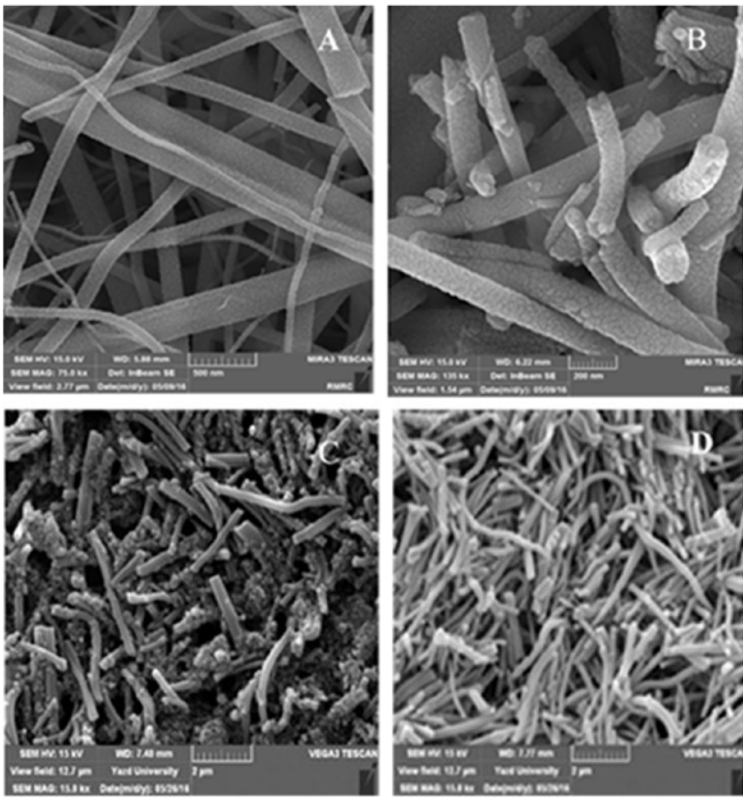

Fig. 1. SEM images of TiO_2 nanofibers (A), TiO_2@carbon nanofibers (B), TiO_2@carbon (NFs)-Ni (C) and TiO_2(NF)-Ni (NPs) (D)

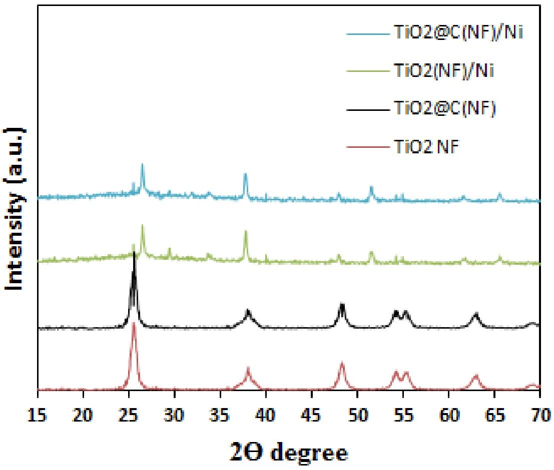

Fig. 2. XRD patterns of the TiO_2 NFs, TiO_2@C NFs, TiO_2 NFs-Ni and TiO_2@C NFs-Ni

(101), 37.9 (004), 48.0 (200), 54.8 (105), 55.4 (211) and 63.8 (112), respectively, which were attributed to the anatase TiO_2. The diffraction peaks of the TiO_2 nanofibers were sharp and intense, indicating the highly crystalline character of the nanofibers. The curves of TiO_2@carbon nanofibers, TiO_2 (NF)-Ni (NPs) and TiO_2@carbon (NFs)-Ni also exhibited the diffraction peaks of anatase TiO_2. And, the graphitic carbon peak at $2\Theta = 25.6$ for TiO_2@carbon nanofibers was too weak to see [51]. To verify whether Ni (NPs) was deposited to TiO_2 and TiO_2@carbon NF during the electrochemical process, XRD patterns of the TiO_2 (NF)-Ni (NPs) and TiO_2@carbon (NFs)-Ni were recorded and compared. The diffraction peaks at 51.5° corresponded to the (2 0 0) facets of the Ni crystal, respectively [52].

Electrocatalytic effect of TiO_2@C- Ni for oxidation of ethanol

The impression of scanning rates on the CV response of the TiO_2@C- Ni/GC electrode was investigated in 0.1 M NaOH solution, and the results are shown in Fig. 3A. For TiO_2@C- Ni/GC electrode redox with increased scanning rates peak current increased, inset Fig. 3A shows both anodic and cathodic peak currents have linear response to the scan rates ranging from 0.01 - 0.3 V s^{-1}. This can be ascribed to the electrochemical activity of an immobilized redox on the surface with a surface-controlled process [53]. The surface coverage r* can be estimated according this equation [54]:

$$I_p = n^2 F^2 A r^* / 4RT \qquad (1)$$

where r* is the surface coverage of redox sample, n is the number of transferred electrons (1 for Ni^{2+}/Ni^{3+}), v is the scan rate, A is the surface area of the electrode, all other symbols have their conventional concept. The surface coverage of TiO_2@C- Ni /GC electrode was estimated to be $r^*_a = 6.22\times 10^{-7}$ mol cm^{-2} for anodic peak currents.

Fig. 4 shows the comparative CV responses from the electrochemical oxidation of 2 M ethanol at the TiO_2@C- Ni /GC in 0.1 M NaOH (curve d), TiO_2- Ni /GC in 0.1 M NaOH and 2 M ethanol curves (c), and (b) and (a) are the voltammograms of TiO_2@C- Ni /GC and bare GCE, respectively, curve (b) in 0.1 M NaOH, curve (a) bare GCE in 0.1 M NaOH with 2 M ethanol. It clear that the current of catalyst in 2 M ethanol at scan rate of 100 mV s^{-1} is higher than other electrodes. Denoting that the TiO_2@C- Ni /GC catalyst can oxidation ethanol, the enhanced electrocatalytic activity of TiO_2@C- Ni /GC is due to the nanofibrous morphology increase the activity. To investigate the roles of C on TiO_2 surface in the electrochemical oxidation of ethanol, the cyclic response of ethanol at the TiO_2- Ni /GC (curve c) and TiO_2@C- Ni /GC (curve d) electrodes were recorded. The results indicated that the presence of C on TiO_2 surface exhibited 58.66%, improvement the peak current for ethanol. Although, the specific surface area of the nanoparticles is more than the nanofibers but the large axial ratio of the nanofibers increases the electrons transfer with the catalyst which results in modified the electrocatalytic process [55], and carbon materials as the matrix improve the conductivity.

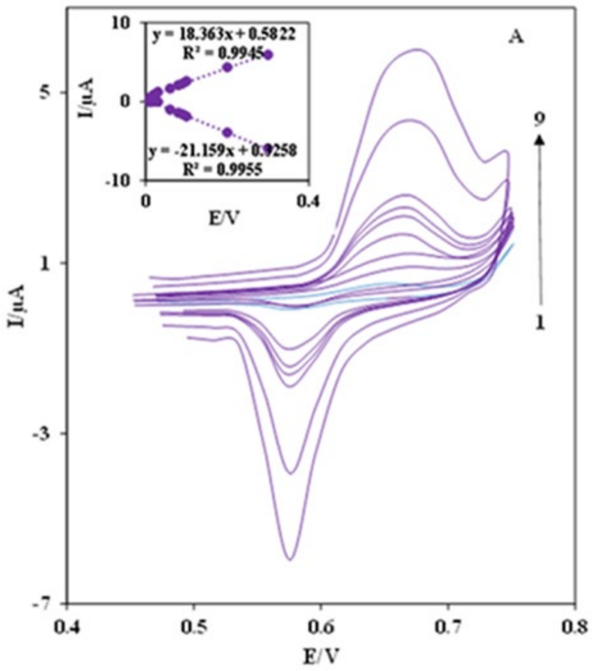

Fig. 3. (A) CVs of the TiO_2@C- Ni/GC electrode in 0.1 M NaOH at different scan rates: 0.01, 0.02, 0.03, 0.06, 0.08, 0.09, 0.1, 0.2 and 0.3 Vs^{-1} from 1 to 9 respectively. Inset Plots of peak current versus scan rate.

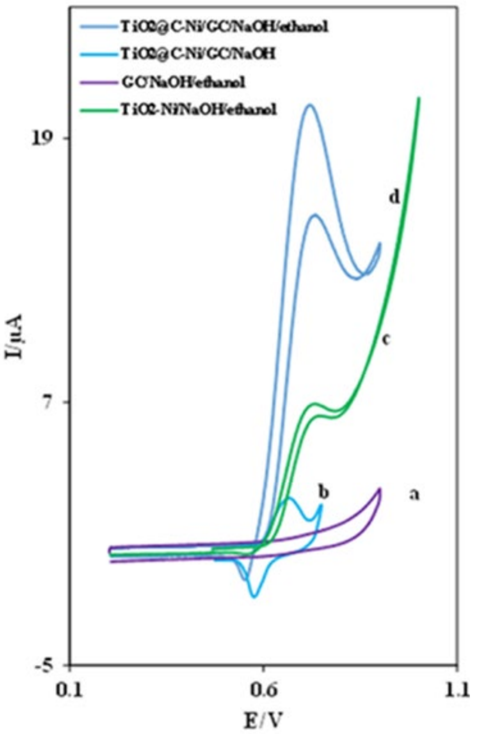

Fig. 4. CVs of the GC electrode in 0.1 M NaOH (a), TiO_2@C-Ni /GC electrode in 0.1 M NaOH (b), TiO_2-Ni /GC in 0.1 M NaOH and 2 M ethanol (c) and TiO_2@C- Ni /GC in 0.1 M NaOH and 2 M ethanol (d), scan rate 100 mVs^{-1}

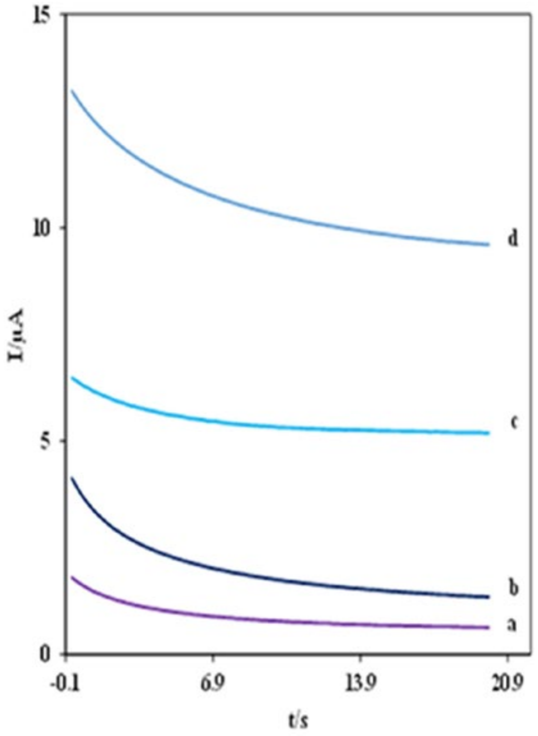

Fig. 5. Chronoamperograms of GC electrode in 0.1 M NaOH (a), GC electrode in 0.1 M NaOH and 2 M ethanol (b), TiO_2@C- Ni /GC electrode in 0.1 M NaOH (c), TiO_2@C- Ni /GC electrode in 0.1 M NaOH and 2 M ethanol (d)

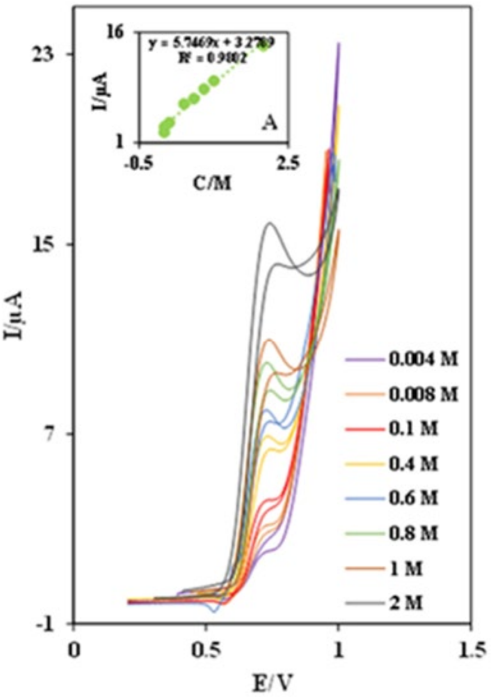

Fig. 6. Cyclic voltammograms for the prepared TiO_2@C- Ni /GC electrode at different ethanol concentration: 0.004, 0.008, 0. 4, 0.6, 0.8, 1.0 and 2 M ethanol in 0.1 M NaOH at scan rate 50 mVs^{-1} and 25 °C.inset (A) Plots of anodic peak current versus different concentration of ethanol

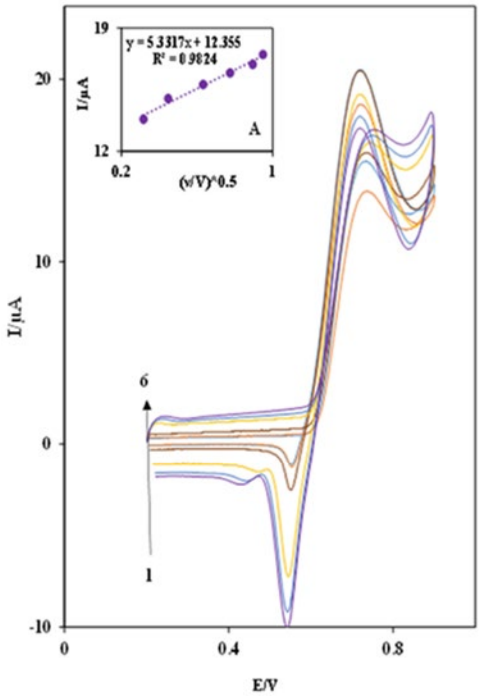

Fig. 7. CVs curves of the as-prepared TiO_2@C- Ni /GC electrode in 0.1 M NaOH solution in the presence of 2 M ethanol at different scan rates : 0.1, 0. 2, 0. 4, 0.6, 0.8 and 0.9 Vs^{-1} from 1 to 6 respectively, inset (A) the corresponding plot of peak current I_p vs. potential sweep rate $v^{1/2}$

The chronoamperometry method was utilized for comparison of the effect of different electrodes in ethanol oxidation. Fig. 5 shows the results of chronoamperometry measurements of TiO_2@C- Ni /GC electrode in 0.1 M NaOH and 2 M ethanol (d), TiO_2@C- Ni /GC electrode in 0.1 M NaOH (c), GC electrode in 0.1 M NaOH and 2 M ethanol (b), GC electrode in 0.1 M NaOH (a). The results showed that the TiO_2@C- Ni /GC electrode in 0.1 M NaOH and 2 M ethanol electrode have high current in comparison with other electrodes. This because of the electrocatalytic properties of nanofibers in the TiO_2@C- Ni /GC electrode for ethanol oxidation, and the improvement in the activity of TiO_2@C-Ni /GC electro-catalyst for ethanol oxidation maybe related to the uniform dispensation of metal nanoparticles on the TiO_2@C NFs support. It is said that the addition of Ni decreased the overpotential and NiOOH formed on the surface of the catalyst, increases the catalytic activity for ethanol oxidation which is in according to the results of cyclic voltammetry of ethanol oxidation.

Fig. 6 shows CV of different ethanol concentration in 0.1 M NaOH and scan rate 50 mVs^{-1}. The results show the good electrocatalytic activity of nanofibers. Increasing the ethanol concentration in the alkaline solution increase the anodic current, with increasing ethanol concentration the peak potential shifted positively, showing kinetic limitation. Anodic peak in the reverse scan in the ethanol oxidation is because of the more oxidation of ethanol molecules due to regeneracy of the active (Ni^{+2}/Ni^{+3}) on the electrode surface which were coating by intermediates, ethanol molecules or reaction products in the forward scan. Therefore, the efficient utilization of high alcohol contents is an important performance parameter for corresponding catalysts. Inset (A) shows plots of the anodic peak currents (I_p) were linearly dependent on concentration of ethanol.

Fig. 7 shows the influence of the scan rate on the electrocatalytic activity of 2 M ethanol by TiO_2@C-Ni/GC electrode and 0.1 M NaOH in the range of 0.1 to 0.9 V s^{-1}. It can be seen, the anodic current increases with increasing the scan rate. As shown in (Inset A in Fig 6); plots of the anodic peak currents (I_p) were linearly dependent on $v^{1/2}$ in the range of 0.1 to 0.9 V s^{-1}; this linear relationship display that the nature of the redox process was controlled by diffusion manner.

CONCLUSION

In this paper, we reported a victorious method to generate TiO_2@C NFs, glucose used as a carbon source and present here fibrous TiO_2@C core–shell nanocomposites and new method for ethanol oxidation based on Ni nanoparticles (NiNPs) decorated TiO_2@C (NFs) is presented. TiO_2@C-Ni is new catalyst that exhibits performance in ethanol oxidation application based on these reasons. First, Ni nanoparticles, when well dispersed and with good particle size, show good catalytic activity for ethanol electro-oxidation due to ability of Ni to adsorb OH^- ions in the form of Ni $(OH)_2$. Second, the high electric conductivity of carbon boost current collection. Third, a 1D TiO2 NFs provides the maximum accessibility for active species and catalysts and enhances the effective mass transfer of reactants due to the large axial ratio of the nanofibers. This work opens new avenue to synthesize more effective catalyst involve nanofiber to be applied in ethanol oxidation process.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.The authors wish to thank the Yazd University Research Council, IUT Research Council and Excellence in Sensors for financial support of this research.

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