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Nickel nitride nanoparticles as efficient electrocatalyst for effective electro-oxidation of ethanol and methanol in alkaline media

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ABSTRACT

In this paper, nickel nitride (Ni_3N) nanoparticles with spherical structure are successfully synthesized by urea glass route. The morphology and structure of the as-prepared nanoparticles are characterized by scanning electron microscopy and X-ray diffraction. The electrocatalytic properties of the synthesized Ni_3N for ethanol and methanol oxidation in alkaline media were investigated using cyclic voltammetry and chronoamperometry. A peak current of about 200 μA for ethanol and 100 μA for methanol oxidation was recorded during ethanol and methanol oxidation under the test condition of adding 1.0 M alcohols in 0.1 M NaOH solution. The stability of the catalyst was investigated using steady state chronoamperometry for 1000 s. The results show that the nickel nitride exhibits excellent electrocatalytic activity that is very promising catalyst for fuel cell application.

1. Introduction

In recent years, fuel cells due to decrease in fossil fuel reserves and the serious environmental pollution caused by the use of these fossil fuels, have attracted extensive attention [1]. Fuel cells can be used as green power sources and highly efficient power source in transportation and portable electronic devices [2]. In direct alcohols fuel cells (DAFCs), alcohol is directly oxidized with oxygen from the air to carbon dioxide and water to generate electricity [3]. Alcohols, like methanol and ethanol, are suitable candidates for DAFCs [4,5]. The use of methanol as a fuel has several advantages such as: low pollution emission and low operating temperature. Furthermore, methanol can be cheaply produced through large-scale chemical process and methanol is a liquid at normal ambient temperatures, thus it can be easily and inexpensively stored [6]. Ethanol has a higher volumetric energy density and lower toxicity in comparison with methanol, and has been viewed as a renewable fuel because it can be produced from biomass fermentation [7]. Despite these advantages, several important limitations exist in the practical application of alcohols in the field of fuel cells, such as relatively slow kinetics and continuous poisoning of the catalysts due to the presence of intermediates generated in the alcohols oxidation reaction [8,9].

In electrochemistry, electrocatalysis offers reductions in over-potential and increase in the magnitude of voltammetric peak heights, allowing high kinetics to be more achievable [10–15]. It is known that platinum (Pt) is widely used as a catalyst in DAFCs due to the rapid kinetics of the oxidation and reduction reactions taking place on its surface [16,17]. However, the high cost of Pt and Pt-based catalysts, limited Pt resources, and easy poisoning by even a trace of CO or CHO during the oxidation of alcohols are major problems [18,19]. To overcome this issue, many researches have been focused on the non-noble metals or their complexes for substitution of precious metals. Among these materials, metal Ni [20,21], Ni-alloy [22,23] and Ni-compounds [24–28] because of their low cost, electrochemical stability, resistance to poisoning, and high catalytic activity toward the electro-oxidation of alcohols are regarded as good candidates [29]. As an alternative to metals and their oxides, metal nitrides attract a lot of attention thanks to their excellent catalytic activities in a variety of reactions for energy related applications [30–32]. On the other hand, the presence of nitrogen strongly influences the electronic properties of the metal by increasing the density of electrons on the surface. Consequently, metal nitrides are found to have higher (electro)catalytic activities in reduction reactions, compared to the corresponding pure metals [33–35].

The “urea glass route” is a simple, scalable and versatile approach for synthesizing various metal carbides and nitrides [36]. The urea-glass-route is a carbothermal reduction in presence of a N-/C-source [37]. The key feature of the ‘urea glass technique’ lied in the formation of the gel-like/glassy starting materials composed of a polymeric complex between metal precursors and urea and an ambient treatment for the transformations to the corresponding carbides and nitrides [38]. This method is an easy approach that minimizes the use of toxic solvent and needs no purification. In fact, this is a simple and safe method to produce nitrides using urea as nitrification agent replacing high pressure ammonia, required in many other synthesis pathways forming

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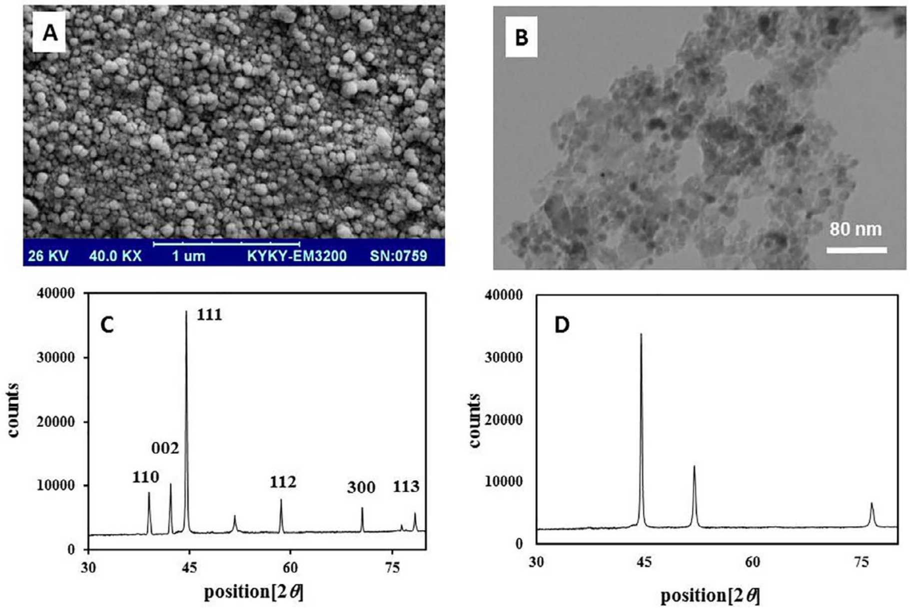

Fig. 1. (A) SEM (B) TEM image of Ni_3N nanoparticles with different magnification, XRD pattern of the synthesized nanoparticles at 370 °C (C) and 470 °C (D).

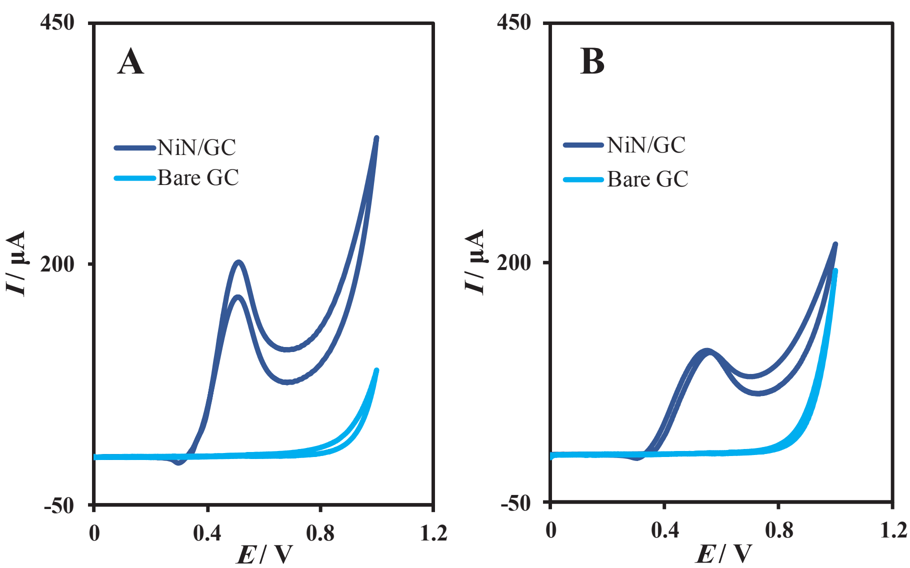

Fig. 2. CVs of the GCE and NiN/GC in 0.1 M NaOH solution containing 1.0 M ethanol (A) and 1.0 M methanol (B) with the scan rate of 100 mV s^{-1}.

nitrides [39].

With an aim of developing cost-effective but efficient DAFCs catalyst, in this study, we report the application of nickel nitride (Ni_3N) nanoparticles for ethanol and methanol oxidation in alkaline media by a simple and non-toxic method. Nickel nitride (Ni_3N) nanoparticles serves as an effective platform for the electro-oxidation of ethanol and methanol in alkaline media. The formation of nickel nitride was confirmed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and their electrocatalytic properties are evaluated by electrochemical methods. The results show that the nickel nitride exhibits excellent electrocatalytic activity that is very promising catalyst for fuel cell application.

2. Experimental section

2.1. Apparatus and chemicals

A potentiostat/galvanostat (SAMA 500, electroanalyzer system, I.R. Iran) was used to carry out the electrochemical experiments. A saturated calomel electrode (SCE), platinum wire and modified glassy carbon electrode were used as reference, auxiliary, and working electrodes, respectively. A Metrohm model 691 pH/mV meter was also used for pH measurements.

All of the materials used in this work were used as received, without further purification, if not stated otherwise. Nickel (II) nitrate hexahydrate, methanol, ethanol, urea and other reagents from Merck. Nafion (5.0 wt% ethanol solution) were purchased from Sigma-Aldrich.

2.2. Synthesis of nickel nitride nanoparticles

In a typical experiment, nickel (II) nitrate hexahydrate (870 mg) and urea (720 mg) were dissolved in approximately 3.0 mL of ethanol. The mixture was magnetically stirred for 12 h until a clear light-green solution was obtained. Then the sample was thermally treated for 5 h at 370 °C under a flowing N_2 atmosphere.

2.3. Preparation of NiN/GC modified electrode

The glassy carbon electrode (GCE, 3 mm diameter) was polished with Al_2O_3 power, rinsed twice by deionized water and then dried at