

Full Paper

Synthesis and Characterization of Nickel Molybdate Nano-powders in the Presence of Carboxymethyl Cellulose as a New Capping Agent and its Application on Electrochemical Determination of Ethanol

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Abstract- Nickel molybdate (NiMoO₄) nanopowders were prepared by a new method in low temperature. For the first time, we used carboxymethyl cellulose as a new capping agent in synthesis procedure. The formed nickel molybdate products have been characterized by means of UV–vis diffuse reflectance spectroscopy, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and energy dispersive X-ray microanalysis (EDX). Glassy carbon electrode modified with NiMoO₄ nanopowders was prepared and used for oxidation of ethanol and methanol. The study of the different scan rates indicates a diffusional process for oxidation of ethanol. The detection limit obtained for ethanol was also 3.8 mM.

Keywords- Nickel molybdate, Nanopowders, Carboxymethyl cellulose, Electrochemical Determination, Ethanol

1. INTRODUCTION

Nano-structured semiconductor materials have attracted considerable attention in nanoscience and nanotechnology due to their better physico-chemical properties compared with their same bulk materials [1-13].

Ethyl alcohol or alcohol is a volatile and flammable liquid which has various applications, such as disinfectant solvents and modern fuels. Its most important applications is using as a psychoactive substance. Excessive consumption of ethanol causes drunkenness and anesthesia. Ethanol acts as a suppressing agent in nervous system which causes complications such as sensory disorder, motor disorder and ultimately death, so the amount of ethanol consumed in beverages and blood should be controlled [14,15].

Several methods have been used to synthesize this nanomaterial such as sonochemical, hydrothermal, sol-gel, chemical precipitation methods [16–27]. However, by using the above conventional methods, nickel molybdate nanopowders were synthesis comparatively large in size with irregular morphology and inhomogeneity. Here in, carboxymethyl cellulose was used as a capping agent to synthesize nickel molybdate nanopowders by precipitation method. This capping agent is a derivative of cellulose, there are of the groups (OH) on the carbon chain. This (OH) plays an important role in the dispersion method of nickel molybdate nanopowders. Also, the glassy carbon electrode was modified with NiMoO₄ nanopowders and its ability in electrocatalysis for oxidation of methanol and ethanol which can be used as fuel in fuel cells will be evaluated.

2 EXPERIMENTAL

2.1. Synthesis of nickel molybdate nanopowders

Ammonium heptamolybdate tetrahydrate, Ni(NO₃)₂·6H₂O and carboxymethyl cellulose were used as starting materials. At first, 3 mmol of ammonium heptamolybdate tetrahydrate and 3 mmol carboxymethyl cellulose was dissolved in 40 mL of water in 60 °C, and then aqueous solutions including 3 mmol nickel nitrate was added to it. Afterwards, a solution consist of NaOH was added drop wise into the above mentioned solution under magnetic stirrer for 12 min at 30 °C. Next, final precipitates were dried in vacuum at 25 °C for 90 min. The as-prepared products were characterized by FT-IR, SEM, TEM and XRD.

2.2. Materials and physical measurements

All chemicals were purchased from Merck and used without purification. Powder X-ray diffraction (XRD) patterns of the as-synthesized nickel molybdate were recorded by applying a diffractometer of Philips Company with X'PertPromonochromatized Cu K_α radiation (k=1.54 Å). SEM images of nickel molybdate were visualized by employing a Tescan mira3 field emission scanning electron microscope (FESEM). Perkin Elmer FT-IR spectrometer was used

to analyze the surface functional groups. Transmission electron microscopy (TEM) images were obtained using a Philips EM208 TEM at an accelerating voltage of 200 kV.

The Voltammetric experiments were performed with Autolab PGSTAT-302 (Eco Chemie B. V.) potentiostat/galvanostat instrument controlled by a computer using GPES software. A typical three-electrode system was used with a glassy carbon electrode as the working electrode, an Ag/AgCl (3 M KCl) and a Pt wire as the reference and counter electrodes, respectively.

2.3. Preparation of electrode modified by nickel

In order to prepare a modified electrode, glassy carbon electrode is first cleaned using sandpaper, and the electrode posed in a mixture of ethanol and acetone was placed in an ultrasonic bath for 10 min to remove the contaminants over surface and then washed with distilled water. Then, to modify the electrode, 1 mg of synthesized NiMoO₄ nanopowders was dispersed into the 10 mL distilled ethanol and 2 μ L of this mixture was placed on the electrode surface and dried at the laboratory temperature.

3. RESULTS AND DISCUSSION

In Fig. 1 nickel molybdate nanopowders prepared with carboxymethyl cellulose as a new capping agent have been shown. Due to polymeric structure of carboxymethyl cellulose, nanopowders with sphere like in the size of 50 nm have been prepared. The TEM results (Fig. 2) further confirmed these observations and data.

Considering XRD pattern of compounds, one can obtain chemical structure and crystal size of the compounds [28-40]. XRD patterns of nickel molybdate nanopowders are shown in Fig. 3. The spectrum of bare nickel molybdate nanopowders shows a series of diffraction peaks at the position of 26.32° ((112) line), 32.18° ((002) line), 43.18° ((200) line), and 54.63° ((222) line) which is in good agreement with the standard JCPDS file of nickel molybdate nanopowders tetragonal phase (space group I41/a, JCPDS No. 85-0588). Crystalline sizes is calculated from Scherrer equation, $D_c = K\lambda/\beta\cos\theta$, where β is the width of the observed diffraction peak at its half maximum intensity (FWHM), K is the shape factor, which takes a value of about 0.9, and λ is the X-ray wavelength (Cu K α radiation, equals to 0.154 nm) were about 12/3 nm for nickel molybdate nanopowders.

The FT-IR spectrum of nickel molybdate display in Fig 4. FT-IR spectrum containing a broad band around 3400 cm^{-1} is due to the hydroxyl stretching mode of water molecules adsorbed on the surface of the sample [41-43]. A band appears at 1634 cm^{-1} may be due to combination band of O-H stretching. This spectrum shows an absorption at 1111 cm^{-1} which was related to C-O bond stretching mode. The characteristic two strong bands of NiMoO₄ appear at 532 and 452 cm^{-1} are assigned to Mo-O and Ni-O vibrations, respectively.

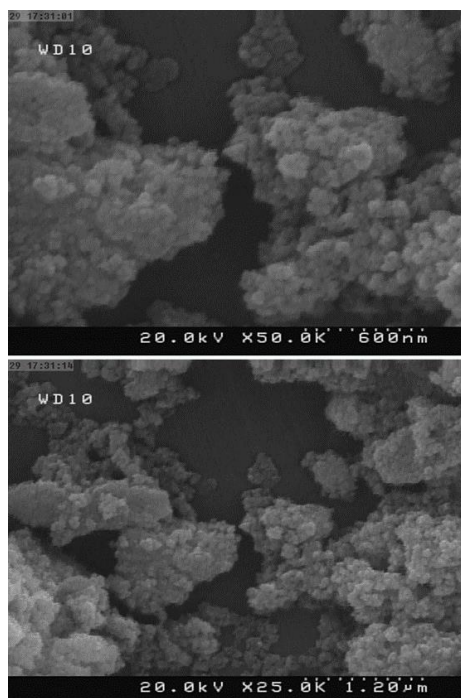


Fig. 1. SEM images NiMoO₄ nano-powders obtained in the presence of carboxymethyl cellulose as capping

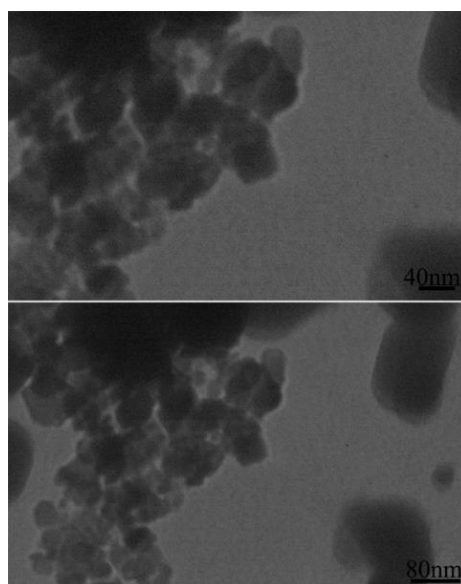


Fig. 2. TEM images of NiMoO₄ nano-powders obtained in the presence of carboxymethyl cellulose as capping

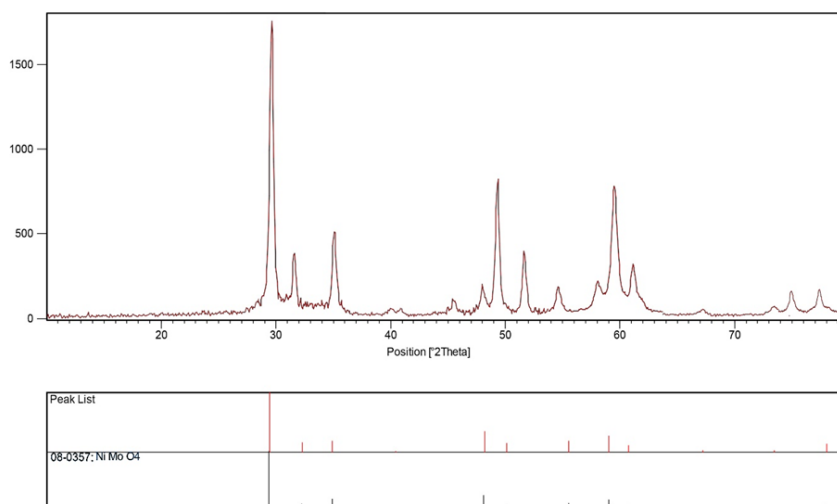


Fig. 3. XRD pattern of NiMoO₄ nano-powders obtained in the presence of carboxymethyl cellulose as capping

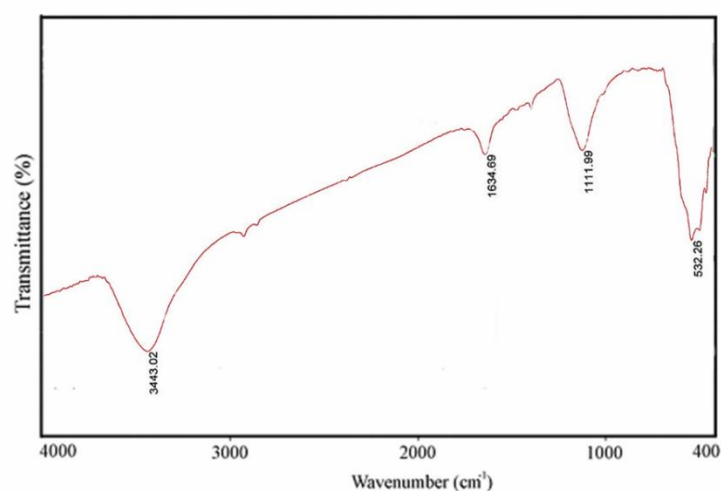


Fig. 4. FT-IR spectra of NiMoO₄ nano-powders obtained in the presence of carboxymethyl cellulose as capping

3.2. Electrochemical performance of methanol and ethanol

Today different nanostructures are used in electrochemical detection of different compounds [44-49]. Metal oxide nanostructures have also various applications in this area [50]. Therefore the synthesized NiMoO₄ nanopowders was used for methanol and ethanol measurement. The electrochemical behavior of methanol and ethanol at the surface of the electrode modified with NiMoO₄ nanopowders was studied using cyclic voltammetric technique to give information about the performance of modified glassy carbon electrode. For this purpose, the studies were performed in 0.1 M KOH in the absence and presence of

methanol and ethanol at the scan rate of 0.1 mV/s. Fig. 5a shows the voltammogram obtained from a glassy carbon electrode modified with nickel molybdate in 0.1 KOH. The existence of an oxidation and reduction peak for modified electrode is indicative of the electroactivity of this compound. After adding the methanol and ethanol (1 M) separately, it was observed that oxidation peak for NiMoO₄ nanopowders was increased and its reduction peak was decreased (Fig. 5b, c). The change in oxidation peak of NiMoO₄ nanopowders is originated from the electrocatalytic activity for oxidation of methanol and ethanol which the electrocatalytic activity is shown better for ethanol.

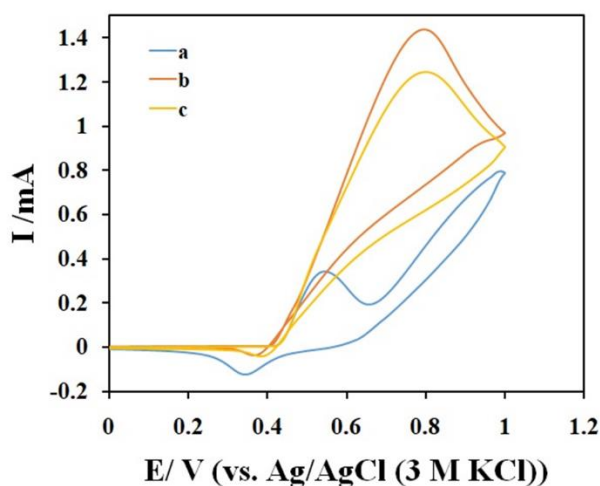


Fig. 5. (a) Cyclic voltammogram of glassy carbon electrode modified with NiMoO₄ nanopowders in 0.1 KOH, scan rate=0.1 V/s; (b) Cyclic voltammograms of glassy carbon electrode modified with NiMoO₄ nanopowders in the solution contains 0.1 M KOH and ethanol and methanol (1 M) with a scan rate of 0.1 V/s

3.3. Investigation of electrocatalytic behavior of glassy carbon electrode modified with nickel at different scan rates in the presence of ethanol

Cyclic voltammograms at different scan rates (0.01-0.25 V/s) were plotted for oxidation of ethanol (1 M) in 0.1 M KOH, as shown in Fig. 6a. Figure 6b shows that there is a linear relationship between square root of scan rate and peak current. This linear relationship indicates that the overall oxidation process of ethanol at the surface of this electrode is controlled by diffusion. Figure 6c shows the normalized current diagram ($I V^{-1/2}$) versus the scan rate, which indicates a negative slope of the electrocatalytic nature of the process.

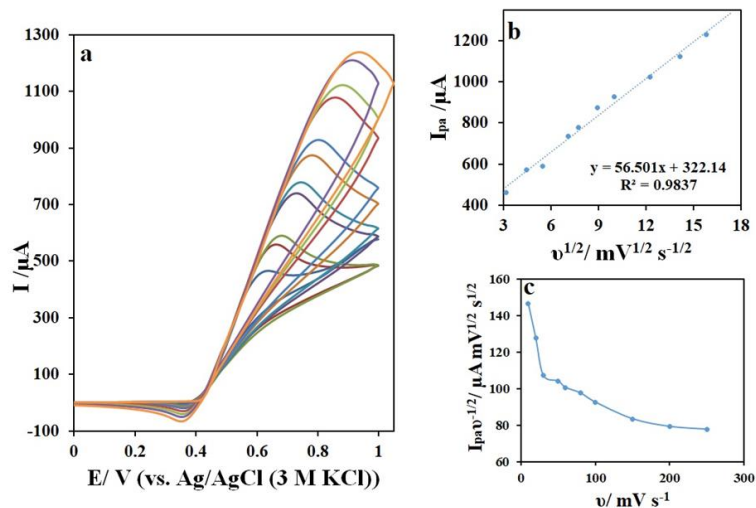


Fig. 6. Cyclic voltammogram of electrode modified with NiMoO₄ nanopowders in 0.1 M KOH solution and ethanol (1 M) at different scan rates; (b) The plot of peak currents against the $v^{1/2}$; (c) Variation of the normalized current ($I_p v^{-1/2}$) with scan rate

3.4. The study of electrochemical behavior of modified electrode in different concentrations of ethanol

The relationship between ethanol concentration and its oxidation current are shown in the presence of various concentrations of ethanol (10-120 mM). It is observed that the value of anodic peak current increases with increasing the ethanol concentration at concentrations range from 10-120 mM (Fig. 7a,b). The detection limit was also obtained from the relation $\text{LOD}=3\text{ S/M}$, which its numerical value is 3.8 mM.

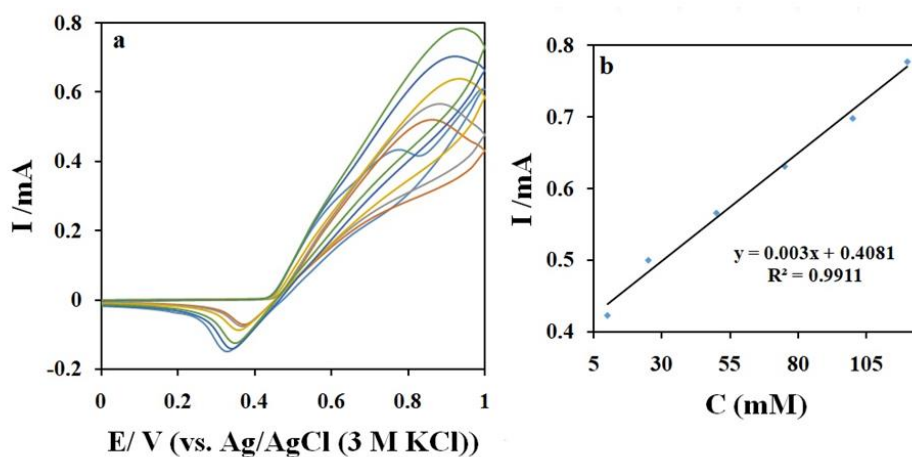


Fig. 7. (a) Differential pulse voltammogram at different concentrations of ethanol; (b) Current diagram versus ethanol concentration

4. CONCLUSION

Here in, nickel molybdate nanopowders were successfully synthesized by a precipitation route at low temperature. Results showed that uniform morphology and size particle is obtained in the presence of carboxymethyl cellulose. The electrocatalytic properties of the electrode modified with NiMoO₄ nanopowders were tested in ethanol and methanol, and it was observed that the behavior of modified electrode in ethanol was better than methanol. The diffusion nature of the current and also electrocatalytic nature of oxidation process of ethanol were tested by investigation of various scan rates. Finally, the detection limit obtained for oxidation of ethanol (3.8 mM) was in the linear range (10-120 mM).

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