

Facile and green synthesis of CuO nanoparticles and electrocatalytic activity of CuO nanoparticles/conductive polymer composite film

Ali Ehsani^{a,*}, Reyhaneh Asgari^b, Akbar Rostami-Vartooni^a, Hamid Mohammad Shir^b, Ali Yeganeh-Faal^b

^aDepartment of Chemistry, Faculty of science, University of Qom, Qom, Iran.

^bDepartment of Chemistry, Payame Noor University, Iran.

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ABSTRACT

In this work, CuO nanoparticles (CuO NPs) was prepared by a simple and green method using Rosmarinus officinalis extract containing phenolic constituents as both the chelating and the stabilizing agents. CuO nanoparticles/polyorthoaminophenol composite (CuO NPs/POAP) as electro-active electrodes for electrocatalytic oxidation of methanol with good uniformity are prepared by electropolymerization. Composite of CuO NPs/POAP was synthesized by cyclic voltammetry (CV) methods and electrochemical properties of film were investigated by using electrochemical techniques. New composite modified electrode shows a significantly high response for methanol oxidation. This method of synthesis of the catalyst and composite has the advantages of high yields, elimination of chemical reagent and simple methodology. Catalytic efficiency remains unaltered even after several repeated cycles.

Keywords: Nanoparticles, Conductive polymer, Electrosynthesis, Catalyst.

1. Introduction

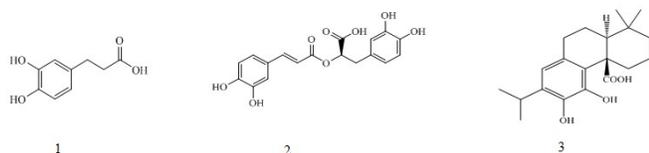
CuO nanostructures have been extensively investigated because of their promising applications in various fields such as catalysis, batteries, semiconductors, supercapacitors, solar cells, sensors, nanofluid and photo detectors [1-4]. Rosemary (Rosmarinus officinalis) is a valuable and important medicinal and aromatic plant, which belongs to the lamiaceae family and it grows in most regions of Iran. In recent decades, antioxidant compounds from rosemary have received increasing interest for their use instead of synthetic antioxidant in food industry and medicine [5,6].

Caffeic acid (1) and its derivatives such as rosmarinic acid (2) are the most important constituents of rosemary [7-9]. These phenolic compounds have an antioxidant effect [10]. Moreno and coworker suggest that the antimicrobial rosemary extracts efficacy was associated with their specific phenolic composition such as carnosic (3) and rosmarinic acids [10].

In this work, CuO NPs was prepared by a simple and

green method using Rosmarinus officinalis extract containing phenolic constituents as both the chelating and the stabilizing agents. The catalytic performance of the prepared catalyst was investigated for electrocatalytic oxidation of methanol. During the past few years, a large number of papers have been published concerning electrocatalytic properties of platinum group metals and their alloys incorporated into the polymeric backbone. It has been shown that such modified electrodes with Pt micro particles exhibit a better catalytic effect than smooth platinum for the oxidation of methanol [11-15]. Although metals such as Pt and Pt-Ru are very active in the anodic oxidation of methanol, they are too expensive for practical applications. The use of Ni and Cu as the catalysts for alcohol electro-oxidation is of interest because it is an inexpensive metal. Many electrodes that include Ni and Cu as a component in their manufacture can be used as catalysts in fuel cells. Ni and Cu are commonly used as an electrocatalyst for both anodic and cathodic reactions in organic synthesis and water electrolysis. One of the most important uses of Cu and Ni as a catalyst is to oxidize alcohols.

*Corresponding author email: a.ehsani@qom.ac.ir
Tel: +98 25 3210 3038; Fax: +98 21 3285 4973



Scheme 1. constituents of different compounds of rosemary.

Several investigations on the electro-oxidation of alcohols on Ni and Cu have been reported [16-21]. We have combined the advantageous features of polymer modification, dispersion of metallic or metal oxide particles into an organic polymer. In this work, we combined the above-mentioned advantageous features with the aim of the electrocatalytic oxidation of methanol by the use of poly(*ortho*-aminophenol) as a conductive polymer. In the present work CuO Nps/POAP composite was synthesized by cyclic voltammetry (CV) methods and electrochemical properties of film were investigated by using electrochemical techniques, viz. CV and electrochemical impedance spectroscopy (EIS). This method of synthesis of a catalyst and composite has the advantages of high yields, elimination of chemical reagent, low cost and simple methodology. The catalytic efficiency remains unaltered even after several repeated cycles and suitable as an anode material in fuel cell.

2. Experimental

2.1. Instruments and reagents

All reagents were purchased from the Merck and Aldrich chemical companies and used without further purification. X-ray diffraction measurements were performed with a Philips powder diffractometer type PW 1373 goniometer. It was equipped with a graphite monochromator crystal. The X-ray wavelength was 1.5405 Å and the diffraction patterns were recorded in the 2θ range (10-60) with scanning speed of 2°/min. Morphology and particle dispersion was investigated by scanning electron microscopy (SEM) (Cam scan MV2300). The chemical composition of the prepared nanostructures was measured by EDS performed in SEM. All electrochemical experiments were carried out by an Autolab General Purpose System PGSTAT 30 (Eco-chime, Netherlands). Saturated Calomel Electrode (SCE), a Pt wire and a graphite (G) electrode were used as the reference, counter and working electrodes, respectively. All studies were carried out at 298 ± 2 K.

2.2. Preparation of *Rosmarinus officinalis* extract

Rosemary plant was collected from university of Qom (Qom, Iran). 10 g of dried powder of rosemary leaves and roots was extracted by heating at 80°C in 50 mL distilled water for 25 min and the aqueous extract was centrifuged at 7000 rpm to obtain the supernatant as

extract. This solution of the extract is used for the synthesis of CuO NPs.

2.3. Preparation of CuO NPs

For green synthesis of CuO NPs, CuCl₂·2H₂O was dissolved in 100 ml of distilled water under magnetic stirring at 50 °C temperature. The addition of the above extract causes the formation of dark brown precipitate which then transforms into CuO by heat treatment. After 30 min, the mixture was centrifuged, washed with distilled water and then dried at 70°C for 1 h. Finally, crystalline CuO NPs were obtained after calcination at 300°C for 3 h in furnace

2.4. Preparation of CuO NPs/POAP

The CuO NPs were first dispersed in an aqueous solution containing an ionic surfactant. Then, electroactive monomer *ortho*-aminophenol (OAP) was added into the above mixture and finally electrochemical reaction was preceded at the surface of the graphite electrode. Films of composite were formed on the graphite surface using a OAP monomer solution (0.01 M tyramine in 0.1 M LiClO₄ and 0.1M HClO₄, 0.005 M SDS and 10% CuO) for CuO/POAP and (0.01 M OAP in 0.1 M LiClO₄, 0.1M HClO₄, 0.005 M SDS and 10% CuO NPs) for CuO NPs/POAP under ultrasonic irradiation. The electropolymerization was carried out by potential cycling (40 cycles at a scan rate of 50 mV/s between -0.2 and 0.9 V versus SCE.

3. Results and Discussion

The CuO NPs was prepared by a simple and inexpensive method using aqueous extract of the leaves and roots of *Rosmarinus officinalis*. The extract of the plant not only functioned as chelating agents, but also served as a stabilizer for prepared CuO NPs. It will be expected that the presence of phenolic components (Scheme 1) in the extract could be responsible for the formation of Cu complexes which then transform into CuO by heat treatment at 300°C for 3 h. As shown in Fig. 1, the insoluble Cu complexes were formed in the presence of phenolics acids in the rosemary extract. The obtained CuO NPs was fully characterized by FT-IR, XRD, FE-SEM and EDS.



Fig. 1. Photograph of *Rosmarinus officinalis* leaves and root extract (A) and synthesized Cu complexes produced after bio reaction (B).

Fig. 2 shows the UV-vis spectra of *Rosmarinus officinalis* extract. The observed bands are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of benzene rings and carbonyl groups in the extract compounds. The constituents of aqueous extract could be adsorbed on the surface of metal nanoparticles, possibly by interaction through π -electrons interaction. Hence, the extract acts as the stabilizer as well as the chelating agents.

Fig. 3 shows the XRD pattern of CuO NPs. All the diffraction peaks could be clearly indexed to monoclinic phase of CuO, which agreed with the data of the Joint Committee on Powder Diffraction Standards file (JCPDS No.05-0661).

The SEM images (Fig. 4) showed that the particle sizes of the CuO NPs, which were found to be spherical in shape and are in the range of 10–50 nm. In the EDS spectrum (Fig. 5), peaks related to Cu (61.23 %W/W) and O (27.33 %W/W) were observed. Presence of the Au in the diagram is related to mounted Au in SEM analysis.

Composite films were applied to electrooxidation of methanol in alkaline media. Fig. 5a shows cyclic voltammograms of CuO NPs/POAP modified graphite electrode in 0.1 M NaOH solution in the presence of methanol at a potential sweep rate of 10 mV s⁻¹.

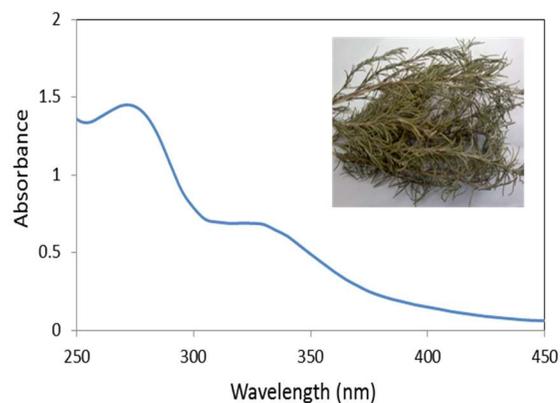


Fig. 2. UV-vis spectrum of *Rosmarinus officinalis* leaves and root extract.

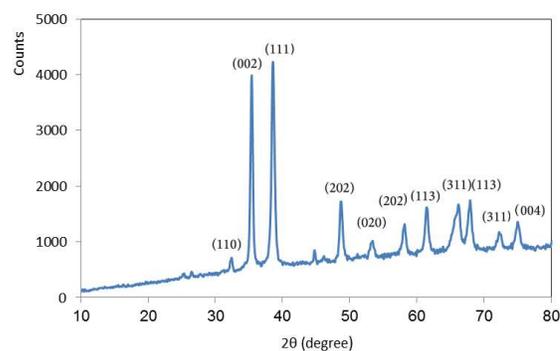


Fig. 3. XRD pattern of CuO NPs.

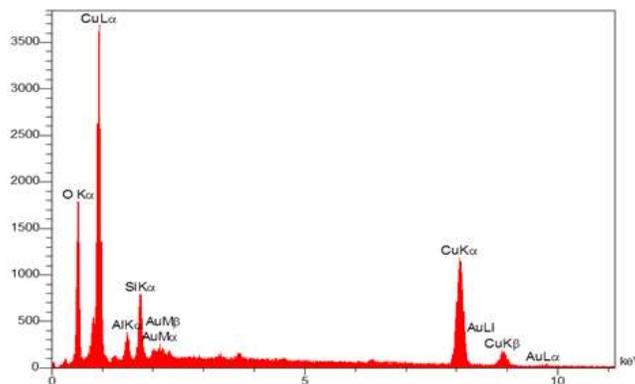
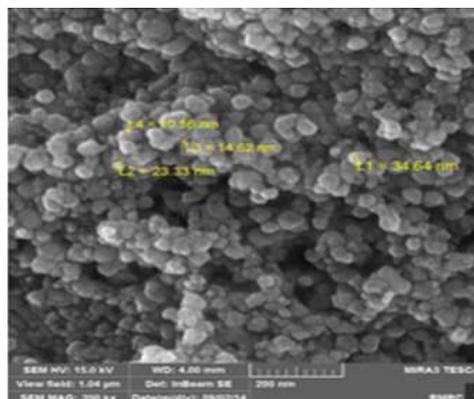
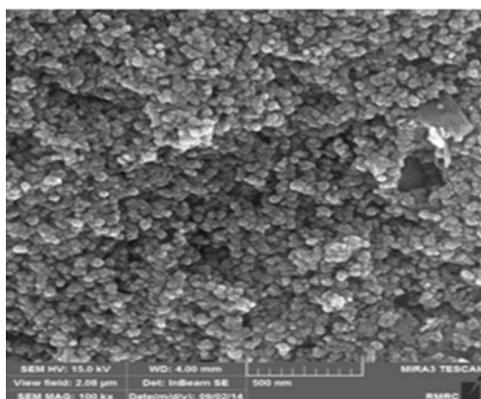


Fig. 4. Typical EDS spectrum and FE-SEM images of CuO NPs in different magnification.

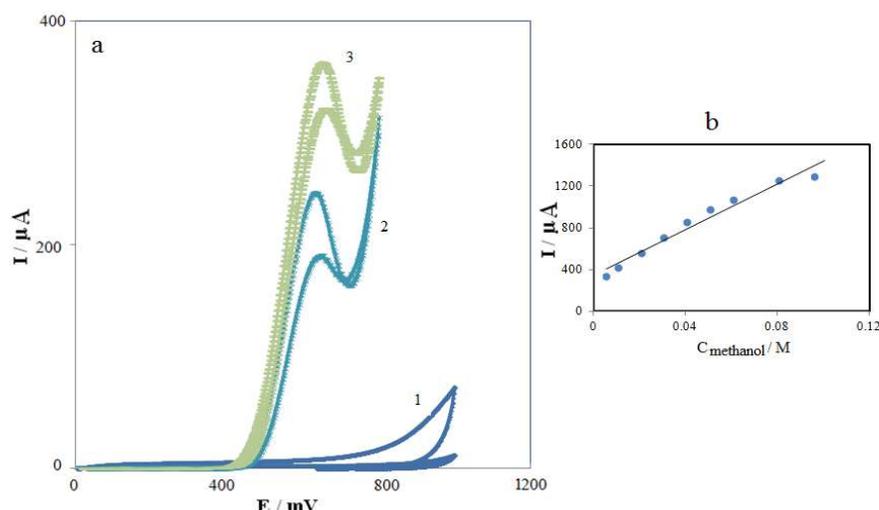


Fig. 5. (a) Cyclic voltammograms of CuO/POAP (2) and CuO NPs/POAP (3) modified graphite electrode in 0.1 M NaOH solution in the presence of 0.005 methanol at a potential sweep rate of 10 mV s⁻¹. (1) Shows voltammograms in the absence of methanol. (b) Shows dependency of the anodic peak current on the concentration of methanol in solution.

The larger methanol response at the CuO NPs/POAP with respect to CuO/POAP is proposed to be the nanostructure effect which enhances the catalytic properties of copper oxide through fine dispersion of the catalyst particles into the conductive polymer matrix. It results in a drastic increase in the surface area. The anodic current in the positive sweep was proportional to the bulk concentration of methanol and any increase in the concentration of methanol caused an almost proportional linear enhancement of the anodic current (Fig. 5b). So, catalytic electrooxidation of methanol on modified electrode seems to be certain. Meanwhile, results show reasonable current for methanol electrooxidation in comparison to already published papers [22,23]. It is observed that the current of electro-oxidation of methanol is almost constant in

300 cycles due to the stability of electrocatalyst in this cycle number and indicating that methanol reacted with the surface and no poisoning effect on the surface was observed.

At CuO NPs/POAP modified graphite electrode, oxidation of methanol appeared as a typical electrocatalytic response in alkaline media by Cu(OH)₂/CuOOH [22]. Schematic of the catalyst preparation and electrocatalytic oxidation of methanol is shown in Fig. 6. The anodic electrochemical reactions can be summarized as follows:

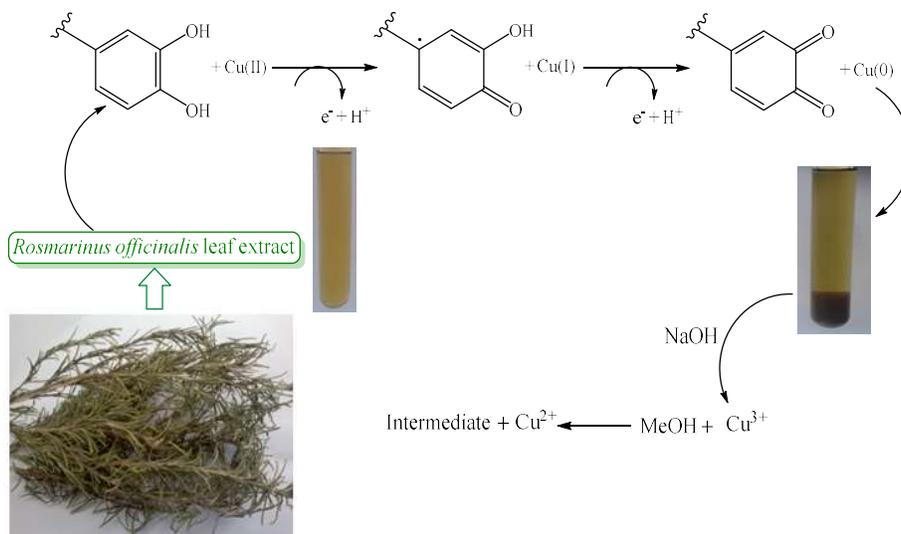
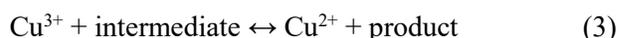
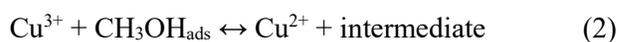
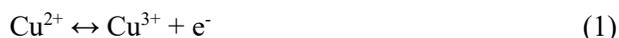


Fig. 6. Bioreduction of metallic ions using the *Rosmarinus officinalis* and electrocatalytic oxidation of methanol.

Fig. 7 presents the Nyquist diagrams of CuO NPs/POAP modified graphite electrode in different concentration of the methanol. In the methanol's concentration range of 0.005- 0.02M a steady decrease of the diameter of the semi-circle is witnessed. Diagrams consist of a small semicircle terminated to depressed capacitive semicircles at low frequency end of the spectrum. The equivalent circuit compatible with the Nyquist diagram recorded in the presence of methanol was depicted in Fig. 7. To obtain a satisfactory impedance simulation of ethanol electro-oxidation, it is necessary to replace the capacitor C with a constant phase element (CPE) in the equivalent circuit [22-30]. The most widely accepted explanation for the presence of CPE behavior and depressed semicircles on solid electrodes is microscopic roughness, causing an inhomogeneous distribution in the solution resistance as well as in the double-layer capacitance. The parallel combination of charge transfer resistance R_1 and constant phase element CPE_1 accounts for the injection of electrons from the conductive polymer to the back metallic contact. R_2 and CPE_2 represent the methanol oxidation. As increasing methanol concentrations decreases the diameters of semicircle, and charge transfer for methanol electrooxidation on the surface CuO NPs/POAP modified graphite electrode.

4. Conclusions

CuO NPs was prepared by a simple and green method using *Rosmarinus officinalis* extract containing phenolic constituents as both the chelating and the stabilizing agents. We have demonstrated a simple and general strategy, namely, in situ electropolymerization

by using the ionic surfactant as electrolyte, for dispersing CuO NPs within conducting films. CuO NPs/POAP modified graphite electrode shows reasonable catalytic performance for the electrocatalytic oxidation of methanol.

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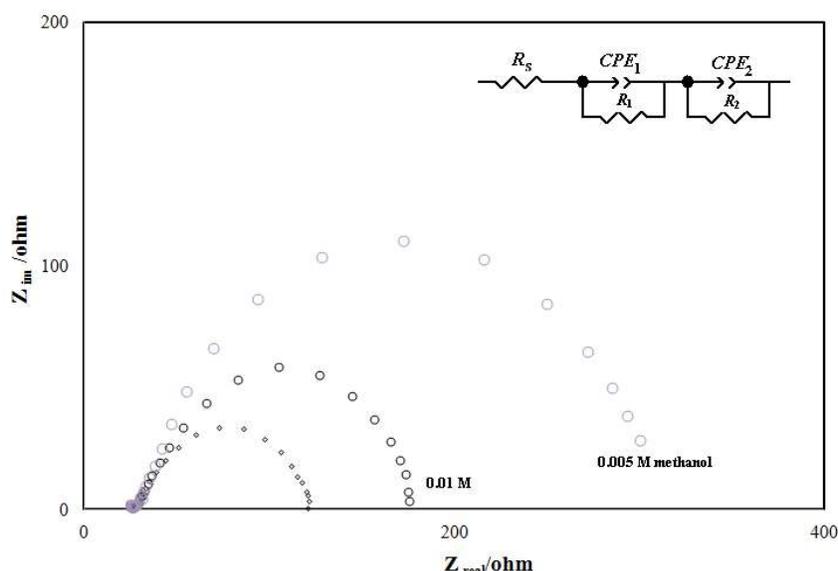


Fig. 7. Nyquist diagrams of CuO NPs/POAP modified graphite electrode recorded at 600 mV dc-offset in the presence of different concentration of methanol in 0.1 M NaOH solution.

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