



# Application of nano-sized nanoporous zinc 2-methylimidazole metal-organic framework for electrocatalytic oxidation of methanol in alkaline solution



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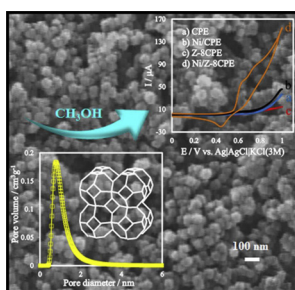
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## HIGHLIGHTS

- ZIF-8 nanoparticles are synthesized using a rapid and template-free method.
- For the first time, nickel species doped ZIF-8 modified CPE (Ni/ZIF-8CPE) is prepared.
- Ni/ZIF-8CPE is used as an electrocatalyst for methanol oxidation.
- The modified electrode shows good catalytic activity and acceptable stability.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this work, a novel non-platinum group metals (non-PGM) catalyst based on modified zinc 2-methylimidazole metal-organic framework (ZIF-8) is proposed and used for electrooxidation of methanol. Nano-sized particles of nanoporous ZIF-8 are synthesized at room temperature using a simple template-free method. The synthesized ZIF-8 nanoparticles are characterized by X-ray diffraction, scanning electronic microscopy and nitrogen adsorption-desorption techniques. In order to decrease the overvoltage of methanol oxidation on carbon paste electrode (CPE), nickel species doped ZIF-8 modified carbon paste electrode (Ni/ZIF-8CPE) is fabricated as a modified electrode. Electrochemical techniques such as cyclic voltammetry and chronoamperometry are used to investigate the electrocatalytic activity of Ni/ZIF-8CPE toward methanol oxidation in alkaline solution. Cyclic voltammetry results show that oxidation current is considerably increased using Ni/ZIF-8CPE in comparison with unmodified CPE. Catalytic rate constant of methanol oxidation on Ni/ZIF-8CPE is obtained using chronoamperometric studies. Besides the good catalytic activity of the modified electrode toward methanol oxidation, it has other advantages such as simple preparation, ease of operation, good stability and low cost, which can be promising in the field of preparation of non-PGM electrocatalysts for application in fuel cells.

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## 1. Introduction

Metal-organic frameworks are a relatively new type of nanoporous crystalline materials which in their structure, metal-centered units are connected together by organic linkers. They

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have good characteristics such as large specific surface areas, high pore volumes, well-ordered nanopores and flexible frameworks. Zeolitic imidazolate frameworks are a subfamily of metal-organic frameworks which are constructed by coordination bonds between transition metal cations and imidazolate anions to form tetrahedral frameworks with a three-dimensional extended structure. Zeolitic imidazolate frameworks have been widely used as gas adsorbent [1], catalysts [2,3], separator membranes [4] and chemical sensors [5]. Zinc 2-methylimidazole metal-organic framework (ZIF-8) is one of the most attractive members of zeolitic imidazolate frameworks which has the formula of  $\text{Zinc}(2\text{-methylimidazolate})_2$ , and crystallizes with a sodalite structure (Fig. S1) [6,7]. The structure of ZIF-8 contains large cavities with diameter of 11.6 Å which are connected through small channels with diameters of 3.4 Å [6,8]. Since many metal ions even in hydrated state have ionic radii smaller than 2 Å (in the case of six-coordinated Ni(II), it is less than 1 Å) [9] and with considering the pore size and flexibility of ZIF-8 framework, it is supposed that these species can easily insert into the pores and channels. In addition, pore diameter and flexible framework of ZIF-8 give it the ability of efficient separation and entrapment of some molecules such as hydrogen [10]. ZIF-8 also has other advantages such as template-free synthesis and thermal stability together with chemical resistance to solvents such as benzene, methanol and water. ZIF-8 shows exceptional resistance toward hydrolysis in alkaline media so that it can remain unchanged for about 24 h in 0.1 and 8 M aqueous sodium hydroxide (NaOH) solutions at 100 °C [6].

Nowadays humans are facing a global energy crisis, thus, the use of renewable resources of energy is very important. Fuel cells (FCs) are good candidates for this purpose which are being applied in the efficient storage and conversion of energy [11]. They have advantages such as operation in low temperature, low pollution for environment and direct conversion of a chemical reaction energy into electricity [12]. Methanol can be used as fuel in FCs due to its good properties such as easy operation, transportation and storage [13]. Direct methanol fuel cells (DMFCs) have limitations such as poisoning of the catalyst and existence of high oxidation overpotential at the surface of electrodes. In order to overcome these problems, various electrodes with electrocatalytic behavior toward the oxidation of methanol have been introduced. Some of the proposed electrodes are based on noble metals, transition metals and metal oxides which can be used individually or together with some support materials such as zeolites and mesoporous materials [14,15]. As we know, the most common catalysts in fuel cells are platinum and platinum group metals (PGM), which are very expensive and scarce. Thus, application of non-PGM electrocatalysts is a long-term demand of scientists [16]. For this purpose, some efforts have been focused on the preparation of platinum-free catalysts which uses metal-organic frameworks instead of traditional catalyst support materials [17–19]. Metal-organic framework based catalysts due to their large surface to volume ratio provide high adsorption of electroactive species which can accelerate the charge transfer kinetic of the electrochemical reaction [20,21]. Most of metal-organic frameworks have been used in direct hydrogen fuel cells because of their good proton conductivity, but fewer have been tested for using in alkaline DMFCs [22–24]. Moreover, some studies showed the effective role of N-containing ligands in ZIF-based electrocatalysts for application in fuel cells [25,26].

To the best of our knowledge, no nickel species doped ZIF-8 (Ni/ZIF-8) has been used as non-PGM electrocatalyst for methanol oxidation in alkaline solution. In the current work, nanoporous ZIF-8 nanoparticles were firstly synthesized using a template-free method and then modified by the adsorption of nickel species in the structure of nanoparticles to fabricate nickel species doped ZIF-8 carbon paste electrode (Ni/ZIF-8CPE). The electrocatalytic activity

of the modified electrode toward the oxidation of methanol was investigated by cyclic voltammetry and chronoamperometry in alkaline solution.

## 2. Experimental

### 2.1. Apparatus and chemicals

Zinc nitrate (98.5%), 2-methyl imidazole (99%), graphite powder (99.5%), nickel chloride (98%), methanol (99.9%) and NaOH (99%) were purchased from Merck and used without further purification. High viscosity paraffin (density:  $0.88 \text{ g cm}^{-3}$ ) obtained from Fluka was used as the pasting liquid for the carbon paste electrode. All solutions were diluted with double distilled water. The solutions were used for electrochemical measurements without deoxygenation. All experiments were performed at room temperature (ca. 25 °C). X-ray diffraction (XRD) pattern were recorded on a Bruker D8 advance diffractometer employing  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) within the  $2\theta$  range of 4–40°. The structure and surface morphology of nanoparticles were studied by scanning electron microscopy (SEM; EM-3200, KYKY). Langmuir and Brunauer–Emmett–Teller (BET) surface areas, pore volume and pore-size distribution of the sample were determined by analyzing nitrogen physisorption isotherms (BET, Quantachrome, Nova series instrument). In order to provide information about the elemental composition of modified electrode surface, energy dispersive X-ray spectroscopy (EDS) was performed using scanning electron microscope (VEGA\TESCAN-LMU). Electrochemical studies were performed by a bipotentiostat/galvanostat (Dropsens,  $\mu\text{STAT 400}$  instruments). An  $\text{Ag|AgCl|KCl}(3 \text{ M})$  and a platinum wire were used as reference and auxiliary electrodes, respectively.

### 2.2. Synthesis of ZIF-8 nanoparticles

ZIF-8 nanoparticles were synthesized according to a previously published procedure with some modifications [27]. In a typical procedure, 50 ml of methanolic solution of Zinc nitrate (0.049 M) and 50 ml of methanolic solution of 2-methylimidazole (0.197 M) were prepared. Then, two solutions were mixed under stirring for several minutes. After 1 h, product was separated from methanol by centrifugation and then washed with fresh methanol. Centrifugation and washing steps were repeated three more times to remove unreacted reactants from the product. Finally, the precipitate was dried in a vacuum oven at room temperature.

### 2.3. Electrode preparation

In order to prepare modified carbon paste electrode, ZIF-8 and graphite powder with a weight ratio of 3:7 were mixed in the presence of diethyl ether. After the evaporation of diethyl ether, several drops of paraffin oil were added by mixing and the resulting paste was placed at the bottom of a glass tube with internal radius of 2 mm. A Cu wire was inserted into the glass tube to establish electrical connection. Afterward, the surface of the fabricated electrode was polished on a paper and then immersed in a 0.1 M aqueous solution of nickel chloride for 5 min. From the initial experiments it was found that 5 min is the optimum time for the adsorption of nickel at the surface of modified electrode. Non-adsorbed species were removed by rinsing the surface of the electrode with deionized water to obtain Ni(II) doped ZIF-8 modified CPE (Ni(II)/ZIF-8CPE). When Ni(II)/ZIF-8CPE is placed in 0.1 M NaOH solution, adsorbed Ni(II) ions precipitate in the form of  $\text{Ni}(\text{OH})_2$  and give nickel species doped ZIF-8 modified CPE (Ni/ZIF-8CPE). The role of ZIF-8 in electrocatalytic oxidation of methanol was investigated by fabrication of another modified electrode

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