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# Pt–Ni bimetallic composite nanocatalysts prepared by using multi-walled carbon nanotubes as reductants for ethanol oxidation reaction

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## ABSTRACT

The multi-walled carbon nanotubes (MWNTs) are introduced as reductants to prepare bimetallic PtNi<sub>x</sub> composite nanocatalysts via a hydrothermal reaction for the investigation of ethanol oxidation reaction (EOR). The crystal structure and elemental analysis of PtNi<sub>x</sub>/MWNTs nanocatalysts are characterized by X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS), respectively. The morphologies of these nanocatalysts are observed by transmission electron microscopy (TEM) and scanning electron microscope (SEM). The results reveal that the PtNi<sub>x</sub> nanocatalysts with a nanoparticle size ranging from 6 to 13 nm are immobilized on the surface of MWNTs. The electrocatalytic activities of the PtNi<sub>x</sub>/MWNTs nanocatalysts for EOR in alkaline media are examined using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA). The onset potential of EOR in the nanocatalyst of PtNi<sub>x</sub>/MWNTs is negatively shifted for about 190 mV as compared to that in the nanocatalyst of Pt/MWNTs. The current for the forward anodic peak of EOR in the PtNi<sub>3</sub>/MWNTs nanocatalyst is about 2.5 times higher than that of pure Pt/MWNTs.

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## Introduction

Recently, the low-temperature fuel cells such as direct alcohol fuel cells (DAFCs) are attracting considerable attention. They serve as eco-friendly techniques to produce electricity by direct electrochemical conversion of the organic molecules and oxygen into water and carbon dioxide. Among various

kinds of fuel cells, direct ethanol fuel cell (DEFC) is considered as a promising power source not only for portable electronics devices but also for electric vehicles due to its high energy density (8.0 kWh kg<sup>-1</sup>), green emission and ambient operation conditions [1]. Ethanol is easier to transport than hydrogen and less toxic than other alcohols such as methanol. Also, ethanol can be produced in large quantities from agricultural products such as sugar cane, wheat and corn [2]. Therefore,

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developing novel catalysts towards ethanol oxidation reaction (EOR) has turned into a hot topic in the research field of electrochemistry. Although platinum (Pt) has been recognized as the best catalyst for EOR at low temperature, it can be easily poisoned by reaction intermediates due to a strong interaction between CO and the Pt surface [3]. Therefore, a number of Pt-based binary or ternary catalysts, such as Pt–Sn [4], Pt–Ru [5], Pt–Pd [6], Pt–Sn–Mo [7], Pt–Pb–Bi [8], are generated towards EOR with the low cost while maintaining the high electrocatalytic activity toward EOR compared to the Pt catalyst alone. However, except the work done by Ko et al. [9], there are few papers regarding the electrocatalytic activity of Pt–Ni bimetallic catalyst toward the EOR in alkaline media. Only some related works have been reported on the Pt–Ni bimetallic catalysts for methanol oxidation reaction (MOR), oxygen reduction reaction (ORR) and formic acid oxidation reaction (FAOR) [10–18].

Up to now, two typical methods for generating Pt–Ni nanoparticles have been developed. One is the chemical reduction reaction. For example, Wu et al. [12] reported the preparation of graphene-supported hollow Pt–Ni nanocatalysts, in which  $K_2PtCl_6$  and  $NiCl_2 \cdot 6H_2O$  were utilized as the precursors and  $NaBH_4$  a reducing reagent. In this work, the electrocatalysis of Pt–Ni toward methanol oxidation reaction (MOR) in a  $H_2SO_4$  solution was investigated. Another one is the electrochemical reduction reaction [19]. Habibi et al. [20] synthesized Pt–Ni alloy nanoparticles at potential of  $-0.4$  V vs. a saturated calomel electrode (SCE) from an  $0.1$  M  $Na_2SO_4$  aqueous solution containing  $H_2PtCl_6 \cdot 5H_2O$  and  $NiCl_2$ , and studied the electrooxidation of 2-propanol and 2-butanol on this alloy nanoparticles in an acidic media. However, the preparation of Pt–Ni nanoparticles by a facile process of hydrothermal reaction has not been reported so far.

Although Pt–Ni bimetallic or alloy nanoparticles have been widely applied for MOR, the reasons for the introduction of Ni to increase the currents and to reduce the onset potential for methanol oxidation on Pt–Ni electrodes are still unclear. For example, Mathiyarasu et al. [13] studied the MOR in a  $0.5$  M  $H_2SO_4$  solution and proposed that the surface redox species Ni oxide, which were formed during the electrooxidation process due to the oxygenation of  $CO_{ads}$ , were contributed to the improvement of oxidation current of MOR. However, Abdel Rahim et al. [14] suggested that in the presence of Ni, the number of active sites of Pt was increased through an electron donation process from Ni to Pt due to the transformation of  $Ni(OH)_2$  to  $NiOOH$ . Ko et al. [9] addressed that Ni could activate water molecules and provide preferential sites for OH adsorption at lower potential than Pt. The abundant  $-OH_{ads}$  species could completely oxidize the CO product to form  $CO_2$  and avoid electrode poisoning. However, no direct proofs were presented in this work except two references. Unfortunately, no direct interpretations were found in these two references as well. Meanwhile, there are many proposed reasons for enhancing the electrocatalytic activity of Pt by the addition of Ni. For example, some reports believed that the alloyed Ni could increase the  $d$  vacancy in the valence band  $5d$  orbital of Pt and cause the improved electrocatalytic activity and durability of the Pt–Ni/Ni electrodes as compared to the Pt [15]. Other works thought that the introduced Ni could modify the electronic structure of Pt due to the charge

transfer from Ni to Pt, which leads to a lower density of states at the Fermi level. This may promote the electrocatalytic performance of Pt [21]. Although many works concerning Pt–Ni materials have been published recently [22–26], the exact catalytic mechanism of Pt–Ni catalyst towards the oxidation of small organic molecules is still unknown.

As a typical catalyst support for fuel cells, carbon nanotubes (CNTs) attract a great deal of attention due to its unique properties, such as high specific surface area, electrical conductivity, and good thermal and chemical stability [27] compared to other carbon materials, such as graphene and carbon nanofiber [28,29]. Anchoring metal nanoparticles on CNTs has turned into an interesting research topic because of the key roles of CNTs and metal nanoparticles in the field of electrocatalysis, biosensors [30]. To the best of our knowledge, the immobilization of Pt–Ni composite nanoparticles onto CNTs by a hydrothermal reaction method without adding any other reductants has not been published yet, though we have successfully immobilized Pt nanoparticles on the surface of multi-walled carbon nanotubes (MWNTs) [31].

In this work, five kinds of  $PtNi_x/MWNTs$  nanocatalysts with different molar ratios of Pt to Ni have been prepared by a hydrothermal reaction without introducing any other reductants. The  $PtNi_x/MWNTs$  nanocatalysts have been characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscopy (TEM). The electrocatalytic activities of the nanoparticles for EOR are investigated through cyclic voltammetry (CV) and chronoamperometric curves. The mechanism for the electrocatalytic performance enhancement of  $PtNi_x/MWNTs$  catalyst towards EOR in alkaline solution was discussed in details.

## Experiment

### Materials

Deionized water was used to prepare the aqueous solutions. MWNTs (purity >95%) with diameter of 10–20 nm diameter were purchased from Shenzhen nanotech port Co., Ltd. (China). All electrodes were obtained from Tianjin Aida Co., Ltd (China). All other chemicals were analytical grade and used without further purification.

### Preparation of $PtNi_x$ nanoparticles onto MWNTs

$3$  mL  $5 \times 10^{-3}$  M  $H_2PtCl_6 \cdot 6H_2O$  and an appropriate amount of  $Ni(CH_3COO)_2 \cdot 4H_2O$  were dissolved in deionized water with a molar ratio of Pt to Ni of 1:1, 1:2, 1:3 and 1:4, respectively. Then  $10$  mg MWNTs were added into the above solution and ultrasonicated for  $30$  min. The resultant suspension solution was placed in a well-sealed autoclave at room temperature and transferred to a box-type furnace. The temperature of the furnace was increased to  $200$  °C within  $30$  min and kept for  $2$  h to accomplish the hydrothermal reaction process. The hydrothermal reaction process was implemented in a SRJX-8-13 box-type furnace equipped with a KSY 12-16 furnace temperature controller. After cooling down to room temperature, the filtered samples were thoroughly washed with deionized

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