



A simple and effective route for preparation of platinum nanoparticle and its application for electrocatalytic oxidation of methanol and formaldehyde



Jahan-Bakhsh Raof^{a,*}, Sayed Reza Hosseini^b, Sharifeh Rezaee^a

^a Electroanalytical Research Laboratory, Department of Analytical Chemistry, Faculty of Chemistry, University of Mazandaran, 47416-95447 Babolsar, Iran

^b Nanochemistry Research Laboratory, Faculty of Chemistry, University of Mazandaran, 47416-95447 Babolsar, Iran

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ABSTRACT

In this work, a new and facile method for preparation of platinum nanoparticles (Pt-NPs) at the surface of glassy carbon electrode (GCE) is reported. Firstly, nickel nanoparticles (Ni-NPs) as sacrificial templates are uniformly electrodeposited onto the GCE by using potentiostatic method at a fixed potential (-1.0 V vs. Ag | AgCl | KCl (3 M)) in 0.5 M H₂SO₄ solution. Then, Pt-NPs are prepared through a spontaneous and irreversible process via galvanic replacement reaction (GRR) between PtCl₆²⁻ and Ni-NPs. The obtained results indicate that the Ni-NPs are completely replaced with Pt-NPs in acid solution. The obtained results from cyclic voltammetry and chronoamperometry reveal that the Pt-NPs demonstrate an enhanced electrocatalytic activity for methanol and formaldehyde oxidation. The effect of several parameters such as electrodeposition potential, NiSO₄ concentration, electrodeposition and GRR time for methanol oxidation as well as stability of the modified electrode has been investigated.

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1. Introduction

To date, among the different transition metal particles, platinum (Pt) due to its unique physical and chemical characteristics, including high durability and specific activity is quite noticeable from others as electrocatalyst [1,2]. However, the high cost and limited supply of Pt are limiting factors. So, the use of Pt particles at nano-scale by controlling the morphology and surface structure is an effective way to reduce the amount of the required Pt and enhance the electrochemical activity [3,4]. Since, catalysis is a surface phenomenon; Pt particles with small sizes demonstrate high activity and display excellent resistance against poisoning effect by CO_{ads} species, which are formed during the methanol oxidation. Formation of multiple Pt-carbon bonds is less at Pt particles with small sizes, in comparison with bulk Pt [5,6]. So, researches have been focused on the exploration of novel synthetic routes to prepare ultrafine nanostructured Pt catalysts.

So far, most studies have been focused on the diverse physical and chemical methods for fabrication of fine noble metal nanoparticles [7]. By considering the potential preparation methods for production of the metal NPs, one of the most plausible ways is metal exchange reaction [8,9]. Galvanic replacement reaction (GRR) as one of typical and

convenient route was widely used for the synthesis of metal NPs by applying particles of various transition metals such as Ni, Cu, Fe, and Co [10,11]. This method has attracted much attention due to its simplicity of operation, cost effectiveness and simple equipment. The GRR is a single step and irreversible reaction which is reliant on the difference in standard electrode potentials of the various elements [12]. The spontaneous reaction occurs between the solid metal (i.e., template) and ions of a second metal having higher electrode potential which leads to the deposition of more noble elements and dissolution of the less noble components.

Until now, many works have been made towards the synthesis of Pt nanoparticles (Pt-NPs) or designing of Pt-based bimetallic catalysts and Pt nano-materials with different shapes such as nano-cages, nano-tubes and nano-porous films by GRR with different active metals. For example, Qiu et al. [13] fabricated bimetallic Pt-Au thin films with different Pt/Au ratios by GRR with hierarchical Co thin film. Kuang et al. [14] synthesized hollow Pt nano-spheres/carbon nanotube nano-hybrids by using silver NPs. Also, Tegou et al. [15] prepared mixed Pt/Au by GRR with Ni layers. Mohl et al. [16] prepared CuPd and CuPt bimetallic nanotubes by using Cu, Pt and Pd. Xie et al. [17] synthesized Pd@M_xCu_{1-x} (M = Au, Pd and Pt) nano-cages with porous walls and a yolk-shell structure through the GRR. Bansal et al. [18] prepared Ni-Cu nano-porous surface for catalysis by the GRR.

Recently, we have made Cu-Pt bimetallic NPs at the surface of poly(8-hydroxyquinoline) film by using Cu as sacrificial and Pt as second

* Corresponding author.

E-mail address: j.raoof@umz.ac.ir (J.-B. Raof).

metal [19]. Our literature survey indicates that the fabrication of the Pt-NP modified GCE (Pt-NP/MGCE) by using Ni nanoparticles (Ni-NPs) as sacrificial templates has not been reported. Hence, in the present investigation, at first the Ni-NP electrodeposition was performed onto the GCE surface and Pt-NPs were then prepared by GRR and their efficiency towards the electrocatalytic oxidation of methanol was investigated. The experimental data reveal that the Pt-NP/MGCE showed excellent performance in the methanol oxidation and formaldehyde oxidation.

2. Experimental

2.1. Reagents and materials

NiSO₄·6H₂O (99%, Fluka) was used in the preparation of Ni deposition solution. H₂PtCl₆·6H₂O (Merck) and NaOH (99%, Merck) were used as received. Methanol and formaldehyde from Merck were of analytical grade. Sulfuric acid (98%, Fluka) was used for the preparation of the supporting electrolyte. K₃Fe(CN)₆, K₄Fe(CN)₆ (99%, Fluka) and KCl (99%, Merck) were used for impedance studies. The solvent used in this work for preparation of the samples was double distilled water.

2.2. Electrochemical measurements

The electrochemical experiments were carried out by using a potentiostat/galvanostat (SAMA 500-C Electrochemical analysis system, Sama, Iran) coupled with a personal computer (PC). Electrochemical impedance spectroscopy (EIS) was performed by an Autolab model PGSTAT 30 with FRA software version 4.9 (Eco Chemie, The Netherlands). The three-electrode system consists of the GCE (1.5 mm in diameter) as working electrode substrate, Ag|AgCl|KCl (3 M) as reference electrode and a Pt wire as an auxiliary electrode. The surface morphology and elemental analysis of the deposits were evaluated by scanning electron microscopy (SEM, model VEGA-Tescan, Razi Metallurgical Research Center, Tehran, Iran) equipped with an energy dispersive spectrometer (EDS).

2.3. Preparation of the Ni nanoparticles

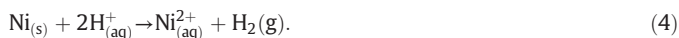
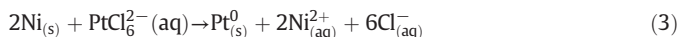
Prior to surface modification, the GCE was carefully polished with polishing cloth and alumina slurry until a mirror finish was obtained. To remove the alumina residues that might be trapped at the surface, the polished electrode was placed in ethanol and sonicated for 5 min. Then, the electrode was rinsed thoroughly with distilled water. After that, Ni-NPs were electrodeposited potentiostatically at -1.0 V vs. Ag|AgCl|KCl (3 M) for 500 s in 0.5 M H₂SO₄ solution containing 0.5 M NiSO₄ according to reaction (1). Also, associated with deposition of Ni-NPs, hydrogen bubbles were released via hydrogen evolution reaction as a competitive reaction according to reaction (2).



2.4. Preparation of the Pt-NP/MGCE

After Ni-NP electrodeposition, the electrode was immediately immersed in 0.5 M H₂SO₄ solution containing 5.0 mM H₂PtCl₆ for 20 min to let GRR between Ni⁰ and Pt^{IV} ions proceeds. Since, the standard reduction potential of the Pt^{IV}/Pt⁰ pair (+0.73 V vs. SHE) is higher than the Ni²⁺/Ni⁰ pair (-0.25 V vs. SHE), Ni-NPs can be oxidized by PtCl₆²⁻ according to following replacement reaction (3) and removed from

the surface into the electrolyte solution. Also, in the meantime, Pt^{IV} is reduced and deposited on the electrode surface. It should be noted that during the GRR, Ni-NPs are dissolved into the solution via a reaction between Ni-NPs with H⁺ as a competitive reaction (4):



It is obvious that the displacing metal in comparison with sacrificial metal manifests oxidation state (4:2). So, according to stoichiometry of the redox reaction, during the reaction by deposition of a Pt atom at the electrode surface, two Ni atoms leach in the surrounding aqueous environment. Hence, on the basis of both reactions (3 and 4), all deposited Ni-NPs release from the electrode surface. Afterwards, when the Pt-NP/MGCE was prepared, it was removed and rinsed with distilled water. The geometric surface area ($A_g = 0.018$ cm²) was used to calculate the current density, except for the comparison of the methanol oxidation and formaldehyde oxidation. All experiments were performed at ambient temperature.

3. Results and discussion

3.1. Electrochemical properties of the modified electrodes

In order to ascertain the electrochemical response of the prepared modified electrode, after accomplishing Ni-NP electrodeposition, the Ni-NP/MGCE was thoroughly rinsed with distilled water and 15 potential cycles were conducted between 0.2 and 0.8 V in 0.1 M NaOH solution until stable cyclic voltammogram was obtained (Fig. 1A

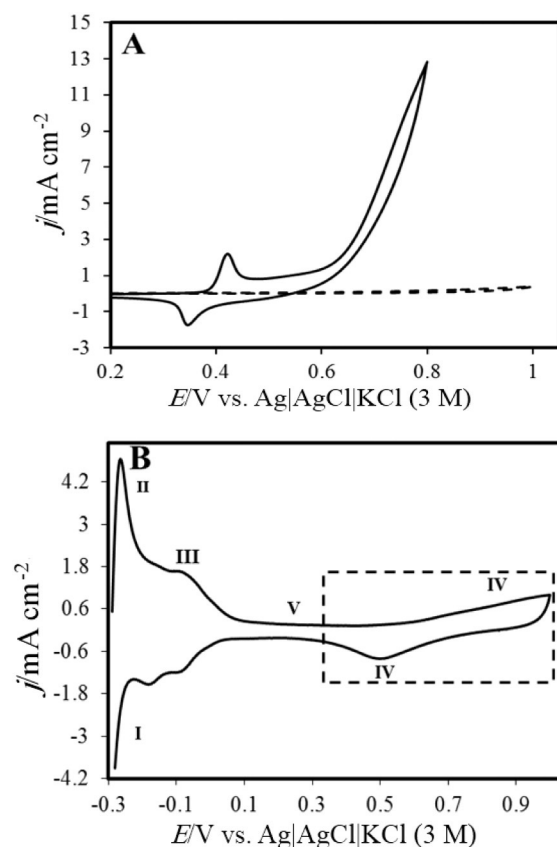


Fig. 1. (A) 15th CV signal of the Ni-NP/MGCE in 0.1 M NaOH (solid line) and 0.5 M H₂SO₄ solution (dotted line) at $v = 50$ mV s⁻¹. (B) CV signal of the Pt-NP/MGCE in 0.5 M H₂SO₄ solution at $v = 50$ mV s⁻¹.

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