Pt–Co nanostructures electrodeposited on graphene nanosheets for methanol electrooxidation

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HIGHLIGHTS

- Co nanoparticles were electrodeposited on graphene modified GC electrode (Co/G/GC).
- Pt–Co nanostructures were loaded on Co/G/GC by galvanic replacement reaction.
- The physical and electrochemical properties of Pt–Co/G/GC were investigated.
- The Pt–Co/G was used as the anode electrocatalyst for methanol electrooxidation.
- The onset potential of methanol oxidation at Pt–Co/G/GC occurred at low potential.

ABSTRACT

Glassy carbon electrode modified by Pt–Co nanostructures decorated on graphene nanosheets (Pt–Co/G/GCE), is fabricated. Co nanostructures are electro-deposited on graphene modified GC electrode and then Pt nanostructures are loaded on the surface of modified electrode by galvanic replacement reaction between Co nanostructures and H_2PtCl_6. The physical and electrochemical properties of Pt–Co/G/GCE are investigated by scanning electron microscopy, energy dispersive X-ray, cyclic voltammetry and chronoamperometry. The morphology of as-prepared graphene nanosheets is investigated by transmission electron microscopy. The prepared Pt–Co/G is used as the anode electrocatalyst for methanol electrooxidation. The fabricated electrocatalyst exhibits an enhanced electrocatlytic performance for methanol electrooxidation.

1. Introduction

Fuel cells are promising efficient alternative energy sources for portable and vehicular applications. Among various types of fuel cells, direct methanol fuel cells (DMFCs) have attracted much more attentions due to their interesting properties such as low operating temperature, high power density and relatively quick start-up [1–4]. However, the practical development of DMFCs is limited by poor activity of methanol electrooxidation activity and high cost of noble metal catalysts [1]. Metal and semiconductor nanoparticles have attracted tremendous attention in various fields such as catalysis, photography, optics, biological and chemical sensor [5–8]. Pt and its alloy nanoparticles are among the best electrocatalysts for methanol electrooxidation [9]. There are different approaches to improve the electrocatalytic activity of a catalyst toward methanol electrooxidation such as incorporation of a second element to Pt or controlling the morphology (size and shape) [10–14]. Recently, many researchers have developed Pt-based alloy catalysts with high activity for the oxygen reduction reaction (ORR) such as Pt–Ru, Pt–Pd, Pt–Co and Pt–Sn [15–17]. Besides, these Pt-based alloy catalysts have good tolerance to CO poisoning as compared with pure Pt [18,19]. It has been found that Pt–Co alloys have high activity and excellent tolerance to CO poisoning in comparison with pure Pt catalysts [20–22], and Co is much cheaper than precious metal Ru.

Support effects are well known to affect catalyst activity. So, the support materials have an important role in catalytic behavior of catalyst. The supporting materials and their surface conditions highly affect catalytic activity of the Pt catalyst [23]. The supporting materials with high surface area reduce the metal loading while

keeping the high catalytic activity. Recently, graphene, one of the carbon materials, has been a good candidate as support materials [24–26]. Graphene has gained interests in many fields of application, because of its unique electronic, optical and chemical properties and its potential applications in nanomaterials and nanotechnology [27]. The-two dimensional layered structure of graphene, provides large specific surface area, which makes it suitable for immobilizing various substances such as metal, nanoparticles, biomolecules and etc. Electron transfer through graphene is sensitive to adsorbed molecules, because every atom in a graphene is a surface atom [28]. When graphene is used as an electrode, the electron transfer is promoted which makes graphene an inexpensive alternative to carbon nanotubes [29]. Also, the layered structure of graphene makes it possible to use both sides of it as support for catalysts; this makes graphene a promising catalyst carrier [30].

Galvanic replacement reaction (GRR) is a type of electroless deposition. In a chemical oxidation–reduction reaction, metal ions with higher standard potential are reduced and templates with lower standard potentials are oxidized [31]. Recently, it has been proved that this simple and spontaneous process is an attractive approach for the growth of structures directly on metal or semiconductor substrates such as deposition of Au on Si [32], Ag/Pd on Si [33], Cu on Si [34], Pt on Ti [35], Au on Ge [36], Pt on Ge [37], Cu on TaN [38], Cu on Al [39], Zn on Al [40], Ni on Al [41], Pd on Ag [42], Pt/Au on Cu [43], Au on Cu [44], Ag on Cu [45], and Au on Ag [46], and other combinations.

Therefore, in the present work, with respect to advantages of graphene nanosheets and galvanic replacement reaction, the modified electrode was prepared by galvanic replacement. In this way, we report a simple and rapid route for preparation of the bimetallic Pt–Co catalyst through a method based on partially replacement of metallic Co by Pt using immersion of the Co/G/GCE in H_2PtCl_6 solution. The general objective of the present work is to obtain the Pt–Co/G/GCE for electrocatalytic oxidation of methanol which has significant attraction in DMFCs.

2. Experimental

2.1. Chemical and reagents

The solvent used for the electrochemical studies was twice distilled water. Graphite powder (particle diameter = 0.1 mm), sulfuric acid, hexachloroplatinic (IV) acid hexahydrate, cobalt (II) sulfate heptahydrate and methanol were purchased from Merck. Sodium hydroxide was purchased from Fluka.

2.2. Instrumentation

Scanning electron microscopy and energy-dispersive X-ray analysis (EDX) were done using KYKY-EM3200 and VEGA – TESCAN – XMU electron microscope. The morphology of graphene was determined by a PHILIPS CM30 transmission electron microscopy (TEM). Electrochemical studies were performed in a three-electrode cell with Pt–Co/G/GC as working electrode, a Pt wire as counter electrode and Ag|AgCl as reference electrode using a computer-controlled potentiostat/galvanostat (μ-Autolab TYPE III, Eco Chemie BV, Netherlands).

2.3. Preparation of graphene nanosheets

Graphene oxide (GO) was prepared with the Hummers method and purified [47], then chemical reduction of GO to graphene was carried out [48]. Fig. 1 shows TEM image of graphene nanosheets. As can be seen, they are rippled like a silk weave due to extremely
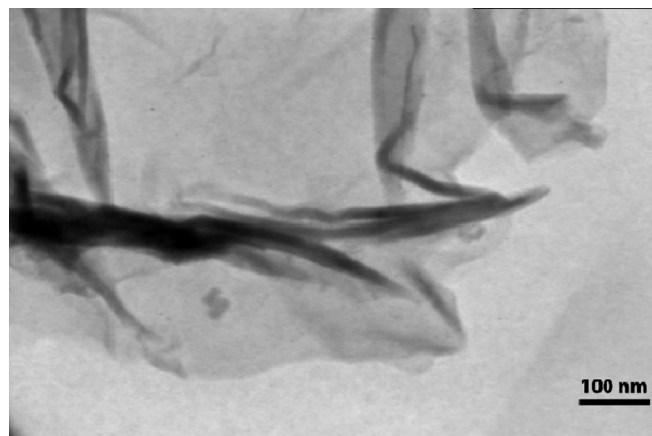

Fig. 1. TEM image of graphene nanosheets.

small thickness of graphene, suggesting a flexible structure of graphene sheets.

2.4. Preparation of Pt–Co/G/GCE

GC electrode was polished with alumina slurry down to 0.05 μm on a polishing cloth followed by sonicating in distilled water and absolute ethanol. 1.0 mg graphene was dispersed in 1.0 mL water using high power ultrasound. A 5.0 μL portion of the resulting graphene nanosheets dispersion was measured and the syringe was put over the GC electrode. The graphene sheet suspension was then dropped on the electrode, which was dried in an oven (70 °C) to evaporate the solvent. The resultant was graphene nanosheets modified GC electrode (G/GCE). For electro-deposition of Co nanostructures on G/GCE, the fabricated G/GC electrode was immersed in 0.02 M $CoSO_4$ + 0.1 M Na_2SO_4 solution. A cyclic scan in the potential range from 0.6 V to −1.0 V was performed (Fig. 2) as mentioned elsewhere [49] and the Co nanostructures modified G/GC electrode (Co/G/GCE) was obtained. The oxidation peak at −0.33 V is attributed to oxidation of electrodeposited Co nanostructures on Co/G/GCE and the reduction peak at −0.86 V is due to reduction of Co^{2+} on the Co/G/GCE. Owing to increase in amount of the electrodeposited Co nanostructures caused by increasing the
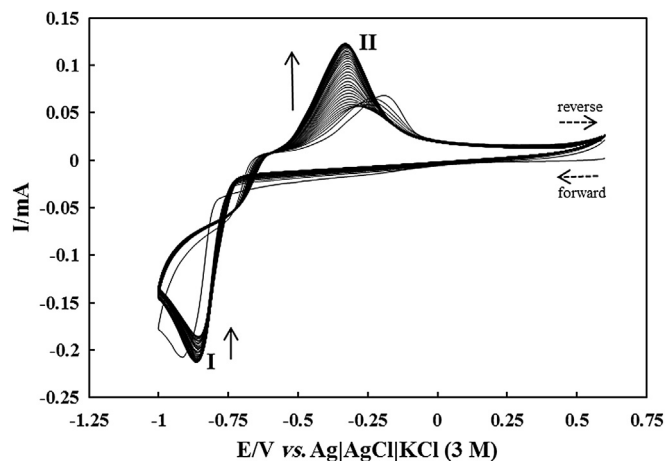

Fig. 2. CVs of graphene/GCE in 0.02 M $CoSO_4$ + 0.1 M Na_2SO_4 at $\nu = 50$ mV s^{-1}, number of potential cycles: 45.