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Preparation of graphene/Nile blue nanostructure on glassy carbon electrode: Decoration with platinum nanoparticles and application for electro-oxidation of methanol

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ABSTRACT

Well-dispersed Pt nanoparticles supported on Nile blue functionalized graphene nano-sheets were successfully prepared on glassy carbon (GC-GNs-NB-Pt) electrode by a facile and effective two-step electrochemical method. Further electrode was fabricated where NB was formed and attached onto the surface in its polymer form (GC-GNs-NB_{poly}-Pt). The Pt decorated GNs-NB nanostructures were characterized by field-emission scanning electron microscopy (FESEM), energy dispersive X-ray diffraction (EDX) microanalysis, Raman spectroscopy and electrochemical methods. The results showed a three-dimensional nanostructure for Pt nanoparticles decorated onto the functionalized GNs-NB surface. The characterized electrodes were tested for electrochemical oxidation of methanol in H₂SO₄. A comparison between the synthesized electrodes; GC-GNs-Pt, GC-GNs-NB-Pt and GC-GNs-NB_{poly}-Pt, in terms of their electrochemical performance, revealed that the GC-GNs-NB-Pt benefits of a large and exceptional electrocatalytic activity for methanol oxidation. This improved activity could be attributed to the NB playing a crucial role in dispersing and stabilizing of Pt on GNs-NB platform.

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Introduction

In order to resolve the problem of energy dilemma and environmental pollution, scientists are researching alternative energy sources. Methanol oxidation reaction (MOR) has potential applications in transportation and portable electronic devices because of its superb energy density, low purulence, simplicity and safe operation [1–3]. Despite the important improvements so far made in the performance of MOR, there remain a number of technical barriers against its widespread

application. The major problem in the development of MOR is its slow kinetics which leads to high over-potentials, currently the high cost Pt is used as the state-of-the-art electrocatalyst for MOR [4,5]. To overcome these problems, great efforts have been devoted to enhance the electrocatalytic activity of the alternative available catalysts having relatively lower costs and acceptable characteristics; activity and stability [6].

Over the past few years, several methods have been developed for the synthesis of Pt nanostructures, however, most of these methods are difficult to be controlled, making them exceedingly challenging. For example, the amount of

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loaded Pt, its efficiency and stability in Pt-based electrocatalysts are the main properties pertinent to the type of support [7,8]. The amount of loaded Pt catalysts is immediately correlated with the unit cost of fuel cell manufacturing which in turn is an important factor for commercialization. A good support should not only provide high precision catalyst nanoparticles and good electron transfer but also increase long-term consistency of the catalyst nanoparticles by slowing down their sintering rate and allowing fast mass transport of reactants and products at the fuel cell electrodes, resulting in better device performance [9,10].

In the past two decades, many different carbon based materials have been used as electrocatalyst supports for preparation of the Pt-based electrocatalysts for MOR [11,12]. Graphene nanosheets (GNs) have been developed for various potential applications due to their exceptional electronic, optical, high charge mobility and large surface area properties [13–17]. The GNs, as the catalytic supports, have been incorporated into many functional materials to form nanocomposites for application in fuel cells [12] and many other aspects of electrochemical technology [18,19], due to their unique advantages, such as the large surface area, novel electron transfer property.

However, due to some inherent drawbacks, such as its chemical inertness, the application of GNs has been limited [20,21]. These drawbacks could be overcome by further functionalize the GNs in order to improve their surface properties, leading to formation of GNs based nanocomposites. The GNs-based nanocomposites formed via decorating of GNs with metal nanoparticles, e.g. with Au-NP, Pt-NP [22], promise new opportunities for developing the next generation of catalysts. These nanocomposites are of scientific and industrial interests due to the synergistic effect of two or more functional components [23,24]. There are many imaginative methods for decorating metal nanoparticles onto GNs based nanocomposites, each offering varying degrees of control of particle size and distribution [25,26]. One type of these methods is based non-covalent functionalization of GNs, resulting in higher activity and more stability for decorating nanoparticles [22].

The functionalization of GNs can be performed by covalent or non-covalent methods [27,28]. Non-covalent functionalization is preferable for catalyst support applications, since it enables attachment of molecules through supermolecular interactions such as π - π stacking, and thus, preserves (conserves) the intrinsic electronic and structural properties of GNs [29]. Therefore, it is important to modify the surface of GNs by proper techniques and materials [22], enabling control distribution of the metal nanoparticles on the substrate, and avoid deterioration of the electronic network of GNs [30]. A promising method could be based on using organic conducting films such as Nile blue (NB) [31,32] or toluidine blue (TB) [33,34].

However, to the best of our knowledge, there is no report on the preparation and application of GC-GNs-NB-Pt nanostructures for electrocatalytic oxidation of methanol. In the present study, a new two-step electrochemical approach is established to synthesize the nanostructured GNs-NB-Pt onto the GC surface by using NB and graphene oxide (GO) as the starting materials. The surface of GC-GNs-NB is further

modified by Pt nanoparticles. The electrocatalytic activity of GC-GNs-NB-Pt nanostructured electrode is completely examined for methanol oxidation by cyclic voltammetry (CV), chronoamperometry and electrochemical impedance spectroscopy (EIS).

Experimental

Material and reagents

Potassium hexachloroplatinate (K_2PtCl_6), graphite powder (Sigma-Aldrich® < 2 micron), sodium nitrate ($NaNO_3$), methanol, potassium permanganate, sulfuric acid (98%) solution, hydrogen peroxide solution (30%), NB and other chemicals were of analytical grade obtained from commercial sources (Sigma-Aldrich® or Merck®), and used without further purification. All solutions were prepared with deionized/distilled water. The testing solutions were saturated with high purity Ar, depend on the experimental conditions.

Synthesis of composites and modifications of the GC electrode surface

The GO was synthesized according to the Hummers' method [35], partially modified by us [24] (see Supporting Information, Section Introduction, Fig. S1). The GC (0.0314 cm²) was polished with alumina powder (0.3 down to 0.05 μ m) on a polish cloth, and then, washed ultrasonically in ethanol/water/ethanol each step for a few minutes to get clean GC electrode. A set of clean GC electrodes was prepared and modified according to previous work [36].

Briefly, separate suspension solutions of GO and mixture of NB and GO composite were prepared for deposition, named as GO_{ssd} and GO-NB_{cssd}. Volumes of 20 μ L of the GO_{ssd} and GO-NB_{cssd} were selected and dropped onto the surface of clean GC electrodes separately, and allowed to dry and form GC-GO and GC-GO-NB electrode, respectively.

- (i) A set of the GC-GO-NB electrodes was placed into the cell containing 0.1 M KNO_3 solution, and its potential was cycled between 0.000 and -1.300 V vs. Ag/AgCl at 20 mV s⁻¹ (~7 cycles) to reduce GO to GNs [23,36], and absorb the GNs and NBs onto the GC simultaneously [37]. The constructed electrode is named GC-GNs-NB nanostructured electrode.
- (ii) Another set of the GC-GO-NB electrodes was treated in the same conditions as (i), but its potential was cycled between +1.300 and -1.300 V to reduce GO to GNs, and absorb the GNs and NBs onto the GC simultaneously by electrochemical polymerization of NB [38]. The constructed electrode is named GC-GNs-NB_{poly} nanostructured electrode (see Supporting Information, Fig. S2).
- (iii) A set of the GC-GO electrodes was treated as (i) to reduce GO to GNs electrochemically and form GC-GNs.
- (iv) The Pt-contained modified electrodes; GC-GNs-Pt, GC-GNs-NB_{poly}-Pt and GC-GNs-NB-Pt, were prepared by electrodeposition of Pt nanoparticles onto the related electrode surface at constant DC potential, $E_{DC} = -0.2000$ V vs. Ag/AgCl reference electrode, for 300 s in

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