Electrochimica Acta 157 (2015) 149–157

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Synthesis of highly dispersed Pt nanoclusters anchored graphene composites and their application for non-enzymatic glucose sensing

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ARTICLE INFO

Article history:
Received 24 October 2014
Received in revised form 20 December 2014
Accepted 19 January 2015
Available online 21 January 2015

Keyword:
Graphene
Pt nanoclusters
Non-enzymatic sensor
Glucose oxidation
Electro-catalytic activity

ABSTRACT

A facile and clean method by using ascorbic acid as mild reductant was developed to synthesize nanocomposites of graphene and platinum nanoclusters (PtNCs/graphene), in which Polyvinyl-Pyrrolidone (PVP) was added during the one-step reductive process so as to improve the dispersity of PtNCs on the graphene and decrease the size of PtNCs. By several characterization methods such as X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS), we demonstrated that Pt nanoclusters have successfully anchored on the surface of graphene sheets with average diameter of 22 nm. It was found that with the assistant of PVP, Pt nanoclusters appeared with smaller particle size and narrower particle size distribution. Cyclic voltammetry and amperometric methods were used to evaluate the electro-catalytic activity of the synthesized nanocomposites toward the oxidation of glucose in neutral media (0.1 M PBS, pH 7.4). The PtNCs/graphene exhibited a rapid response time (about 3 s), a broad linear range (1 mM to 25 mM), good stability, and sensitivity estimated to be 1.21 $\mu A\,cm^{-2}\,mM^{-1}$ (R = 0.995, 71.9 $\mu A\,cm^{-2}\,mM^{-1}$ vs. geometric area). Additionally, the impact from the oxidation of interferences can be effectively limited by choosing the appropriate detection potential. These results indicated a great potential of PtNCs/graphene in fabricating novel non-enzymatic glucose sensors with high performance.

1. Introduction

In recent years, glucose biosensor has drawn considerable attention for its widely applications in different areas such as blood glucose sensor, wastewater treatment, food and textile industry, biofuel cell, and environment monitoring [1–3]. Glucose biosensor based on the immobilization of glucose oxidase on various substrates has been the research topic during the past several decades [4–7]. These enzyme-based sensors show good selectivity and high sensitivity in the detection of glucose. However, there are also some inevitable drawbacks from the intrinsic nature of enzyme itself, for instance the activity of enzyme can decrease with the passage of time, be easy affected by the temperature and pH value. The tedious immobilization process of enzyme could be another barrier which limits their further applications [6–8]. To overcome these issues, many attempts have been devoted to non-enzymatic glucose biosensors based on direct catalytic oxidation of glucose on the surface of electrode, which exhibits conveniences and advantages to avoid these drawbacks [2,4,9].

The performance of non-enzymatic glucose biosensors much depended on the catalytic activity of catalyst materials towards glucose oxidation. Considering the high specific surface area, excellent conductivity and catalytic activity, metal nanomaterials has become the research focus of electrocatalyst for glucose sensing [10,11]. Nowadays, various metal nanomaterials such as platinum (Pt) [6,10,12], gold (Au) [7,13], palladium (Pd) [3,9] and nickel (Ni) [11,14] have been modified on the surface of electrode as eletrooxidation materials in nonenzymatic glucose sensors. Among them, platinum nanomaterial is of great promise for its extraordinary performance in the electro-oxidation of glucose [12,15,16]. However, platinum nanomaterials easily lose their activity during the detection of glucose due to the agglomeration of nanomaterials and poison effect of chemisorbed intermediates [10,15]. And the limit supply of Platinum in nature also prevented it from being an efficient commercial catalyst [17,18]. Therefore well

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http://dx.doi.org/10.1016/j.electacta.2015.01.085
0013-4686/

dispersed Pt nanomaterials supported by proper carbon material would be effective way to reduce the Pt loadings and prevent nanomaterials aggregation, which would keep the electrocatalyst stable during the robust electrochemical measurement [19].

On the other hand, novelty two-dimensional nanomaterial, graphene and its derivatives has attracted considerable interests from both experimental and theoretical scientific communities due to its extraordinary properties including high surface area, strong mechanical strength, good biocompatibility, and ease of functionalization and mass production for the catalysis application [20–22]. Therefore, graphene is considered to be the best candidate as the support materials of platinum nanoparticles for their catalysis application [14,23]. The excellent properties of graphene not only provide large surface area for loading Pt nanoparticles so as to generate more active catalytic sites but also efficiently accelerate the electron transfer between electrode and detection molecules [24,25]. The combination of Pt nanoparticles and graphene would open a new avenue for constructing glucose sensor platform with high performance. Many efforts have been made in preparing Pt nanoparticles and graphene composites. However, the materials are often lack of high sensitivity and selectivity, which is a main challenge to overcome [23,26,27].

In our previous study, an efficient and clean method has been successfully employed to prepare PtNCs/graphene composite for the application of direct methanol fuel cell (DMFC), in which graphene oxide and Pt ion precursor were reduced within one-step process and low-cost, environmentally friendly ascorbic acid was chosen as the reductant [28]. However, the dispersion and size control of Pt nanoparticles on the graphene was still not dissolved. In addition, the investigation of the performance of the PtNCs/graphene composite on glucose sensing is still deserved. As the further researching in the current work, Polyvinyl-Pyrrolidone (PVP) used as dispersing agent to synthesize highly dispersed Pt nanoclusters for nonenzymatic sensing of glucose. The main effect of the surfactant was to reduce or eliminate conglobation and increase the dispersity of Pt nanoclusters during the experiment process [29,30]. The synthesized PtNCs/graphene composites were characterized using various techniques, including TEM, FE-SEM, XRD and XPS. Then the catalytic activity, selectivity and stability of the composites towards glucose oxidation were investigated and compared to those of PtNCs/graphene without using PVP, blank bulk Pt electrode and Pt nanoclusters no (PtNCs) or a carbon black (Vulcan) support (PtNCs/Vulcan). Furthermore, the real sample analysis was performed to verify the practicability. All the results show that the synthesized PtNCs/graphene exhibited excellent catalytic activity toward glucose oxidation in neutral solution (PBS, 0.1 M, pH 7.4). Therefore, the obtained PtNCs/graphene (PVP) has a great potential using in fabricating novel non-enzymatic glucose sensors with high sensitivity, stability, and selectivity.

2. Experimental

2.1. Chemicals

K_2PtCl_4 was obtained from Aldrich Chem Co. Graphite were purchased from Alfa Aesar. Glucose, Ascorbic acid (AA), Uric acid (UA), 4-acetamidophenol (AP), Vulcan, and Polyvinyl-Pyrrolidone (PVP) were purchased from Sinopharm Chemical Reagent Co. All the chemicals were of analytical grade. Phosphate buffer solution (PBS, 0.1 M, pH 7.4) was made up from Na_2HPO_4 and NaH_2PO_4. Solutions of AA, UA, and AP were prepared using PBS solution immediately before each experiment. In all the procedures, the deionized pure water was prepared with Kertone Ultrapure Water System P60-CY (Kertone Water Treatment Co.Ltd resistivity > 18 MΩ.cm).

2.2. Apparatuses

The morphology of the PtNCs/graphene was characterized with a field-emission scanning electron microscopy (SEM, ZEISS, Germany) and a transmission electron microscopy (TEM FEI TECNAI20, USA and HRTEM EM-2100F, Japan). X-ray diffraction analysis (XRD) was carried out with the D/Max-3C diffractometer (made in Japan). X-ray photoelectron spectroscopy analysis (XPS) was carried out with Phoibos 150 (Specs, Germany). Thermogravimetric analysis (TGA) was taken with a thermogravimetric analyzer (Perkin-Elmer TGA-7, USA). All electrochemical measurements were performed with a 550 electrochemical workstation (Gaoss Union Instrument Company, Wuhan, China) in a conventional three-electrode cell. Pt wire electrode was used as counter electrode, and Ag/AgCl electrode was applied as the reference electrode. Before TEM observation, PtNCs/graphene was dispersed into ethanol with sonication for several minutes and casted on the copper mesh and then dried in the ambient condition for TEM observation.

2.3. Procedures of preparing PtNCs/graphene

The graphite oxide powders were prepared from the graphite according to a modified hummer's method. To obtain graphene oxide (GO), 25 mg graphite oxide was dissolved in 50 ml water and exfoliated by ultrasonic treatment for 1 h. After that, 400 mg PVP was added into the solution as the surfactant, the solution was kept stirring for 1 h. Then 2 ml 0.1 M K_2PtCl_4 was added into the above solution under stirring. 500 mg ascorbic acid was added in the solution at last. The mixture was kept stirring for 12 h at a temperature of 85 °C with the reflux condition. Finally, the collected solid sample was separated by centrifugation and then thoroughly washed with ethanol and deionized water and then dried in a vacuum oven at room temperature for TEM, FE-SEM characterizations and electrochemical measurements. The PtNCs/graphene (synthesized without PVP) was prepared by the same procedure in the above description, while no PVP was added as the surfactant. Pt nanoclusters (PtNCs) and PtNCs/Vulcan were synthesized as well via similar procedure with no support and with Vulcan XC-72 as supporting material. By thermogravimetric analysis (TGA), the Pt loadings in different catalysts were tested to be 39.31% in PtNCs/graphene, and 55.14% in PtNCs/graphene (synthesized without PVP).

2.4. Fabrication of PtNCs/graphene working electrode

12 mg PtNCs/graphene (PVP) composites were well-dispersed in 2 ml DMF by ultrasonic treatment. Then, 5 μl well-distributed catalyst suspension was spread by pipette onto the surface of glassy carbon (GC) disc electrode (diameter: 3 mm) which had been polished with 1, 0.3 and 0.05 μm alumina to mirror finish. The working electrode was kept at a room temperature in vacuum furnace until dry. The PtNCs/graphene (synthesized without PVP) working electrodes were prepared by the same procedure above.

3. Results and discussion

3.1. The characterization of morphology and structure of PtNCs/graphene composite

The transmission electron microscopy (TEM) image of PtNCs/graphene synthesized without PVP was shown in Fig. 1A, in which micro-length wrinkles are clearly visible. The wrinkles which corresponded to defects in the carbon lattice is due to the remnants of the epoxy reaction [31]. Besides, a great quantity of Pt nanoclusters responded as black dots were detected on the surface