



Electrodeposited gold nanostructures at Nafion–poly(*o*-phenylenediamine) modified electrode and its electrocatalytic application



Perumal Rameshkumar, Ramasamy Ramaraj*

School of Chemistry, Centre for Photoelectrochemistry, Madurai Kamaraj University, Madurai 625 021, India

ARTICLE INFO

Article history:

Received 24 October 2014

Received in revised form 13 January 2015

Accepted 18 January 2015

Available online 27 January 2015

Keywords:

Au nanostructures

Poly(*o*-phenylenediamine)

Nafion

Modified electrode

Oxygen reduction

ABSTRACT

A facile method to prepare gold (Au) nanostructures at the Nafion–poly(*o*-phenylenediamine) (Nf–PPD) composite film modified electrode (ITO or GC/Nf–PPD/Au) and its application toward the electrocatalytic reduction of oxygen in acidic medium are reported. The formation of Au nanostructures at the Nf–PPD composite film modified electrode was monitored by *in-situ* spectroelectrochemical method. The *o*PD monomer was oxidatively polymerized during the electrodeposition of Au nanostructures. The Nf–PPD/Au modified electrode was characterized by cyclic voltammetry, scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses. The composite film formed on the electrode surface was dissolved in ethanol and the Au nanostructures were characterized by high resolution transmission electron microscopy (HRTEM) analysis. The HRTEM images showed the formation of ginger shaped Au nanostructures by a fusion growth process at the Nf–PPD film. The GC/Nf–PPD/Au modified electrode displayed a better electrocatalytic activity in terms of peak current density, mass activity and stability toward oxygen reduction reaction (ORR) in acidic medium than the other controlled modified electrodes investigated in this work. The presence of PPD and Au nanostructures in the Nf matrix at the modified electrode showed a synergistic catalytic activity in the ORR.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, conducting polymers (CPs) have found increasing importance in the fabrication of nanodevices [1] and chemical sensors [2] because of their metal-like conductive nature. The CPs based on aniline derivatives have been extensively studied [3]. Among them, poly(*o*-phenylenediamine) (PPD) is an interesting CP due to its conductance [4], electrochromic [5] and photoelectronic [6] properties. PPD was extensively used for the construction of electrochemical biosensors [7–10], PPD was mostly prepared by an electrochemical oxidation of *o*PD monomer [4,11]. Moreover, the preparation of PPD–metal nanocomposites has received much attention and profound applications in the field of electrocatalysis [12,13]. PPD was used as an affinity support for the Au NPs [14,15] and the PPD–Au composite finds applications in electrocatalysis. The PPD/Au modified electrode was used as L-lysine biosensor by immobilizing lysine oxidase on the electrode [16] and also used as signal tag for sensitive electrochemical detection of prolactin [17]. The PPD/Au film was used as a novel biocompatible interface

for the immobilization of antibody to detect antigen [18]. Recently, our group has reported the preparation of multi-branched cactus like Au nanostructures encapsulated in Nf–PPD composite film through an electroless synthetic route [19].

The fabrication of catalytically active and stable electrocatalysts for oxygen reduction reaction (ORR) is an important field of research. Platinum (Pt) has been widely used as single metal electrocatalyst for ORR [20,21]. Also, palladium (Pd) and Pt–Pd alloys have been studied extensively as electrocatalysts for the ORR [22,23]. Though the Pt based electrocatalysts have been used in proton exchange membrane fuel cells (PEMFCs), the poor kinetics of cell reactions and the high cost of Pt is still a limiting factor [24,25]. Therefore, toward the usage of Pt alternative electrocatalysts Au NPs modified electrodes were widely studied for ORR [26–28]. The Au NPs have received much attention in electrocatalysis reactions due to their large surface area, bio-compatibility and high conductivity [29,30]. Furthermore, the combination of Nf and Au NPs improves the efficiency of electrocatalytic reactions because Nf serves as a stabilizer for metal NPs and creates protonic conducting pathway for the reactions [29,31,32]. Recently, our group has reported the electrocatalytic ORR in both acidic and alkaline media using electrodeposited raspberry-like Au nanostructures modified

* Corresponding author.

E-mail address: ramarajr@yahoo.com (R. Ramaraj).

electrode [33]. The ORR study in acidic medium at the Au nanostructures modified electrode is particularly important for kinetic studies since Au is the only metal that has an oxide-free surface at the ORR potential region [34].

In the present work, we report a simple fabrication method to prepare Au nanostructures on Nf-PPD composite film modified electrode (ITO or GC/Nf-PPD/Au). The electrocatalytic properties of the GC/Nf-PPD/Au modified electrode were studied for ORR in acidic medium and the catalytic performance was systematically investigated at all the other controlled modified electrodes. The combination of PPD and Au nanostructures at the modified electrode revealed synergistic catalytic activity in the ORR.

2. Experimental

2.1. Materials

Gold(III) chloride (HAuCl₄) and Nafion perfluorinated ion-exchange resin (equiv. wt. 1100, 5 wt.% solution in lower aliphatic alcohols/H₂O mixture) were purchased from Sigma-Aldrich. *o*-Phenylenediamine was received from Merck and it was twice recrystallized before use [35]. All glassware was thoroughly cleaned with aqua regia and rinsed extensively with distilled water prior to use. (Precaution: Aqua regia is highly corrosive and it should be handled with extreme care.).

2.2. Preparation of GC/Nf-PPD/Au modified electrode

6 μ L of 0.1% Nf solution was drop-casted on GC electrode surface and allowed to dry at room temperature for an hour. The thickness of the Nf film coated on the electrode was calculated as 1 μ m using the following relation [36] (The same film thickness was maintained at the ITO modified electrode also).

$$\text{Thickness of Nf film}(\mu\text{m}) = \frac{\text{Amount of Nf} \times 10^4}{\text{Area of the electrode} \times \text{Density}} \quad (1)$$

The ITO/Nf or GC/Nf electrode was immersed in aqueous solution of 0.1 M *o*PD for 10 min to form the ITO/Nf-*o*PD or GC/Nf-*o*PD modified electrode. At this modified electrode, Au nanostructures were electrodeposited at an applied potential of -0.2 V (Hg/Hg₂Cl₂) for 300 s by dipping the electrode in an electrolyte solution containing 3 mM HAuCl₄ and 0.5 M H₂SO₄. The prepared modified electrode is represented as ITO/Nf-PPD/Au or GC/Nf-PPD/Au and the other Au nanostructures modified electrodes were prepared for controlled experiments by following similar procedure. For the preparation of GC/PPD or GC/Nf-PPD modified electrodes, GC or GC/Nf electrodes was immersed in aqueous solution of 0.1 M *o*PD for 10 min and then washed with distilled water. The adsorbed *o*PD molecules on the electrode surface were electrochemically polymerized by recording 20 cycles between -0.2 and 1.2 V in 0.5 M H₂SO₄ at a scan rate of 50 mV s⁻¹.

2.3. Characterization techniques

The absorption spectra of the Au nanostructures were recorded on an Agilent 8453 spectrophotometer. Scanning electron microscopic (SEM) images of Au nanostructures modified electrodes were collected using a HITACHI (Model S-3400) instrument. X-ray diffraction (XRD) patterns were obtained with a Bruker AXS D8 Advance instrument. High resolution transmission electron microscopy (HRTEM) analysis was performed on a JEOL JEM 2100 instrument operated at 200 kV. The sample for HRTEM analysis was prepared by dropping the sample solution on a carbon-coated copper grid and dried at room temperature. Electrochemical

characterization was carried out using a CH Instruments electrochemical workstation (model-760D).

2.4. Electrochemical studies

All the electrochemical studies were performed in a single compartment three-electrode cell at room temperature. The GC or ITO modified electrode and a platinum wire were used as working and counter electrodes, respectively. Calomel electrode was used as reference electrode. GC electrode was polished with alumina slurry (0.05 micron) and cleaned by potential cycling between +1 and -1 V in 0.1 M H₂SO₄ before each experiment. The electrochemical measurements for ORR were carried out in O₂ saturated 0.5 M H₂SO₄ solution. The modified GC electrode was used for all electrochemical experiments and the modified ITO electrode was used for *in-situ* spectroelectrochemical studies.

3. Results and discussion

3.1. Preparation of GC/Nf-PPD/Au electrode

The fabrication of GC/Nf-PPD/Au electrode was carried out by using the following procedure. The GC/Nf electrode was immersed in a deaerated 0.1 M *o*PD monomer solution for 10 min. The electrostatic attraction between the sulfonate groups of Nf and the protonated amine groups of *o*PD [19] led the formation of Nf-*o*PD film on the electrode (GC/Nf-*o*PD). At this modified electrode, Au nanostructures were electrodeposited at an applied potential of -0.2 V for 300 s by dipping the electrode in an electrolyte solution containing 3 mM HAuCl₄ and 0.5 M H₂SO₄. When the Nf/*o*PD film was dipped in HAuCl₄ solution, *o*PD was oxidized by Au³⁺ and the oxidized *o*PD monomer underwent polymerization leading to the formation of PPD at the Nf film. During the oxidative polymerization, a radical cation of *o*PD monomer initially forms and followed by polymerization leading to the formation of phenazine ring [19,37]. Schematic illustration of fabrication of GC/Nf-PPD/Au electrode is shown in scheme 1. Fig. 1 shows the cyclic voltammogram recorded for the GC/Nf-PPD/Au electrode in 0.5 M H₂SO₄ and it showed the characteristic redox peaks for both Au [32] and PPD [38]. The oxidative peak observed around 1.25 V is due to the oxidation of Au to its oxide and the corresponding reduction of Au oxide was observed at 0.8 V. In addition to the characteristic Au electrode behavior, a pair of reversible peaks attributed to the redox behavior of PPD film was observed in the negative potential region for PPD. This observation suggests that both Au and PPD showed the characteristics electrochemical behavior and this reveals that the electrodeposited Au nanostructures are electrochemically active at the Nf-PPD film coated electrode.

The influence of pH on the redox behavior of PPD was understood by recording the cyclic voltammograms for the GC/Nf-PPD/Au electrode using phosphate buffer solution (PBS) at different pHs (Fig. 2). The redox potential of PPD shifted linearly toward more negative potential when the pH was increased from 3 to 7 (Fig. 2B) and the plot of redox potential of PPD versus pH showed a slope value of 65 mV/pH. The pH dependence of redox potential of PPD indicates that the redox reaction involves two electron and two proton transfer [19,39]. Also, the reduction peak of Au shifted cathodically when the pH was varied systematically. The plot of reduction peak potential versus pH provided a slope value of 98 mV/pH (inset of Fig. 2B), which is close to the reported value thereby confirming the formation monomolecular layer of Au oxide in the oxidative scan [40]. Cyclic voltammograms recorded in 0.5 M H₂SO₄ for all the Au modified electrodes are shown in Fig. S1. From the voltammograms the electrochemically active surface areas (EASA) were calculated and the values are summarized

Download English Version:

<https://daneshyari.com/en/article/218492>

Download Persian Version:

<https://daneshyari.com/article/218492>

[Daneshyari.com](https://daneshyari.com)