



Electrodeposited gold dendrites at reduced graphene oxide as an electrocatalyst for nitrite and glucose oxidation



Manivannan Shanmugam, Kyuwon Kim *

Electrochemistry Laboratory for Sensors & Energy (ELSE), Department of Chemistry, Incheon National University, Incheon 406-772, Republic of Korea

ARTICLE INFO

Article history:

Received 15 February 2016

Received in revised form 5 June 2016

Accepted 10 June 2016

Available online 11 June 2016

Keywords:

Cyclodextrin

Electrodeposition

Glucose

Gold dendrites

Reduced graphene oxide

Nitrite

ABSTRACT

Herein we present, electrodeposition of gold dendritic nanostructures (Au-DNs) at reduced graphene oxide (RGO) functionalized with β -cyclodextrins (CD). The structural features of the Au-DNs and their interfacing mechanism with RGO are characterized by UV–Visible, FESEM, EDX, XPS, XRD and Raman analysis. The growth mechanism of Au-DNs at RGO–CD support has been elucidated using FESEM measurements. The CD induces the formation and plays a crucial role in shaping the dendrite morphology of Au nanostructures at RGO–CD along with the ad layer of ammine functionalized silicate sol–gel matrix (TPDT). The combined effect of RGO and Au-DNs provoked the synergistic electrocatalytic activity towards the nitrite and glucose electrooxidation.

© 2016 Published by Elsevier B.V.

1. Introduction

The chemical and physical properties of gold (Au) nanostructures (NSs) depends on their size and shape, these properties are tunable through control of morphology and structure [1,2]. Au NSs have shown great potential in nanocatalysis where the catalytic efficiencies are size and shape-dependent [3]. Various methods have been developed to prepare different size and shaped Au NSs [4–7]. Among the different morphologies of Au, dendritic NSs have attracted great attention because of their potential applications in several fields and importance in understanding the growth mechanism. Most of the dendritic NSs are the result of either growth of anisotropic particles or directional interactions between isotropic particles in the medium [2]. Graphene (GR), which consists of a two dimensional single layer of sp^2 hybridized carbon atoms, has attracted a great deal of attention from both experimental and theoretical scientific communities [8,9]. However, GR have a strong tendency to agglomerate irreversibly or restack to form graphite in aqueous medium due to its hydrophobic properties which will lower its catalytic ability [10]. Thus, chemical modifications on GR become essential to improve its stability and introduce special functionalities. Furthermore, it is demonstrated that GR and its derivatives along with metal NSs were the promising candidate for electrochemical applications [11,12] and stability of the composite can be improved via hybridization between the NSs and sp^2 dangling bonds at GR resident effect sites [12,13]. Therefore, tremendous progress [11,14–16] over

the past decade in the shape-controlled synthesis of Au NSs in particular; decorating GR derivative with dendritic NSs is an essential step for fabricating the functional devices and it remains a challenge.

The silicate network prepared through hydrolysis of N^1 -(3-trimethoxysilylpropyl)diethylenetriamine monomer led to the water soluble amine functionalized silicate sol–gel matrix (TPDT) and is a highly porous, high thermal stability, chemical inertness and rich in primary and secondary amine groups [17], which has been used as supporting matrix for the synthesis of nanomaterials and fabrication of the modified electrodes [18,19]. Furthermore, TPDT can interact with the functional groups (carboxyl, epoxy and hydroxyl) of GR and reduced graphene oxide (RGO) due to its active amine groups, which makes it to be an ideal candidate for supporting GR and its derivatives and further extend its application [20]. The β -cyclodextrin (CD) is a water-soluble, environmentally friendly, can improve the solubility and stability of functional materials and this cyclic oligosaccharide having a hydrophilic exterior and a hydrophobic interior cavity [21]. In addition, CDs can be attached at the GR and RGO sheets by strong hydrogen bonding to make them more hydrophilic [22]. Nitrite (NO_2^-) which is a typical inorganic pollutant to environment and human health is widely used as food additive, fertilizing agents and corrosion inhibitor [23]. Moreover, NO_2^- can become poisonous at high concentrations to animals and human beings because it probably results in generation of carcinogenic nitrosamines [24,25]. Also excessive NO_2^- in the body can lead to the irreversible oxidation of hemoglobin to methemoglobin [26]. Therefore, accurate and economic detection and determination of NO_2^- has attracted much attention. Glucose oxidation reaction has been an important subject in analytical chemistry for the past few

* Corresponding author.

E-mail address: kyuwon_kim@inu.ac.kr (K. Kim).

decades due to their applications as fuel, medical applications and food industries [27]. Au NSs are attractive electrode material for the glucose oxidation in alkaline media [28].

Recently, GR has been found as the promising supporting materials for variety of mono- and bi-metallic NSs and used as an electrocatalyst for fuel cell applications. For instance, Jena and co-workers [12] developed the Pd supported GR for methanol oxidation and Berry and co-workers [14] reported the snow flake-like Au NSs supported on GR by seed mediated growth. To attach metallic NSs on GR both external reducing agents [15,16,29] and electrodeposition methods [30] were previously used. Furthermore, by electrodeposition the metallic NSs can be facily attached on GR surface and size and shape can be easily tuned by altering experimental parameters also no stabilizer/capping agents were required. In this study we present an environmentally friendly method to attach Au-NDs on RGO with the assistance of pre-attached CD for the first time. Synergistic electrocatalytic activities toward NO_2^- and glucose oxidation are observed and enzyme-free NO_2^- sensor is also developed.

2. Experimental section

2.1. Materials and methods

Graphite (powder <20 μm), Gold (III) chloride hydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), β -cyclodextrin (CD), N^1 -(3-trimethoxysilylpropyl) diethylenetriamine (silane monomer used to prepare TPDT), L-ascorbic acid (AA), sodium nitrite and D-(+)-glucose were received from Sigma-Aldrich. All the chemicals were of analytical grade and were used as received. Absorption spectra were recorded with Thermo Scientific Evolution 60S UV-Visible spectrophotometer. FESEM images were recorded with JEOL JSM-7800F instrument. XRD profiles were recorded using Smart Lab (Rigaku) instrument. Raman spectra were recorded with WITTEC alpha 300 instrument. XPS spectra were recorded with ULVAC-PHI 5000 Versa Probe instrument. Indium tin oxide (ITO, (dimension: $2 \times 1 \text{ cm}$) and its modified forms were used as working electrode. Pt wire served as a counter electrode and Ag/AgCl (in 3 M NaCl solution) was used as a reference electrode. All the electrochemical experiments were conducted in a single compartment three electrode cell using an Ivium Technologies electrochemical work station. Nitrogen gas (N_2) was bubbled for 30 min prior to each experiment.

2.2. Synthesis of TPDT

A homogeneous TPDT was prepared [14] by the addition of 25 μL of 1 M TPDT silane monomer into 5 mL of aqueous solution under vigorous stirring and the stirring was continued for another 60 min.

2.3. Synthesis of RGO-CD nanosheets

GO was prepared from graphite by a modified Hummers method [31]. The detailed synthetic procedure of RGO-CD hybrid nanosheets

is found elsewhere [19,32]. Briefly, 20 mL of GO (2 mg/mL) was ultrasonicated for 2 h to yield a yellowish brown dispersion. Subsequently, 20 mL of CD aqueous solution (0.01 M) was mixed with GO dispersion and stirred for 1 h. Then, 80 mg of AA was added to the reaction mixture. The mixture was stirred at room temperature for 48 h. The resultant black dispersion was centrifuged and washed with water for five times and then dried in an oven. The RGO nanosheets were prepared by following the above procedure in the absence of CD.

2.4. Fabrication of the ITO/TPDT/RGO-CD/Au electrode

The modified electrode was fabricated as illustrated in Fig. 1, known amount (50 μL) of TPDT solution was drop casted on the ITO electrode surface and allowed to dry at room temperature for 1 h and referred as ITO/TPDT electrode. The thickness of the film coated on electrode was calculated as 1 μm [33]. Subsequently known amount of RGO-CD solution was drop casted on ITO/TPDT electrode and allowed to dry at room temperature and referred as ITO/TPDT/RGO-CD electrode. The Au NSs were electrodeposited at the modified electrode by applying a potential of -0.2 V (Ag/AgCl) for 300 s in an electrolyte solution containing 3 mM HAuCl_4 and 0.5 M H_2SO_4 [33]. The prepared modified electrode was referred as ITO/TPDT/RGO-CD/Au electrode. The modified electrodes were washed, dried and used for further experiments. The modified electrodes were stored at room temperature when it's not in use. The electrochemically active surface area (ECSA) was calculated from the charge consumed to form the Au oxide monolayer at the different modified electrodes using equation 1 and was used to obtain the current density plots [33].

$$\text{EASA} = Q/Q^* \quad (1)$$

where 'Q' is the charge required to form an oxide monolayer on the surfaces of Au NSs and 'Q*' is calibration factor with a value of $390 \mu\text{C cm}^{-2}$.

2.5. NO_2^- and glucose electrocatalysis at Au NSs modified electrodes

The NO_2^- and glucose electrocatalysis at the Au NSs modified electrodes were studied by recording the cyclic voltammograms (CVs). During the measurements, 1 mM of sodium nitrite was added to the 0.1 M PBS (pH 7.2) electrolyte and 10 mM glucose was added to the 0.5 M KOH electrolyte solution for NO_2^- and glucose electrocatalysis, respectively. The experiments were carried out at the room temperature (25°C) with a potential window of 0 to 1.2 V and -0.9 to 0.6 V for NO_2^- and glucose electrocatalysis, respectively. The NO_2^- sensor experiments were carried out by square wave voltammetric technique in the potential range of 0 to 1 V, with the step potential of 5 mV, amplitude of 25 mV and frequency of 25 Hz.

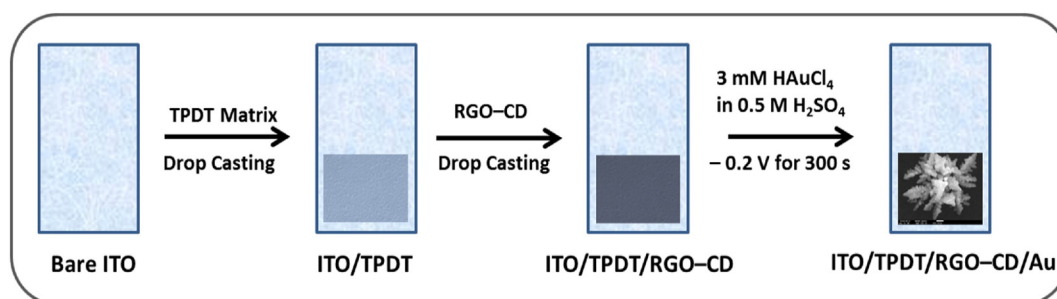


Fig. 1. Schematic representation of fabrication of the ITO/TPDT/RGO-CD/Au electrode.

Download English Version:

<https://daneshyari.com/en/article/217773>

Download Persian Version:

<https://daneshyari.com/article/217773>

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