Electrochimica Acta 236 (2017) 212–220

Contents lists available at ScienceDirect

Electrochimica Acta

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

Electrocatalytic application for gold nanoparticles decorated sulfur-nitrogen co-doped graphene oxide nanosheets and nanosized cobalt tetra aminophenoxy phthalocyanine conjugates

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ARTICLE INFO

Article history:
Received 31 December 2016
Received in revised form 13 March 2017
Accepted 20 March 2017
Available online 21 March 2017

Keywords:
Cobalt tetraaminophenoxy phthalocyanine
Graphene oxide nanosheets
Hydrogen peroxide
Electroreduction

ABSTRACT

Sulfur and nitrogen affinity for gold is utilized to self-assemble gold nanorods (AuNRs) on S, N doped or S/N co-doped graphene oxide nanosheets (SGONS/AuNRs, NGONS/AuNRs or SNGONS/AuNRs) for enhancement of the electrocatalytic activity of nanosized cobalt tetra aminophenoxy phthalocyanine (complex **1**) towards hydrogen peroxide detection. Of the electrodes containing AuNRs, **1**-SNGONS/AuNRs-GCE gave the lowest limits of detection (LOD) of 0.012 μM followed by **1**-SGONS/AuNRs-GCE and **1**-AuNRs-SNGONS(seq)-GCE both with LOD of 0.016 μM. This work shows that in the absence of GONS (when AuNRs are alone and in the presence of **1** in **1**/AuNRs-GCE), unfavorable detection limits are obtained and that doping of GONS is important in improving LOD. **1**-SNGONS/AuNRs-GCE showed concentration dependent mechanisms resulting in two adsorption Gibbs energies (ΔG^o) of −18.55 kJ mol^{-1} and −17.35 kJ mol^{-1} at high and low concentrations, respectively.

1. Introduction

Gold nanoparticles have been employed in electrocatalysis and have been shown to improve the electrode performance, both in terms of detection currents and overpotential [1]. Graphene oxide nanosheets (GONS) on the other hand increase surface area and improve conductivity of conventional electrodes [2–4]. Doping GONS with multiple functionalities such as sulfur and nitrogen can create anchoring sites on GONS for attachment of other nanomaterials such as gold nanoparticles (AuNPs). The two (GONS and AuNPs) can therefore be used in combination for electrode modification and their synergistic properties exploited for improved electrocatalytic detection. Composites of pristine graphene oxide and gold nanoparticles have been investigated for electrocatalytic properties [5–8]. On the other hand, metallophthalocyanines (MPcs) have been exploited for electrocatalytic detection of analytes such as hydrogen peroxide [9,10], nitrite [11,12], hydrazine [13] and L-cysteine [14,15].

In this work, we report for the first time on the effect of composites of gold nanorods (AuNRs) with sulfur/nitrogen co-doped GONS (SNGONS) on the electrocatalytic behavior of a nanosized MPc. The effect of individually doped sulfur (SGONS) and nitrogen doped (NGONS) on the electrocatalytic behavior of the nanosized MPc will also be evaluated. The choice of this combination has been greatly influenced by the high affinity of sulfur and nitrogen based compounds for gold``, coupled with the electrocatalytic nature of both gold nanoparticles and graphene based nanomaterials. Our previous work has demonstrated improved electrocatalysis of hydrogen peroxide on gold nanorods decorated multiwalled carbon nanotubes [10], hence the need to investigate the effect of gold nanorods on both pristine and doped graphene oxide nanosheets towards electrocatalysis. We have also earlier on demonstrated that nanosizing phthalocyanines improve the electrocatalytic behavior of MPcs [16] hence nanoparticles of cobalt tetra aminophenoxy phthalocyanine (represented as complex **1**, Fig. 1) are employed in this work. Cobalt (II) is employed as a central metal ion due to the well-known [17] electrocatalytic activity of CoPc derivatives. The aminophenoxy substituents were employed since they are bulky and improve solubility. The amino groups in complex **1** may also link to AuNPs, in addition to the latter also linking to S or N atoms of SNGONS. Hydrogen peroxide is employed as a test analyte.

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http://dx.doi.org/10.1016/j.electacta.2017.03.154
0013-4686/