

The influence of gold nanoparticles on the electroactivity of nickel tetrasulfonated phthalocyanine

Audacity Maringa and Tebello Nyokong*

Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

Dedicated to Professor Nagao Kobayashi on the occasion of his 65th birthday

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ABSTRACT: We report on the electrodeposition of gold nanoparticles (AuNPs) on a glassy carbon electrode (GCE) followed by deposition of nickel tetrasulfonated onthalocyanine (NiTSPc) film by electropolymerization (poly-NiTSPc-GCE) to form Poly-NiTSPc/AuNPs-GCE. The presence of the gold nanoparticles caused a lowering of the anodic and cathodic peak separation (ΔE_p) of ferricyanide from 126 mV on poly-NiTSPc to 110 mV on poly-NiTSPc/AuNPs. The electrooxidation of nitrite improved on modified electrodes compared to GCE, with the latter giving $E_p = 0.78$ V and the modified electrodes gave $E_p = 0.62$ V or 0.61 V. Poly-NiTSPc/AuNPs-GCE had higher currents compared to poly-NiTSPc-GCE. This indicates the enhancement effect caused by the AuNPs. Electrochemical impedance spectroscopy and chronoamperometric studies also showed that poly-NiTSPc/AuNPs-GCE was a better electrocatalyst than poly-NiTSPc-GCE or An NPs-GCE.

KEYWORDS: gold nanoparticles, nicket tetrasulfonated phthalocyanine, nitrite, electrocatalysis.

INTRODUCTION

Metallophthalocyanines (MPcs) have been employed to modify electrodes using a Griety of methods such as electropolymerization [1–5], self-assembled monolayer formation [6, 7] and adsorption [8, 9]. The resulting electrodes have been used for the detection of many analytes including nitrite [9, 10].

On the other hand, metal nanoparticles (such as gold [11–13], silver, [14, 15] palladium [16, 17] and platinum [18, 19]) have attracted a lot of attention as electrocatalysts. In some cases, alloys of these metals have been employed to enhance the electrocatalytic activity [20, 21]. In order to improve the electrocatalytic activity of metal nanoparticles, special attention has to be paid to the synthesis methods. This is because the reactivity of nanoparticles is dependent on their size, composition and morphology [20].

The combination of metallophthalocyanine with metal (such as gold) nanoparticles results in improved electrocatalysis [22–24]. We have previously showed that the presence of gold nanoparticles on tantalum phthalocyanine enhanced the detection of bisphenol A [22]. Pal and Ganesan showed that the incorporation of AuNPs onto mercaptopropyl silica-cobalt phthalocyanine (MPS-CoPc) [23] resulted in significant increase in current and considerable decrease in oxygen reduction potential.

Alencar *et al.* found that the presence of AuNPs in a layer by layer arrangement of PAH-AuNP/NiTSPc {poly(allylamine hydrochloride)-gold nanoparticles/ nickel tetrasulfonated phthalocyanine} enhanced the catalytic detection of H_2O_2 [24]. In all the three cases, gold nanoparticles were first synthesized in solution, and then linked to the phthalocyanines, followed by adsorption onto the bare electrode. The use of adsorption has limitations as far as reproducibility is concerned since the adsorbed modifiers may leach from the electrode.

To avoid the leaching from preformed conjugates of AuNPs with Pc, AuNPs nanoparticles were synthesized

[◊]SPP full member in good standing

^{*}Correspondence to: Tebello Nyokong, email: t.nyokong@ ru.ac.za, tel: + 27 46-6038260, fax: + 27 46-6225109