



# Electrocatalytic activity of bimetallic Au–Pd nanoparticles in the presence of cobalt tetraaminophthalocyanine



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## ABSTRACT

Au and Pd nanoparticles were individually or together electrodeposited on top of polymerized cobalt tetraaminophthalocyanine (poly-CoTAPc). When Pd and Au nanoparticles are co-deposited together, the electrode is denoted as Au–Pd (co-deposited)/poly-CoTAPc-GCE. X-ray photoelectron spectroscopy (XPS) was used to show the successful deposition of AuNPs, PdNPs and Au–Pd (co-deposited). The scanning electrochemical microscopy showed that Au–Pd (co-deposited)/poly-CoTAPc-GCE (with current range of 9.5–13.5  $\mu$ A) was more conducting than Au–Pd (co-deposited)-GCE (with current range of 8–12  $\mu$ A). Electrochemical impedance spectroscopy (EIS) showed that there was less resistance to charge transfer for Au–Pd (co-deposited)/poly-CoTAPc-GCE compared to the rest of the electrodes. Au–Pd (co-deposited)/poly-CoTAPc-GCE showed the best activity for the electrooxidation of hydrazine in terms of limit of detection (0.5  $\mu$ M), hence shows promise as an electrocatalyst for electrooxidation of hydrazine.

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## 1. Introduction

Bimetallic nanoparticles have been used for various electrochemical reactions [1–14], including ethanol electro-oxidation [3,12,13], formic acid electro-oxidation [10,11,14], reduction of benzyl chloride [15] and hydrazine detection [16,17]. Bimetallic nanoparticles are based on two different metals and show improved catalytic activity compared to pristine metal nanoparticles, this has been attributed to the synergetic effect of the bimetallic nanoparticles. Yen et al. [18] found out that of the two nanoparticles, one has high performance in electroactivity and the other influences the electrocatalytic activity or prevents poisoning problem. The unique electrocatalytic behavior of bimetallic nanoparticles is attributed to their electronic structures which are quite distinct from those of the pure nanoparticles [19].

We have recently reported that there was an improvement in the electrocatalytic detection of hydrazine when both CoTAPc and Pd nanoparticles (NPs) were employed in electrode modification [20]. The presence of both AuNPs and CoTAPc also showed improved electrocatalytic activity [21]. In this work, cobalt tetraaminophthalocyanine (CoTAPc) was electropolymerized onto a glassy carbon electrode (GCE), followed by the co-electrodeposition of Pd and Au nanoparticles, the electrode is represented as Au–Pd (co-deposited)/poly-CoTAPc-GCE, Scheme 1. This is the first

time bimetallic NPs are employed together with a phthalocyanine for electrocatalysis.

Bimetallic nanoparticles containing Pd and Au have showed selective electrocatalytic oxidation of analytes [22], making the electrocatalytic detection much more enhanced, hence were chosen in this work. Phthalocyanines on the other hand are well known electrocatalysts, whose electrocatalytic activity has been shown to improve in the presence of nanoparticles, as stated above. This is the first time that Pcs are combined with more than one type of nanoparticle for electrocatalytic applications. The study clearly shows that when both Au and Pd nanoparticles and phthalocyanine, are present, the overpotentials are greatly reduced compared to when individual nanoparticles are combined with phthalocyanines.

We have recently shown that the best catalytic activity is obtained when CoTAPc was electropolymerized first followed by electrodeposition of AuNPs on top. The electrocatalytic activity was larger than when CoTAPc was electropolymerized on top of electrodeposited of AuNPs [21]. Thus, in this work only the electrodes where CoTAPc is electropolymerized before the electrodeposition of Pd–Au NPs will be presented. Electrodes where AuNPs are deposited first followed by PdNPs and vice versa were also studied and are represented as Pd/Au–GCE and Au/Pd–GCE (in the absence of CoTAPc), and Pd/Au–poly-CoTAPc-GCE and Au/Pd–poly-CoTAPc-GCE (in the presence of CoTAPc), respectively. The data is compared to electrodes where PdNPs [20] or AuNPs separately (in the absence and presence of CoTAPc) are employed.

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