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Characterization and electrocatalytic behaviour of glassy carbon electrode modified with nickel nanoparticles towards amitrole detection

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ABSTRACT

We report on the synthesis of Ni nanoparticles (NiNPs) and their application in electrocatalysis in comparison with nickel phthalocyanine (NiPc). UV–vis spectroscopy, powder X-ray diffraction, transmission electron microscopy and electron paramagnetic resonance were used in the characterization of NiNPs. Cyclic voltammetry and electrochemical impedance spectroscopy were used in electrocatalytic studies of amitrole on the glassy carbon electrode modified with NiNPs. The apparent and catalytic rate constants for amitrole on the NiNP-GCE were found to be 2.58×10^{-5} cm s^{-1} and 1.11×10^{3} M^{-1} s^{-1}, respectively.

1. Introduction

Magnetic nanoparticles have found potential applications in therapeutic and diagnostic testing [1], magnetic resonance imaging [2,3], drug delivery [2–5] and bio-sensing [6]. Specifically, nickel nanoparticles have attracted much attention because of their application in catalysis, medical diagnostics and magnetic applications [7]. The major advantage of using nickel nanoparticles as electrode modifiers for carbon electrodes and for electrocatalysis of a wide variety of analytes is that they are a suitable substitute for noble metals due to their low cost [8], while having good electrical conductivity.

Nickel nanoparticles have been produced by several methods including by surfactant mediated synthesis [9], chemical reduction method [10] and solvothermal method [11]. The latter is a simple method which results in pure products. Different morphologies of Ni nanoparticles have been produced by using different solvents. The morphology and particle size of metal nanoparticles may in addition be controlled by reaction temperature, the concentration of metal precursor and the type of reducing agents.

In this paper we report on the synthesis of Ni nanoparticles (NiNPs) using chemical reduction method utilizing ethylene glycol as a solvent and sodium borohydride as a reducing agent. The NiNPs are used as electrode modifiers in comparison with nickel phthalocyanines (NiPc) and using amitrole as a test analyte. NiNPs functionalized with enzymes have been employed for the electrocatalytic detection of bisphenol A [12]. NiNPs have also been used for the detection of methanol when immobilized on graphene [13]. Alcohols have also been electrocatalysed using NiNPs on boron doped diamond [14]. The NiNPs in reference 14 were produced by electrodeposition from $Ni(NO_3)_2$ solution. NiO NPs have been used for oxygen reduction [15]. In this work pre-formed NiNPs (instead of electrodeposition or NiO NPs) were employed and converted into O–Ni–O bridges (in NaOH solution) following adsorption onto the glassy carbon electrode (GCE) as discussed below. This allows us to compare the catalytic activity of the NiNPs to that of NiPc, where the latter is also transformed into O–Ni–O bridges in NaOH following adsorption onto the GCE. Immersion of Ni (or its macrocylic complexes) adsorbed on electrode surfaces in alkaline solution results in the formation of $Ni(OH)_2$, which have a characteristic Ni(III)/Ni(II) couple in cyclic voltammetry [16]. For nickel phthalocyanine (NiPc) complexes, O–Ni–O bridges are known to form between the macrocycles following cyclic voltammetry cycling in basic media [17–19]. Such O–Ni–O bridged complexes show better catalytic activity than before the formation of these bridges [17,20].

Thus in this work, the electrocatalytic behaviour of NiNPs is compared with that of NiPc following transformation in alkaline media. Metallophthalocyanines (MPcs) exhibit a rich electrochemical behaviour due to the accessibility of a range of oxidation states centred on the Pc unit and on the central metal [21]. MPcs are very good electrochemical catalysts and as such they have been used for the detection of many analytes [22]. Since Pcs and especially NiPc are well known as electrocatalysts [22], the electrocatalytic activity of nickel nanoparticles (NiNPs) are compared with those of NiPc individually or as mixture. Amitrole, a heterocyclic herbicide

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