A sensitive electrochemical nitrate sensor based on polypyrrole coated palladium nanoclusters

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ABSTRACT
This study examines the synthesis and characterization of polypyrrole coated palladium nanocluster (Pd NCs-PPy) composites and their application in nitrate detection at pH = 7.0. The synthesis was performed via the direct reduction of an aqueous solution of Pd (CH3COO)2 in the presence of pyrrole monomers in NaOH. X-ray diffraction and field emission scanning electron microscopy observations showed that the Pd cations were completely reduced to Pd with the formation of Pd NCs-PPy cluster morphology, respectively. Electrochemical properties of the Pd NCs-PPy electrode were studied by differential pulse voltammetry (DPV), cyclic voltammetry and electrochemical impedance spectroscopy. From the DPV results, the estimated limit of detection, limit of quantification (S/N = 3) for the two linear segments (lower and higher concentration of nitrate) are 0.7444, 2.4815 and 0.4535, 1.5117 lM, respectively. The sensitivity of these two linear segments is 0.124 and 0.204 lA lM/C0 1 cm2/C02, respectively. Results from the reproducibility experiments show that the Pd NCs-PPy is feasible for the quantitative determination of certain concentration ranges of nitrate.

1. Introduction
Polypyrrole (PPy), an electroactive polymer, has wide applications in various fields of research due to its excellent properties [1]. Recent investigations have shown that PPy or its composites with metal oxides and metals such as silver and palladium are useful for the fabrication of different type of devices, due to their good conductivity and reductive ability [2–7]. On the other hand, recent results have confirmed the effects of size and morphology of the nanocomposites on the catalytic properties [8,9]. It is clear that the catalyst efficiency can be increased with the increase of the surface area. Therefore, based on this important factor, the most important research is focused on the synthesis of electroactive polymer in the presence of noble metal or metal oxide nanoparticles [10,11]. On the other hand, the cost and the type of metal or metal oxide nanoparticles are other important factors which must be considered.

Recently, it is clearly recognized that nitrate pollution of water sources is a huge problem for the society. Several techniques have been proposed for the efficient removal of nitrate, but such applications are limited by their expensive cost [12–16]. On the other hand several methods such as spectrophotometry, chromatography and electrochemistry have been used for nitrate reduction or sensing [17]. Among these different methods, electrochemistry has numerous advantages such as low cost, simplicity, high sensitivity and selectivity. A viable method for the detection of nitrate is based on its electroreduction in the presence of metallic or bimetallic catalyst [18–21,17]. A noble metal such as palladium or its alloy can be used as a catalyst for the reduction and sensing of nitrate. Recent reports have shown that palladium and bimetallic catalyst such as copper–palladium, or other metal catalysts can be used for nitrate electroreduction in acidic [22–24] and basic [25,26] media, although the majority of ground and drinking waters are close to neutral pH. Therefore, the focus on the type of catalysts for the sensing or electroreduction of nitrate without any pretreatment is an interesting area of research. Most of the reports on nitrate electroreduction or sensing in neutral media gave very small ranges of nitrate concentrations [23,27]. In this