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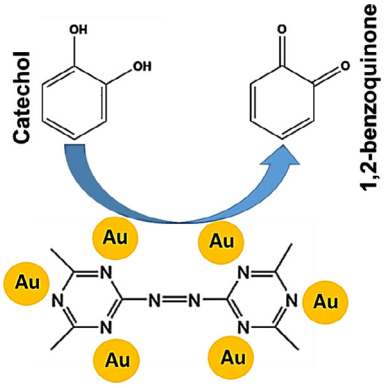
One pot electrochemical synthesis of poly(melamine) entrapped gold nanoparticles composite for sensitive and low level detection of catechol

Selvakumar Palanisamy [a], Sayee Kannan Ramaraj [b,e], Shen-Ming Chen [a,*], Te-Wei Chiu [b,*], Vijayalakshmi Velusamy [c,*], Thomas C.K. Yang [d], Tse-Wei Chen [a], Sonadevi Selvam [e]

[a] Electroanalysis and Bioelectrochemistry Lab, Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, No. 1, Section 3, Chung-Hsiao East Road, Taipei 106, Taiwan, ROC
[b] Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, 1, Sec. 3, Zhongxiao E. Rd., Taipei 106, Taiwan
[c] Division of Electrical and Electronic Engineering, School of Engineering, Manchester Metropolitan University, Manchester M1 5GD, United Kingdom
[d] Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, No. 1, Section 3, Chung-Hsiao East Road, Taipei City, Taiwan
[e] PG & Research Department of Chemistry, Thiagarajar College, Madurai-09, Tamil Nadu, India

GRAPHICAL ABSTRACT



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ABSTRACT

A simple and cost effective synthesis of nanomaterials with advanced physical and chemical properties have received much attention to the researchers, and is of interest to the researchers from different disciplines. In the present work, we report a simple and one pot electrochemical synthesis of poly(melamine) entrapped gold nanoparticles (PM-AuNPs) composite. The PM-AuNPs composite was prepared by a single step electrochemical method, wherein the AuNPs and PM were simultaneously fabricated on the electrode surface. The as-prepared materials were characterized by various physicochemical methods. The PM-AuNPs composite modified electrode was used as an electrocatalyst for oxidation of catechol (CC) due to its well-defined redox behavior and enhanced electro-oxidation ability towards CC than other modified electrodes. Under optimized conditions, the differential pulse voltammetry (DPV) was used for the determination of CC. The DPV response of CC was linear over the concentration ranging from 0.5 to 175.5 μM with a detection limit of 0.011 μM. The PM-AuNPs composite modified electrode exhibits the high selectivity in the presence of range of potentially interfering compounds including dihydroxybenzene isomers. The sensor shows excellent practicality in CC containing water

* Corresponding authors.
E-mail addresses: smchen78@ms15.hinet.net (S.-M. Chen), tewei@ntut.edu.tw (T.-W. Chiu), V.Velusamy@mmu.ac.uk (V. Velusamy).

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samples, which reveals the potential ability of PM-AuNPs composite modified electrode towards the determination of CC in real samples.

1. Introduction

Recent years, the monitoring of phenols and its analogous compounds has received greater attention due to their prime toxicity to animals, plants and aquatic organisms [1]. In particular, catechol (CC) is an isomer of dihydroxybenzene, has poor degradability in water and the large amount is released into the fresh water from the pesticides, dyes and pharmaceutical industries [2]. The U.S Environmental Protection (EPA) Agency and the European Union (EU) has stated that CC is a serious environmental pollutant due to its poor degradability and high toxicity in the biological environment [3,4]. Hence, the development of reliable and robust methods for the detection of trace levels of CC is very important. To date, number of analytical methodologies have been developed and used for the reliable detection of CC including electrochemical methods [5–9]. Compared with available methods, electrochemical methods are widely used for the detection of CC due to its simplicity, portability and high sensitivity [10]. It is well-known that CC is highly electroactive on conventional carbon electrodes such as glassy and screen printed carbon electrodes, though the selectivity and reproducibility of the electrode is quite challenging due to the fouling of oxidation signals, higher oxidation working potential and response to other compounds [3]. Hence, different approaches or modifiers have been used on the electrode surfaces to attain the better selectivity and improved sensitivity for the detection of CC.

In recent years, different nano and micro material modified electrodes have been employed for the reliable detection of CC, and they can also offer better selectivity, lower oxidation potential with improved sensitivity [11–15]. For instance, carbon nanomaterials and metal nanoparticles are widely used for selective detection of CC due to their unique physical and chemical properties [3,11–17]. Among them, metal nanoparticles are found considerable interest in the modified electrodes owing to the large active sites and high conductivity [18]. In particular, Au-NPs are commonly used for broad range of applications including the electrochemical sensing of small molecules [3]. On the other hand, poly (melamine) (PM) is an important polymer, has been widely used for the construction of electrochemical sensors due to its extreme stability and presence of abundant nitrogen functional groups [19–23]. The abundant functional groups and extreme hydrophilicity of PM is often more helpful for the surface functionalization with small molecules. Up to now, very few reports have been reported for the synthesis of PM with metal nanoparticles [19,20], while they not yet been used for electrochemical sensing of dihydroxybenzene isomers.

The motivation of the present work is to synthesize the AuNPs-PM composite by single step electrochemical method for the first time. The schematic representation for the single step electrochemical fabrication of PM-AuNPs composite is shown in Fig. 1. The resulting AuNPs-PM composite is used for the sensitive and low potential detection of CC. The combined unique properties of AuNPs and PM are result into the high sensitivity, selectivity and lower oxidation potential for CC than discrete PM and AuNPs modified electrodes.

2. Experimental

2.1. Materials and methods

Melamine was obtained from Sigma–Aldrich and used as received. Potassium gold (III) chloride trihydrate ($KAuCl_4{\cdot}3H_2O$) was purchased from Strem chemicals (USA). Catechol was purchased from Sigma–Aldrich. NaH_2PO_4 and Na_2HPO_4 were purchased from Sigma–Aldrich and Avantor Performance Materials Inc, Center Valley, U.S.A, respectively. The phosphate buffer solution (PBS) pH 7.0 was prepared using 0.05 mol L^{-1} Na_2HPO_4 and NaH_2PO_4 solutions in double distilled water. All other chemical were used in this study were obtained from Aldrich and the solutions were prepared using doubly distilled water without any further purification.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were performed using a computerized CHI 1205b and CHI750a electrochemical work stations. The scanning electron microscopic (SEM) images were acquired using Hitachi S-3000 H electron microscope. Transmission electron microscopic image of the composite was taken using JEM 2007 model transmission electron microscope (TEM). Elemental analysis (EDS) of the composite was analyzed using HORIBA EMAX X-ACT attached Hitachi S-3000 H scanning electron microscope. Thermo SCIENTIFIC Nicolet iS10 instrument was used for the Fourier transform infrared spectroscopy (FTIR) measurements. Typical three electrode setup which consisting of glassy carbon electrode as a working electrode, a saturated Ag/AgCl reference electrode and a platinum electrode as an auxiliary electrode in the electrochemical experiments. All measurements were carried out at a room temperature in an inert atmosphere unless otherwise stated.

2.2. Single step electrochemical synthesis of PM-AuNPs composite

To prepare PM–AuNPs composite, first 1 mM $KAuCl_4{\cdot}3H_2O$ solution prepared using 0.5 M H_2SO_4 and melamine (1 mM) was added into the solution and sonicated for 10 min. Then pre-cleaned GCE was immersed in the aforementioned solution and 10 constitutive CV cycles were performed in the potential ranging from 0 to 1.5 V at a scan rate of 50 mV/s [18]. The schematic representation for the

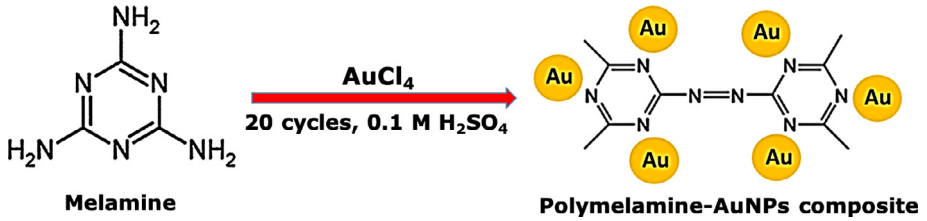

Fig. 1. Schematic representation of one pot electrochemical preparation of PM–AuNPs composite.