Sensors and Actuators B 143 (2010) 547–554

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Platinum nanoparticle decoration of carbon materials with applications in non-enzymatic glucose sensing

Dhanraj Rathod [a], Calum Dickinson [b], Denise Egan [a], Eithne Dempsey [a,*]

[a] Centre for Research in Electroanalytical Technologies (CREATE), Department of Science, Institute of Technology Tallaght, Tallaght, Dublin 24, Ireland
[b] Materials Surface Science Institute, University of Limerick, Limerick County, Limerick, Ireland

ARTICLE INFO

Article history:
Received 25 June 2009
Received in revised form
16 September 2009
Accepted 30 September 2009
Available online 9 October 2009

Keywords:
Non-enzymatic glucose sensor
Nanocomposite
Platinum nanoparticle

ABSTRACT

Nanocomposites of ethylene glycol protected platinum nanoparticles were prepared in the presence of activated carbon (AC), multi-walled carbon nanotubes (MWNTs) and carbon nanofibres (CNFs) at 20% (w/w) Pt loading and their potential in non-enzymatic glucose sensing evaluated. Physical and electrochemical characterization of these hybrid materials was enabled using transmission electron microscopy (TEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and cyclic voltammetry. The average platinum nanoparticle diameters, as determined from TEM and XRD measurements, were 2 ± 1 to 3 ± 1 nm. The electrochemically active surface area of the platinum nanoparticles were found to be 91, 78 and 128 $m^2\,g^{-1}$ for Pt-C, Pt-MWCNT and Pt-CNF respectively, as determined by the hydrogen adsorption/desorption phenomenon, using cyclic voltammetry in H_2SO_4. The nanomaterials were applied to the direct non-enzymatic quantization of glucose over its physiological range in the absence of the enzyme glucose oxidase. Hydrodynamic amperometric at $E_{app} = 0.55$ V vs. Ag/AgCl in phosphate buffer (pH 7.4) was employed and the materials responded linearly to glucose (at pH 7.4, 298 K) over the range 2–20 mM ($R^2 = 0.99$) with sensitivity 1.07, 1.10 and 0.52 $\mu A\,mM^{-1}\,cm^{-2}$ for Pt-C, Pt-MWCNT and Pt-CNF respectively.

1. Introduction

The controlled synthesis of platinum nanoparticles (Pt NPs) is an attractive goal in the development of highly active platinum catalysts for sensor and fuel cell applications [1–3]. Attachment of metal nanoparticles to carbon nanomaterials is not only of great interest in the modification of the properties of pristine carbon nanotubes but also in the preparation of novel hybrid materials for various applications e.g. biosensors, heterogeneous catalysts and as nanoelectrodes in next generation high performance fuel cells and batteries [4–10]. This is made possible by their high chemical stability, unique electrical properties and high surface to volume ratios. A recent review has given an account of the use of carbon nanotubes as a support material for the dispersion and stabilization of metal and semiconductor nanoparticles [11] while another report has focused on the synthesis, assembly and surface functionalization of nanostructures with applications in nanosensors and nanoelectronics [12,13].

Nanostructures of transition metals, such as platinum, have significant application potential not only in sensor technology but in photocatalysis, optical, electronic and magnetic devices [2,14–18]. For decades, carbon nanotubes and fibers have attracted attention due to their high mechanical strength, high thermal conductivity, high electrical conductivity and excellent chemical stability in aggressive media. As a result, these materials have been employed as templates for the synthesis of various transition metal nanoparticles for different technological applications such as enzyme based sensing [19–21]. Well dispersed Pt nanoparticles in carbonaceous materials have also been used as catalysts in polymer electrolyte membrane fuel cells (PEMFCs), direct methanol fuel cells (DMFC) and for hydrogen oxidation as well as the oxygen reduction reaction (ORR) [22–24].

Currently, commercial glucose sensors rely on immobilized enzymes for selective recognition and quantitative analysis. However, the thermal and chemical instability of enzymes is still a significant issue in the practical application of such devices, particularly in the area of continuous monitoring. A recent review by Park et al. [25], outlines advances in non-enzymatic glucose sensing and describes the mechanism of direct electrochemical glucose oxidation under various pH conditions. Recent innovative approaches in the development of nanomaterials, together with a clearer understanding of the mechanism of direct glucose oxidation, has meant that the goal of non-enzymatic glucose sensing is close to being realized.

One such example is an amperometric enzyme-less glucose sensing system based on nanoporous platinum embedded within

---

* Corresponding author. Tel.: +353 1 4042862; fax: +353 1 4042404.
E-mail address: Eithne.dempsey@ittdublin.ie (E. Dempsey).

0925-4005/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2009.09.064

a microfluidic chip comprised of a microfluidic transport channel network and a miniaturized electrochemical cell (sensitivity 1.65 μA cm^{-2} mM^{-1} over the range 1–10 mM glucose) [26]. Other examples include Pt-Ir nanomaterials prepared by a hydrothermal method, and exploited for amperometric glucose sensing by Holt-Hindle et al. [27], Pt and Au nanoparticles synthesized using tetra aniline, for electrocatalysis of glucose [28], non-enzymatic flow injection analysis of glucose performed at a nickel electrode [29], porous gold formed using the hydrogen bubble dynamic template synthesis [30] and detection at a Cu–O nanowire modified Cu electrode [31]. Other materials which have been recently reported include a nickel powder sol gel composite electrode [32], Pd doped copper oxide nanofibres [33], porous CuO_2 microcubes [34], an Au nanowire array [35] and a 3D inverse opal gold film electrode [36].

There are fewer reports which exploit the unique combined properties of both carbon nanomaterials and metallic nanoparticles for direct glucose electrocatalysis. Some examples include the electrodeposition of Pt-Pd nanoparticle alloy on CNTs for glucose oxidation in neutral and alkaline media which was examined by Cui et al. [37], gold decorated carbon nanotubes employed by Manesh et al. [38] and restructured carbon nanotubes [39]. A recent report by Myung et al. [40] examines Pt, Cu_2S and SnO_2 hybrid nanostructures grown using the solvothermal method on double-walled and multi-walled carbon nanotubes, with the double-walled series responding best to both glucose and hydrogen peroxide oxidation.

To date, many of the non-enzymatic glucose sensing reports suffer from limited linear range, poor selectivity and operate only in either acidic or basic conditions, thus severely limiting their applications in the area of diabetic monitoring and control. In this work, we present the synthesis and decoration of uniform sized Pt nanoparticles in different carbon matrices and report their application in glucose electro-oxidation over the physiological range in the absence of enzymes, with evidence of effective discrimination against structurally related sugars and electroactive interferents.

2. Materials and methods

2.1. Reagents

Sulphuric acid, nitric acid, hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$), ethylene glycol (EG), Nafion® (5% solution in a mixture of lower aliphatic alcohols and water), activated carbon (AC), multiwall carbon nanotubes (MWNTs, 6–13 nm diameter), carbon nanofibers (CNF) (∼100 nm diameter) were used as received from Sigma–Aldrich. Ultrapure water purified with Purelab option water equipment (ELGA Co. Ltd.) was used exclusively in all experiments (resistivity 17 MΩ cm).

2.2. Characterization techniques

The size and distribution of the Pt nanoparticles was determined by means of transmission electron microscopy (TEM) using a JEOL 2011 operated at 200 kV using a LaB_6 filament equipped with a Gatan Multiscan Camera 794. The X-ray diffraction (XRD) patterns of the catalysts were obtained using a Rigaku D/MAX-PC 2500 X-ray diffractometer with a Cu Kα (Kα = 1.5405 Å) radiation source operating at 40 kV and 200 mA. The materials were electrochemically evaluated using cyclic voltammetry (CV) using an electrochemical work station (CH Instruments Inc. 420A). Experiments were performed in 0.5 M H_2SO_4 saturated with nitrogen and contained within a conventional three-electrode cell using an Ag/AgCl aq. reference electrode and a Pt wire counter electrode. Thermogravimetric analysis (TGA) was performed using a Thermal Advantage Q50 with platinum pan, balance N_2 flow 40 ml min^{-1} and sample N_2 flow 60 ml min^{-1}.

2.3. Synthesis of Pt/C, Pt/MWNT and Pt/CNF hybrid nanocomposite

Prior to the synthesis of the platinum nanoparticles, carbon nanotubes and nanofibres were treated by heating at reflux in 30% (v/v) HNO_3 at 353 K for 24 h followed by filtration using 0.45 μm Millipore hydrophilic polycarbonate membrane, with the aid of vacuum pump (1 atm), and washed thoroughly with deionized water. The materials were then dried under vacuum at 383 K for 12 h. Platinum nanoparticles were synthesized by the polyol process, in which ethylene glycol acts as both a reducing agent and capping agent, to control the particle size, uniformity and distribution of the platinum nanoparticles during the synthesis in the presence of activated carbon and acid functionalized carbon nanotubes and nanofibres [41–44].

In a typical synthesis, 53 mg of H_2PtCl_6 (20 mg Pt representing 20% (w/w) loading) was dissolved in 180 ml of EG:H_2O solution (3:2). 80 mg of activated carbon was added to 90 ml of EG:H_2O solution (3:2), followed by sonication for 30 min to achieve a homogenous solution. The hexachloroplatinic acid solution was then added drop wise to the carbon solution using a dropping funnel over a 3 h period. The reaction mixture was heated under reflux at 413 K for 8 h with constant stirring before being allowed to cool to room temperature. The solution was filtered using a 0.45 μm pore size Millipore polycarbonate membrane, followed by washing with hot deionized water and isopropyl alcohol until all chloride ions were removed, as confirmed by the silver nitrate test after each washing. The sample was then dried in a vacuum oven at 383 K for 12 h. The same procedure was followed for decoration of Pt nanoparticles on acid functionalized MWNTs and CNFs. The weight percent of platinum nanoparticles was maintained at 20% (w/w) in all cases.

2.4. Electrochemical testing

Prior to testing, glassy carbon electrodes were polished with 0.5 μm alumina powder, washed with deionized water and then dried at room temperature. 2 mg of Pt-C was dispersed in 1 ml water:isopropyl alcohol mixture (3:1) and a calculated amount of Nafion® solution (1% (v/v)) added to the dispersion to maintain the Pt-C:Nafion® ratio of 8:1. This mixture was then sonicated for 30 min to achieve a uniform dispersion of the particles in solution. 10 μl of this suspension was then cast onto the surface of a glassy carbon electrode and allowed to dry in air for 1 h. The same procedure was adopted for the Pt-MWNT and Pt-CNF samples. Amperometric experiments were carried out in phosphate buffer solution (pH 7.4) at E_{app} = 0.55 V vs. Ag/AgCl for the direct electro-oxidation of glucose.

3. Results and discussion

As carbon nanotubes and fibers are chemically inert, the activation of their surfaces using acid treatment was essential for attachment of metal nanoparticles, improving deposition and nucleation on the surface. This activation results in a greater degree of hydrophilicity for the functionalized carbon nanomaterials, as reflected by enhanced dispersion in aqueous solution. Fig. 1(a) shows the visual changes in aqueous solutions of MWNT and CNF (5 mg ml^{-1}) before and after surface modification reflecting the highly uniform and stable (>6 months) distribution of the nanomaterials in water. The resultant surface functional C=O and COOH groups at the tips and sidewall defect sites were confirmed by FTIR and Fig. 1(b) shows the spectra for nitric acid treated CNF and MWNTs indicating the presence of the carbonyl group at 1626 cm^{-1} and 1635 cm^{-1} respectively. The broad peak