



Short Communication

A silicon nanoparticle-based polymeric nano-composite material for glucose sensing

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ABSTRACT

A novel non-enzyme glucose sensing material has been prepared by incorporating ultrasmall (1–3 nm) silicon nanoparticles in polyaniline, a conducting polymer, as a nano-composite material (NCM). When deposited on electrodes, the composite material with three-dimensional loading of the nanoparticles showed a significantly enhanced amperometric response to glucose, compared to the nanoparticles deposited on bare electrodes and electrodes immobilized with the enzyme, glucose oxidase. The linear range of the glucose response of NCM electrodes covered both the hypo- and hyper-glycaemic glucose levels. The sensitivity of the NCM electrodes was $2.5 \mu\text{A cm}^{-2} \text{mM}^{-1}$. The NCM electrodes' selectivity for glucose against interfering agents was achieved by covering the composite material with a Nafion membrane. The glucose response of Nafion-NCM electrodes was characterized with single 1 μl drops of glucose-solution, showing a sensitivity of $2.2 \mu\text{A cm}^{-2} \text{mM}^{-1}$. The NCM electrode's long-term *in vitro* glucose response appeared to be reasonably stable over a period of 40 days.

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1. Introduction

Today's glucose biosensors use the enzyme, glucose oxidase (GOx), as sensing element [1]. The primary issue of using GOx as sensing element is the inherent instability of the enzyme, which makes the enzyme prone to thermal and chemical deformation/denaturation during fabrication, storage or use [2]. The changed enzyme conformation will produce detrimental effects on the *in vivo* performance of glucose biosensors [3]. For home-blood glucose monitoring, blood sample size of 3 μl [4] is required to meet the sensitivity requirement of enzyme-based biosensors. The large sample size collected by pricking fingertips causes discomfort for patients and results in a low compliance rate of using the sensors by patients who needs several tests daily [5]. To reduce the discomfort, blood samples could also be collected in less sensitive regions of the body such as the forearm. Since the density of capillary vessels in these regions is much less than in the fingertips, the sample volume collected by one pricking action is much smaller than 3 μl [5]. Thus, one of the priority tasks in glucose-sensor research is to work with much smaller samples while satisfying the sensor's sensitivity requirement. It is believed that inorganic sensing materials can be used to replace enzyme in order to eliminate the issues mentioned.

Recently, we have shown that the ultrasmall silicon nanoparticles (USiN), when deposited on a bare electrode, show the essential characteristics of glucose sensing element [6,7]. The most noted

characteristic observed was that the glucose response of USiN is significantly higher than that of the enzyme GOx. Furthermore, USiN shows selectivity for glucose against major interference agents, and the sensing electrode provides long-term stability. In this article, we describe the synthesis of a nano-composite material (NCM) by incorporating USiN in polyaniline (PANI), a conducting polymer, in order to develop USiN as a practical sensing material for glucose sensing. Conducting polymers such as PANI with its nanoporous structure has been used as supporting materials for the dispersion of metal catalyst nanoparticles in order to prepare high performance electrocatalytic materials [8]. Conducting polymers adhere firmly to electrodes and show stability under device operation [9]. In the present work, the NCM was developed to control and optimize the amount of USiN on the sensing electrode in order to control the sensing signal level. The incorporation of USiN in PANI resulted in a three-dimensional (3D) loading of the particle. Additionally, PANI offers an anchorage for USiN to be firmly attached to the electrode and PANI works as nanowires for transmitting electrons collected from glucose to the electrode. We show that electrodes coated with NCM possess three essential properties for glucose sensing: (1) significantly enhanced amperometric response to glucose, (2) a wide linear range of the amperometric response that covers both the hypo- and hyper-glycaemic glucose levels, and (3) glucose selectivity against major interference agents existing in the body fluid. As a demonstration of the potential applications of the composite material in glucose sensing, small-volume glucose samples were used to characterize the composite material's glucose amperometric response, which showed similar sensitivity as that obtained with large-volume samples.

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The NCM electrode's long-term *in vitro* glucose response appeared to be reasonably stable. Our results indicate that the composite material is a novel non-enzyme sensing material for glucose sensing applications.

2. Materials and methods

USiN were made by electrochemical etching of a (1 0 0)-oriented p-type (1–10 Ω cm) silicon wafer in hydrofluoric acid and hydrogen peroxide followed by shaking off the particles from the etched wafer using ultrasound in water or organic solvents such as benzene, isopropyl alcohol and tetrahydrofuran (THF) [10]. This etching technique can be used to prepare 1-nm particles (USiN1) and 2.8-nm particles (USiN2.8), depending on etching conditions. Under UV excitation, USiN1 generates blue spontaneous emission with a measured band-gap of 3.5 eV and USiN2.8 generates red emission with a 2 eV band-gap. Fig. 1a shows the spontaneous emissions of the two kinds of particle. Monte Carlo simulation of the USiN1 particle suggests a filled fullerene structure of $\text{Si}_{29}\text{H}_{24}$, in which a central core silicon atom and four other silicon atoms are arranged in a tetrahedral coordination and the 24 remaining silicon atoms undergo a H-terminated bulk-like (2×1) reconstruction of dimer pairs on (0 0 1) facets (six reconstructed surface dimers) [11].

Polyaniline (PANI) was prepared by electrochemical polymerization of aniline monomers (Sigma Aldrich) [12] on heavily doped ($\rho < 0.005 \Omega$ cm) n-type silicon wafers, which contained the native oxide. The wafers were first cleaned with ethanol, isopropanol and de-ionized water and then covered with a mask to achieve a working area of about $1 \text{ mm} \times 1 \text{ mm}$ for the polymerization process. The polymerization was carried out in an electrochemical cell with the silicon wafer as the working electrode. The deposition of PANI films was obtained by cycling the cell potential between 0 and 0.8 V at 50 mV/s for 1000 cycles in a solution that contained 0.1 M aniline and 1 M HCl. The nano-composite was prepared by first mixing a water-based USiN (10 μM) with a solution, which contained 0.1 M of aniline and 1 M HCl (with a volume ratio of 6:4), followed by performing the electrochemical polymerization described to co-deposit the composite material on silicon wafers.

The electrochemical cell was a conventional three-electrode cell, controlled by a potentiostat (CH Instrument 660C). A commercial Ag/AgCl (3 M KCl) electrode was used as the reference electrode, and a platinum wire was used as the counter electrode. Cyclic voltammetry measurements were performed with the potential scanned at 50 mV/s. Detection of glucose was performed with silicon wafers containing the nano-composite material as the working electrode. Glucose was dissolved in a phosphate buffer solution (PBS) and then introduced into the cell for measurements. De-ionized water ($\rho = 18.2 \text{ M}\Omega$ cm, Direct Q3, Millipore) was used to prepare 100 mM PBS at pH 7. The 0.015 in-diameter Ag/AgCl wire that was used as the reference electrode for the small-volume measurement was purchased from A-M Systems (Sequim, WA). A pipette (Eppendorf), which transfers 0.5–20 μl sample, was used to collect the 1 μl samples. Scanning electron microscopy (SEM) was performed using an Amray 1820 instrument. The voltammetric measurements presented here were made at room temperature under de-aerated condition.

3. Results and discussion

The morphologies of the electrochemically synthesized PANI and nano-composite material have been studied using SEM. Fig. 1b shows that the electrochemically synthesized PANI has a fibrillar morphology with a cross-sectional dimension of about 150 nm as previously noted [13]. As shown in Fig. 1c, the nano-

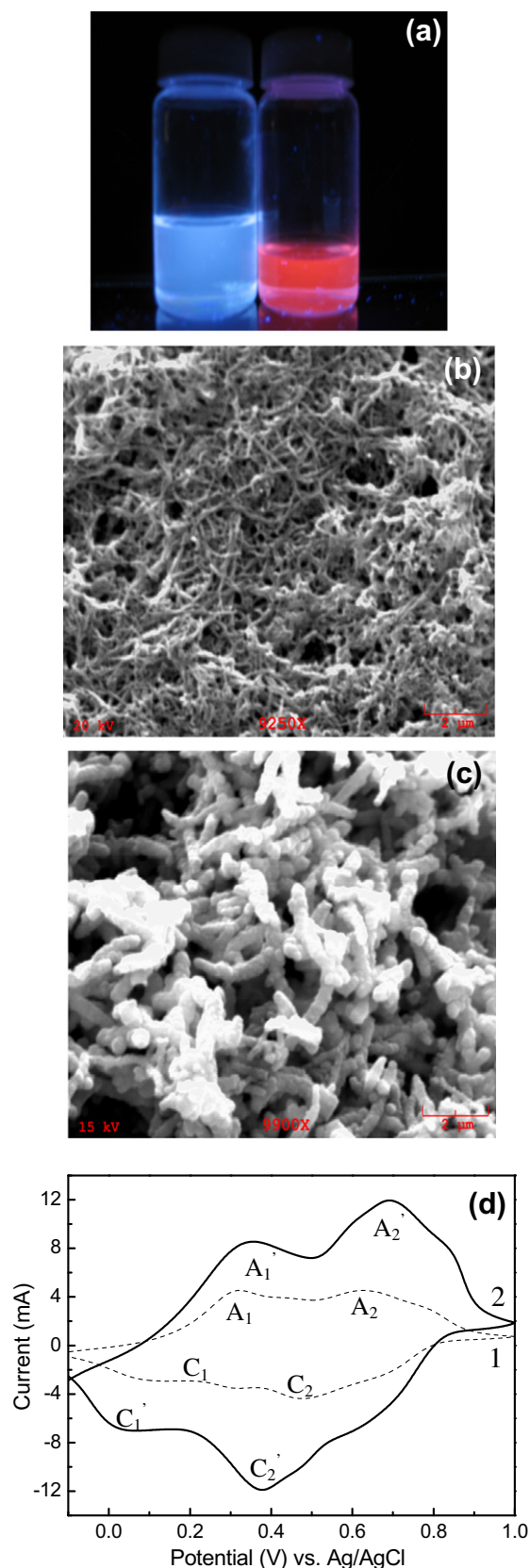


Fig. 1. (a) Spontaneous emission of USiN1 and USiN2.8 under UV excitation, (b) SEM image of the electrochemically synthesized PANI, (c) SEM image of the nano-composite material, (d) Cyclic voltammograms of the electrochemically synthesized PANI (CV1) and the nano-composite material (CV2) deposited on silicon wafers under acidic conditions (1 M HCl). The two pairs of redox peaks, which are characteristics of PANI, appear in both CVs.

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