



Nickel oxide-deposited cellulose/CNT composite electrode for non-enzymatic urea detection



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ABSTRACT

A highly sensitive non-enzymatic urea sensor was fabricated using nickel oxide deposited on a cellulose/carbon nanotube (CNT) composite. The structure and morphological properties of the NiO/cellulose/CNT composite were investigated using X-ray diffraction and scanning electron microscopy. A thin film of the NiO/cellulose/CNT composite was coated on an indium tin oxide glass to fabricate an amperometric urea sensor. The composition of the modified electrode and detection conditions (i.e., pH and temperature) were optimized. The prepared electrode exhibited an excellent sensitivity of $371 \mu\text{A mM}^{-1} \text{cm}^{-2}$ with a fast response time of 4 s. The electrode also showed high stability with only a 3.6% decrease in its sensitivity after storage for two months under ambient conditions. In addition, the feasibility for urea analysis in urine samples was demonstrated.

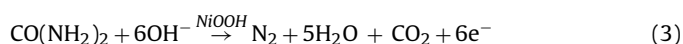
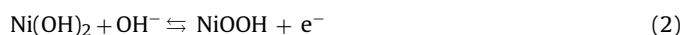
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1. Introduction

Monitoring the level of biologically important molecules, such as urea, glucose, creatinine, and dopamine, in the human body is a vital issue in biochemical and medical diagnostics [1–3]. Various types of biosensors, including enzymatic biosensors, have been used intensively in the detection of such molecules owing to its selectivity, simplicity, and reliability [4–7]. However, the critical issue encountered with the enzymatic biosensors is denaturation of the enzyme, which results in poor stability. Moreover, enzymatic biosensors often fail to generate a strong electrical signal and require mediators to transport electrons. In contrast, non-enzymatic biosensors comprising metals and metal oxides are considered to be potential substitute for enzymatic biosensors because of their excellent redox flexibility and stability [8,9].

A variety of metals, alloys, and metal oxides, such as Pt, Rh, Pt-Rh, Cu/Cu oxide, Zn/Zn oxides, Ni/Ni oxides, and Co/Co oxides, have been widely used for the detection of different molecules. Among them, Ni and Ni oxides have been extensively documented for the direct electro-catalytic oxidation of biochemical molecules such as urea [10,11] and glucose [12,13]. Nickel-based catalysts are relatively cheaper and demonstrate superior catalytic properties for urea oxidation in alkaline medium as compared with other metals/metal oxides. In our earlier study, a Ni-based catalyst was

observed to exhibit good catalytic activity for the electrochemical oxidation of urea [14]. The mechanism of electrochemical oxidation of urea on Ni-based electrodes in alkaline media can be represented with the following reactions [15]:



A common problem with Ni-based catalysts is the degradation and expansion of the catalyst structure during the oxidation reaction, which adversely affects their catalytic performance. Furthermore, such structures have a tendency to self-assemble, forming agglomerations, which reduces their specific surface area and decreases their electrochemical activity [16]. To overcome such problems, supporting materials, such as carbon nanotubes, graphene, and cellulose nanofibers, have been employed. Cellulose and its derivatives, by virtue of their large functionality (hydroxyl, ether, esters groups, etc.), have been found to be good supporting materials for the anchorage of different metal/metal oxide structures, providing a good platform for the construction of bio-sensing devices [17]. Mahadeva and Kim [18] deposited tin oxide onto a cellulose scaffold to fabricate a urea sensor, which exhibited good chemical stability and sensitivity.

Carbon nanotubes (CNTs) have also garnered much attention as a supporting material for sensor fabrication due to their outstanding properties such as high electron conductivity, high chemical and thermal stability, and high surface area [19]. Amalgamations of

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cellulose with CNTs benefit from the advantages of the properties of both the individual materials and thus can provide an improved support material. Qi et al. [20] synthesized quasi-one-dimensional CNT/cellulose composite fibers with good electrical conductivity. The CNT networks formed with support of the functionalized cellulose structure exhibited significant improvement in their electrical and mechanical properties [21,22].

In the present work, a novel electrode employing nickel oxide deposited on a cellulose/CNT composite was prepared for the non-enzymatic sensing of urea. The structural, morphological, and electrochemical properties of the electrode were investigated. The prepared electrode exhibited excellent sensitivity for urea detection.

2. Experimental

2.1. Materials

CNTs (multi-walled, diameter 20 nm, length 5 μm) were purchased from Carbon Nano Material Technology Co., Ltd. Sigmacell cellulose (type 101, highly purified fibers), nickel nitrate hexahydrate (98.5%) were purchased from Sigma-Aldrich. All other chemicals used in this work were reagent grade products. Indium tin oxide (ITO) glass (<20 X/square) was used as a base electrode and was cut into a rectangular shape of 5 mm in width and 20 mm in length. The working area of the ITO glass for the electrochemical tests was controlled at 0.25 cm^2 using masking tape.

2.2. Preparation of cellulose fibrils from orange peel

Natural cellulose was prepared from orange peel waste by removing the oil, color, and pectin following a previous method [23]. First, dried orange peel was immersed into a solution of water/ethanol (15:85) at 80 $^{\circ}\text{C}$ for 20 min to remove the colored materials and oils, after which the solid portion was separated by centrifugation. This extraction step was repeated until the sample was free from color. The sample was then washed with de-ionized (DI) water. Similarly, metal constituents were removed using ammonium oxalate solution (50 mM in water) at 20 $^{\circ}\text{C}$ for 1 h, and pectin was removed using 0.18 wt% HCl at 80 $^{\circ}\text{C}$ for 1 h and 0.2 wt% NaOH at 5 $^{\circ}\text{C}$ for 1 h. The sample was then washed with DI water and dried in an oven overnight. The resulting cellulose was denoted Cel-1. Commercial cellulose (Sigmacell cellulose), denoted Cel-2, was used without further purification.

2.3. Preparation of NiO/cellulose/CNT composites

The NiO/cellulose/CNT composites were fabricated via a hydroxide thermal decomposition method. First, a CNT-dispersed solution in *N,N*-dimethylformamide (DMF, 1 mg mL^{-1}) was prepared using a sodium dodecyl sulfate surfactant. Similarly, a cellulose-dispersed solution in DMF (1 mg/mL) was also prepared using a 2% cationized starch. The CNT and cellulose solutions were mixed at a CNT/cellulose ratio of 1:9, unless specified otherwise, and homogenized for 2 h at room temperature. To this dispersion, a pre-calculated amount of nickel nitrate hexahydrate was added, and the dispersion was stirred for 3 h. Sodium borohydride (as a reducing agent) was then slowly added with a Ni/Na ratio of 1:2.5, and stirred for 1 h. The precipitated $\text{Ni}(\text{OH})_2$ /cellulose/CNT composite material was filtered and washed with DI water and acetone repeatedly. Finally, the precipitate was heated at 280 $^{\circ}\text{C}$ for 4 h in order to convert $\text{Ni}(\text{OH})_2$ on the cellulose/CNT network into NiO and thus to obtain a NiO/cellulose/CNT composite.

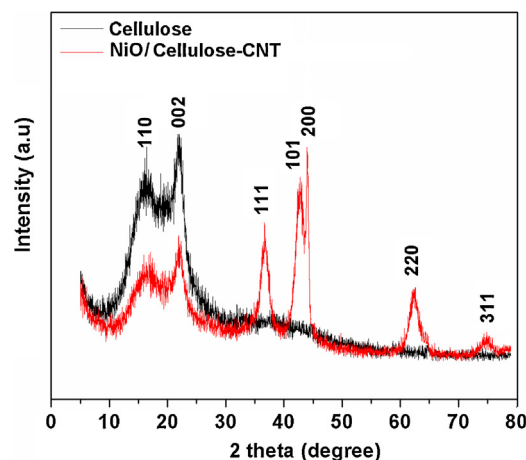


Fig. 1. XRD patterns of cellulose and a NiO/cellulose/CNT composite.

2.4. Electrode fabrication

The electrodes were fabricated by a vacuum-assisted deposition method. First, the NiO/cellulose/CNT composite was dispersed into DMF at a concentration of 1 mg mL^{-1} . An aliquot of the NiO/cellulose/CNT dispersion was filtered through an Anodisc membrane that was attached to a suction filter apparatus. After filtration, the membrane was air-dried. The membrane was then placed on the ITO glass, and dipped into a 0.1 M NaOH aqueous solution for 10 min during which the Anodisc membrane was etched away leaving a uniformly NiO/cellulose/CNT coated ITO glass. It was then washed repeatedly with DI water and dried in a vacuum oven at 60 $^{\circ}\text{C}$ overnight. The NiO/cellulose/CNT/ITO electrode was then covered by an encapsulating membrane, a polyion complex (PIC) of poly-L-lysine and polystyrene sulfonate, as described in a previous report [14].

2.5. Analysis

The morphology and compositional analysis of the NiO/cellulose-CNT composites were characterized using a scanning electron microscope (SEM, Hitachi S-4700; Hitachi Ltd., Tokyo, Japan), and energy dispersive X-ray spectroscopy (EDX). Powder X-ray diffraction (XRD) analysis of the samples was performed using an X-ray diffractometer (Rigaku D/MAX-2200, Japan) with $\text{Cu-K}\alpha$ radiation at a wavelength of 1.5406 \AA .

Cyclic voltammetry and chronoamperometry measurements were carried out using a potentiostat-galvanostat (VSP, Biologic-Science Instruments, 38640 CLAIX, France). All the electrochemical measurements were conducted at room temperature using a conventional three-electrode system (wherein Ag/AgCl was the reference electrode, a platinum wire was the counter electrode, and the sample was the working electrode).

3. Results and discussion

3.1. Characterization of NiO/cellulose/CNT composite

The XRD patterns of cellulose and the NiO/cellulose/CNT composite are shown in Fig. 1. The cellulose sample (Cel-1) exhibits two prominent peaks at $2\theta = 16.2^{\circ}$ and 21.9° , attributed to the (110) and (002) reflections of cellulose, respectively [24].

The NiO/cellulose/CNT composite showed peaks for cellulose, (002) and (101) reflection peaks at $2\theta = 21.9^{\circ}$ and 42.8° , respectively; peaks for CNT; and characteristic peaks at $2\theta = 36.7^{\circ}$, 44.1° ,

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