



Laser synthesis and tailor-design of nanosized gold onto carbon nanotubes for non-enzymatic electrochemical glucose sensor



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ABSTRACT

The non-enzymatic cyclic and pulse voltammetric detection of glucose using pulsed laser deposited gold nanostructures onto carbon nanotubes electrodes is described for the first time. Several synthesis conditions have been considered in order to obtain various morphologies for the Au film. Among all the synthesized Au nanostructures, it is found that an Au film deposited under vacuum with 10,000 laser pulses displays a high electroactive surface area of 6.55 cm² and a roughness factor of 13.2. In addition, this electrode exhibits a low onset potential of -0.28 V vs. Ag/AgCl for glucose oxidation. A linear square-wave voltammetric response for oxidation of glucose was observed up to a glucose concentration of 50 mM with a sensitivity of 25 $\mu\text{A cm}^{-2} \text{mM}^{-1}$ and a detection limit of 0.1 mM. Finally, owing to its versatile capabilities such as robust control of the surface morphology, control of the stoichiometry and ultra-low loading of noble catalyst, it can be expected that the pulsed laser deposition (PLD) technique will emerge as a fabrication tool for on chip miniature-sized sensors in the near future.

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1. Introduction

Highly sensitive and selective glucose detection is critical in point of care and clinical diagnostics, such as diabetes diagnostics and management [1]. Non-enzymatic electrochemical oxidation of glucose is being considered and explored as an alternative to enzymatic glucose oxidation but also in the hope of improving the sensitivity and selectivity towards the oxidation of glucose.

Platinum was the first material discovered showing an electrocatalytic effect in response to glucose oxidation [2]. However, a glucose sensor using a Pt electrode suffers from poisoning by adsorbed intermediates. Indeed, the kinetics and mechanism of glucose electro-oxidation to gluconic acid on pure Pt surfaces involve the formation of some intermediates (e.g., adsorbed CO) [3], which poison the electrode surface, and interfering species, such as acetaminophen, ascorbic acid (AA) and uric acid (UA) resulting in low sensitivity and poor selectivity. Alloys-based amperometric glucose sensors containing Pt, Ru, Pb, Au, Cu, Bi, Pb, Tl, and W have been reported as promising enzyme-free sensors with the goal of improving the sensitivity and selectivity of the electrodes towards the electro-oxidation of glucose [4 and references therein]. Nevertheless, the application of these sensors is hindered either by the

toxicities of heavy metal elements present in the alloys or by their instability and easy dissolution at normal operation conditions. In contrast, an Au electrode appears to be a more active electrocatalyst for glucose oxidation in neutral and alkaline electrolytes and does not exhibit the strong poisoning effect of adsorbed intermediates [5]. Over the past two decades the development of non-enzymatic glucose sensors has risen at a significant rate. The fabrication of a wide variety of nanomaterials has introduced a plethora of selective and highly responsive glucose sensors. The reader is encouraged to read the excellent reviews of Chen et al. [4], Park et al. [6] and Toghiani and Compton [7] for more information.

Partially due to its excellent biological compatibility, gold is one of the most inspiring materials for the fabrication of different kinds of biosensors. In order to improve the electrocatalytic activity and sensitivity of gold towards glucose oxidation in non-enzymatic sensors, several strategies have been explored towards the use of nanostructured Au in electrodes in recent years. Works earlier than 2010 are reported in the review of Toghiani and Compton [7]. After 2010, a number of new and promising approaches have been reported including sputtered gold particles layers [8], gold nanoparticle and conducting polymer-polyaniline-based nanocomposites [9], nanoporous black gold surfaces [10], gold nanostructures on phosphorus doped diamond-like carbon surfaces [11], ordered gold nanowires synthesized by utilizing anodic aluminium oxide (AAO) templates in combination with direct electrodeposition [12], aligned carbon nanotube modified carbon fibres

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coated with gold nanoparticles embedded in a polymer film [13], and gold nanoparticles anchored onto polypyrrole nanofibers by hydrogen bonding [14].

In this work, we report the development of a multi-layered electrode that includes the current collector (a conducting carbon paper), the catalyst support (carbon nanotubes, CNTs) and the nanostructured Au catalyst. The Au films were fabricated by pulsed laser deposition (PLD), whereas CNTs were grown by chemical vapour deposition (CVD). The formation of Au film catalysts was studied as a function of the PLD deposition conditions, such as background atmosphere (i.e., vacuum vs. helium (He) gas), which allowed us to obtain various morphologies of the deposited Au. Thus synthesized Au films were then characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The electroactive surface area (ESA) of the Au films was evaluated in H₂SO₄ solution with cyclic voltammetry (CV), whereas the glucose electrooxidation was studied with CV and square wave voltammetry (SWV) in a pH 7.2 phosphate buffer containing various concentrations of glucose.

2. Materials and methods

2.1. Material synthesis

PLD-deposited nickel film was used as the catalyst for the growth of CNTs onto carbon paper (CP, Toray). The CNTs were grown by CVD at 700 °C using acetylene (carbon source), hydrogen and argon (gas carrier) with flow rates of 20, 140 and 100 sccm, respectively. Full experimental details regarding the synthesis of the CNTs can be found elsewhere [15].

Gold was deposited on CNTs by PLD at room temperature by means of a pulsed KrF excimer laser ($\lambda = 248$ nm, pulse width = 17 ns, and repetition rate = 50 Hz) and by using a pure polycrystalline Au target (99.99%, Kurt J. Lesker Co.). Prior to deposition, the PLD chamber was evacuated with a turbo pump (2×10^{-5} Torr). The fluence was fixed to 4 J cm^{-2} and the target-to-substrate distance was set to 50 mm. The Au catalyst films were deposited under vacuum (UV), under 0.5 Torr of He and under 2 Torr of He with the number of pulses being 10,000 (10 kp) or 50,000 (50 kp). During deposition, the Au target was continuously rotated and translated in order to obtain a uniform ablation over the entire target surface. A detailed description of the PLD setup has been given elsewhere [16]. Table 1 summarizes the synthesis conditions used for the deposition of the Au samples under current investigations.

2.2. Material characterization

The morphologies of the CNT/Au structures were examined by means of SEM (JEOL-JSM-6300F or JEOL, JSM-7401F) and TEM (JEOL-JEM-2100F operating at 200 kV). The surface composition was studied by XPS via a VG Escalab 220i-XL equipped with an Al K α source (1486.6 eV). The anode was operated at 10 kV and

Table 1
Au samples and their corresponding synthesis conditions.

Denotation ^a	Number of laser pulses	Au loading ($\mu\text{g cm}^{-2}$)	Background pressure
Au10kp _{UV}	10,000	53	Under vacuum
Au10kp _{0.5T}	10,000	53	0.5 Torr of He
Au10kp _{2T}	10,000	53	2 Torr of He
Au50kp _{UV}	50,000	265	Under vacuum
Au50kp _{0.5T}	50,000	265	0.5 Torr of He
Au50kp _{2T}	50,000	265	2 Torr of He

^a kp, UV and T stand for kilo pulses, under vacuum and Torr, respectively.

20 mA. The pass energy of the analyzer was fixed at 20 eV. All samples were analyzed with a spot size of $250 \mu\text{m} \times 1000 \mu\text{m}$ located approximately in the centre of the samples. A survey spectrum ranging from 0 to 1300 eV was first acquired and then higher resolution multiplex scan spectra of Au 4f were obtained. The crystalline structure of all samples was determined by XRD using a Bruker D8 Advance diffractometer equipped with a Cu K α source. The diffractometer was operated at 40 kV and 40 mA. All diffractograms were acquired in the grazing incidence diffraction (GID) scan mode with an incident angle of 2° , 2θ angular step size of 0.05° and acquisition time of 5 s per step.

2.3. Electrochemical measurements

Prior to the electrochemical measurements, the surface of the working electrode was cleaned electrochemically by potential cycling in 0.5 M H₂SO₄. The electrochemical properties of the Au electrodes were investigated using CV and SWV in a deaerated phosphate buffer saline (PBS) solution (pH 7.2, Sigma–Aldrich) with glucose (D-(+)-glucose, ACS reagent grade, Sigma–Aldrich). All the electrochemical measurements were carried out at room temperature using a three-compartment electrochemical cell with an Ag/AgCl, 3 M NaCl reference electrode and a platinum coil as a counter electrode. Measurements and data acquisition were conducted with an Autolab potentiostat/galvanostat from Eco Chemie.

3. Results and discussion

3.1. Structure characterization

Fig. 1 shows typical SEM images of Au deposited onto CNTs under different conditions. Considerable differences in the surface morphology can be noticed between the various deposits. Fig. 1a shows that the surface of CNTs is homogeneously coated with a rough Au film. The CNT/Au morphology is reminiscent of a coral. Gold films deposited under He atmosphere (Fig. 1b and c) are made of particles that tend to gather into highly compacted large grains in a fashion reminiscent of cauliflower or broccoli-like arrangements at high He pressure (Fig. 1c). The PLD involves complex physical processes of laser–material interaction during the impact of the high-power pulsed radiation on a solid target under different background gas pressure that yield to different morphologies. The study of such processes is beyond the scope of this paper. More details regarding the influence of the atmosphere on the physical processes of laser–material interaction can be found elsewhere [17–19].

The XRD pattern (Fig. 2a) shows five peaks corresponding to the {1 1 1}, {2 0 0}, {2 2 0}, {3 1 1} crystallographic planes of the face-centred cubic (fcc) gold, indicating the deposited gold has the fcc crystalline structure. The average crystallite size was estimated to range between 20 and 35 nm from the (1 1 1) diffraction peak using the Debye–Scherrer equation, whereas the lattice parameter was found to be 4.076 for all the Au samples.

Typical high-resolution XPS Au 4f core level spectrum shown in Fig. 2b displays two peaks whose maximum intensities are located at binding energy of 84.1 and 87.7 eV. These two maxima correspond to Au 4f_{7/2} and 4f_{5/2} core levels, respectively. The binding energy difference of 3.6 eV is consistent with Au in a metallic state [20].

TEM images of the CNT/Au films synthesized under various PLD conditions are shown in Fig. 3. We should emphasize that our samples were subjected to TEM analyses as prepared and it is indeed very challenging to analyze because of the compactness of the Au films (Fig. 1), the high agglomeration of the particles, the dark underneath carbon fibres substrate, and the CNTs that move a lot during analysis, particularly during the high-resolution analysis. A

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