Technical Communication

Fabrication of Nickel-Gold Microsensor Using In Situ Laser-Induced Metal Deposition Technique

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In this work we report two-step in situ laser-induced synthesis of bimetallic micro-sized structures based on nickel and gold exhibiting good electrical conductivity and high electrocatalytic activity. This synthesis was carried out using consecutive deposition of nickel and gold on the sur-face of glass-ceramics upon laser irradiation at 532 nm from aqueous and organic solutions con-taining the salts of the corresponding metals. The electrochemical properties of the obtained nick-el-gold microsensor were investigated using voltammetric methods. We observed that the calcu-lated limit of detection (LOD) and sensitivity of the synthesized material with respect to glucose sensing are $1.8 \square M$ and $2670 \square A \text{ mM-1}$ cm-2, respectively.

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1. Introduction

Development of simple and reliable methods for fabrication of new metallic and bimetallic small-sized structures with good electrical conductivity and electrochemical properties is rather critical for many areas of medicine, science, and industry [1-3]. There are a lot of methods that can be used for the aforementioned purposes; however, most of them exhibit some significant drawbacks. For example, pulsed laser deposition (PLD), which is widely applied for synthesis of metal nanoparticles [4], is not suitable for deposition of the thick metal layers due to low metal deposition rate and essential difficulties in control of the thickness of the deposited metal structures. In turn, laserinduced forward transfer (LIFT) technique, dealing with deposition of thin metal films on the dielectric surface. demonstrates low level of metal localization [5]. Another example, laser-induced chemical vapor deposition (LCVD) despite the fact that it is decent technique for copper deposition may lead to low adhesion of a metal on the surface of a dielectric and results in codeposition of impurities in the resulting deposit, moreover, this technique requires implementation of expensive vacuum equipment [6]. Finally, direct laser writing (DLW) as effective analog of similar approaches exploits complicated procedures and expensive equipment [7]. In opposite to all mentioned above, in this work, we propose to use simple, cheap, and reliable method based on the method of laser-induced chemical liquidphase deposition of metals from solution on the surface of different dielectrics (LCLD). In this method the reduction of a metal in the local volume of a solution occurs within the focus of the laser beam resulting in deposition of porous micro-sized metallic structures on the surface of a dielectric substrate [8,9]. The strong points of LCLD include consumption of low cost reagents as well as implementation of simple equipment and procedures. Furthermore, this technique allows us to produce microdeposits of different metals with high resolution at reasonable rates [10,11].

In our previous studies we showed that the materials synthesized by LCLD have highly developed surface area, good electrical conductivity and biocompatibility along with high catalytic and electrocatalytic activity [12,13]. In addition, we observed that these materials can be used as enzymeless sensors for detection of such important disease markers in human blood as hydrogen peroxide and glucose. Indeed, it is known that non-enzymatic sensors, in which electron transfer proceeds directly on the electrochemically active centers of a sensor, have stronger analytical signal, better sensitivity and accuracy in comparison with enzymatic ones [14,15]. Moreover, nano- and micro-sized bimetallic structures used for enzymeless sensing attract even more interest due to their higher catalytic activity, better stability, sensitivity, and selectivity [16,17]. This phenomenon can be explained by the fact that introduction of a second metal to a catalytic material gives the opportunities for catalytic fine-tuning provided by bimetallic complementarity and synergism. In turn, such approach allows decreasing the amount of more expensive second metal while keeping the advantages of the bimetallic system mentioned before.

Thus, in the current work, we synthesized porous bimetallic microstructures based on nickel and gold known as quite promising metals for non-enzymatic sensing due to their high catalytic activity, chemical stability, and electrical conductivity. The nickel-gold microsensor was obtained using in situ laser-induced metal deposition technique and its electrochemical properties were studied using voltammetric methods.

2. Materials and methods

All chemicals and reagents used in this work were of analytical and pharmaceutical grade commercially available (Sigma Aldrich) and distilled water was used throughout the experiments. The full description of the experimental setup used for in situ laser-induced synthesis of nickel-gold microsensor has been published elsewhere [8] and the schematic picture of this setup is shown in Fig. 1. Briefly, the output from a continuous wave 532 nm diode-pumped solid-state Nd:YAG laser is split into two portions. The first portion is focused in an area between the plating solution and dielectric placed in the experimental cell. This cell is moved vertically and horizontally by the computer controlled a X-Y translation stage in such a way that the focused laser beam is virtually writing the metal lines of any size and shape on the surface of different dielectric substrates. The second portion of the 532-nm output travels to web camera used for in situ monitoring the laser-induced metal deposition process. As a result, we synthesized 1-cm-long nickel-gold lines on the surface of crystalline glass-ceramics material (Sitall ST-50-1) [8] at the scanning speed of $2.5 \ \mu m \ s^{-1}$.



Fig. 1 The experimental setup used for laser-induced deposition of nickel-gold microsensor (line): 1-cw 532-nm diodepumped solid-state Nd:YAG laser, 2-mirrors, 3-splitting cube, 4objective lens, 5-the experimental cell, 6-neutral density flter, 7web camera, 8-personal computer, 9- the computer controlled motorized stage.

Magnification and numerical aperture of the objective lens (Fig. 1) were $50 \times$ and 0.95, respectively. The laser spot size was about 4–5 µm and corresponding power density equals approximately to 2.1 mW µm⁻².

Morphology of the obtained nickel-gold lines was investigated using scanning electron microscopy (SEM). Their atomic composition was studied by means of energy dispersion of X-ray spectroscopy (EDX). The EDX-system was coupled with a Zeiss Supra 40 VP scanning electron microscope equipped with X-ray attachment (Oxford Instruments INCA X-act).

For identification of the crystallization phase of nickelgold microstructures X-ray diffraction (XRD) patterns were recorded on a Bruker D2 Phaser diffractometer equipped with LynxEye detector using CuK α radiation in the 2 θ angle range of 0°-100°. The sample size was 25 μ m².

The electrochemical properties of nickel-gold deposits were studied using cyclic voltammetry and amperometry (potentiostat, Elins P30I). All measurements were conducted at room temperature in a standard three-electrode cell using a platinum wire as counter electrode, a Ag/AgCl/3.5 mol/kg KCl reference electrode and the deposited lines as working electrodes. The sweep speed of the potential was set at 50 mV s⁻¹. The read speed was 50 points per second. The current range of the device was set at 100 μ A. Voltammetric measurements of the sensor activity of nickelgold electrodes towards D-glucose were performed in 0.1 M sodium hydroxide within the potential range varied from -1000 to 1000 mV directly after bubbling the cell with argon for half an hour. The solutions of D-glucose of different concentrations were added to background solution (0.1 M NaOH) with simultaneous stirring.

3. Results and discussion

The in situ laser-induced synthesis of 175 µm wide and 10 mm long nickel-gold microstructures with low electrical resistance (~7 Ω) was performed in two steps at laser power of 1 W. The laser spot size was about 4-5 µm and such difference with respect to the width of the synthesized material can be explained, according to our previous work [8], by analysis of the temperature distribution in the area irradiated with a laser beam. It was shown that the temperature at the focused laser spot reaches ~1000 °C resulting in the activation of the dielectric surface in the adjacent region. Thus, the generation of the very first portion of copper nucleates takes place at the focus of the laser beam (4-10 μ m). Then, the temperature rapidly drops outside the focused laser spot and two more temperature zones appear, in which autocatalytic reaction of copper reduction and further solidification of copper structures occur. The size of these zones can reach more than 50 µm each and they can be varied by changing the laser power and the scanning speed, and, in turn, definitely affect the size of the deposited structures.

In the first step of the synthesis, we obtained nickel deposit (line) on the surface of glass-ceramics from aqueous solution containing nickel (II) chloride using 532-nm excitation wavelength. Further, in the second step, gold particles were deposited on the surface of nickel line from solution of triphenylphosphine gold (I) chloride in N,N-dimethylformamide (DMF) using the same source of laser irradiation. The compositions of solutions used in the LCLD experiments are shown in Table 1.

The scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were implemented for investigation of the surface morphology and elemental composition of the deposited microsensor. The results of these studies are demonstrated in Fig. 2. It was observed that two-step laser-induced synthesis leads to deposition of gold particles on the surface of the pre-deposited nickel.

 Table 1
 The compositions of solutions used for two-step in situ
 laser-induced synthesis of nickel-gold microsensor.

| Reagents | Ni | Au |
|-----------------------------|------------|------------|
| $NiCl_2 \times 6H_2O$ | 0.02 mol/L | - |
| $KNaC_4H_4O_6 \times 4H_2O$ | 0.07 mol/L | - |
| NaOH | 0.10 mol/L | - |
| (Ph ₃ P)AuCl | - | 0.03 mol/L |

The resulting nickel-gold layer has both discontinuous and continuous character, in which gold is deposited in the form of individual droplets with a diameter of 40-220 nm and their agglomerates (Fig. 2b and d). EDX analysis shows a clear separation of nickel and gold phases (Fig. 2a and c). This may indicate that the deposition takes place in relatively mild conditions, without gold melting process. In addition, EDX analysis revealed an excess of oxygen, carbon, and other elements that can be associated with the glass-ceramics material. XRD measurements demonstrate the presence of a multi-phase multi-component system containing metal phases of gold and nickel, as well as some components of glass-ceramics such as $MgSiO_3$ and TiO_2 (Fig. 3a), which, in turn, is consistent with the result of the EDX analysis.



Fig. 2 SEM images (b and d) of nickel-gold microsensor (line). EDX spectra (a and c) taken from two spots 1 and 2 of nickel-gold line.

The sensor activity of nickel-gold electrode towards glucose was investigated by recording cyclic voltammograms (CVs) in 0.1 M NaOH solution containing different concentration of D-glucose (Fig. 3b). According to the obtained CV, the electrocatalytic oxidation reaction of glucose to gluconic acid occurs at 0.5 V. Furthermore, the electrochemical properties of the synthesized nickel-gold deposit were also studied using amperometry. Fig. 3c illustrates typical amperometric response of this deposit to consecutive additions of D-glucose with applied potential at 0.5 V. It is clearly seen here that the increase of concentration of the analyzed substrate is followed by the increase of the analytical signal from background solution. Besides, Fig. 3d shows that nickel-gold line exhibits a linear range of concentrations between 0.25 and 50 µM for D-glucose sensing. For calculation of limit of detection (LOD) we used the following equation: LOD = 3S/b, where S is the standard deviation of the signal and b is the slope of the calibration curve (Fig. 3d). The calculated LOD is 1.8 µM and the maximum sensitivity is 2670 μ A mM⁻¹ cm⁻² with respect to glucose detection.



Fig. 3 (a) XRD patterns of nickel-gold microsensor (line). (b) Typical CV of nickel-gold line recorded in solution containing 30 μ M D-glucose. (c) Amperogram of nickel-gold line measured after consecutive additions of D-glucose of different concentration with applied potential at 0.5 V. (d). The linear dependency of Faraday current measured using amperometry on the concentration of D-glucose.

Herein, the low detection limit and high sensitivity towards glucose detection revealed by nickel-gold microsensor can be explained by large surface area of this sensor and the electrocatalytic synergy of nickel and gold. It should be also pointed out that the synthesized material has good stability and reproducibility (Fig. 4).



Fig. 4 (a) Stability of nickel-gold microsensor stored at ambient conditions in a period of ten days (each column corresponds to the averaged 10 measurements; where Ω_0 is the averaged electrical resistance of nickel-gold line measured at each day, whereas Ω is the lowest electrical resistance of nickel-gold line measured at the first day). (b) The relative standard deviation of values related to the electrochemical response to 5 μ M of D-glucose in 0.1 M NaOH for three nickel-gold lines produced at the identical conditions (I₀ and I are the maximum Faraday currents measured for the first and second two Ni-Au sensors at 0.5 V, respectively).

Indeed, nickel-gold deposit exhibits no significant changes in electrochemical and physical properties (Fig. 4a) during repeated use (~100 times). In turn, the relative standard deviation of values related to the electrochemical response to 5 μ M of D-glucose is roughly 7-9% for three nickel-gold lines produced at the identical conditions showing a decent reproducibility of this sensor (Fig. 4b).

Finally, it should be emphasized that the sensor characteristics represented by the synthesized nickel-gold microsensor are comparable and even better than those revealed by many similar analogs due to lower limit of detection and higher sensitivity [18-21].

4. Conclusions

Within the framework of the current project, we synthesized conductive bimetallic microstructures based on nickel and gold with high sensor activity towards glucose using two-step in situ laser-induced metal deposition technique. It was observed that nickel-gold microsensor exhibits the linear dependence Faraday current vs. the concentration of D-glucose between 0.25 and 50 µM. In turn, the calculated limit of detection is 1.8 μ M and the sensitivity is 2670 μ A mM⁻¹ cm⁻² with respect to D-glucose detection. In comparison with the similar analogs, the synthesized material demonstrates rather good electrochemical characteristics apparently due to large surface area of this material and the electrocatalytic synergy of nickel and gold. Thus, it is possible to conclude that laser-induced metal deposition technique is rather perspective in fabrication of electrocatalytically active bimetallic microstructures for further application in development of new non-enzymatic sensors.

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