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Graphene Paper-Gold Nanostructured Electrodes Obtained by Laser Dewetting for High Sensitive Non-Enzymatic Glucose Sensing

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Abstract: Electrodes for non-enzymatic glucose sensing based on gold nanostructures onto graphene paper (GP-AuNPs) have been obtained inducing dewetting, by laser annealing, of 8 nm-thick Au layer deposited by sputtering. Molten-phase dewetting of gold layer, which produces the formation of spherical nanoparticles (AuNPs), was achieved by nanosecond laser annealing using a pulsed (12 ns) Nd: yttrium aluminum garnet YAG laser operating at 532 nm. The Surface of the electrode presents gold rich regions consisting of graphene nanoplatelets covered by spherical AuNPs. The sizes of AuNPs are in the range of 10–150 nm. Glucose was detected at a potential of 0.17 V vs SCE, which corresponds to the intense peak of two electrons oxidation. Highest sensitivity of 600 μA mM^{-1} cm^{-2} of glucose detection was obtained. The resulting sensitivity, detection limit and linear range of glucose detection are very promising since comparable to the actual state of art results for nanostructured gold electrodes which are, however, produced by complex multi-steps processes.

Keywords: Graphene paper; Gold nanoparticles; Dewetting; Laser annealing; Electrochemical Glucose sensing

1. Introduction

Fast, sensitive and specific sensing of glucose is an important issue in many scientific and technological fields including health [1], food [2], environmental monitoring [3], and genomics [4]. Non-enzymatic electrochemical sensors provide high stability, low production costs and tolerance to broad range of operating conditions. Gold nanostructures present a low electro-oxidation potential of glucose, around 0.2 V, which is preferable to obtain high sensor specificity and low interference by other organic redox active materials. Furthermore, the advantages of graphene materials used as substrate include low cost, high electrical conductivity and large electrochemical potential window (~2.5 V in 0.1 mM phosphate buffered saline). Herein, we propose a method for the preparation of graphene-gold nanostructured electrodes for non-enzymatic glucose detection which is based on laser dewetting of 8 nm gold layer deposited onto graphene paper. Advantages of the proposed process can be summarized in the low cost, simplicity, high purity of the electrode, absence of toxic materials and low generation of dangerous waste during the production compared with other methods.

2. Results

The fabrication of gold nanostructures on graphene paper was based on the liquid state dewetting (laser annealing) of 8 nm gold layer deposited by sputtering onto graphene paper [5]. Molten-phase dewetting of gold layer, which produces the formation of spherical nanoparticles (AuNPs), was achieved by nanosecond laser annealing using a pulsed (12 ns) Nd: yttrium aluminum garnet YAG laser operating at 532 nm. Figure 1a reports representative SEM pictures of graphene paper substrate (no gold) after laser irradiation at fluence of 0.5 J cm^{-2}. The laser beam irradiation produces the formation of numerous nanoplatelets as consequence of exfoliation of graphene layers from the substrate.

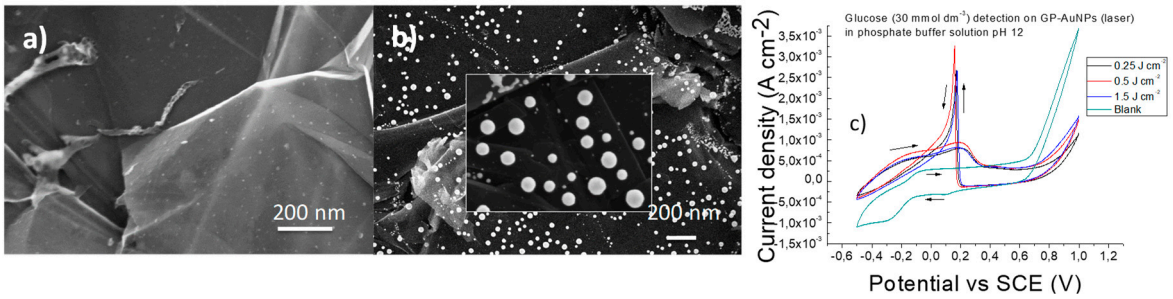

Figure 1. Representative SEM pictures of: (**a**) graphene paper after laser irradiation at fluence of 0.5 J cm^{-2}; (**b**) Au layer 8 nm thick after laser annealing at fluence of 0.5 J cm^{-2}; (**c**) voltammograms of glucose 30 mmol dm^{-3} at pH 12 buffer solution detected with GP-AuNPs electrodes laser annealed at 0.25, 0.5 and 1.5 J cm^{-2}.

Similar structures have been observed at fluence of 0.25 and 1.5 J cm^{-2}. Figure 1b reports representative SEM picture of GP-8 nm Au layer laser irradiated at fluence of 0.5 Jcm^{-2}. The surface is characterized by the presence of graphene platelets covered with spherical AuNPs. The sizes of AuNPs are in the range of 10–150 nm. Figure 1c reports the voltammograms at scan rate of 20 mV s^{-1} of glucose 30 mM in phosphate buffer solution at pH 12, obtained with electrodes irradiated at 0.25, 0.5 and 1.5 J cm^{-2} of fluence, respetively. The three electrodes show similar response. In the forward scan two peaks are observed at 0.19 V and 0.45 V (less pronounced) vs SCE, which are assigned to the formation of gold hydroxide/glucose oxidation to gluconolactone and to the oxidation of the gold hydroxide layer, respectively. In the backward scan, the peak corresponding to the two electrons oxidation of glucose is located at 0.17 V vs SCE. The peak is characterized by significant intensity and sharpness. Current calibration curve (not shown) is characterized by a linear detection range from 2.5 μM to 8 mM. Highest sensitivity of 600 μA mM^{-1} cm^{-2} was obtained in the linear range of the curve.

3. Conclusions

The advantages of the proposed process are the low cost, simplicity, high purity of the electrode, absence of toxic materials and low generation of dangerous waste during the production. The electrode performances present good values compared to recent studies related to the detection of glucose on gold nanostructured surfaces.

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Conflicts of Interest: The authors declare no conflict of interest.

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