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On the preferential crystallographic orientation of Au nanoparticles: Effect of electrodeposition time

Mohamed S. El-Deab*

Department of Chemistry, Faculty of Science, Cairo University, Cairo, Egypt

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ABSTRACT

The crystallographic orientation of Au nanoparticles electrodeposited at glassy carbon (nano-Au/GC) electrodes (prepared by potential step electrolysis) is markedly influenced by the width of the potential step. The oxygen reduction reaction (ORR) and the reductive desorption of cysteine have been studied on nano-Au/GC electrodes. Furthermore, electron backscatter diffraction (EBSD) technique has been used to probe the crystallographic orientation of the electrodeposited Au nanoparticles. That is, Au nanoparticles prepared in short time (5–60 s) have been found rich in the Au(1 1 1) facet orientation and are characterized by a relatively small particle size (ca. 10–50 nm) as well as high particle density (number of particles per unit area) as revealed by SEM images. Whereas Au nanoparticles prepared by longer electrolysis time (>60 s) are found to be much enriched in the Au(1 0 0) and Au(1 1 0) facets and are characterized by a relatively large particle size (>100 nm). EBSD patterns provided definitive information about the crystal orientations mapping of Au nanoparticles prepared at various deposition times.

1. Introduction

Nanometer-scale materials are continuously attracting considerable attention due to their unusual and fascinating properties [1–5]. The decrease of the size of materials down to the nanometer range leads to a tremendous change of their surface, electronic and optoelectronic properties compared with their bulk metal counterparts [6,7]. The use of gold nanoparticles has been rapidly extended to several applications in electronics, optoelectronics, electroanalysis [8,9] as well as chemical and electrochemical catalysis [4,10–13]. In this regard, the preparation of tailored design nanostructures in terms of size and crystallographic structure is a subject of unequivocal importance [14–17].

Electrodeposition is among the most familiar binder-free technique used for the preparation of nanoparticles. It is a facile technique which results in the direct attachment of the nanoparticles to the substrate in addition to the facile control of the characteristics of the metal (or metal oxide) (e.g., size, crystallographic orientation, mass, thickness and morphology of the nanostructured materials) by adjusting the operating conditions and bath chemistry [17–21] in contrast to other techniques which require several steps and consume relatively longer time, such as sol–gel [22,23], micelle-based cluster generation [24,25] and metal vapor synthesis routes [26,27].

This paper addresses the influence of the electrodeposition time on the crystallographic orientation of Au nanoparticles deposited on glassy carbon (nano-Au/GC) electrodes. SEM, XRD and electron backscatter diffraction (EBSD) techniques are used to characterize the electrodeposited Au nanoparticles in terms of size and preferential facet orientation. Furthermore, the reductive desorption of cysteine and the oxygen reduction reactions in alkaline medium are used as probing electrochemical reactions to monitor the variation of the crystallographic orientation of the electrodeposited Au nanoparticles with time.

2. Experimental

The working electrode was a GC rod of 3.0 mm diameter sealed in a Teflon jacket leaving an exposed geometric surface area of 0.07 cm^2. A spiral Pt wire and an Ag/AgCl/KCl (sat) were the counter and the reference electrodes, respectively. Prior to the electrodeposition of Au nanoparticles, the GC electrode was polished with aqueous slurries of alumina powder (particle size down to 0.06 μm) with the help of a polishing microcloth then sonicated for 10 min in Milli-Q water. Au nanoparticles were electrodeposited from 0.5 M H_2SO_4 + 1.0 mM $Na[AuCl_4]$ solution by applying potential step electrolysis from 1.1 to 0.0 V vs. Ag/AgCl/KCl(sat) [20,28]. The duration of the potential step electrolysis was varied from 5 to 900 s to obtain Au deposits with different characteristics (cf. Table 1). The thus-prepared Au nanoparticles-electrodeposited GC electrodes were characterized electrochemically in a deoxygenated (i.e., N_2-saturated) 0.5 M H_2SO_4 solution (cf. Fig. 1). The self-assembled

* Tel.: +202 3567 6603; fax: +202 3572 7556.
E-mail address: msaada68@yahoo.com.

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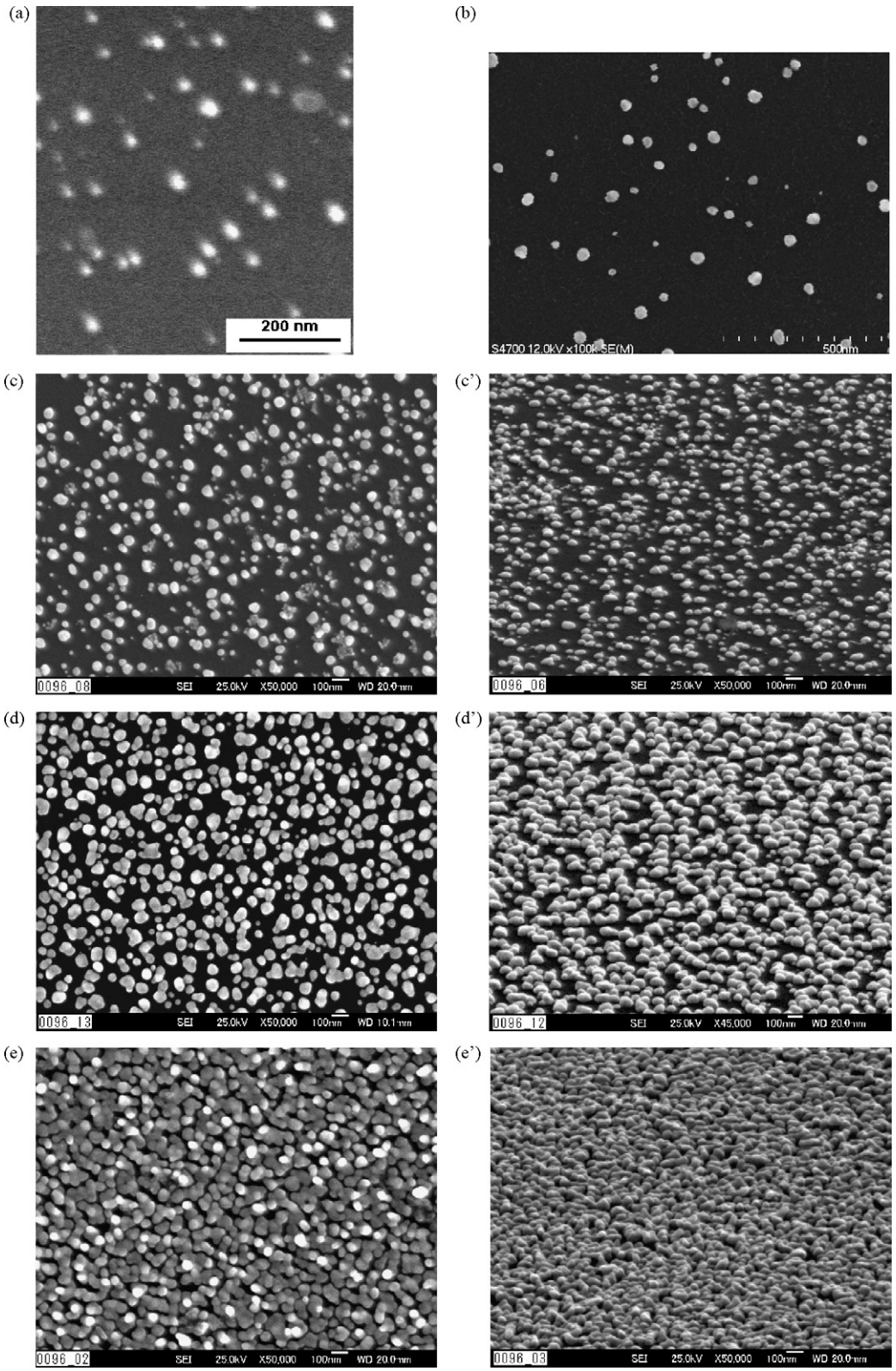

Fig. 1. SEM micrographs of Au nanoparticles electrodeposited onto GC electrodes from 0.5 M H_2SO_4 containing 1.0 mM $Na[AuCl_4]$ by applying potential step electrolysis from 1.1 to 0 V vs. Ag/AgCl/KCl(sat) with a step width of (a) 5, (b) 10, (c,c′) 60, (d,d′) 300, (e,e′) 900 s. Note that images c′–e′ are taken at an inclination of 70° of the sample.

monolayer (SAM) of cysteine [HS-CH_2-CH(NH_2)-COOH] was prepared by immersing the nano-Au/GC electrodes into an aqueous solution of 1.0 mM cysteine for 20 min. The reductive desorption experiments were carried out in a deoxygenated 0.5 M KOH solution. For the oxygen reduction measurements, O_2 gas was bubbled directly into the cell containing 0.5 M KOH to obtain an O_2-saturated solution and during the measurements O_2 gas was flushed over the cell solution. Electrochemical measurements were performed in a three-electrode cell using EG&G potentiostat (model 273A) at room temperature. The current densities were calculated on the