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Electrochemically stable gold nanoclusters in HOPG nanopits

M. Limat [a], G. Fóti [a], M. Hugentobler [b], R. Stephan [b,1], W. Harbich [b,*]

[a] Electrochemical Engineering Group, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland
[b] Institut de Physique des Nanostructures, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

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ABSTRACT

Gold nanoparticles on highly oriented pyrolytic graphite (HOPG) electrodes are synthesized. They are stabilized in nanosized pits of well defined depth in the graphite surface. These pits are created by energetic cluster impact followed by etching under a well controlled oxygen atmosphere. We succeeded in the preparation of highly dispersed and stable Au electrodes with gold particles with a mean diameter smaller than 5 nm. The stability of the gold nanostructures for electrochemical applications has been tested by performing cyclic voltammetric measurements in 0.5 M H_2SO_4. While conventionally prepared sputter deposited electrodes show highly unstable structures in this size range, Au clusters stabilized in the nanosized containers are stable.

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1. Introduction

Gold nanoparticles have attracted considerable interest in the past decade due to their geometrical, electronic and chemical properties which differ drastically from those of bulk materials [1,22]. Gold is known as an extremely stable and established weak chemisorber, therefore a poor catalyst. The seminal work of Haruta [23,22] has shown that gold shows surprisingly strong catalytic activity when dispersed as nanoparticles on a substrate. Goodman and coworkers [39] clearly delimited the size range to be below 5 nm. Since then a new field opened up known as nanocatalysis by gold [24]. Gold exhibits remarkable electrocatalytic activity, higher than that of other transition metals towards many reactions like catalytic hydrogenation of unsaturated alcohols and aldehydes [35], CO oxidation [4,20–22], selective hydrocarbon oxidation [26] and O_2 reduction [14,41]. The detailed mechanisms of this exceptional activity are not well understood yet. Numerous studies have been performed over the last years to better understand the electrochemical properties of gold nanoparticles in heterogeneous catalysis and surface electrochemistry. Gold catalyst systems, i.e. supported Au nanoparticles, can be used for applications in pollution control, chemical processing and fuel cells. It is not only the promising technical performance gold catalysts can provide [9], but also an economical challenge, because of the lower price of gold against platinum, which is the currently used catalyst.

In the perspective to prepare stable electrocatalysts, several groups investigated the electrocatalytic activity of metallic nanoparticles like platinum [33,37], silver and gold [41,33] deposited on boron-doped diamond (BDD) electrodes. In our research group, a new technique for the preparation of stable and applicable gold nanoparticles supported on boron doped diamond has been developed [33]. Gold deposits have been assumed to agglomerate at specific actives sites of the BDD film corresponding to the surface defects. Ultrafine Gold particles on carbon substrates (glassy carbon) have first been considered as substrates by Yahikozawa et al. [40] and Tateishi et al [38]. Highly oriented pyrolytic graphite (HOPG) has also to be considered as a support because it is an attractive electrode material due to its wide potential window in aqueous media with a low background current. Furthermore this support is inert and chemically stable [31]. HOPG electrodes have been widely investigated due to their strong anisotropic surface properties [3].

The basal plane of HOPG having all carbon bonds saturated is extremely inert with a small energy barrier for adatom diffusion. Consequently it is difficult to stabilize nanoparticles on the surface terraces and aggregation takes place at monoatomic step edges [11,12,15,18]. This results in a strongly anisotropic distribution of nanoparticles on the surface like metallic chains [12], a difficult size control and even more important in a small particle density. A possible way to stabilize very small nanostructures is to pin the particles via the creation of defects to the surface [7,8,30,10,17,19]. However these structures although to some extent stable under vacuum conditions at room temperature alter upon exposure to atmospheric conditions or when immersed in solutions. Instead of

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[*] Corresponding author.
E-mail address: wolfgang.harbich@epfl.ch (W. Harbich).

[1] Present address: Institut de Science des Matériaux de Mulhouse, (IS2M) - LRC CNRS 7228 Université de Haute-Alsace, 4 rue des frères Lumière, 68093 Mulhouse Cedex, France.

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stabilizing the particles by partial implantation of the cluster atoms one can imagine to keep them in place on strongly nanostructured surfaces.

HOPG is a model candidate for such type of substrates. Kappes and coworkers [5,6] where the first to create controlled nanosize pits in ion bombarded HOPG. These pits could be created by selective etching of defects introduced by ion beam impact. Several groups, including the authors have followed this idea [16,25,2,27,32,34,36].

In the following we describe the application of this method to the preparation of stable HOPG electrodes for electrochemical processes. Very small gold clusters ($\leq$5 nm) are fixed in these nanopits and show to be surprisingly stable. The nanosized gold deposits are characterized by scanning tunneling microscopy (STM), scanning electron microscopy (SEM) and cyclic voltammetry (CV).

2. Phenomenological description

The preparation of highly dispersed nanosized particles on a substrate by physical vapor deposition or sputtering involves two basic processes: nucleation and particle growth. These processes strongly depend on the bond energy of the contributing atoms to the surface and the surface corrugation for diffusion and often take place simultaneously. Suitably chosen experimental conditions may favor one process over the other hence one may tailor the granulometric properties of the dispersion.

Electrochemical deposition processes are mostly characterized by growth rather than nucleation leading to the formation of very large clusters without completion of the first monolayer. As a consequence, the size of the clusters is difficult to control and exceeds easily the desired range of some tens of nanometers. Aiming to prepare metal nanoparticles of tailored size less than 10 nm and well adhered to the HOPG substrate we separate nucleation and particle growth. The process, sketched in Fig. 1, consists of three consecutive steps: (1) implantation of gold clusters (Au_5 in this case) at a well defined impact energy on the HOPG surface to create the desired number of defects, (2) etching of these pits under controlled temperature and oxygen atmosphere, and (3) gold deposition by evaporation onto the substrate at 400 °C. The application of this method is limited to small surface loading of the deposited material, typically not exceeding a few monolayer equivalent but is perfectly suited to produce very small supported clusters.

An atomically clean HOPG surface containing only a small fraction of edge planes ($<5\%$) is exposed to Au_5 clusters with an appropriate kinetic energy ($\sim$3 keV). The bombardment involves permanent displacements of surface and subsurface carbon atoms. These displacements (defects) create dangling bonds which serve as oxidation sites for the successive etching step. Au_5 clusters have been chosen for their size is large enough to guarantee a well defined defect depth (3–4 monolayers) [36] and to avoid implantation of other metals than the desired electrode material. Control of the defect density is easily achieved via the bombarding time.

During the second step the defects are opened into nanosized pits. The carbon-oxygen reaction is highly dependent on the nature of the carbon sites. Carbon atoms with saturated bonds (the ones in the basal plane) are much more inert than the ones with dangling bonds. At temperatures below 700 °C, oxidation is initiated mainly at defects on the basal plane, or edge atoms on monoatomic steps while intact basal plane atoms remain unaffected. The oxidation removes carbon atoms from the basal plane of graphite and creates new vacancies. This process continues until the penetration depth of defect production is reached. The diameter of the pit however continues to grow and is largely dependent on the oxidation time.

The third step consists in evaporation of gold under high vacuum conditions ($p \approx 10^{-4}$ Pa). The carbon electrode is heated to 400 °C which confers sufficient energy to the gold atoms to migrate into the pits. The number of individual nanoparticles depends on the pit density while the cluster size is defined by the total gold load on the surface.

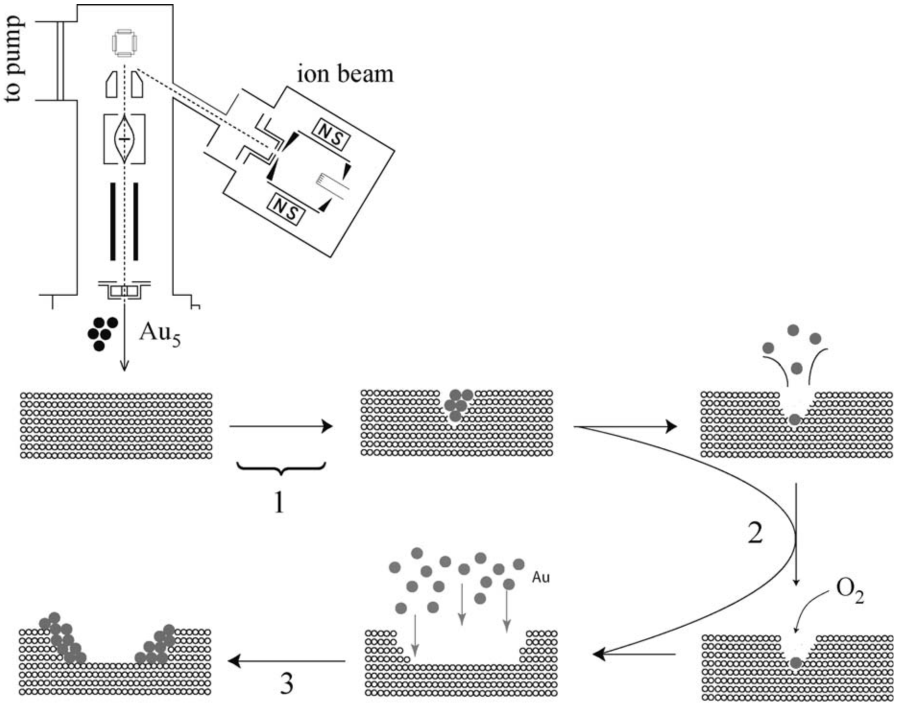

Fig. 1. Schematic representation of the nanostructuring of HOPG consisting in the following three-steps: Au_5 implantation into the atomically clean HOPG surface (1), etching of the created defects under well controlled oxygen partial pressure and temperature (2), gold deposition by thermal evaporation under high vacuum conditions (3).

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