

Superior Electrocatalytic Activity of Au (110)-like Gold Nanoparticles towards the Oxygen Evolution Reaction

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This study is concerned with the electrocatalytic evolution of oxygen gas at novel gold nanoparticles (nano-Au) modified glassy carbon (GC) electrodes in 0.5 M KOH. The electrochemical measurements show a superior enhancement of the nano-Au/GC towards the oxygen evolution reaction (OER) compared to bulk GC and Au electrodes. That is, the onset potential of the OER is shifted by ca. 600 mV in the negative direction compared with bulk Au and unmodified GC electrodes. The enrichment in the Au (110) facet orientation (of the electrodeposited nano-Au) [1] at the expense of other low facet orientations induces a favorable geometric arrangement of the Au surface atoms which is believed to facilitate the OH⁻ adsorption and, hence, the charge transfer process during the water electrolysis into molecular oxygen. Thus, the OER is accelerated and realized at less positive potential.

Keywords: Nanoparticles; Water electrolysis; Oxygen evolution; Facet orientation.

1. INTRODUCTION

A considerable attention of the recent research in electrocatalysis is focused on the discovery of electrode materials with excellent electrochemical stability and activity towards typical electrochemical reactions. Electrocatalytic oxygen evolution on various electrode materials and from various electrolyte solutions is one of the most frequently studied electrode reactions. The reasons for this are both theoretical and practical, since this gas represents major product of several industrial electrolytic processes. It is the most common anodic reaction coupled with many of the cathodic processes occurring in aqueous solutions. Some metal oxide-based electrodes have been reported to catalyze the oxygen evolution reaction (OER). Among them Ni and Co oxides have been extensively

studied [2–9]. In general, when oxygen evolution takes place on a metallic electrode, the surface is already covered with an oxide layer. Also, various Mn oxides have been reported to catalyze the OER; the extent of catalysis is based on the synthesis method of the electrode as well as on the nature of the dopant such as Mo or W [10–13]. Recently, a significant enhancement is obtained upon the modification of Au electrode with manganese oxide nanoparticles [14].

Gold nanoparticles are also well known by their unexpected high catalytic activities toward several electrocatalytic reactions. Considerable attention has been directed to the preparation of gold nanoparticles because of their fascinating properties and potential applications in many fields [15–28]. The overall performance of gold nanoparticles-based electrodes is highly depending on their size, shape, crystallographic orientation and method of preparation as well as the structure and the properties of the support material [29–37]. One attractive technique for the fabrication of gold nanoparticles based electrode could be achieved, for example, by the immobilization of the chemically prepared colloidal Au nanoparticles on a gold support with the help of a short chain dithiol [38]. Kolb et al in their recent publications have described a new technique for depositing metals like Pd, Pt and Rh atop SAM, which form nanometer-sized and monoatomic islands with new electronic properties [39–42]. All the above mentioned researches utilize Au substrate for the fabrication of Au nanoparticle assemblies. Whereas, the current study aims to the employing of Au nanoparticles fabricated atop modified carbon substrate. The fabrication of gold nanoparticle atop GC electrode can be achieved via the grafting of amino group onto the surface of the electrode. The electrochemical grafting of nitrogen-containing compounds has been investigated by several groups, and the electrochemical introduction of various amines has been successfully carried out [43–45]. Recently, Uchiyama et al succeeded in the electrochemical grafting of amino group onto glassy carbon (GC) by electrolysis in carbamic acid solution [46].

In the present study, gold nanoparticles are chemically deposited atop amino group-grafted GC electrode. The gold nanoparticles modified glassy carbon electrode has been examined as a novel anode for the electrocatalytic evolution of oxygen gas from alkaline medium (N_2 -saturated 0.5 M KOH).

2. EXPERIMENTAL

The fabrication of gold nanoparticles atop the amino group-grafted GC is achieved via the following three consecutive steps [1]. Firstly, amino groups were introduced onto the surface of the carbon substrate according to the procedure reported recently by Uchiyama et al. who have succeeded in the electrochemical grafting of glassy carbon (GC) with amino groups [30] by potentiostatic electrolysis in carbamic acid solution for 90 min at 1.0 V vs. Ag/AgCl/KCl(sat). Secondly, a solution of 1.0 mM H_2SO_4 was dropped dropwise on the NH_2 -grafted carbon substrate (e.g. GC electrode) to protonate the $-NH_2$ group to $-NH_3^+$. Then, to anchor the $[AuCl_4]^-$ ions on the surface of the GC electrode, the grafted GC electrode was immersed in 1.0 mM H_2SO_4 containing 1.0 mM $Na[AuCl_4]$ solution for 10 min followed by washing with 1.0 mM H_2SO_4 to remove the electrostatically unbound $[AuCl_4]^-$. Thirdly, the anchored $[AuCl_4]^-$ ions were electrochemically reduced in 1.0 mM H_2SO_4 by

scanning the potential from 0.7 to 0 V vs. Ag/AgCl at 0.1 V s⁻¹. To characterize the redox waves of gold nanoparticle modified GCEs; CVs were carried out in N₂-saturated 0.1 M H₂SO₄. The potential was cycled between 0.0 and 1.5 V vs. Ag/AgCl and the potential scan rate was 0.1 V s⁻¹.

The morphological characterization of the prepared gold nanoparticle was carried out by Atomic Force Microscopy (AFM) using basal plane highly oriented pyrolytic graphite (HOPG) substrates anchored with gold nanoparticle by applying the same methodology mentioned above. VN-H1V8 VN Viewer (KEYENCE Nanomicroscope, Japan) was used to get the AFM images.

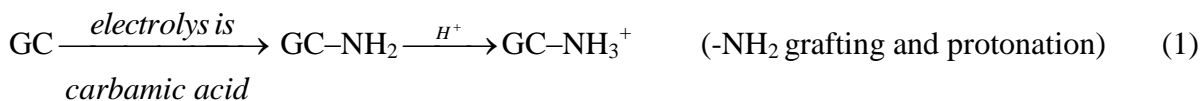
The XPS data were acquired with glassy carbon electrodes (d = 6.0 mm), which were prepared as mentioned above. The XPS spectra were recorded by ESCA-3400 electron spectrometer (SHIMADZU) using an unmonochromatized X-ray source with Mg K alpha (1253.6 eV) anode.

The electrocatalytic activity of the gold nanoparticles modified GC towards the oxygen evolution reaction (OER) was examined in N₂-saturated 0.5 M KOH solution at a potential scan rate of 20 mV s⁻¹. All the electrochemical measurements were performed at room temperature (25 ± 1°C) in a conventional two-compartment Pyrex glass cell (having a total volume of ca. 25 cm³) using a computer controlled BAS 100 B/W electrochemical analyzer.

3. RESULTS AND DISCUSSION

3.1. Preparation and characterization of the modified GC electrodes:

A series of the above mentioned procedure for the fabrication of Au nanoparticles on the NH₂-grafted glassy carbon electrode can be schematically described as follows [1]:



AFM image (not shown) depicts that no Au nanoparticles were fabricated on the carbon substrate (highly oriented pyrolytic graphite (HOPG)) subjected to the above mentioned procedures except for the -NH₂ grafting step. On the contrary, Au nanoparticles of ca. 100-200 nm in diameter could be grown up on the -NH₂ grafted HOPG substrates (Figure (1)). This implies the necessity of the grafting step, i.e., the introduction of the amino group onto the surface of the carbon substrate, for the successful immobilization of Au nanoparticles on the electrode surface.

Similarly, Au nanoparticles could be also assembled onto GC surface grafted with -NH₂ groups. Figure (2b) shows the characteristic cyclic voltammograms (CV) obtained at the Au nanoparticles-assembled GC electrodes in N₂-saturated 0.1 M H₂SO₄. The observation of typical surface oxidation and reduction peaks similar to those of a bulk gold electrode assures a successful

anchoring of the Au nanoparticles to the NH_2 grafted GC substrate. As shown in Figure (2a), such CV response characteristic of Au electrode was not observed for GC electrode subjected to 0 min of grafting.

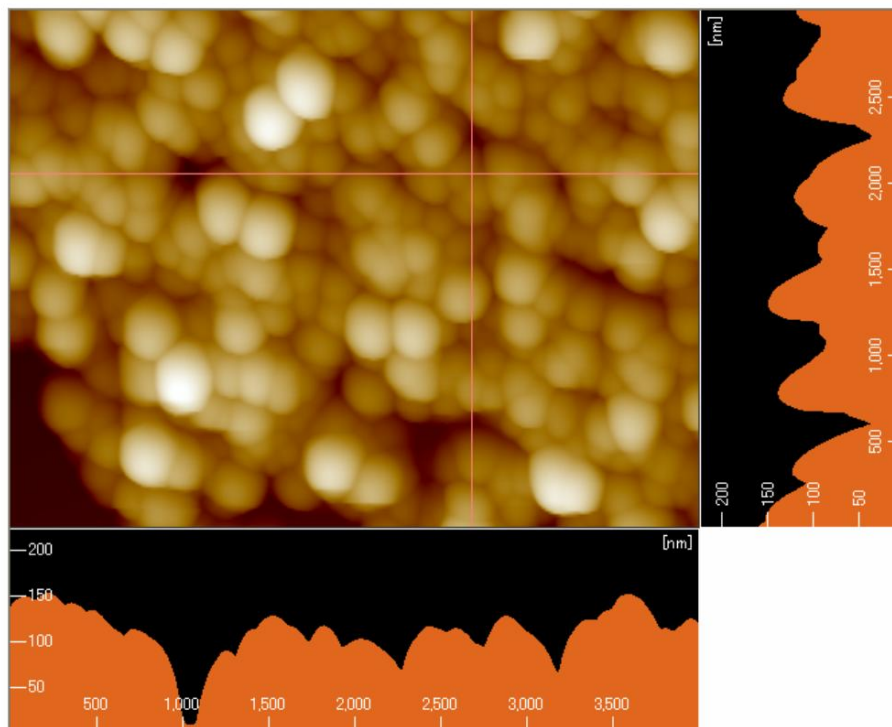


Figure 1. AFM image obtained for the Au nanoparticles anchored at HOPG substrate. Note that $-\text{NH}_2$ groups has been grafted onto HOPG prior to anchoring of Au by electrolysis in carbamic acid solution for 90 min at 1.0 V vs. Ag/AgCl/KCl(sat).

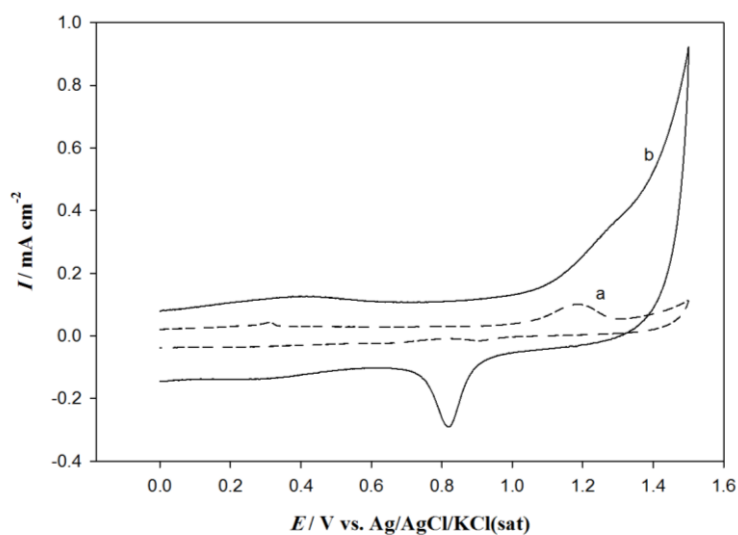
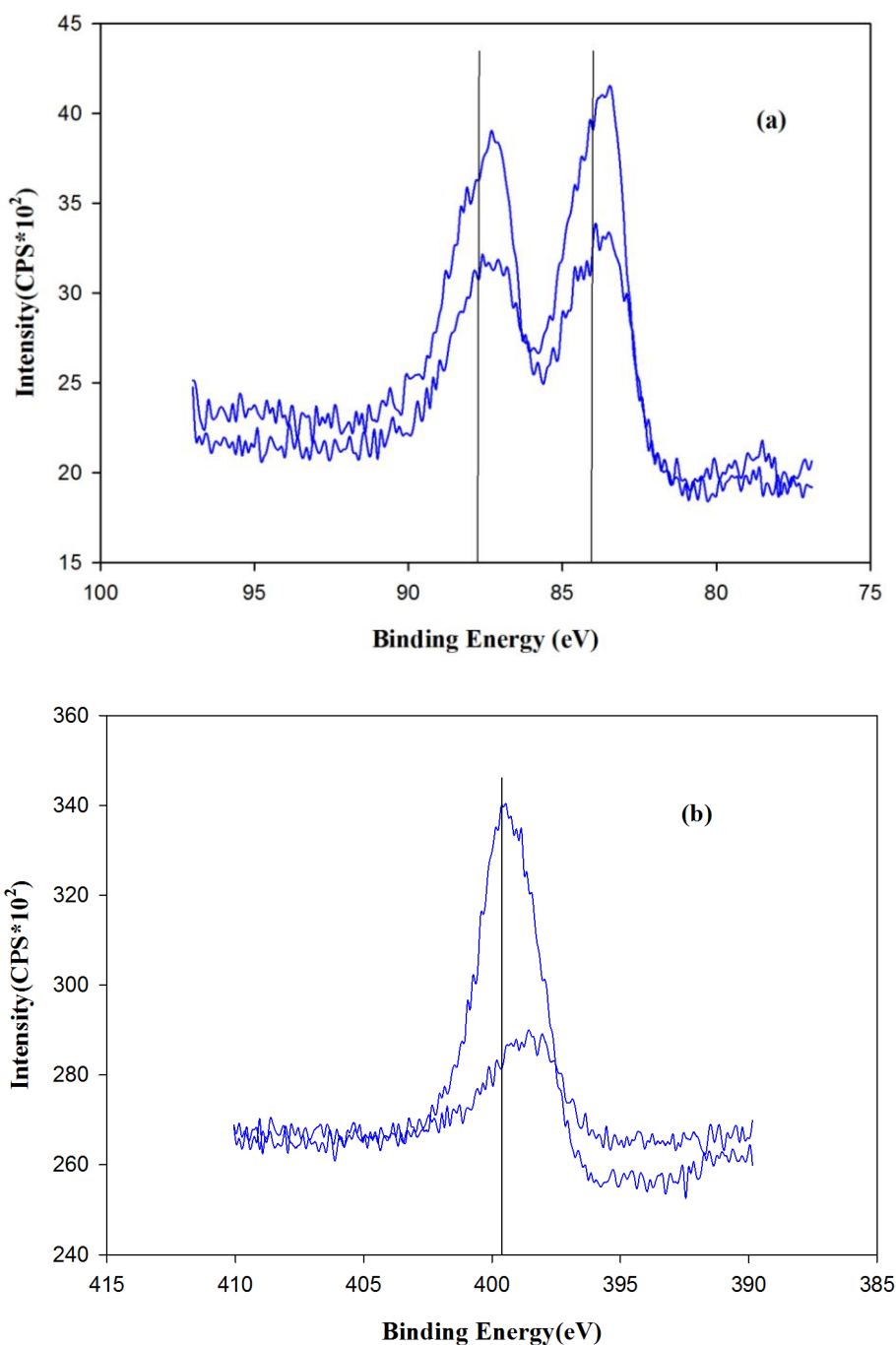


Figure 2. Characteristic CVs of Au nanoparticles anchored on $-\text{NH}_2$ grafted GC measured in N_2 -saturated 0.1 M H_2SO_4 . Potential scan rate: 0.1 V s^{-1} . Note that the GC electrodes were subjected to (a) 0 and (b) 90 min time of grafting.

Further confirmation of the formation of the Au nanoparticles and the necessity of the $-\text{NH}_2$ grafting step was accomplished by the XPS measurements and the results are shown in Figure (3). This figure shows the XPS spectra of (a) Au 4f, (b) N 1s and (c) O 1s of the gold nanoparticles modified GC electrode which was subjected to 90 min of grafting. The vertical solid lines in Figure (3a) refer to the binding energies for elemental Au. Inspection of Figure (3) reveals the following points: (i) There is a significant negative shift of the binding energies for the Au 4f of the gold nanoparticles compared to that of the bulk gold, i.e., a shift from 87.7 and 84.0 eV for $4f_{5/2}$ and $4f_{7/2}$, respectively, of bulk Au to 86.9 and 83.2 eV in the gold nanoparticles samples.



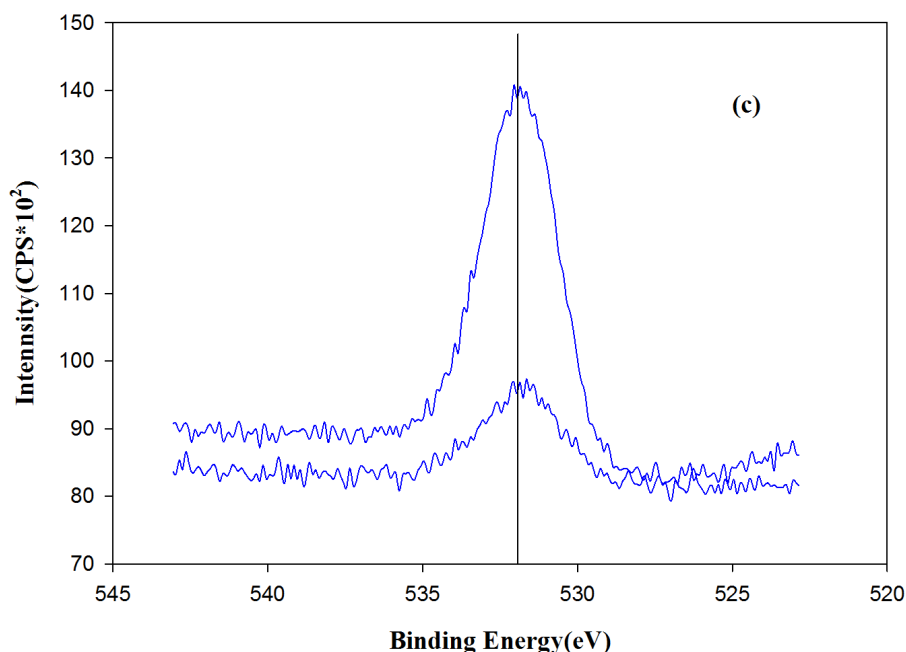


Figure 3. XPS spectra of (a) Au 4f and (b) N 1s and (c) O 1s of gold nanoparticles modified GC electrode subjected to 90 min of grafting. Note that: The black vertical lines in Fig. (3a) refer to the binding energies for elemental Au and in Fig. (3b) to nitrogen in the form of C-NH₂. The lower spectra are for the same sample after etching.

This fact indicates a change in the electronic structure of Au nanoparticles. This might originate from the change in the facet orientation. Interestingly, the thus-prepared Au nanoparticles are found highly rich in the Au (110) facet orientation [1]. (ii) Figure (3b) indicates that nitrogen exists in the form C-NH₂. The negative shift of the 1s binding energy of nitrogen after etching of the GCEs sample from 399.5 eV to 398.3 eV indicates that nitrogen exist in $-N=$ cyclic structure beneath the outermost few layers of GC electrode. (iii) The XPS spectra for oxygen (Figure 3c) show O 1s peak at 531.5 eV correspond to $-OH$ group, which can be attributed to the extensive electrolysis of GC electrode at 1.0 V in 0.1 M carbamate aqueous solution (pH 8.9).

3.2. Activity towards the OER and origin of enhancement:

The electrocatalytic activity of the gold nanoparticles modified GC towards the oxygen evolution reaction (OER) was examined in N₂-saturated 0.5 M KOH solution. Figure (4) shows linear scan voltammograms (LSVs) at a potential scan rate of 20 mV s⁻¹ for the OER measured in N₂-saturated 0.5 M KOH solution at (a) bare gold, (b) unmodified GC, (c) NH₂-grafted GC and (d) gold nanoparticles modified GC electrodes. This figure shows a significant enhancement of the polarization behavior of the gold nanoparticles modified GC electrode towards the OER. That is, a 600 mV negative shift of the onset potential of the current flow has been obtained upon the modification of the GC electrode with gold nanoparticles. This surprising enhancement can be explained as follow:

The sequence of the elementary steps for oxygen evolution is frequently assigned as follows [47-49]:



The rate determining step for oxygen evolution in alkaline media is frequently assigned to the adsorption and the initial charge transfer, i.e., Reaction (4) [50].

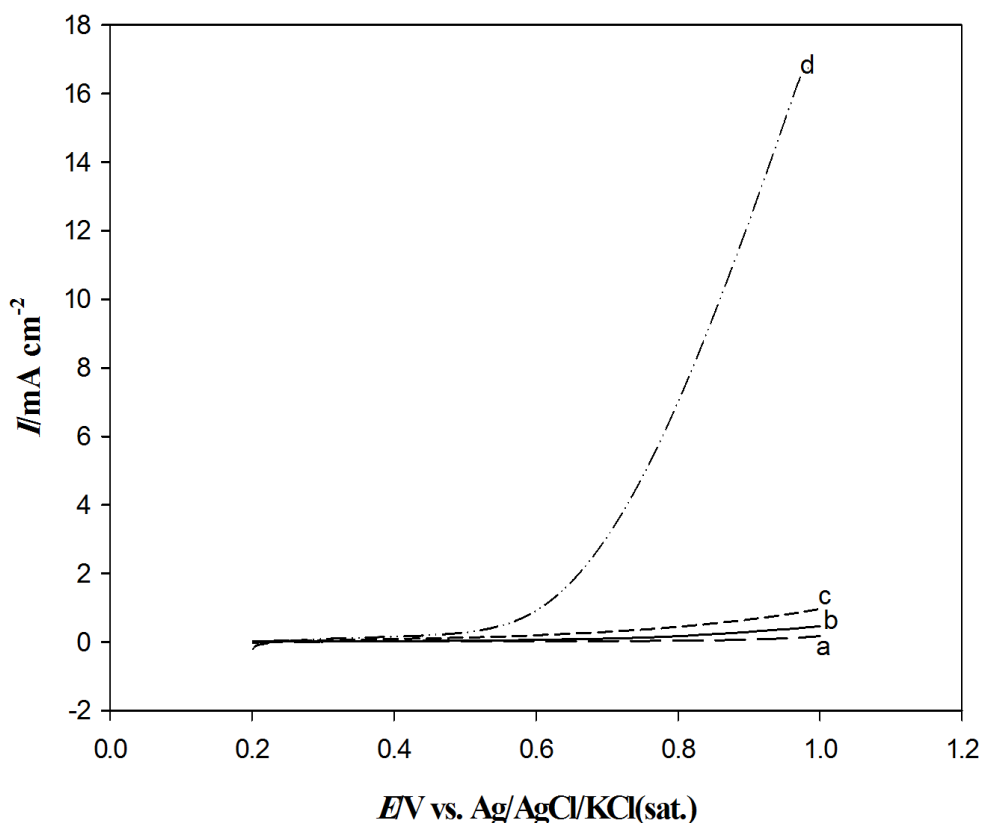
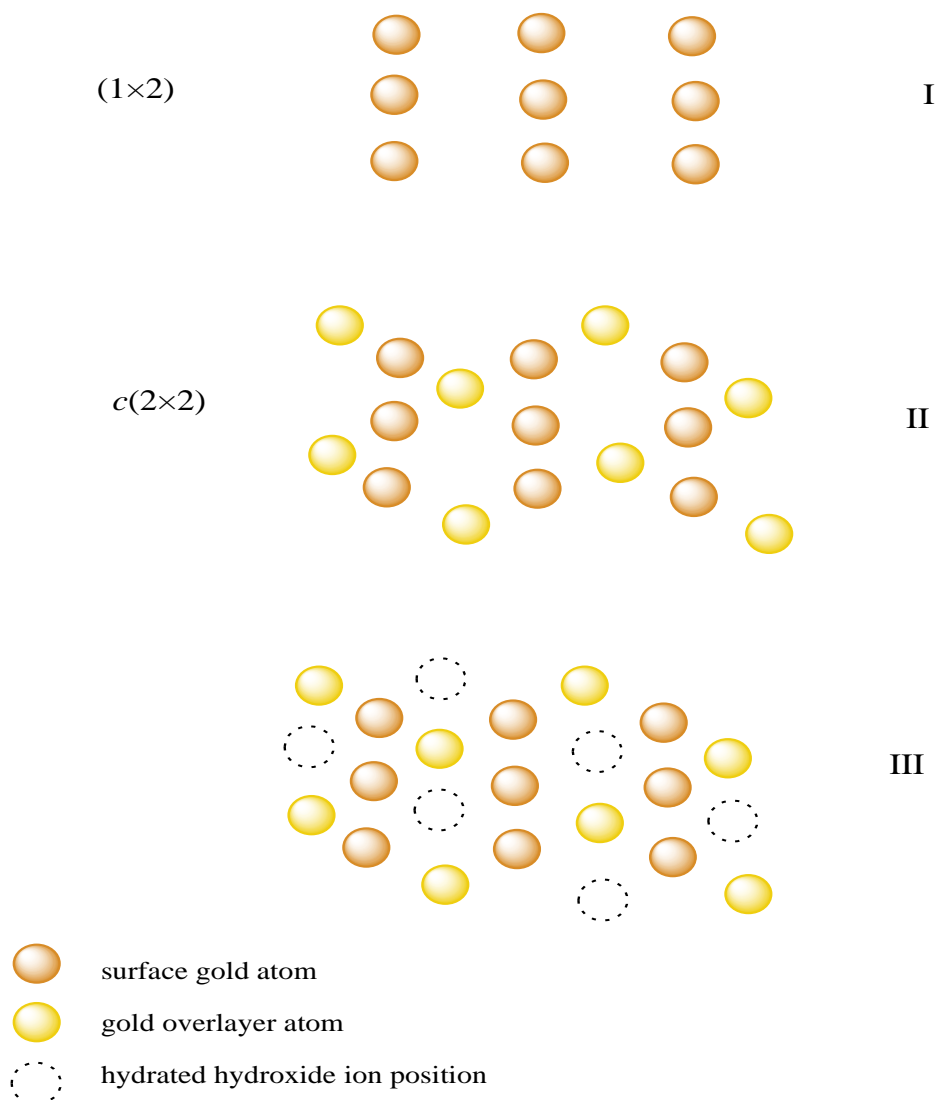


Figure 4. Linear Scan Voltammograms (LSVs) for the OER in N_2 -saturated 0.5 M KOH solution at (a) bare gold, (b) bare GC, (c) $-\text{NH}_2$ grafted GC and (d) gold nanoparticles modified GC electrodes. Potential scan rate: 20 mV s^{-1} .

In the present case, the Au nanoparticles are enriched in the Au(110) facet orientation as depicted from the reductive desorption experiments (measured in N_2 -saturated 0.5 M KOH solution) of a short chain thiol (typically cysteine) self-assembled on the surface of the Au nanoparticles [1].

It is well known that Au (110) single crystal exhibits a (1×2) surface structure. However, it is transformed to a (1×1) surface structure upon complete oxidation [51]. Throughout the pre-oxidation and the oxidation region, the surface becomes more disordered and may go through some stable intermediate structures [51]. Upon the complete oxidation, the structure changes from (1×2) to (1×1) but the surface may go through an intermediate stable structure consisting of (1×2) and (1×1) in co-existence (see Scheme 1) [51].



Scheme 1. A sketch of the proposed structural changes of the Au (110) surface atoms: (I) Au (110) surface structure, (II) the surface structural transformation throughout the oxidation and preoxidation state of Au surface atoms and (III) the extra hollow site generated during the structural transformation.

This structure looks like a (1×1) and also called a centered rectangular structure [51]. The correct notation for this central structure is $c(2\times 2)$. It represents an ordered (1×1) structure with a

centered (2×2) overlayer (see Scheme 1). The extra hollow sites which are formed during this transformation could be filled by adsorption of spectator anions from the solution phase. Hydroxide ions are typical candidate for this process which, if contained in a hydrated sphere, could be of the order of the size of a gold atom. The size of the hydroxide ion is 1.37 Å and the size of a water molecule is of the order of 1.5 Å [52]. As shown in Scheme (1), one could safely assume that a hydrated hydroxide sphere of ~3.4 Å in diameter would fit easily in the hollow site left which will stabilize the $c(2\times 2)$ structure. This would, certainly, facilitate the sequential coupling of the adsorption and the initial discharge of OH⁻, Reaction (4). This point of view is supported by XPS results that show a change in the oxygen peak position and structure with the peak corresponding to the Au-OH state [53]. Thus, the mechanism suggested above might furnish a plausible explanation for the observed enhancement of the OER at the gold nanoparticles enriched with the Au(110) facet orientation.

4. CONCLUSION

The current study introduces a novel Au nanoparticles-based electrocatalyst for water electrolysis in alkaline media. That is, a shift of the onset of the OER by about 600 mV to the negative direction was achieved at the Au (110)-like gold nanoparticles modified GC electrode. Gold nanoparticles (enriched in Au (110) facet orientation) are thought to facilitate the favorable adsorption of OH⁻ anions and, thus, the charge transfer during the water discharge into molecular oxygen could be achieved at a reasonably low anodic polarization.

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