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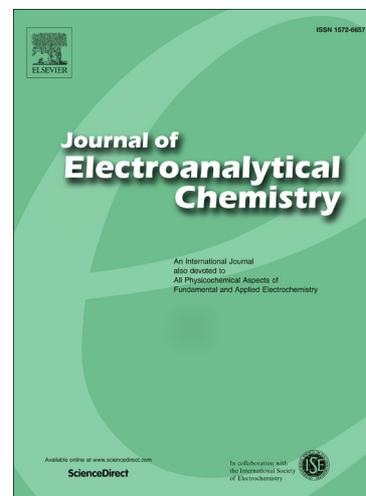
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Abstract

Gold electrocatalysts seems to be an interesting material for application in Alkaline Fuel Cells (AFC) since several studies have reported the electro-catalytic activity of gold-based catalysts for various heterogeneous catalyzed oxidation reactions like oxidation of small organic molecules. In this paper, we synthesized Au nanoparticles (AuNps) dispersed onto Vulcan carbon substrate using a straightforward glycerol method in order to study the pathway electro-oxidation of alcohols, like glycerol, 1,2-propanediol and 1-propanol in alkaline medium. TEM images showed a good dispersion of the gold nanoparticles on the carbon support and the particle mean size ranging from 3 to 14 nm. The structure of gold is face centered cubic (fcc) indicated by XRD and the metal loading was 18 % evaluated by EDS technique. Cyclic voltammetry was mainly used to evaluate the electrochemical activity of the Au NPs towards the oxidative transformation of alcohols. Electrochemical results proved that Au/C Nps are more active to oxidize glycerol than 1,2-propanediol and 1-propanol, while higher current density was obtained for the diol. *In situ* FTIR measurements showed different pathway for each alcohol. For glycerol electro-oxidation, the main byproducts from reaction were formate and oxalate ions. It was already suggested that gold in alkaline medium oxidized glycerol more promptly than others alcohols. The electro-oxidation of 1,2-propanediol led to acetate and hydroxyacetone ions while the *in situ* FTIR spectrum for electrooxidation of 1-propanol suggests that propanoate is the only the product of 1-propanol electro-oxidation over Au/C.

1. Introduction

The most of noble metals, like gold, are very inert and remarkably resistant to oxidation. The nobleness and inertness of gold is explained in terms of the degree of filling of the antibonding states on adsorption and the degree of orbital overlap with the adsorbate¹. As a result, gold was traditionally considered as a very poor catalyst or electrocatalyst². However, in recent years several studies have reported the electrocatalytic activity of gold-based catalysts for various heterogeneous catalyzed oxidation reactions, like borohydride³ and small organic molecules, like ethanol⁴, glycerol^{5,6} and ethylene glycol⁷.

Koper et al.⁶ showed the oxidation activity of a series of similar alcohols with varying pK_a on gold electrodes in alkaline solution. The authors concluding that the high oxidation activity on gold electrode, compared to platinum electrode, is related to high resistance of gold toward the formation of poisoning surface oxides.

In this context, gold electrocatalysts seems to be an interesting catalyst for application in Alkaline Fuel Cells (AFC)⁸. It is known that electrocatalytic activity is strongly related to structure surface of catalysts⁹. In addition the catalyst composition, the catalyst particle size in the nanometric range has also been demonstrated to be important to deliver improved catalytic performances.

In this way, several synthesis methods are employed in order to obtain a homogeneous catalyst with high surface area. A variety of methods of synthesis, such as polyol¹⁰ and microwave assisted¹¹, may be employed in the production of Au Nps, for example. The polyol method typically consists in refluxing a mixture of a precursor salt (e.g., $AuCl_3$ or $AgNO_3$), a stabilizing agent [e.g., poly (vinyl pyrrolidone) (PVP)] and a polyalcohol (e.g., ethylene glycol) at ~160–240 °C for 2–12 h, which requires a long time and energy consuming. The microwave-assisted approach also requires high temperature and has the further inconvenience of

demanding a microwave generator. It was recently reported an environmentally friendly route to produce gold³ and silver¹² nanoparticles using glycerol as reducing agent in alkaline medium. Glycerol is a greener option since it is non-toxic and readily biodegradable under aerobic conditions.

In this paper, Au Nps dispersed onto Vulcan carbon were synthesized using glycerol method³ as catalysts for oxidation of small organic molecules. Electrocatalysis of simple organic molecules is becoming increasingly important in areas such as the development of alternative fuel sources¹³. Although the electrocatalytic oxidation of methanol and ethanol have been examined extensively^{14,15}, there has been much less effort on the study of saturated C3 alcohols and polyols.

Among monohydric and polyhydric alcohols, the electrochemical oxidation of C3 alcohols (1-propanol, 1,2-propanediol and glycerol) are attractive for investigating the electrochemical properties of different kind of alcohols and the influence of the structure of molecular chain in relation to performance of electrooxidation on Au NPs. In this way, the electrooxidation of 1-propanol can provide useful insights for the oxidation of other complex alcohols.

The electrocatalytic oxidation of 1,2-propanediol was investigated since the cyclic voltammetric response of this diol depends on electrode morphology¹⁶. Moreover the structure of diols, with two or more oxidatively accessible groups, can potentially provide some information into the factors relevant to the electrocatalytic oxidation of hydroxyl-containing species¹⁶.

Glycerol has been drawing increased attention of researchers. Glycerol is the main co-product of the biodiesel fabrication via trans-esterification reaction¹⁷ and, nowadays, its production exceeds the demand of traditional trades. In the field of renewable energy glycerol has been regarded as an alternative fuel in Direct Alcohol

Fuel Cells (DAFCs)¹⁸. If completely oxidized to CO₂, the glycerol electro-oxidation reaction involves 14 electrons, which is quite favorable from an energetic point of view¹⁹.

The electrocatalytic oxidation of some C3 alcohols is also attractive as a preparation method. For example, the preparation of glyceric acid²⁰ and lactic acid²¹ by glycerol and 1,2 propanediol oxidation has been reported and would provide a pathway for the sustainable production of these valuable products. Thus, this system can be useful as a chemical reactor to add value to the alcohol by producing more valuable chemicals. Gold nanoparticles were physical-chemically characterized by Transmission Electron Microscopy (TEM), X-ray Energy Dispersive Spectroscopy (EDS) and X-ray Diffraction (XRD).

2. Experimental

2.1 Synthesis of Carbon-Supported Au-NPs

For the production of gold nanoparticles, a facile green route based on co-reduction of Au³⁺ by glycerol in alkaline medium at room temperature was used to synthesize nanoparticles anchored onto a carbon support³. The synthesis of the catalyst consisted in sonicating 80 mg of XC-72 Vulcan carbon in 60 mL of ultrapure water and then adding a fixed amount of AuCl₃ under stirring to promote homogenization. Afterwards, another aqueous solution containing glycerol and NaOH was added to give the following concentrations: 1.02 mmol L⁻¹ Au³⁺, 1.0 mol L⁻¹ glycerol and 0.01 mol L⁻¹ NaOH. The black suspensions were kept during 30 min. under stirring at room temperature and then washed, filtered and dried at 80 °C for 12 h.

2.2 Physical and Chemical Characterization

The TEM analyses were performed in order to investigate the composition, morphology, size and distribution of gold particles onto carbon substrate. The experiments were conducted using a TEM FEI Tecnai with an accelerating potential of 200 kV. For preparation of sample the copper-coated grid was immersed in a suspension containing 1.0 mg of catalytic powder (Au/C) and 5 mL of isopropanol alcohol, after then the solvent was evaporated at room temperature. The EDS technique was employed to determine the amount of metal onto carbon Vulcan. The XRD was also used to observe the diffraction pattern and to estimate the average crystallite size from Scherrer's equation²²:

$$D = k\lambda / B \cos \theta \quad (1)$$

where D is the average crystallite size in angstrom, k is a coefficient taken here as 0.9, λ is the wavelength of the X-rays used (1.5406 Å), B is the full width at half maximum of the diffraction peak, given in radians, and θ is the angle at the position of the peak maximum, given in degrees.

2.3 Electrochemical Characterization

The electrochemical experiments were assessed in a conventional three-electrode cell. A catalytic layer of Au/C on a glassy carbon disc, a platinum foil and a Reversible Hydrogen Electrode (RHE) in 0.1 mol L⁻¹ NaOH were employed as working, counter and reference electrodes, respectively. A glassy carbon disc ($\phi_{OD} = 5$ mm, geometric area = 1.540 cm²) was used as substrate to support active layers of Au/C. For the preparation of the catalytic layer, 1.0 mg of the catalytic powder was

suspended in a mixture containing 1 mL of isopropyl alcohol and 24 μL of a Nafion solution (6 wt % in low aliphatic alcohol, from DuPont). After ultrasonic homogenization, 20 μL of this ink were dropped onto the glassy carbon disc and the solvent was then evaporated at room temperature. Firstly, electrochemical measurements were performed in 0.1 mol L⁻¹ NaOH solution prepared with ultrapure water to determine the Au electrochemical surface area via oxide reduction charge, due to the weak hydrogen adsorption/desorption on Au surface. For calculate the Au/C surface area it was considered the oxide reduction peak at around 1.05 V vs. RHE, considering a conversion factor of 386 $\mu\text{A cm}^{-2}$ for polycrystalline Au²³.

Afterwards alcohol oxidation on Au/C electrode was performed in 0.1 mol L⁻¹ NaOH + 0.1 mol L⁻¹ of alcohol (glycerol, 1,2-propanediol and 1-propanol) solutions.

All the electrochemical experiments were conducted with a computer-controlled potentiostat (Solartron 1285, controlled by Core software). Cyclic Voltammetry (CV) was carried out in the range of 0.05 to 1.5 V vs. RHE at 50 mV s⁻¹ with O₂-free solution. FTIR spectroscopy experiments were carried out in a Nicolet Nexus 670 spectrometer equipped with a liquid nitrogen cooled MCT detector. *In situ* experiments were performed in a three-electrode spectro-electrochemical cell with an IR transparent window (CaF₂) attached to the bottom of the cell. More information concerning the cell are described elsewhere²⁴. Briefly, a movable piston supports the working electrode. Gold wire connected to the working electrode passes through the piston and keeps the electric contact. The CaF₂ window function as a transparent cover for the cell and, also, as a wall against which the working electrode is pressed to obtain a thin film of the electrolytic solution. The working electrode was prepared by depositing an ultrathin layer of catalyst ink (same as used in the conventional electrochemical experiments) over a glassy carbon disk attached to the piston of the cell. In such a way, during the FTIR measurements, the absorption of the infrared

beam by solution is minimized. FTIR spectra were taken in the wavenumber region between 1000 and 4,000 cm^{-1} , and in the range of 0.05 to 1.5 V vs. RHE at 2.0 mV s^{-1} . An average spectra was recorded for each 0.1 V of sweeping, and the first one (between 0.05 and 0.15 V) was taken as background. The spectra resolution was set to 4 cm^{-1} . Reflectance spectra were calculated as the ratio (R/R_0) where R represents a spectrum at the sample potential and R_0 is the spectrum collected at 0.05 V. Positive and negative bands represents the consumption and the production of substances at the sample potential, respectively.

3. Results

3.1. Characterization of the gold nanoparticles supported on Vulcan carbon

The mean size and corresponding particle size distribution and average size of gold nanoparticles on Vulcan carbon support were evaluated from TEM images, displayed in Fig. 1a. Images showed that gold nanoparticles have spherical shape and are distributed over the carbon substrate. Au/C powder presents non-agglomerated gold nanoparticles; one can identify nanoparticles in the range of 3 to 14 nm, according to account for statistical size distribution (Fig. 1b). According to Garcia et al.²⁵ during the Au reduction process, Au nuclei form rapidly, favoring a larger dispersion of the Au nuclei onto to the substrate. The variation of the gold nanoparticles size is probably due to the absence of stabilizer in the reaction medium during the synthesis, many studies have reported the use of PVP as stabilizer agent, nevertheless researchers have already shown that the presence of PVP may interfere in the catalytic activity^{26,27}. Thus, the PVP could be beneficial if removed after the synthesis process. However, some studies showed that the commonly cleaning procedures are not enough to remove it²⁸.

Figure 1

XRD pattern for Au/C catalyst are presented in Fig. 2 Spectra show the typical reflection of face centered cubic (fcc) crystalline structure of gold²⁹ with the absence of any metal oxide reflection. Considering the (220) crystallographic plane we estimated the average crystallite size by application of the Scherrer's equation²². The absence of broad peak evidences large crystallite size of gold nanoparticles. The crystal size value is close to 19 nm, typical value obtained by this metal nanoparticles synthesis route²⁵. The presence of large crystal can be explained in terms of a large growth of the metal nuclei in the absence of a capping protecting agent³⁰. Indeed, controlled particle sizes by chemical reduction with glycerol can be easily achieved under the presence of polyvinylpyrrolidone (PVP) as “protecting” agent³.

Figure 2

We observed that the crystallite size obtained by XRD were higher than the particle size measured by TEM. It can be due to the portion of the sample that each technique analyses. Whereas TEM scans only a small area of the sample, XRD takes an average of a great portion. Thus, an isolated big crystallite could interfere in the average result.

As already mentioned, EDS technique was used to evaluate the amount of metal (gold) on Vulcan carbon. Analysis showed that the amount of metal is near to the nominal values, which was around 18 wt. % of metal dispersed on the carbon, indicating that the glycerol is efficient as reducing agent in the synthesis of catalysts.

3.2 Electrochemical oxidation of alcohols on Au/C in alkaline medium.

Figure 3

Cyclic voltammogram profile for Au/C electrocatalyst in alkaline medium is showed in Fig. 3a. The small peak at around 1.3 V is assigned to the oxide formation film. The reverse scan peak is attributed reduction of the oxides of gold a potential of about 1.05 V³¹ of a few monolayers of Au(OH)₃ and Au³⁺ species. It is possible to note that the profile is not well defined probably because Au nanoparticles are surrounded by a carbon layer.

Fig. 3b shows typical voltammograms recorded during the electro-oxidation of 0.1 mol L⁻¹ 1-propanol, 1,2-propanediol and glycerol in alkaline medium (0.1 mol L⁻¹ NaOH). For all curves, in the positive going scan, there are: a peak that starts at the “onset potential” (we consider the potential value that the oxidation current reaches the double of the background current), then rises to a maximum value called “peak potential - E_p” and subsequently drops near to zero, due to oxidation of the electrode surface. In the negative going scan, the electrode surface is reactivated due to reduction of oxides and the current arises again, leading to another peak that is smaller than that observed in the positive going scan. The onset potential for 1-propanol oxidation is around 0.9 V vs. RHE. The peak potential occurs at 1.14 V and the maximum current obtained was 5.8 mA cm⁻². The reactivating of the electrode occurs at 1.1 V and the current was about 0.74 mA cm⁻². Similar voltammogram

profile was obtained for electro-oxidation of 1,2-propanediol on Au/C electrocatalyst (Fig. 3b), where the onset potential for oxidation occurs at 0.7 V vs. RHE, that means 200 mV lower than the onset potential for 1-propanol oxidation. The maximum current density obtained for 1,2-propanediol oxidation was 67 mA cm^{-2} at 1.2 V. The reactivating of the electrode surface occurs close to 1.2 V and the maximum current density was about 23 mA cm^{-2} .

For glycerol electro-oxidation, in the anodic potential scan the onset potential is around 0.6 V vs. RHE, about 300 mV lower than the onset potential for 1-propanol and 100 mV lower than 1,2-propanediol. The peak current occurs at 1.2 V and the maximum current density was 120 mA cm^{-2} . The reactivation in the negative going scan occurs around 1.1 V and the maximum current density was about 72 mA cm^{-2} . Thus, the glycerol shows the best performance of electrooxidation among the studied alcohols. This is in agreement that the peak currents depend on the number of hydroxyl groups in the molecular chain: the more hydroxyl in a molecule, the higher the peak current^{32,33}. Lamy et al.³² showed that the presence of two vicinal OH groups seems to favour the adsorption of two adjacent carbons and probably the breaking of C-C bond, leading to higher current densities. Furthermore, the results showed in Fig. 3 corroborates with results obtained by Koper et al.⁵, lower the pKa of alcohols higher the oxidation reactivity. They conclude that the alcoholate is the electroactive specie, so lower is the pKa, higher is the dissociation that leads to alcoholate anion. It is known that molecules with more OH species (consequently lower pKa) have greater oxidative activity. Therefore, glycerol (pKa = 14.1) shows to be more reactive molecule compared to 1,2-propanediol (pKa = 14.9) and 1-propanol (pKa = 16), in alkaline medium⁶. Both higher current density and lower onset potential evidence better interaction between glycerol and gold metal surface, compared to other alcohol.

3.2.1 *In situ* Infrared Spectroscopy Measurements

Fig. 4. displays FTIR spectrum for Au/C, obtained during the electro-oxidation of three different polyalcohols: 1-propanol (A), 1,2-propanediol (B) and glycerol (C), in the wavenumber region ranging between 1,000 and 2,500 cm^{-1} .

Figure 4

Common features can be observed in the three sets of spectra. In potentials higher than 0.75 V absorption bands relative to products formation start appears. However, at lower potentials no faradaic current in the voltammograms (Fig. 3), is observed indicating that no pre-adsorption steps are present. It was already suggested that oxidation of glycerol over gold in alkaline medium leads directly to more oxidized products, *i.e.* glycerate, without preceding by steps that leads to less oxidized ones, *e.g.* glyceraldehyde⁵. Afterwards, the higher potentials show bands of products between 1000 and 1600 cm^{-1} that do not change with the increasing potential, but only grow in intensity. In addition, they did not showed bands of CO (1850 or 2060 cm^{-1})^{34,35} or CO₂ (2343 cm^{-1})^{36,37} in all range of potential. Although the set of spectra for 1-propanol (Fig. 4a) seems to be complex at first time, they are identical to the spectra of propanoate ion, growing in intensity from 0.95 V to higher potentials. The absence of other bands suggests that propanoate ion is the only major product of 1-propanol electrooxidation over Au/C. This is a strong evidence that no C-C bond breaking occurs during electrooxidation of 1-propanol over Au/C. Janata et al.³⁸ mentioned that the main step for the n-propanol oxidation is its dehydrogenation. Afterwards, the dehydrogenated specie is further oxidized to propionic acid. However, González-Velasco et al.³⁹ showed that no traces of corresponding propionate ion were obtained

in the n propanol oxidation on gold in basic solution. These results are in agreement with the FTIR data obtained.

A different behavior was obtained for 1,2-propanediol electrooxidation (Fig. 4b). Absorption bands at 1,550 and 1,417 cm^{-1} are assigned for acetate ion, while the sharp peaks at 1,720, 1,360, 1,190 and 1,090 cm^{-1} suggest the formation of hydroxyacetone. The formation of acetate indicates the breaking of the C-C bond, leading to the formation of one carbon compounds, like formate ion, due the presence of bands at 1,580 and 1,350 cm^{-1} overlapped with bands assigned for acetate and hydroxyacetone ions. At the same time, bands of 1,2-propanediol consumption are detected at 1,138, 1,089 and 1,043 cm^{-1} . González-Velasco et al.⁴⁰ studied the mechanism of electrooxidation of 1,2- propanediol on a gold electrode in an alkaline electrolyte by Nuclear Magnetic Resonance (NMR) after different periods of electrolysis. Lactate, acetate and formate ions were identified as stable reaction products. In addition, 1,2-propanediol oxidation may proceed along two different pathways, via 2- hydroxypropanal and via hydroxyacetone. Methylglyoxal may be formed by further hydroxyacetone oxidation and then partially transformed into the anion of lactic acid. After cleavage of the C-C bond in the anions of pyruvic and lactic acid, anions of formic, acetic and carbonic acid may be formed. This fact is confirmed by the formation of acetic acid and CO, in the oxidation of pyruvic acid on gold^{16, 40,41}. The formation of these products is also possible by rupture of the C-C bond in -CO-COH, -COH-CHO and -COH-COOH groups⁴⁰. The FTIR sets of spectra indicate that the 1,2-propanediol oxidation on Au/C occurs via hydroxyacetone with subsequent rupture of the C-C bond leading to acetate ion.

For glycerol electro-oxidation on Au/C electrocatalyst (Fig. 4c), all spectra starting from 0.85 V show a band at 1,580 cm^{-1} and a pair at 1,350 and 1,380 cm^{-1} , typical of formate ions. Another band less intense at 1,308 cm^{-1} indicates the

formation of oxalate ion. The band at $1,047\text{ cm}^{-1}$ is feature of glycerol consumption, it starts to appear at the same potential that the first band related to formate and oxalate ions, suggesting that formic acid and oxalate are the main products from glycerol electro-oxidation reaction catalyzed by Au/C⁴².

From an economic point of view, the oxalate produced by glycerol oxidation is interesting because it can add value to this alcohol.

In order to facilitate the understanding, Figure 5 summarizes the products formed from the electro-oxidation of alcohols studied C3 detected by FTIR spectroscopy.

Comparing the different C3 alcohols, is possible conclude that the presence of vicinal OH groups leads to C-C bond breaking, and oxidized products with 1 and 2 carbons atoms were observed. The same is not observed in n-propanol as described before. These *in situ* FTIR results are in agreement with the density current observed to each alcohol by voltammetry cyclic.

4. Conclusions

Green Au nanoparticles dispersed onto Vulcan carbon were successfully synthesized. TEM images showed that gold nanoparticles have spherical shape and are distributed over the carbon substrate with nanoparticles size in the range from 3 to 14 nm. Electrochemical results appointed that green gold nanoparticles has interesting catalytic activity. Glycerol electro-oxidation presented higher density current compared to 1,2-propanediol and 1-propanol, this seems to corroborate with Koper at al, lower the pKa of alcohols higher the oxidation activity. *In situ* FTIR spectrum showed different pathway for each alcohol. For glycerol electro-oxidation, the main byproducts from reaction were formate and oxalate ions, according to band at $1,580$

cm^{-1} , a pair at 1,340 and 1,380 cm^{-1} , and 1,308 cm^{-1} , respectively. Electro-oxidation of 1,2-propanediol leads to acetate (bands at 1,550 and 1,417 cm^{-1}) and hydroxyacetone ions (peak at 1,720 cm^{-1}) while the *in situ* FTIR spectrum for electro-oxidation of 1-propanol suggests that propanoate is the only the byproduct of 1-propanol electro-oxidation on Au/C.

In general, results showed that the increasing activities with presence of vicinal OH groups are associated with C-C bond breaking, leading to more oxidized products with 1 and 2 carbon atoms.

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CAPTIONS FOR FIGURES

Figure 1. TEM images (a) and related particle size distribution (b) of the Au/C catalysts.

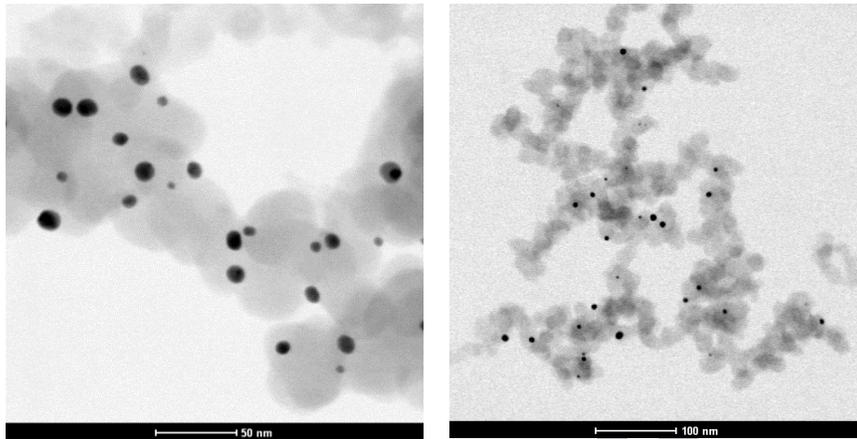
Figure 2. XRD spectra for Au/C catalyst.

Figure 3. Cyclic voltammograms for Au/C electrocatalysts. A) in NaOH 0.1 mol L⁻¹ and B) in NaOH 0.1 mol L⁻¹ + alcohols (glycerol, 1,2-propanediol and 1-propanol) 0.1 mol L⁻¹. Scan rate at 50 mV s⁻¹.

Figure 4. FTIR SPAIRS spectra for Au/C in NaOH 0.1 mol L⁻¹ + alcohols 0.1 mol L⁻¹. (a) 1-propanol, (b) propane-1,2-diol and (c) glycerol. Scan rate at 2.0 mV s⁻¹.

Figure 5: Possible reaction mechanism of the electro-oxidation of alcohols C3 in alkaline medium.

A



B

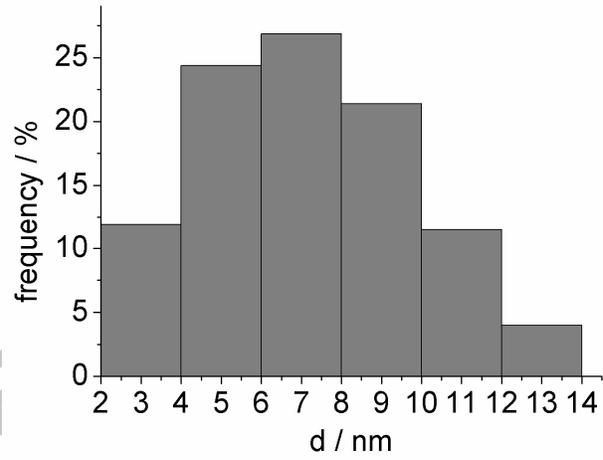
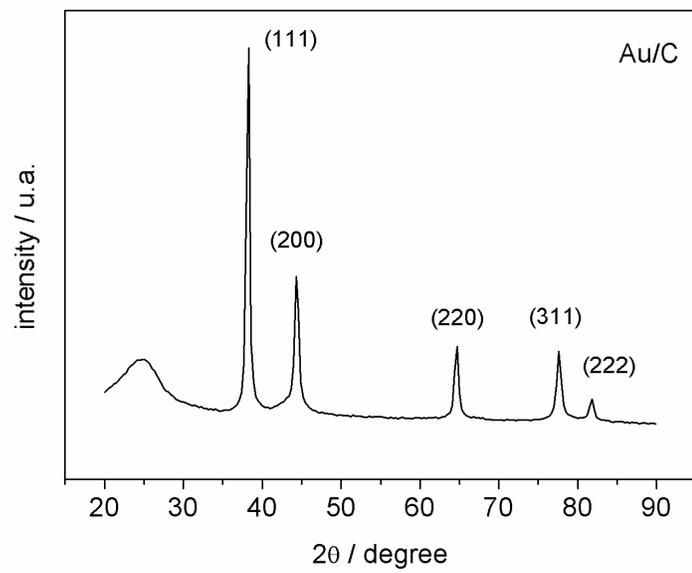


Figure 1

**Figure 2**

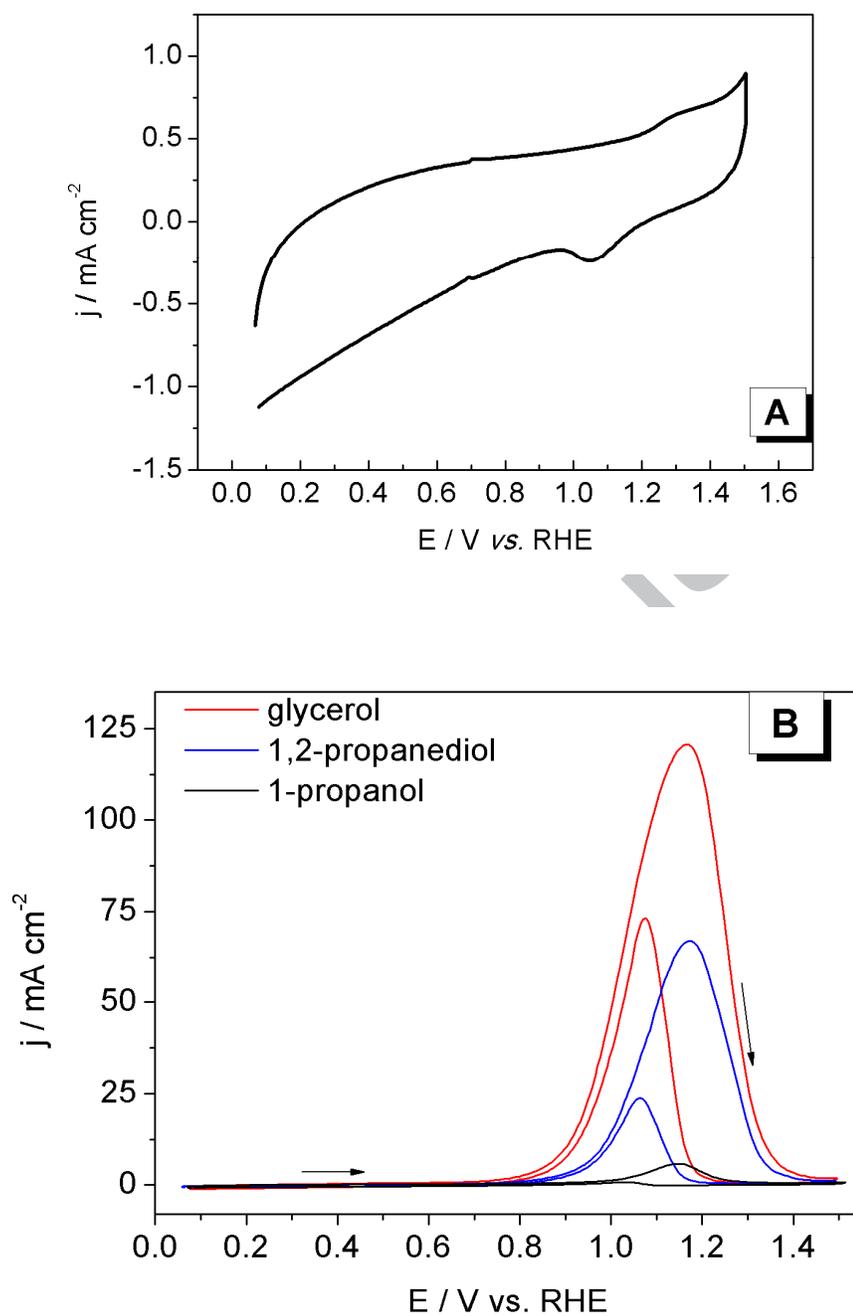


Figure 3

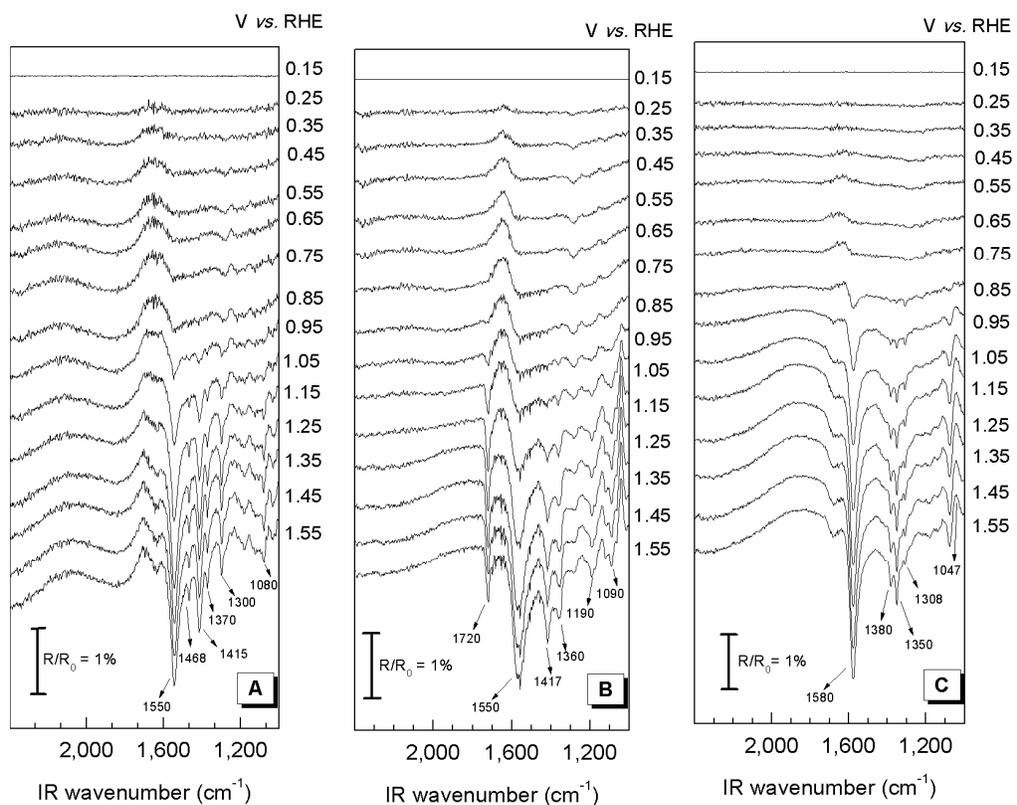


Figure 4

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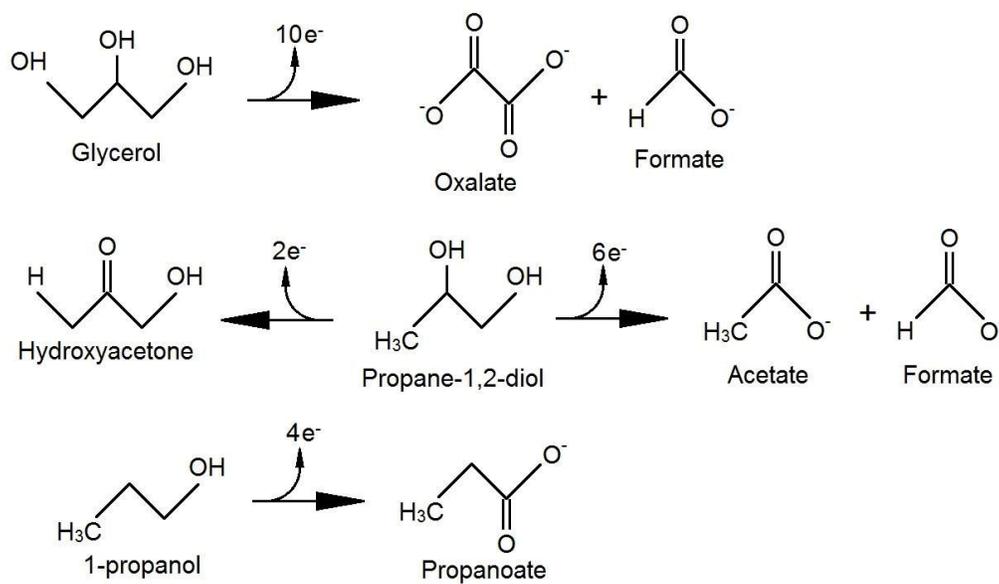


Figure 5

Research Highlights

- Au/C can be easily prepared by chemical reduction with glycerol.
- The electro-oxidation of C3 alcohols catalyzed by Au nanoparticles can lead to added value byproducts.
- The increasing in the activities are related with presence of vicinal OH groups are associated with C-C bond breaking.

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