Searching for Authentic Nano-electrocatalytic Effects:
A Joint Experimental and Computational Approach.
The Electrooxidation of Nitrite and of L-Ascorbate on Gold
Nanoparticle-Modified Glassy Carbon Electrodes

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Abstract

The investigation of electrocatalytic nanoeffects is tackled via joint electrochemical measurements and computational simulations. The cyclic voltammetry of electrodes modified with metal nanoparticles is modeled considering the kinetics of the electrochemical process on the bulk materials of the different regions of the electrode, that is, the substrate (glassy carbon) and the nanoparticles (gold). Comparison of experimental and theoretical results enables the detection of changes in the electrode kinetics at the nanoscale due to structural and/or electronic effects.

This approach is applied to the experimental assessment of electrocatalytic effects by gold nanoparticles (Au NPs) in the electrooxidation of nitrite and L-ascorbate. Glassy carbon electrode is modified with Au NPs via seed-mediated growth method. Divergence between the kinetics of these processes on gold macroelectrodes and gold nanoparticles is examined. Whereas claimed electrocatalysis are not observed in the electrooxidation of nitrite, electrocatalytic nanoeffects are verified in the case of L-ascorbate. This is probably due to that the electron transfer process follows an adsorptive mechanism. The combination of simulation with experiments is commended as a general strategy of authentication, or not, of nanoelectrocatalytic effects.

Keywords: electrocatalytic nanoeffects; gold nanoparticles; electrode modification; nitrite electrooxidation; L-ascorbate electrooxidation
1. Introduction

Extensive works are devoted to the development of nanotechnology with ground-breaking applications in (electro)catalysis [1,2], chemical analysis [3,4], medicine [5], material science [6],… Geometric and electronic features of materials can vary with size affecting their physical (electrical, optical, magnetic, mechanic) and chemical properties [2,7-9]. Understanding and controlling the behavior of nano-sized materials is essential for the efficient progress of nanoscience and it demands the development of methodologies for the preparation of structure-controlled nanoparticles (NPs) and the analysis of their characteristics.

In electrochemistry metal nanoparticles are widely employed for the modification of the electrode surface in order to develop (bio)sensors and energy production cells [1-4] as well as for environmental applications [10]. Nanoparticle-modified electrodes provide large effective surface area, enhanced mass transport and high control over local environment [4]. In addition, the reduction of the amount of material enables the decrease of fabrication costs and environmental impact. In many cases modification with nanoparticles just leads to the increase of the surface area without affecting the electrode kinetics with respect to the bulk material. The aim of this paper is identifying authentic nano-effects, that is, changes of the electron transfer kinetics at the nanoscale.

A widely-used strategy for electrode modification with metal nanoparticles is the drop-cast deposition of chemically prepared NPs. Synthesis of nanoparticles by reduction of a metal salt enables a better control of the size and structure of nanoparticles [11-13] though it often requires the use of capping agents that can alter the electrochemical response of both nanoparticles and substrate-electrode [14,15].

Regarding characterization techniques, transmission electron microscopy (TEM), scanning electron microscopy (SEM), scanning tunneling microscopy (STM), atomic force microscopy (AFM) and X-ray diffraction (XRD) are commonly employed [8]. Electrochemical methods are also valuable to obtain
information about metal nanoparticles [16,17] given that the electrochemical response of electrode processes is influenced by the properties of the electrode material. When the “particular” properties of nanosized materials give rise to enhanced electrode kinetics, electrocatalytic effects are observed. Major issues in nanoelectrochemistry are related to the detection of these effects and their relationship with structural and/or electronic properties of the nanosized material in comparison with the bulk material.

Many examples of electrocatalysis have been claimed in the literature when modifying electrodes with noble metal nanoparticles, such as gold, platinum and silver NPs [4]. Apart from the importance of understanding the nature of electrocatalysis, such effects are potentially very valuable in electroanalysis and energy production given that the triggering of the electrode reaction is facilitated. Moreover, the investigation of these phenomena can provide further insight into the factors governing electron transfer processes.

In most cases, electrocatalysis is tentatively identified from the reduction of the overpotential where the electrode reaction occurs and the increase of the magnitude of experimental voltammograms. Nevertheless, the corroboration of electrocatalytic effects must be carried out more carefully given that modification of electrodes involve changes in the electrode-solution interface that can mimic the effects expected when the electrode kinetics is enhanced [18-20]. For example, when porous layers are employed for the electrode modification, thin-layer diffusion of the electroactive species trapped between the layers takes place and gives rise to the shift of the voltammograms towards smaller overpotentials. Even in the case of bare electrodes modified with “naked” nanoparticles, the changes observed in the voltammograms might be explained simply by the response of an “array” of assembled nanoelectrodes with the same characteristics as the bulk material.

In this paper we tackle the detection of electrocatalytic nanoeffects by combining electrochemical experiments and computational simulations as summarized in the scheme shown in
Figure 1. Thus, the response of the electrode modified with nanoparticles is first simulated assuming that the particles “retain” the electrode kinetics of the bulk material; this enables us to predict the response in the absence of “nanoeffects”. Separately electrochemical experiments are performed with nanoparticle-modified electrodes, the characteristics of the modification being examined by electrochemical and imaging techniques. Finally, the comparison of simulated and experimental voltammograms enables the detection of differences between the kinetics at the bulk material and at the nanoparticles and, therefore, for revealing authentic nanoeffects.

The theory is applied to the study of two electrode processes of biological and industrial importance for which electrocatalytic effects by gold nanoparticles have been reported repeatedly [4]: electrooxidation of nitrite [21] and L-ascorbate [22-24] in aqueous solution. Modification of glassy carbon (GC) and indium tin oxide (ITO) electrodes with gold nanoparticles gives rise to significant shift of the voltammograms towards smaller overpotentials, which is commonly ascribed to electrocatalytic effects. The nature of these behaviors is investigated in this paper by comparing the theoretical response predicted in absence of nanoeffects with that obtained on a glassy carbon electrode modified with ca. 20-90 nm-diameter gold NPs via the seed-mediated growth method [11-13,25-27]. The comparison of the simulated and experimental results show that electrocatalysis is not observed for the electrooxidation of nitrite. On the other hand, the authentic enhancement of the electrooxidation kinetics of L-ascorbate on gold nanoparticles with respect to gold macroelectrodes is pointed out. The origin of such electrocatalytic nanoeffects is likely associated with the adsorptive mechanism of this electron transfer process.
2. Experimental

2.1 Chemical reagents

Sodium sulphate (>99%), sodium nitrite, sodium acetate trihydrate (>99%), acetic acid (>99%), sodium borohydride (98%), gold (III) chloride trihydrate (>99%), trisodium citrate (>99.0%), L-ascorbic acid (>99.0%), hexadecyltrimethylammonium bromide (CTAB), hydrochloric acid (37%), sodium hydroxide (>97%) and lead(II) nitrate (>99.5%), were all purchased from Sigma-Aldrich and used as received without further purification. All the solutions were prepared using deionised water with a resistivity 18.2 MΩ cm (25 ºC).

2.2 Electrode modification with gold nanoparticles

Seed-mediated growth method was used to modify a glassy carbon electrode (GCE) [11-13,25-27]. Glassy carbon electrode was polished with diamond paste (Kenet, Kent, UK) of deceasing size (3, 1 and 0.1 μm) and sonicated in ultrasound bath prior to use. The GCE was immersed in the gold seeding solution containing 18 mL water, 0.5 mL (0.01 M) trisodium citrate, 0.5mL HAuCl₄ (0.01M) and 0.5mL freshly prepared ice-cold NaBH₄ (0.1M) . After immersing in the seeding solution for 30 minutes, the electrode was sequentially rinsed by water and dried with nitrogen. Then the seeded electrode was immersed in the growth solution containing 18 mL CTAB (0.1 M), 0.5 mL HAuCl₄ (0.01 M), and 0.1 mL ascorbic acid (0.1 M) solutions for 2, 10 and 30 min to reach different coverages. The modified electrode was washed thoroughly with deionized water and dried under nitrogen atmosphere before electrochemical experiments.

2.3. Instrumentation

Electrochemical experiments were performed using a three-electrode system with an Autolab PGStat 20 computer-controlled potentiostat (Eco-Chemie, Utrecht, Netherlands). Platinum wire was
employed as counter electrode and the reference electrode was a saturated calomel electrode (SCE, Radiometer, Copenhagen). A bare or modified glassy carbon electrode (GC, 3 mm diameter, BAS, Technical, UK) and a bare gold electrode (1 mm diameter, BAS, Technical, UK) were used as working electrodes. The bare GC electrode was polished before use with diamond paste (Kenet, Kent, UK) of decreasing size (3, 1 and 0.1 \( \mu \text{m} \)). The gold electrode was polished prior to experiments on alumina lapping compounds (BDH) of decreasing size (1 – 0.3 \( \mu \text{m} \)). All of them were sonicated in ultrasound bath prior to use.

Scanning Electron Microscope (SEM) images were obtained on a JEOL 6500F FEGSEM. XPS spectra were recorded on a VG ESCALAB MkII spectrometer.
3. Theory

3.1. Reaction Schemes

The electrooxidation of the nitrite ion in aqueous solution at the working pH of 4.6 on both gold and glassy carbon electrodes is known to proceed by the second order catalytic (DISP2) mechanism [28,29]:

\[
\text{NO}_2^- \xrightarrow{k_2} \text{NO}_2 + e^- \quad (1)
\]

\[
2\text{NO}_2 + \text{H}_2\text{O} \xrightarrow{k_{\text{dis}}2} 2\text{H}^+ + \text{NO}_3^- + \text{NO}_2^- \quad (2)
\]

This process consists of charge transfer at the electrode surface followed by a second-order disproportionation reaction which partially regenerates the starting material (the nitrite ion).

The electrooxidation of L-ascorbic acid at the working pH of 6.8 proceeds by the following scheme [15,30,31]:

\[
\text{AH}^- \xrightarrow{k_1} \text{A}^- + \text{H}^+ + e^- \quad (3)
\]

\[
\text{A}^- \xrightarrow{k_2} \text{DHA} + e^- \quad (4)
\]

\[
\text{DHA} + \text{H}_2\text{O} \xrightarrow{k_{\text{dis}}} \text{HDHA} \quad (5)
\]

such that the two electron, one proton oxidation of L-ascorbate (AH) results in the initial form of dehydro-L-ascorbic acid (DHAA) which undergoes hydrolysis (the product of which can suffer further oxidation [15]). Accordingly, the above scheme has been modelled considering an EEC mechanism.

3.2. Numerical simulation

The simulation methods employed are as used previously by this group for hemispherical particles, [32] and heterogeneous surfaces [33], although this is the first time a simulation of an array of electroactive hemispherical particles on an electroactive surface has been performed. A detailed account of the simulation method is presented in the supporting information, but a summary of the important points is presented below.
Throughout this study, the substrate electrode used consists of a disc of glassy carbon (GC) modified with gold nanoparticles. The supporting glassy carbon substrate is ‘macro’ (radius = 1.5 mm); the size and number of the nanoparticles vary depending on the growing time and were typically in the range 20-90 nm diameter and 2x10⁸ – 6x10⁸ particles respectively. The nanoparticles are assumed to be hemispherical in shape, and the surface coverage by the particles, $\Theta$, is defined as:

$$\Theta = \frac{N \pi r_e^2}{A}$$  \hspace{1cm} (6)

where $N$ is the number of particles, $r_e$ is the radius of a single nanoparticle and $A$ is the area of the GC substrate. For the purposes of simulation, it is assumed that nanoparticles are of uniform size and that they are regularly distributed across the GC surface. Previous studies have demonstrated that for the time scale employed in this work there is little difference between the simulated voltammograms of arrays regularly and randomly distributed [34].

Computationally, the electrode is modelled in a 2-dimensional space through use of the diffusion domain approximation [35,36]. The Butler-Volmer equation with an applied potential waveform appropriate to cyclic voltammetry is used to model electrode kinetics and diffusion is determined by Fick’s second law which is discretised according the ADI method [37]. The simulation method employed allows the current response at each electroactive material (gold nanoparticle and GC electrode substrate) to be recorded separately. The resolution of the voltammetry into separate components in this manner allows for a greater insight into the mass transport phenomena present in the system.
4. Results and Discussion

4.1. Characterization of Au NP-modified GC electrodes

Electrochemical characterization of the modified electrode was carried out immediately following each experiment with nitrite or L-ascorbate. The total coverage of NPS, that is, the surface area of gold nanoparticles, was estimated by the lead deposition method developed by Hernandez et al. [38]. Underpotential deposition (UPD) is commonly used to characterize the electrode surface structure as it is sensitive to the arrangement of atoms. Lead UPD in alkaline solution has proved to be a suitable system to estimate the surface area and morphology of gold NPs [39].

Figure 2 shows the voltammetric profiles of bare glassy carbon and Au/GCE in the presence of 1 mM Pb(NO₃)₂ and 0.1 M NaOH. The surface area of gold nanoparticles can be determined from the stripping peaks. Au(111) contributes to the narrow and sharp stripping peak at potential -0.58 V (vs SCE) and 380 µC cm⁻² is the charge associated with the lead UPD process [38,39]. A broader stripping peak at -0.42 V (vs SCE) corresponds to Au(110) and Au(100) crystal planes. The charge associated with the lead UPD process have been reported to be 330 µC cm⁻² and 340 µC cm⁻² for Au(110) and Au(100) respectively [38].

Scanning electron microscope (SEM) images of the surface of the modified GC electrodes were also obtained in order to evaluate the size and distribution of the nanoparticles. The SEM images of Au/GC electrodes after a growing time of 30 min are shown in Figure 4. Gold nanoparticles show spherical shape, with an average size of ca. 40 nm diameter and a total number of ca. 10⁸ NPs (i.e., ca. 10⁹ NPcm⁻²). The SEM images also point out the monodispersity and even distribution of the particles on the GC surface.

The size of the particles was confirmed to increase during the growing time with an average diameter of ca. 20 nm after 2 min, 30 nm after 10 min, 40 nm after 30 min and 90 nm after 120 min. This gives rise to coverage values of nanoparticles in the range Θ =1 - 8 %.
4.2. “Side effects” of the electrode modification on the electrooxidation kinetics

The adsorption of the surfactant employed in the electrode modification (CTAB) on gold and carbon surfaces has been previously documented in the literature [15,40,41]. Accordingly, its effect on the electrooxidation kinetics of nitrite and L-ascorbate was evaluated in this work.

The effect on the electrooxidation of nitrite and L-ascorbate was examined by recording cyclic voltammograms of both processes on gold and glassy carbon macroelectrodes before (white points in Figure 4) and after immersion in 0.1 M CTAB solution for 30 min and rinse with distilled water (black points in Figure 4). As can be seen in Figure 4.A for nitrite and Figure 4.B for L-ascorbate, the CTAB treatment influences contrarily the electrochemical response on gold and glassy carbon, the kinetics being slowed down in the former and speeded up in the latter. Both effects are more apparent in the case of L-ascorbate giving rise to the “inversion” of the kinetics with respect to the bare electrodes. Thus, whereas at bare electrodes (white points) the process is faster on Au than on GC electrodes, the L-ascorbate electrooxidation is faster on GC than on Au after the “CTAB treatment” (white points). The greater sensitivity of the L-ascorbate electrooxidation to CTAB adsorption points out that the inner-sphere character of this electrode process is higher than the nitrite electrooxidation.

In order to take into account the above effects in our study, the kinetics of both electrooxidation processes were examined on “CTAB-modified” electrodes (referred as CTAB/Au and CTAB/GC hereafter). Thus, bare gold and GC macroelectrodes were immersed in a 0.1 M CTAB solution for a time equivalent to that employed in the growing step of the electrode modification. Then, the electrodes were thoroughly rinsed with water, placed into the nitrite or L-ascorbate solution and cyclic voltammograms were recorded at different scan rates between 50 and 500 mVs⁻¹. From the fitting of the experimental results with the simulation software DigiSim® the quantitative kinetic analysis of both systems was carried out according to the reaction mechanisms discussed in Section 3.1. The values of the diffusion coefficient employed in the simulations were 1.9x10⁵ cm²s⁻¹ for nitrite and 6.0x10⁶ cm²s⁻¹ for L-ascorbate,
both in good agreement with the values reported in the literature \[29,42-44\]. As representative cases, the kinetic parameters obtained after 30 min immersion in the CTAB solution (0.1 M) are given in Tables 1 and 2.

The origin of the contrasting behaviour on gold and GC electrodes was further investigated by examining the adsorption of CTAB on the GC and gold electrode surfaces via X-ray photoelectron spectroscopy (XPS). The spectra of GC electrodes (see Supporting Information) after immersion in 0.1 M CTAB solution for 30 min clearly show the peaks of N1s and Br, confirming the adsorption of CTAB on GC surfaces. In the case of gold electrodes, the presence of Br on the surface was also confirmed (see Supporting Information). On the other hand, the results for N1s were not conclusive since peaks in the binding energy region of nitrogen were observed on gold samples both before and after the CTAB modification. In view of this, cyclic voltammograms were recorded after immersing the gold electrode in a 0.1 M NaBr solution in order to assess the effect of the bromide adsorption on the electrooxidation processes. The effect on the experimental voltammograms (see Supporting Information) was similar to those obtained after immersion in CTAB solution (Figure 4), that is, the shift of the peaks to more positive potentials and smaller peak currents. This along with the XPS results suggests that the Br⁻ adsorption is the main responsible for the kinetic changes described above. Note that this is also in agreement with the contrasting behaviors observed for the electrooxidation kinetics on GC and Au electrodes after the CTAB treatment.

4.3. Electrooxidation of nitrite on Au NP-modified GC electrodes: no nanoelectrocatalysis

Nitrite solutions were prepared at pH 4.6 with a buffer solution containing acetic acid and sodium acetate according to previous studies \[29\]. As can be observed in Figure 4.A, a single oxidative peak at 0.74 V (vs SCE) on CTAB/Au and 0.78 V (vs SCE) on CTAB/GC electrodes is obtained given that the reactant species (NO₂⁻) is regenerated in solution according to the DISP2 mechanism given by Eqs. (1)
and (2). The peak shows a higher density current on gold than on glassy carbon and it is situated at smaller overpotentials as corresponds to a more reversible process [29].

The experimental voltammograms obtained with the glassy carbon electrode modified with gold nanoparticles are shown in Figure 5 (circle points) for different coverage and scan rates. After the modification the shift of the voltammograms towards smaller overpotentials and the increase of the peak current are observed; the larger the gold NP coverage, the more apparent the changes in the voltammetry.

The experimental results were compared with the simulations obtained considering the gold coverage on the GC electrode and the kinetic parameters obtained for bare glassy carbon and gold electrodes (black solid line). In all cases the agreement between experimental and theoretical results is good. The theoretical contributions of the gold nanoparticles (red line) and the GC substrate (gray line) are also plotted. Note that the peaks of both components are situated at similar potentials given that the electrode modification shifts the peak corresponding to the GC component with respect to the bare GC electrode as a result of the consumption of electroactive species by the Au NPs. As expected, the NP component increases with the coverage from 40% for $\Theta = 2\%$ up to 70% for $\Theta = 6\%$ such that the responses obtained are representative and informative about the nanoparticle properties.

From the good agreement of experimental and simulated voltammograms changes in the electrode kinetics of the electrooxidation of nitrite between the bare gold macroelectrode and the gold nanoparticles cannot be inferred. Accordingly, electrocatalytic nanoeffects can be discounted for the conditions of this study given that the electrochemical response observed agrees with that expected for a heterogeneous electrode with two spatial zones of different kinetics, i.e., the glassy carbon substrate and the gold nanoparticles.
4.4. Electrooxidation of L-ascorbate on Au NP-modified GC electrodes: nanoelectrocatalysis

The study of the electrooxidation of L-ascorbic acid was carried out at pH 6.8 (0.1 M PBS). A single oxidative peak at 0.18 V (vs SCE) on CTAB/Au and 0.13 V (vs SCE) on CTAB/GC electrodes is observed corresponding to the two-electron oxidation of L-ascorbate. According to the scheme given by Eqs. (3)-(5), the product of the electrode reaction undergoes hydrolysis and no reductive peak is observed at the scan rates employed (v = 25−100 mVs⁻¹).

According to the results shown in Figure 4.B assuming that the reactivity of L-ascorbate is the same on gold at both the macro- and nano-scales, the modification of GC electrode with Au NPs by seed-mediated growth method is not expected to have a catalytic effect on the response (i.e., increase of the current and decrease of the overpotential) given that the electrode reaction is slower on CTAB/Au. Indeed, the results obtained from digital simulations (see Figure 6.A) show that the cyclic voltammetry is not predicted to be affected by the modification with Au NPs. On the other hand, the experimental results show the shift of the voltammogram towards smaller overpotentials and greater current densities after the electrode modification; the greater the coverage, the more apparent these effects (Figure 6.B). This indicates that the electrode kinetics on the gold nanoparticles is faster than on gold macroelectrode and so the occurrence of electrocatalytic nanoeffects is verified.

Possible reasons of the electrocatalysis can be found attending to that electrooxidation of L-ascorbic acid is structure sensitive and significant differences between the voltammetry on polycrystalline gold electrodes and single crystal electrodes have been reported [15]. Accordingly, the electrocatalytic effects observed can be due to a change of mechanism (i.e., of the relative rates of the two electron transfer steps) associated with the surface structure of gold nanoparticles [45,46]. However, nanoeffects related to particular electronic properties of the nanoparticles should also be considered. The quantitative comparison of the kinetics at gold nanoparticles and single crystal
electrodes is of great interest to elucidate these fundamental aspects. The electrochemical approach for assessment of nanoeffects here presented can contribute to this aim.
5. Conclusions

An electrochemical approach for the detection of nanoeffects has been developed. The electrochemical response of electrodes modified with nanoparticles (NPs) is modeled considering different electrode kinetics on the surface of the substrate-electrode and on the NPs. This enables the evaluation of kinetic changes of electrode processes associated with the use of nanosized materials and therefore the investigation of electrocatalytic nanoeffects.

The theory has been applied to the study of the possible electrocatalysis of the electrooxidation of nitrite and L-ascorbate by gold NPs. Glassy carbon macroelectrodes have been modified with Au NPs of 20-90 nm-diameter via the seed-mediated growth method. By comparison of experimental and simulated voltammograms it is inferred that no differences are observed between the kinetics of electrooxidation of nitrite on gold nanoparticles and on gold macroelectrodes. So, electrocatalytic nanoeffects under the conditions here considered can be discarded. On the other hand, the authentic enhancement of the kinetics of the electrooxidation of L-ascorbate by nano-gold has been confirmed.

The modification of the electrode can affect the surface of the substrate beyond the changes expected from the presence of the nanoparticles. Thus, the adsorption of the surfactant (CTAB) on glassy carbon affects the electrode kinetics of both electrooxidation processes which are faster after the CTAB-modification, particularly in the case of L-ascorbic acid. On the other hand, the bromide adsorption on gold electrodes gives rise to a decrease of the degree of reversibility, although this effect is less apparent than that due to CTAB adsorption.

Acknowledgements

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Table 1. Kinetic parameters for the electrooxidation of nitrite on gold and glassy carbon electrodes after immersion in CTAB solution 0.1 M for 30 minutes. The values are obtained from fitting of experimental cyclic voltammograms at different scan rates: 50-500 mVs⁻¹. See scheme given by Eqs. (1) and (2).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>k⁰ / cm s⁻¹</th>
<th>α</th>
<th>E₀ / mV (vs SCE)</th>
<th>k_{disp} / M⁻³s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB/Gold</td>
<td>0.075</td>
<td>-</td>
<td>776</td>
<td>2.0×10⁶</td>
</tr>
<tr>
<td>CTAB/Glassy carbon</td>
<td>0.013</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Kinetic parameters for the electrooxidation of L-ascorbate on gold and glassy carbon electrodes after immersion in CTAB solution 0.1 M for 30 minutes. The values are obtained from fitting of experimental cyclic voltammograms at different scan rates: 25-100 mVs\(^{-1}\). See scheme given by Eqs (3)-(5).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>(k^0 \times \exp\left(-(1-\alpha)E^o F/RT\right)/\text{cms}^{-1})</th>
<th>(\alpha)</th>
<th>(k / \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB/Gold</td>
<td>4.40\times10^{-4}</td>
<td>1.47\times10^{-4}</td>
<td>0.54</td>
</tr>
<tr>
<td>CTAB/Glassy carbon</td>
<td>2.79\times10^{-4}</td>
<td>1.47\times10^{-2}</td>
<td>0.54</td>
</tr>
</tbody>
</table>
FIGURES

**Figure 1.** Approach followed in this work for the detection of nanoelectrocatalysis of the electrooxidation of nitrite and L-ascorbate by gold nanoparticles combining electrochemical measurements with computational simulations.

**Figure 2.** Cyclic voltammogram corresponding to lead deposition on gold nanoparticles deposited on GC electrode in 1 mM Pb(NO$_3$)$_2$ and 0.1 M NaOH solution. Scan rate: 50 mV s$^{-1}$.

**Figure 3.** Scanning electron microscopy images of a glassy carbon electrode modified with gold nanoparticles by seed-mediated growth method with a growing time of 30 min.

**Figure 4.** Effect of the immersion of the gold and glassy carbon electrodes in a CTAB solution on the electrooxidation of nitrite (A) and L-ascorbate (B). White points correspond to the bare electrodes and black points to the electrodes after 30 min immersion in a 0.1 M CTAB solution and rinse with water. Scan rate: 25 mV s$^{-1}$. Nitrite solution: 2 mM NaNO$_2$, 0.3 M Na$_2$SO$_4$, pH 4.6. L-ascorbate solution: 0.1 mM L-ascorbic acid, 0.1 M PBS, pH 6.8.

**Figure 5.** Experimental (points) and simulated (line) cyclic voltammograms corresponding to the electrooxidation of nitrite on CTAB/Au, CTAB/GC and Au-NP/GC electrodes at different scan rates and coverage (indicated on the graphs). Other conditions as in Figure 4.

**Figure 6.** Experimental (points) and theoretical (line) cyclic voltammograms corresponding to the electrooxidation of L-ascorbate on CTAB/Au, CTAB/GC (A) and on Au-NP/GC electrodes (B) at different coverage (indicated on the graphs). Scan rate: 100 mV s$^{-1}$. Other conditions as in Figure 4.
Kinetics on macro electrodes for electro-oxidation of nitrite or L-ascorbate

Modification of GCE with Au-NPs with different coverage

Characterization of Au-NPs/GCE

Experiments of electro-oxidation with Au-NPs/GCE of nitrite or L-ascorbate

Simulation using “macro” parameters

Change of kinetics of nanoparticles compared with bulk materials

“Positive nanoeffects”: Nanoelectrocatalysis

“Negative nanoeffects”

Does not fit

Fits

VS

No nanoeffects
Figure 2

![Cyclic voltammogram showing comparison between Au-NPs/GCE and GCE.](image)
Figure 3
Figure 4.A
Figure 4.B

![Graph showing the relationship between J (µA/cm²) and E vs SCE (V) for different samples (Au, Au after CTAB, GCE, GCE after CTAB).]
Figure 6.A

![Graph showing current density (J) vs. potential (E vs SCE) with three different data sets: GCE/CTAB (△), μ/CTAB (●), and Simulation (---).]
Figure 6.B

The figure shows a plot of current density ($J / \mu A/cm^2$) vs. potential ($E$ vs. SCE / V) with different coverage levels. The graph includes data points for 8% and 5% coverage, as well as a simulation curve.

- **8% coverage** represented by solid circles.
- **5% coverage** represented by diamond shapes.
- **Simulation** represented by a dotted line.

The plot indicates a peak in current density at specific voltages for each coverage level.
References


Supporting Information

1. Simulation Details

1.1. Electrode Kinetics

For the one-electron oxidation:

\[ A \xrightleftharpoons[k^0, \alpha, E^0]{\beta} B + e^- \]  

the flux of species 'A' normal to the electrode surface at a given applied potential \( E \) is described by the Butler-Volmer equation:

\[
D_A \frac{\partial [A]^o}{\partial x} = k^0 \left[ \exp \left( (1 - \alpha) \frac{F}{RT}(E - E_i^0) \right) [A]^o - \exp \left( -\alpha \frac{F}{RT}(E - E_i^0) \right) [B]^o \right] 
\]

where \( F \) is the Faraday constant, \( R \) is the gas constant, \( T \) is the temperature, \( x \) is a Cartesian coordinate normal to the electrode surface and \([i]^o\) refers to the concentration of the species \( i \) at the electrode surface \((x = 0)\). Given that \( E_i^0 \) is dependent on the redox couple and the surrounding medium, the use of different electrodes can result in a change in the rate constant \( k^0 \) and the transfer coefficient \( \alpha \) for the electrode reaction.

1.2. Numerical Simulation

Modelling the entire 3-dimensional ensemble of nanoparticles directly is not a realistic possibility, but certain assumptions and simplifications can be employed to give a highly accurate approximation. First it is assumed that for a given electrode, all of the nanoparticles are of the same size and are regularly distributed over the GC substrate. Now since the substrate is large and there are a large number of particles, differences due to the altered local environment at the edge of the disc can be considered negligible [1] and so the GC surface
may be treated as though it is composed of a vast array of identical unit cells, each centred around a single nanoparticle. Since each cell is identical, only one need be simulated with the results simply being scaled by the total number of nanoparticles on the GC surface. This is still a 3-dimensional problem (albeit much smaller) and is thus highly computationally demanding. Through the use of the 'diffusion domain approximation' [2,3] each unit cell is approximated as a cylindrical cell of the same area. Previous studies have demonstrated that simulations employing the diffusion domain approximation show very good agreement with experiments [4] and that there is little difference between the simulated voltammetry of arrays of regular and random distribution in most cases, the differences being only significant when very slow scan rates are employed (less than 10 mVs⁻¹) [5].

The use of the diffusion domain approximation renders the cell cylindrically symmetric and therefore allows it to be represented in a 2-dimensional cylindrical polar coordinate system as depicted in Figure S1, which is computationally tractable. The simulation space is therefore a 2D 'slice' of the unit cell with radial coordinate \( r \) and axial coordinate \( z \).

The simulation model is normalized using the dimensionless parameters shown in Table S1. The \((R,Z)\) coordinate system is defined relative to the hemisphere radius while the dimensionless time, \( T \), is defined in terms of the radius and the diffusion coefficient. In this normalized space, the surface of the hemispherical nanoparticle is described by:

\[
R^2 + Z^2 = 1 \quad \text{where } R, Z \geq 0
\]  

The 2-dimensional continuous space is discretized by dividing it up into a finite grid of spatial points as shown in Figure S2. The distribution of spatial points in the region of the nanoparticle is determined by specifying an angular increment \( \Delta \phi \), where \( \phi \) is the angle in radians measured from the \( R \) axis, and calculating the values of \( R \) and \( Z \) at each increment [6], from:

\[
R = \cos \phi \\
Z = \sin \phi
\]  

32
This allows grid points to fit precisely to the curved surface of the spherical particle. The grid spacing expands exponentially from the surface of the nanoparticle in both directions and contracts again in the $R$ direction as the outer boundary of the unit cell is approached, in order to ensure simulation accuracy.

### 1.2.1 Mass transport

As an excess of supporting electrolyte is added in each experiment, the effects of migration may be ignored, and the movement of chemical species in solution is attributed solely to diffusion down a concentration gradient. Diffusion may be modelled by Fick's second law in 2D cylindrical polar coordinates using our normalized coordinate system:

$$\frac{\partial C_i}{\partial T} = \delta_i \left( \frac{\partial^2 C_i}{\partial R^2} + \frac{1}{R} \frac{\partial C_i}{\partial R} + \frac{\partial^2 C_i}{\partial Z^2} \right)$$

where $C_i$ is the normalized concentration of species $i$, $T$ is the normalized time and $\delta_i$ the normalized diffusion coefficient of the species in question.

Homogeneous chemical reactions can be accounted for in the mass transport equation by introducing an additional term for each species involved in a chemical step. Therefore at some point in the solution ($R, Z$), at some arbitrary time, $T$, the rate of change of concentration of each chemical species is given by the sum of the diffusional and reaction terms:

**Nitrite electrooxidation**

$$\frac{\partial C_{NO_2}}{\partial T} = \delta_{NO_2} \left( \frac{\partial^2 C_{NO_2}}{\partial R^2} + \frac{1}{R} \frac{\partial C_{NO_2}}{\partial R} + \frac{\partial^2 C_{NO_2}}{\partial Z^2} \right) + K_{\text{disp}} C_{NO_2}^2$$

$$\frac{\partial C_{NO_3}}{\partial T} = \delta_{NO_3} \left( \frac{\partial^2 C_{NO_2}}{\partial R^2} + \frac{1}{R} \frac{\partial C_{NO_2}}{\partial R} + \frac{\partial^2 C_{NO_2}}{\partial Z^2} \right) - 2K_{\text{disp}} C_{NO_2}^2$$

$$\frac{\partial C_{NO_2}}{\partial T} = \delta_{NO_2} \left( \frac{\partial^2 C_{NO_2}}{\partial R^2} + \frac{1}{R} \frac{\partial C_{NO_2}}{\partial R} + \frac{\partial^2 C_{NO_2}}{\partial Z^2} \right) + K_{\text{disp}} C_{NO_2}^2$$
To perform simulations, the mass transport equation for each species is discretized to the grid of \((R, Z)\) spatial points using the well-known alternating direction implicit (ADI) method [7]. The resulting set of partial differential equations is non-linear, and so it is solved for each species at each successive time step using the iterative Newton-Raphson method [7], subject to the boundary conditions described below. Note that internally, these equations are represented in terms of a conventional set of normalised parameters which reduces the number of solutions by amalgamating parameters that act as scaling factors into parameters that do not.

### 1.2.2 Boundary Conditions and Potential Sweep

At the beginning of the simulation (i.e. \(T=0\)), the concentration of the starting species (\(\text{NO}_2^-\) and \(\text{AH}^-\)) is uniform and equal to its bulk value across the whole simulation space, and that of every other species is 0. In the \(Z\) direction, the simulation space extends as far as \(Z_{\text{max}} = 6\sqrt{T_{\text{max}}}\) where \(T_{\text{max}}\) is the length of time that the simulated experiment will run for. This
distance exceeds the maximum extent of the diffusion layer by the Einstein equation [8], and so the concentration at this point is set to its bulk value. As the system has mirror symmetry about the Z-axis, there can be no material flux through this boundary \((\rho=0)\) and so the boundary condition is simply one of zero flux \((\partial C_i / \partial \rho=0)\). Similarly, as each unit cell is identical, the boundary between them must also have zero flux of material across it.

Finally, both the surface of the Au nanoparticle and at the planar GC surface, a normalized version of the Butler-Volmer equation, described in Section 1, is used as a boundary condition, with different values of dimensionless rate constant, \(K^0\), for each material:

**Nitrite electrooxidation**

\[
D_{\text{NO}_2} \frac{\partial C_{\text{NO}_2}}{\partial N} = -D_{\text{NO}_2} \frac{\partial C_{\text{NO}_2}}{\partial N} = K^0 \left( C_{\text{NO}_2} e^{\beta \theta} - C_{\text{NO}_2} e^{-\alpha \theta} \right) \tag{13}
\]

**L-ascorbate electrooxidation**

\[
D_{\text{AH}} \frac{\partial C_{\text{AH}^-}}{\partial N} = K^0 \left( C_{\text{AH}^-} e^{\beta \theta} - C_{\text{AH}^-} e^{-\alpha \theta} \right) \tag{14}
\]

\[
D_{\text{A}^-} \frac{\partial C_{\text{A}^-}}{\partial N} = -K^0 \left( C_{\text{AH}^-} e^{\beta \theta} - C_{\text{A}^-} e^{-\alpha \theta} \right) + K^0 \left( C_{\text{A}^-} e^{\beta \theta} - C_{\text{DHA}} e^{-\alpha \theta} \right) \tag{15}
\]

\[
D_{\text{DHA}} \frac{\partial C_{\text{DHA}}}{\partial N} = -K^0 \left( C_{\text{A}^-} e^{\beta \theta} - C_{\text{DHA}} e^{-\alpha \theta} \right) \tag{16}
\]

where \(N\) is the spatial coordinate normal to the particle surface.

To simulate cyclic voltammetry, the dimensionless potential, \(\theta\), is swept from some initial value, \(\theta_{\text{initial}}\) to a more oxidising potential, \(\theta_{\text{final}}\) followed by a reverse sweep. At any time, \(T\), the value of \(\theta\) is given by:

**Forward**

\[\theta = \theta_{\text{initial}} + \sigma T\]  \tag{17}

**Backward**

\[\theta = \theta_{\text{final}} - \sigma (T - T_{1/2})\]  \tag{18}
where $\sigma$ is the normalized scan rate and $T_{1/2}$ is the time at which the sweep direction is reversed. The value of $\theta$ is then used in a normalized version of the Butler-Volmer boundary condition. The boundary conditions are summarized in Table S2.

1.2.3 Current Calculations

The normalized current of a single unit cell is the sum of the contributions from the Au nanoparticle and from the planar GC surface:

$$J_{\text{cell}} = 2\pi (J_{\text{Au}} + J_{\text{GC}}) \tag{19}$$

where $J_{\text{Au}}$ and $J_{\text{GC}}$ are related to the rate of consumption of electroactive material at the Au and GC surfaces respectively (see below). The factor of $2\pi$ is necessary because the simulation space is a 2D slice of the cylindrically symmetric unit cell. The total normalized current is equal the current of a single unit cell multiplied by the number of such cells, $N$. The real current may be obtained according to the relation shown in Table S1.

As the simulation grid is rectangular, the flux at each point on the surface of the nanoparticle is found by summing its components in the $R$ and $Z$ directions. The $J_{\text{Au}}$ value is then found by integrating over the surface:

$$J_{\text{Au}} = \delta \int_0^{\pi/2} \left( \frac{\partial C_i}{\partial R} \cos \phi + \frac{\partial C_i}{\partial Z} \sin \phi \right) \cos \phi \ d\phi \tag{20}$$

The $J_{\text{Au}}$ value is similarly found by integrating the particle flux over the whole surface:

$$J_{\text{GC}} = \delta \int_1^{R_{\text{max}}} \frac{\partial C_i}{\partial Z} \ R \ dR \tag{21}$$

The fact that the current response from each material of this composite electrode may be tracked individually can be very useful analytically.
1.2.4 Computation

Simulations were written in C++ with OpenMP for multithreading support and compiled using MSVC++. They were performed with a Dell Precision T5500 with two quad-core hyper-threaded Intel Xeon E5520 processors (16 logical cores, 2.23 GHz). The alternating direction implicit (ADI) method used for simulations in 2-dimensional space is particularly amenable to parallelization: at each time step, multiple calculations may be carried out simultaneously (provided the machine has multiple processor cores), which can decrease runtime considerably. A convergence study was run to determine optimum parameters for spatial and temporal grid densities which gave a good compromise between runtime and simulation accuracy. Typical simulation runtime was in the range 10-20 mins on the machine specified above.
**Table S1.** Dimensionless parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radial Coordinate</td>
<td>$R = \frac{r}{r_e}$</td>
</tr>
<tr>
<td>Normal Coordinate</td>
<td>$Z = \frac{z}{r_e}$</td>
</tr>
<tr>
<td>Time</td>
<td>$T = \frac{D_A t}{r_e^2}$</td>
</tr>
<tr>
<td>Butler-Volmer Rate Constant</td>
<td>$K^0 = k_0 \frac{r_e}{D_A}$</td>
</tr>
<tr>
<td>Concentration of species $i$</td>
<td>$C_i = \frac{c_i}{c_{A,\text{bulk}}}$</td>
</tr>
<tr>
<td>Diffusion Coefficient of species $i$</td>
<td>$\delta_i = \frac{D_i}{D_A}$</td>
</tr>
<tr>
<td>Potential</td>
<td>$\Theta = \frac{F}{RT} \left( E - E_r^0 \right)$</td>
</tr>
<tr>
<td>Scan Rate</td>
<td>$\sigma = \frac{F}{RT} \frac{r_e^2}{D_A} v$</td>
</tr>
<tr>
<td>First Order Rate Constant</td>
<td>$K_1 = \frac{k_r r_e^2}{D_A}$</td>
</tr>
<tr>
<td>Second Order Rate Constant</td>
<td>$K_{\text{disp}} = \frac{k_{\text{disp}} r_e^2 c_{A,\text{bulk}}}{D_A}$</td>
</tr>
<tr>
<td>Current</td>
<td>$J = \frac{1}{FD_A c_{A,\text{bulk}} r_e}$</td>
</tr>
</tbody>
</table>
### Table S2. Boundary conditions.

<table>
<thead>
<tr>
<th>Initial conditions</th>
<th>$T \leq 0$, all $R, Z$</th>
<th>$C_{\text{NO}<em>2} = C</em>{\text{AH}} = 1; C_{\text{others}} = 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bulk</strong></td>
<td>$Z = Z_{\text{max}}$</td>
<td></td>
</tr>
<tr>
<td><strong>Domain boundary</strong></td>
<td>$R = R_{\text{domain}}$</td>
<td>$rac{\partial C}{\partial R} = 0$</td>
</tr>
<tr>
<td><strong>Axial symmetry</strong></td>
<td>$R = 0$, $Z &gt; 1$</td>
<td></td>
</tr>
<tr>
<td><strong>Substrate surface (active)</strong></td>
<td>$Z = 0$, $R &gt; 1$</td>
<td>Butler - Volmer</td>
</tr>
<tr>
<td><strong>Particle surface (active)</strong></td>
<td>$Z^2 + R^2 = 1$, $Z, R &gt; 0$</td>
<td></td>
</tr>
<tr>
<td><strong>Substrate surface (inactive)</strong></td>
<td>$Z = 0$, $R &gt; 1$</td>
<td>$rac{\partial C}{\partial Z} = 0$</td>
</tr>
<tr>
<td><strong>Particle surface (inactive)</strong></td>
<td>$Z^2 + R^2 = 1$, $Z, R &gt; 0$</td>
<td>$rac{\partial C}{\partial Z} = \frac{\partial C}{\partial R} = 0$</td>
</tr>
</tbody>
</table>
Figures S1. Coordinate system of simulation space. The space is angularly isotropic so the coordinate \( \phi \) may be ignored, reducing the space to 2 coordinates: the radial coordinate, \( r \), and the axial coordinate, \( z \).
Figure S2. Discretization of the simulation space. Note the greater density of points at finite spatial boundaries (electrode surface and diffusion domain boundaries).
References


2. XPS results

Figure S3. XPS spectra corresponding to the glassy carbon electrode before (bottom) and after (top) immersion in a 0.1 M CTAB solution for 30 minutes.
Figure S4. XPS spectra corresponding to the gold electrode before (bottom) and after (top) immersion in a 0.1 M CTAB solution for 30 minutes.
3. Effect of the bromide adsorption

Figure S5. Effect of the adsorption of bromide on the gold electrode for the electrooxidation of nitrite (A) and L-ascorbate (B). White points correspond to the bare electrodes and black points to the electrodes after 30 min immersion in a 0.1 M NaBr solution and rinse with water.

Scan rate: 25 mV s\(^{-1}\). Nitrite solution: 2 mM NaNO\(_2\), 0.3 M Na\(_2\)SO\(_4\), pH 4.6. L-ascorbate solution: 0.1 mM L-ascorbic acid, 0.1 M PBS, pH 6.8