A kinetic study of oxygen reduction reaction and characterization on electrodeposited gold nanoparticles of diameter between 17 nm and 40 nm in 0.5 M sulfuric acid

Ying Wang, Eduardo Laborda, Kristopher R. Ward, Kristina Tschulik and Richard G. Compton*

Kinetic and mechanistic studies of the oxygen reduction reaction (ORR) in oxygen saturated 0.5 M sulfuric acid at 298 K at a gold macroelectrode and at an electrodeposited gold nanoparticle-modified glassy carbon electrode are reported. The conditions of electrodeposition are optimized to obtain small nanoparticles of diameter from 17 nm to 40 nm. The mechanism and kinetics of ORR on the gold macroelectrode are investigated and compared with those obtained for nanoparticle-modified electrodes. The mechanism for this system includes two electron and two proton transfers and hydrogen peroxide as the final product. The first electron transfer step corresponding to the reduction of \( \text{O}_2 \) to \( \text{O}_2^- \) is defined as the rate determining step. No significant changes are found for the nanoparticles here employed: electron transfer rate constant \( k_i \) is \( k_{0,\text{bulk}} = 0.30 \text{ cm s}^{-1} \) on the bulk material and \( k_{0,\text{nano}} = 0.21 \text{ cm s}^{-1} \) on nanoparticles; transfer coefficient \( (\alpha) \) changes from \( \alpha_{\text{bulk}} = 0.45 \) on macro-scale to \( \alpha_{\text{nano}} = 0.37 \) at the nano-scale.

1 Introduction

Nanoparticle-modified electrodes are widely used to improve the working efficiency of sensors and fuel cells due to the enhanced effective surface area, mass transport, high control over local environment and possible catalytic properties. Thus, change of electroactivity can be expected considering that nanoparticles may have altered electronic properties, surface structures and electron transfer kinetics with respect to the bulk material depending on their size. For example, there is a dramatic decrease of (111) facets in gold nanoparticles with size below 3 nm, whereas for particles with size bigger than 10 nm, the (111) facets are found to be predominant. White et al. have also suggested that there is a decrease of the density of states from bulk material to nanoparticles.

The above changes at the nanoscale can lead to different electrochemical behaviour on nanosized materials, so-called "nanoeffects". Electrocatalytic effects caused by noble metallic nanoparticles such as platinum, gold and palladium have been extensively studied. These refer to an enhanced electrochemical behaviour leading to the decrease of the signal overpotential and increase of its magnitude. However, the corresponding changes in mass transport also have to be considered when investigating electrocatalytic effects at the nanoscale because the diffusion field will change at nanoparticle-modified electrodes compared to the bulk material. For example, apparent electrocatalytic effects can be caused by thin-layer diffusion on porous film electrodes, where the electro-active species is trapped within pores on the electrode surface leading to the decrease of the overpotential of the voltammograms.

Wet chemistry synthesis and electrodeposition (Table 1) are two commonly used methods for synthesis of nanoparticles. In wet chemistry methods, nanoparticles are usually synthesised through seeding and growing steps. The first seeding process can follow either progressive or instantaneous nucleation. Progressive nucleation leads to broader size distributions because of nucleation and growth happening at the same time, while a more uniform distribution of the particle size is achieved by instantaneous nucleation on a shorter time scale. In the growth step, nanoparticles grow under either kinetic or diffusion control. The size of the nanoparticles under kinetic control conditions has a wider distribution compared to that in the diffusion controlled region. Instantaneous nucleation and diffusion controlled growth is the preferred method to achieve uniform size of nanoparticles. However, surfactants are usually employed in wet chemistry methods to control the particle size and stabilize nanoparticles. In our former study, the cetyl trimethylammonium bromide (CTAB) effect on the kinetics of electro-oxidation of nitrite and L-ascorbic acid...
was confirmed on gold and glassy carbon electrodes. Methods for removal of the surfactant can involve change of the surface morphology and loss or aggregation of nanoparticles. Therefore, an electro-deposition method without additives is employed in this paper to get surfactant-free nanoparticles.

A general experimental and simulation approach was developed to investigate the kinetics of electron transfer reactions on nanoparticles. Thus, the response of a nanoparticle modified electrode is simulated using the diffusion domain approximation and assuming that the particles are of uniform size and evenly distributed on the substrate surface. By fitting the experimental results with the mechanism determined for the bulk material, it is feasible to obtain the kinetics on nanoparticles. This approach was applied to two different systems: the electro-oxidation of nitrite, where authentic catalysis was found not to occur, and the electro-oxidation of L-ascorbic acid, which shows authentic nanocatalysis.

In this paper, the above strategy will be extended to the study of the oxygen reduction reaction (ORR) that has a very significant importance in biological processes and energy transformation, especially in fuel cells. Direct electrodeposition is employed in order to get surfactant-free gold nanoparticles with adjustment of the optimum conditions (concentration of gold salt, deposition time and potential) to control the size and number density of nanoparticles. The ORR kinetics is studied at the resulting modified electrode where, under the conditions of the present study, there is a negligible contribution from the supporting electrode, which provides a “clean window” for the study of the kinetics on nanoparticles. The absence of the distorting effect due to the capping agent or substrate enables an accurate and representative study of the kinetics on gold nanoparticles. Comparisons are made with the same process on gold macroelectrodes.

2 Results and discussion

2.1 Characterization of gold nanoparticles on glassy carbon electrodes

The characterization of Au-NPs/GCE has been performed by the electrochemical method proposed in former studies as well as by Scanning Electron Microscopy (SEM).

Regarding the electrochemical characterization, lead underpotential deposition (UPD) on gold nanoparticles and subsequent anodic stripping of gold in hydrochloric acid are employed to determine the total surface area and amount of gold, respectively. Lead UPD in alkaline solution has proved to be an effective method to estimate the surface area and morphology of gold nanoparticles. A typical cyclic voltammogram of a gold nanoparticle-modified glassy carbon electrode (solid line) and bare glassy carbon (dashed line) in the presence of 0.1 mM Pb(NO₃)₂ with 0.1 M NaOH is shown in Fig. 1. As reported by Hernandez et al., the sharp peak at around −0.56 V (vs. SCE) is assigned to the stripping of lead on the Au(111) crystal plane with a charge transfer per atom of 380 μC cm⁻². Au(100) and Au(110) crystal planes contribute to the broad peak that appears at around −0.39 V (vs. SCE). The charge associated is 340 μC cm⁻² (ref. 30) for the Au(100) plane and 330 μC cm⁻² (ref. 30) for the Au(110) plane.

The amount of electrodeposited gold nanoparticles is determined from anodic stripping of Au-NPs/GCE in 0.1 M HCl. According to previous studies, at the macroscale, the soluble complexes AuCl₂⁻ and AuCl₄⁻ will be formed during the oxidation process of gold in 0.1 M HCl. Our group extended this study to the nanoscale and found that the charge in the stripping process is related to the loading of gold nanoparticles with a value of 1.9 electrons transferred per gold atom. Fig. 2 shows the anodic stripping of a gold nanoparticle-modified glassy carbon electrode in 0.1 M hydrochloric acid. Normally three scans are sufficient to strip all the gold nanoparticles. Thus, by combining the results from lead UPD and anodic stripping,
the number and size of particles can be calculated from the following expressions:

\[ S = 2\pi r^2 \times N \]

\[ Q = 1.9 \times e \times N_A \times N \times \frac{x \times \pi r^3 \rho}{M} \]

where, \( x = 2 \) for hemispherical and \( x = 4 \) for spherical nanoparticles, \( e \) is the electron transfer charge, \( r \) is the average radius of nanoparticles, \( N \) is the number of particles, \( \rho \) is the density of gold, \( M \) is the molar mass of gold and \( N_A \) is the Avogadro constant. This simple and fast procedure has proven accurate in previous studies with chemically synthesized gold nanoparticles.\(^{28,29}\)

SEM has also been employed in the present study to evaluate the size and distribution of gold nanoparticles on the glassy carbon electrode. The SEM image in Fig. 3 shows the glassy carbon surface after electrodeposition for 30 s at \(-0.2 \) V (vs. SCE) in 0.1 mM HAuCl\(_4\) solution. The SEM images obtained have been analyzed with ImageJ software (1.47, National Institutes of Health, USA). The results show gold nanoparticles of rounded shape, evenly distributed on the glassy carbon surface, and with a diameter of 24 ± 9 nm and a total coverage \((= 100 \times N \pi r^2 / A \) where \( A \) is the glassy carbon area) of 8.4 ± 0.7%. The electrochemical characterization for Au-NPs/GCE under the same deposition conditions yields a particle diameter of 35 ± 10 nm; moreover, assuming that the particles are hemispherical, the coverage determined is of 8 ± 1%. These values agree acceptably well with the SEM ones, especially in terms of coverage, which is the factor that predominantly defines the electrochemical response under the conditions of the present study, that is, case 4 of diffusional behaviour to an array of nanoparticles.\(^{32}\)

2.2 The electrodeposition of gold nanoparticles on glassy carbon electrodes

A high density nanoparticle-modified electrode has been prepared by electrodeposition.\(^{17}\) In this method, the seeding and the growing laws of the wet chemistry method still operate but there is another variable in the growing procedure, that is, the Inter Diffusion Coupling (IDC). Deposition at large overpotentials promotes instantaneous nucleation\(^{17}\) and therefore small particle seeds. If a subsequent growing pulse is applied, IDC is found to be the main factor determining the distribution of particle size.\(^{16,17}\) The depletion layer of neighbouring nanoparticles will overlap and, therefore, the size of a nanoparticle strongly depends on the distance to and distribution of its neighbours. Later, Plieth\(^{33}\) and Penner\(^{16}\) found that the influence of IDC is negligible in the electrochemical kinetic controlled region. Forster et al.\(^{17}\) controlled particle size using a double-pulse technique. A first pulse was applied at large overpotentials to generate small seeds followed by a second pulse in the kinetic control region to reach slow growth avoiding generation of more seeds as well as IDC. In the present paper, only the first seeding pulse is applied in order to get smaller nanoparticles.
Fig. 4 depicts the cyclic voltammograms of electroreduction of HAuCl₄ on a bare glassy carbon electrode in 0.5 M H₂SO₄ containing 0.5 mM HAuCl₄. As can be seen, in the first reduction scan gold deposition on glassy carbon occurs at around 0.64 V (vs. SCE), the deposition peak shifting to lower overpotentials for about 70 mV in the second scan and finally stabilizing at 0.75 V (vs. SCE). This decrease in overpotential in subsequent scans points out that electrodeposition on gold deposit is more favourable than on carbon.¹⁷,⁹,¹¹,¹² The small reduction peak increased with scans at around −0.89 V (vs. SCE) may be related to the reduction of gold oxides formed in the reverse oxidation process in the repetitive scan.³⁴ According to these results, deposition potentials between −0.2 V and −0.5 V are chosen in the following studies to get instantaneous nucleation.

Besides the deposition potential, the AuCl₄⁻ anion concentration and the deposition time are the other two main variables in single pulse electrodeposition. Table 2A–C show the correlations between particle size and coverage with these three variables. Regarding the effect of deposition time, the results in Table 2A show that the influence on the particle number is more significant than on the average size. Thus, the particle size does not change significantly for deposition times between 30 s and 0.05 s while the coverage changes from 8% to 4%. Accordingly, increasing the deposition time will lead to a major effect on the number density of nanoparticles but not on the size of nanoparticles. Table 2B and C demonstrate that both concentration and potential are critical in controlling particle size and numbers. A slight decrease of size happens when the concentration drops. However, concentration can decrease the particle size only to a certain extent. A more significant decrease of particle size is achieved by increasing the overpotential which provides a large driving force for deposition. In Table 2C particle sizes smaller than 20 nm are achieved with a deposition potential around −0.5 V (vs. SCE). Deposition potentials more negative than −0.6 V were avoided due to hydrogen discharge.

In conclusion, small gold concentrations and large overpotentials are used for the synthesis of small nanoparticles.

### 2.3 Kinetic studies of the ORR on a polycrystalline bulk gold electrode

The oxygen reduction reaction (ORR) on metal electrode surfaces has been in the spotlight over recent decades.³⁵–⁵⁳ A number of mechanisms for ORR in acid media have been proposed and are still under debate.⁴²,⁵⁰,⁵¹ A series pathway including two electron transfer to hydrogen peroxide or an overall four electron transfer reaction to water is proposed depending on the solution conditions and electrode materials.⁴¹,⁴²,⁵⁰,⁵¹

On polycrystalline gold electrodes in strong acid media, the reduction of oxygen to hydrogen peroxide has been well reported.⁴² Therefore, the following mechanism will be employed in the simulations with the parameters shown in Table 3:

\[
\text{O}_2 + e^- \xrightarrow{k_{o1,1}E^o_{1/2}} \text{O}_2^- \quad (1)
\]

\[
\text{O}_2^- + \text{H}^+ \xrightarrow{k_{eq}k_{01}} \text{HO}_2^- \quad (2)
\]

\[
\text{HO}_2^- + e^- \xrightarrow{E^o_{2/3}} \text{HO}_2^+ \quad (3)
\]

\[
\text{HO}_2^- + \text{H}^+ \xrightarrow{k_{eq}k_{02}} \text{H}_2\text{O}_2 \quad (4)
\]

where, \(k_{0i}\) is the electron transfer rate constant for step \(i\); \(\alpha_i\) the transfer coefficient; \(E^o_i\) the formal potential; \(K_{eq}\) is the equilibrium constant and \(k_{fi}\) the forward rate constant.

### Table 2
Electrodeposition of HAuCl₄ in nitrogen saturated 0.5 M H₂SO₄ at 293.15 K: influence of deposition time (A), concentration (B) and deposition potential (C), surface coverage by nanoparticles (θ) in the table is defined as:

\[
\theta = \frac{N_r^2}{A^2} \times 100, \text{where } N \text{ is the number of particles, } r \text{ is the radius of a single nanoparticle and } A \text{ is the area of the GC substrate}^6
\]

<table>
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<tr>
<th>A</th>
<th>c/mM</th>
<th>Deposition potential/V (vs. SCE)</th>
<th>t/s</th>
<th>d/nm</th>
<th>θ/₀%</th>
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<tr>
<td></td>
<td></td>
<td>0.05</td>
<td>36 ± 1</td>
<td>3.8 ± 0.1</td>
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<table>
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<tr>
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<th>t/s</th>
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<tr>
<td>30</td>
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<tr>
<td></td>
<td></td>
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<td>24 ± 3</td>
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<td>44 ± 8</td>
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<td>35 ± 2</td>
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<td>22 ± 2</td>
<td>8 ± 1</td>
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</table>

* Error bars calculated from 3–20 experimental measurements.

### Table 3
Summary of kinetics of ORR in 0.5 M sulphuric acid at 298 K on a gold macroelectrode and a gold nanoparticle-modified glassy carbon electrode

<table>
<thead>
<tr>
<th>Gold macroelectrode</th>
<th>Au-NPs/GCE</th>
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<tbody>
<tr>
<td>Step 1</td>
<td>(k_{o1,1} = 0.30 \text{ cm}^{-1} \text{ s}^{-1}) (this work)</td>
</tr>
<tr>
<td>(E^o_{1/2} = −0.298 \text{ V (vs. SCE)}) (this work)</td>
<td>(E^o_{1/2} = −0.298 \text{ V (vs. SCE)}) (this work)</td>
</tr>
<tr>
<td>(\alpha_1 = 0.45) (this work)</td>
<td>(\alpha_1 = 0.37) (this work)</td>
</tr>
<tr>
<td>(pK_{a_{HO_2}} = 4.88) (ref. 36)</td>
<td>(pK_{a_{HO_2}} = 4.88) (ref. 36)</td>
</tr>
<tr>
<td>Step 2</td>
<td>(E^o_{2/3} = 1.19 \text{ V (vs. SCE)}) (ref. 60)</td>
</tr>
<tr>
<td>(pK_{a_{HO_2}} = 11.62) (ref. 54)</td>
<td>(pK_{a_{HO_2}} = 11.62) (ref. 54)</td>
</tr>
</tbody>
</table>
The first electron transfer (eqn (1)) leading to the formation of the superoxide ion is thought to be the rate determining step (RDS) regardless of the electrode material and medium. At low pH,\(^\text{42}\) this reaction is followed by fast protonation (step 2) and a further fully driven electron transfer step as shown in eqn (3).

The final product, hydrogen peroxide, is formed by rapid protonation of \(\text{HO}_2^-\), Gold has been acknowledged as having the least adsorption of the noble metals for oxygen species, although adsorption of intermediates, such as \(\text{O}_2^-\) and \(\text{HO}_2^-\), may still happen\(^\text{46,44,47,50}\) and there may be changes between macro and nanogold.

In this work, kinetic studies of ORR on a polycrystalline bulk gold electrode have been carried out in oxygen saturated 0.5 M sulfuric acid solution at 298 K (pH = 0.39). Thermostatic control is essential due to the fact that the solubility, diffusion coefficient and electron transfer kinetics are temperature sensitive. Determinations of diffusion coefficient and concentration are completed on a gold microelectrode \((r_o = 13 \, \mu\text{m})\) via potential step chronoamperometry through the Shoup and Szabo equation (Fig. 5).\(^\text{32}\) The values obtained for the diffusion coefficient and concentration are \((1.26 \pm 0.03) \times 10^{-5} \, \text{cm}^2 \, \text{s}^{-1}\) and \((1.43 \pm 0.02) \, \text{mM}\), respectively, which are in good agreement with the literature.\(^\text{43}\)

The kinetics of ORR on a polycrystalline bulk gold electrode in strong acid media is reported in Table 3 based on the mechanism proposed in eqn (1)–(4). Fig. 3 shows the experimental (solid line) and simulated (dashed line) voltammograms from 25 mV s\(^{-1}\) to 2000 mV s\(^{-1}\). The homogeneous kinetics for steps (2) and (4) are widely reported.\(^\text{46}\) The superoxide ion will protonate rapidly once after it is formed. Kastening and Divisek suggested step two to be diffusion-limited and the acid dissociation constant \(pK_a = 4.88\) for \(\text{HO}_2^-\).\(^\text{46}\) The homogeneous reaction four is also a fast protonation step (diffusion-limited) with \(pK_a = 11.62\) for hydrogen peroxide,\(^\text{44}\) so \(\text{HO}_2^-\) is consumed immediately. Moreover, considering the formal potential value of the redox couple \(\text{HO}_2/\text{HO}_2^-\) (see Table 3), it is expected that step 3 is fully driven, that is, \(\text{HO}_2^-\) is immediately reduced to \(\text{HO}_2\).

Based on the discussion above, the kinetics of step 1 determines the rate of the overall reaction. The standard redox potential for the couple \(\text{O}_2/\text{O}_2^-\) has been determined to be \(-0.21 \, \text{V (vs. SCE)}\) and more negative values for the formal potential of up to \(-0.434 \, \text{V (vs. SCE)}\) (Table 4) have been reported by different means such as thermodynamic calculations and electrochemical measurements. Using \(E^{\circ}_{\text{O}_2/\text{O}_2^-}/\text{C}_0\) and \(k_{o,1}\), as fitting parameters, the values \(E^{\circ}_{\text{O}_2/\text{O}_2^-}/\text{C}_0 = -0.298 \, \text{V (vs. SCE)}\), \(a_1 = 0.45\) and \(k_{o,1} = 0.30 \, \text{cm}^2 \, \text{s}^{-1}\) correspond to the best fitting of the voltammograms from 25 mV s\(^{-1}\) to 2000 mV s\(^{-1}\) shown in Fig. 6. Fig. 7 shows the voltammograms of ORR on Au-NPs/GCE (solid line) and bare GCE (dashed line) in oxygen saturated 0.5 M sulphuric acid at 100 mV s\(^{-1}\) and 298 K. As can be seen, the response from GCE is almost negligible in the range where ORR occurs on Au-NPs/GCE. This allows a more accurate study of the kinetics on the gold nanoparticles.

### 2.4 Kinetic studies of the ORR on Au-NPs/GCE

In the previous section, the kinetic and mechanistic study on bulk gold was reported. The next stage is to investigate the ORR kinetics on gold nanoparticles under the same experimental conditions. Au-NPs/GCE is prepared following the electrodeposition method discussed in Section 2.2. The coverage and size of nanoparticles for each particular Au-NPs/GCE are obtained using the electrochemical characterization method discussed in Section 2.1 immediately after investigation of oxygen reduction. Note that all the studies are based on the first voltammograms with freshly prepared Au-NPs/GCE. Subsequent scans were found to yield irreproducible results that may be due to the poisoning of the gold surface. Conventional cleaning methods of the gold macroelectrode with repetitive scans in nitrogen saturated sulfuric acid have been found to promote defects and alter the morphology of gold nanoparticles.\(^\text{35}\) Moreover, repetitive scans of Au-NPs/GCE in sulphuric acid can lead to detachment of nanoparticles.\(^\text{35,56}\)

A simulation program has been developed under the assumption of the diffusion domain approximation together with hemi-spherical nanoparticles of uniform size and evenly distributed on the substrate as detailed in ref. 28 and 57. The influence of different shape and size on the voltammograms has been investigated prior to the study. Comparison of

<table>
<thead>
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<th>(E^{\circ}_{\text{O}_2/\text{O}_2^-}/\text{C}_0) /V (vs. SCE)</th>
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<th>Ref.</th>
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<td>Tafel plot</td>
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<td>(-0.399)</td>
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<td>(-0.424)</td>
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**Fig. 5** Determination of diffusion coefficient and concentration of oxygen in oxygen saturated 0.5 M sulphuric acid solution at 298 K by Shoup and Szabo equation. The open circles denote simulation and the solid line denotes experiment.
simulated voltammograms of nanoparticles of different size with spherical, hemispherical and disk shapes showed negligible divergence for the conditions of this study, the response being defined almost exclusively by the nanoparticle coverage.

There are two steps in the following study of the ORR kinetics on gold nanoparticles. The first one is to identify whether there is a kinetic change with respect to the bulk material. If so, the second step is to obtain the new kinetics from fitting. The ORR response was recorded on nanoparticles of diameter from 17 nm to 40 nm with coverage from 6.5% to 12.8%. It is worth pointing out that, for suitable simulation, very high coverage should be avoided to prevent the formation of porous films on the electrode. Meanwhile, very low coverage is not preferred because the voltammograms will have a predominant contribution from the glassy carbon substrate. Comparison of experimental voltammograms (solid line) and simulation (open triangle) considering the coverage for nanoparticles and kinetics from bulk gold are shown in Fig. 8 (40 nm) and Fig. 9 (17 nm). It can be inferred that the fitting of the peak current is worse with the increase of the scan rate. Simulated voltammograms with new kinetics (solid circle) are shown in Fig. 8 and 9 from 25 mV s$^{-1}$ to 750 mV s$^{-1}$. Considering the whole range of scan rates, a higher quality fitting is achieved with the best fit parameters shown in Table 3. Fig. 10 shows the correlation of the experimental (open square) and simulated (solid square) peak potentials against natural logarithm of scan rate for a similar coverage (8%). A good linearity ($R^2 = 0.997$) is obtained for experimental data, and these are well fitted with the simulation. In Fig. 11, peak current is plotted as a function of square root of scan rate. A good agreement of experimental and simulated results can be seen. The experimental value $\alpha_{exp} = 0.36$ calculated from the slope of $I_p$ vs. $\sqrt{v}$ in Fig. 11 agrees with the value employed in the simulation of $\alpha_{sim} = 0.37$. 

**Fig. 6** Simulated (circle) and experimental (solid line) voltammograms on the gold macroelectrode in oxygen saturated 0.5 M sulphuric acid solution at 298 K from 25 mV s$^{-1}$ to 2000 mV s$^{-1}$. 

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The electrode kinetics on nanoparticles of diameter from 17 nm to 40 nm have been summarized in Table 3 based on the fitting from 25 mV s$^{-1}$ to 750 mV s$^{-1}$. The transfer coefficient ($\alpha$) changes from 0.45 on bulk material to 0.37 at the nanoscale. Adžić revealed that ORR shows different transfer coefficients ($\alpha$) at different crystalline planes: $\alpha_{(100)} = 0.49$, $\alpha_{(111)} = 0.34$ and $\alpha_{(110)} = 0.49$. Therefore, the change of $\alpha$ here may be related to the different domains of crystalline planes on the nanoparticles. Regarding the rate constant of electron transfer ($k_0$), this is slightly smaller on nanoparticles of diameter from 17 nm to 40 nm (0.21 cm s$^{-1}$) compared to the gold macroelectrode (0.30 cm s$^{-1}$). However, comparing the kinetics on bulk material and nanoparticles (see Table 3), one can infer that the change is not significant. Extraordinary electrocatalytic effects have been reported on gold nanoparticles smaller than 3–5 nm, for example, for the electro-oxidation of carbon monoxide and oxygen reduction reaction.

3 Experimental

3.1 Chemical reagents

Sulphuric acid (H$_2$SO$_4$, Fisher, >95%), gold(III) chloride trihydrate (HAuCl$_4$·3H$_2$O, Sigma-Aldrich, >99%), hydrochloric acid (Sigma-Aldrich, >37%), lead(II) nitrite (Sigma-Aldrich, >99.5%), and sodium hydroxide (Sigma-Aldrich, >97%) were all used as received, without further purification. All the solutions were prepared using deionised water with a resistivity of 18.2 MΩ cm (25 °C).

3.2 Instrumental

All electrochemical experiments were performed using a three-electrode system with an Autolab PGStat 20 computer-controlled potentiostat (Eco-Chemie, Utrecht, Netherlands). A platinum wire was employed as the counter electrode and a saturated calomel electrode (SCE, Radiometer, Copenhagen) was used as the reference electrode. A bare or modified glassy carbon electrode (GCE, 3 mm diameter, BAS, Technical, UK) or a bare gold electrode (2 mm diameter, BAS, Technical, UK) was
employed as working electrodes. The glassy carbon electrode was polished using 3.0, 1.0 and 0.1 μm diamond spray (Kenet, Kent, UK) and the gold electrode was polished with a decreasing size of 1.0, 0.3, 0.05 μm alumina lapping compounds (Bucher, Germany). All of them were sonicated in an ultrasound bath prior to use. Scanning Electron Microscopy (SEM) images were obtained on a LEO Gemini 1530 (Zeiss) using an in-lens detector and a beam voltage of 5 kV.

4 Conclusion
In this work, kinetic and mechanistic studies of oxygen reduction reaction (ORR) on a gold macroelectrode and on an electro-deposited gold nanoparticle (of diameter from 17 nm to 40 nm)-modified glassy carbon electrode have been completed in oxygen saturated 0.5 M sulphuric acid solution at 298 K. An overall ECEC mechanism with two electron, two proton transfers and hydrogen...
peroxide as the final product is found to be consistent with the experimental voltammetry. The first electron transfer step corresponding to the reduction of $\text{O}_2$ to $\text{O}_2^-$ is defined as the rate determining step. For this, the kinetics on the gold macro-electrode is obtained through the fitting of cyclic voltammetry in the range of 25 mV s$^{-1}$ to 2000 mV s$^{-1}$. $E^0_{\text{O}_2/\text{O}_2^-} = -0.298 \text{ V (vs. SCE)}$, $\alpha_{\text{bulk}} = 0.45$ and $k_0_{\text{bulk}} = 0.30 \text{ cm s}^{-1}$. Although these kinetic parameters do not enable to satisfactorily fit the voltammogram of the nanoparticles, the change of kinetics at the nanoscale is not significant, obtaining the following values: $\alpha_{\text{nano}} = 0.37$ and $k_0_{\text{nano}} = 0.21 \text{ cm s}^{-1}$.

Consequently, the electrochemical behaviour for the ORR system of electrodeposited gold nanoparticles of size between 17 nm and 40 nm is not significantly different from that on the bulk material. The small change of electrode kinetics from macro to nanoscale may indicate that gold nanoparticles in the range of diameter from 17 nm to 40 nm are not small enough to observe apparent nanoeffects. Therefore, it will be of interest to extend the strategy to the study of the electrocatalytic activity of smaller gold nanoparticles, where more significant changes of properties (surface site domain and electronic properties) are expected.

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References