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

Ying Wang, Kristopher R. Ward, Eduardo Laborda, Chris Salter, Alison Crossley, Robert M. J. Jacobs, and Richard G. Compton*

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 catalytic effects 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 authentification, or not, of nanoelectrocatalytic effects.

1. Introduction

Extensive works are devoted to the development of nanotechnology with ground-breaking applications in (electro) catalysis, chemical analysis, medicine, material science... Geometric and electronic features of materials can vary with size affecting their physical (electrical, optical, magnetic, mechanic) and chemical properties. 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 as well as for environmental applications.
Nanoparticle-modified electrodes provide large effective surface area, enhanced mass transport and high control over local environment.\textsuperscript{[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\textsuperscript{[11–13]} though it often requires the use of capping agents that can alter the electrochemical response of both nanoparticles and substrate-electrode\textsuperscript{[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.\textsuperscript{[8]} Electrochemical methods are also valuable to obtain information about metal nanoparticles\textsuperscript{[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 nanomaterial 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.\textsuperscript{[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.\textsuperscript{[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:\textsuperscript{[4]} electrooxidation of nitrite\textsuperscript{[21]} and L-ascorbate\textsuperscript{[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\textsuperscript{[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. Theory

#### 2.1. 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

\[
\text{NO}_2^- \overset{k_0}{\rightarrow} \text{NO}_2 + e^- \quad (1)
\]

\[
2\text{NO}_2 + \text{H}_2\text{O} \overset{k_{\text{disp}}}{\rightarrow} 2\text{H}^+ + \text{NO}_3^- + \text{NO}_2^- \quad (2)
\]

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:30-31

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

\[
\text{A}^- \overset{k_2}{\rightarrow} \text{DHA} + e^- \quad (4)
\]
DHA + H₂O $\xrightarrow{k^-}$ HDHA \hspace{2cm} (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). Accordingly, the above scheme has been modelled considering an EEC mechanism.

2.2. Numerical Simulation

The simulation methods employed are as used previously by this group for hemispherical particles, although this is the first time a simulation of an array 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 $2 \times 10^8$–$6 \times 10^9$ 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{2cm} (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.

Computationally, the electrode is modelled in a 2D space through use of the diffusion domain approximation. 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. 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 voltammogram into separate components in this manner allows for a greater insight into the mass transport phenomena present in the system.
3. Results and Discussion

3.1. 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.\textsuperscript{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.\textsuperscript{39} Figure 2 shows the voltammetric profiles of bare glassy carbon and Au/GCE in the presence of 1 mM Pb(NO\textsubscript{3})\textsubscript{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 $\mu$C cm\textsuperscript{-2} is the charge associated with the lead UPD process.\textsuperscript{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 $\mu$C cm\textsuperscript{-2} and 340 $\mu$C cm\textsuperscript{-2} for Au(110) and Au(100) respectively.\textsuperscript{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 3. Gold nanoparticles show spherical shape, with an average size of ca. 40 nm diameter and a total number of ca. $10^8$ NPs (i.e., ca. $10^8$ NP cm\textsuperscript{-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 and 40 nm after 30 min. Due to problems of aggregation\textsuperscript{40} the electrochemical approach could not be used for sizing the nanoparticles obtained with a growing time of 120 min. In this case, SEM images were employed determining a size similar to that for 30 min growing time (i.e., ca. 40 nm diameter). This is a consequence of the effect of the capping agent (CTAB), the adsorption of which on the nanoparticle surface slows down and eventually prevents its growth.

The above sizes of nanoparticles correspond to coverage values in the range $\Theta$ = 1–8%.

3.2. “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.\textsuperscript{15,41,42} 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
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 min. The values are obtained from fitting of experimental cyclic voltammograms at different scan rates: 50–500 mVs\(^{-1}\). See scheme given by Equations (1) and (2).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>(k_0)</th>
<th>(\alpha)</th>
<th>(E^\circ)</th>
<th>(K_{\text{disp}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB/Gold</td>
<td>0.075</td>
<td>–</td>
<td>776</td>
<td>2.0 \times 10^4</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 min. The values are obtained from fitting of experimental cyclic voltammograms at different scan rates: 25–100 mVs\(^{-1}\). See scheme given by Equations (3)–(5).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>(k_0) \times \exp \left( -\left(1 - \alpha \right) E^\circ / F \right) \text{[cm}^\text{s}^{-1}]</th>
<th>(\alpha)</th>
<th>(k) \text{[s}^{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB/Gold</td>
<td>4.40 \times 10^4 \times 1.47 \times 10^4</td>
<td>0.54</td>
<td>1.3 \times 10^3</td>
</tr>
<tr>
<td>CTAB/Glassy carbon</td>
<td>2.79 \times 10^4 \times 1.47 \times 10^2</td>
<td>0.54</td>
<td>–</td>
</tr>
</tbody>
</table>

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 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 2.1. The values of the diffusion coefficient employed in the simulations were 1.9 \times 10^7 \text{cm}^2\text{s}^{-1} for nitrite and 6.0 \times 10^6 \text{cm}^2\text{s}^{-1} for L-ascorbate, both in good agreement with the values reported in the literature.\(^{29,43-45}\) 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.

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-ascorbic acid, 0.1 M PBS, pH 6.8.

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3.3. 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. 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 (\( \text{NO}_2^- \)) is regenerated in solution according to the DISP2 mechanism given by Equations (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.

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

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**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.
3.4. 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 Equations (3)–(5), the product of the electrode reaction undergoes hydrolysis and no reductive peak is observed at the scan rates employed (v = 25 – 100 mV s^{-1}).

According to the results shown in Figure 4B 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 (see Figure 5 and Table 2); the greater the coverage, the more apparent these effects (see Figure 7). 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.[46,47] 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.

On the other hand, the experimental results with the modified electrodes show the shift of the voltammograms towards smaller overpotentials and greater current densities with respect to the theoretical predictions based on the kinetic parameters determined at the macroscale (Table 2); the greater the coverage, the more apparent these effects (see Figure 7). 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.

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Figure 6. Experimental voltammograms (points) corresponding to the electrooxidation of L-ascorbate on CTAB/Au and CTAB/GC. Simulated voltammograms (line) corresponding to 8% coverage are also plotted. Scan rate: 100 mV s^{-1}. Other conditions as in Figure 4.

Figure 7. Experimental (points) and simulated (line) voltammograms corresponding to the electrooxidation of L-ascorbate 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.
4. Conclusion

An electrochemical approach for the detection of nano-effects 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.

5. Experimental Section

5.1. Chemical Reagents

Sodium sulphate (>99%), sodium nitrate, 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 °C).

5.2. Electrode Modification with Gold Nanoparticles

Seed-mediated growth method was used to modify a glassy carbon electrode (GCE). Glassy carbon electrode was polished with diamond paste (Kenet, Kent, UK) of decreasing size (3.0, 1.0 and 0.1 μm) was polished prior to experiments on alumina lapping compounds (BDH) of decreasing size (1.0–0.3 μm). The gold electrode was polished prior to experiments on alumina lapping compounds (BDH) of decreasing size (1.0–0.3 μm). 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.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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