Micro-/nanoelectrode systems have been widely studied due to their potential for electroanalytical and biosensing applications.1,2 They display smaller capacitive charging currents, smaller ohmic drops, enhanced mass transports, faster electrochemical responses, higher current densities, and higher signal-to-noise ratios than those of macroelectrode systems.3-5 However, the low current response is the main disadvantage of using a single micro-/nanoelectrode. This challenge can be overcome by employing arrays or ensembles of micro-/nanoelectrodes operating in parallel.6-8 Moreover, redox cycling is an efficient approach to enhance sensitivities, limits of detection, and steady-state currents of micro-/nanoelectrode systems.4,5 Redox cycling requires at least two working electrodes (or two arrays of working electrodes): a generator and a collector electrode. The electrodes should be located close to each other and individually polarized at different potentials. In dual mode operation, a redox species in solution undergoes a reversible or quasi-reversible oxidation (or reduction) at the generator electrode. The oxidation (or reduction) product diffuses to the collector electrode, and it is converted back to the starting material. The regenerated species, formed on the collector electrode, then diffuses back to the generator where it is again electrolyzed. This cycle continues as long as the electrodes are properly polarized. Therefore, the same redox-active molecule contributes multiple electrons to the measured current, leading to an enhancement of electrochemical response from both generator and collector electrodes.4,5,9,10

The redox-cycling approach has been used for a wide variety of applications. They include measurements of reaction kinetics,4,11 diffusion studies,12 in vitro analysis of dopamine in the presence of ascorbic acid13,14 development of DNA biosensor,15 detection of reaction intermediates,16 development of electrochemical sensors,17-19 and application in bioassays.20,21 The performance of redox-cycling systems is commonly evaluated using two parameters:22 the collection efficiency (η) and amplification factor (A). η is defined as the ratio between the collector current, \( i_{\text{CE,red}} \), and the generator current, \( i_{\text{GE,red}} \), during redox cycling (dual mode):4

\[
\eta = \frac{i_{\text{CE}}}{i_{\text{GE,red}}}
\]  

(1)

And A is given as the ratio between the generator current in dual mode, \( i_{\text{GE,red}} \), and the generator current in single mode (in the absence of redox cycling), \( i_{\text{GE}} \):

\[
A = \frac{i_{\text{GE,red}}}{i_{\text{GE}}}
\]  

(2)

The collector electrode is left at open circuit during single mode operation, while the potential of the generator electrode is biased in the same manner as in the dual mode. The
performance of redox-cycling systems depends on the geometry and design of the electrodes. Improved performance is obtained by decreasing the electrodes’ size as well as the inter-electrode spacing (inter-electrode gap). In these conditions (smaller electrodes and gap), fewer redox-active molecules escape from the redox-cycling trap into the bulk solution. A broad range of redox-cycling systems, with different geometries, has been proposed and investigated over the years. These include dual cylinders, dual discs, dual bands, and interdigitated band electrodes (IBEs). IBEs are a natural evolution from the dual band redox-cycling systems that show greater sensitivities. The performance of IBEs is improved by decreasing the width of the bands, decreasing the inter-electrode gap distance between the generator and the collector, and increasing the height of the bands. Planar interdigitated ring electrodes (IREs) are an important variation of the IBEs. Compton et al. demonstrated that IREs with small radii show larger current enhancements in comparison to IBEs, due to the higher radial diffusion and more efficient mass transport. Important alternatives to the planar interdigitated configurations are vertically separated electrodes. A dielectric (insulating) material defines the inter-electrode gap between the generator and collector electrodes. The gap can be simply tuned by varying the thickness of the dielectric layer through thin film deposition. Vertically separated electrodes provide several advantages over planar electrodes, including highly improved collection efficiency and signal amplification, due to the more efficient trapping of redox-active species. In addition, their three-dimensional nature makes them ideal for lab-on-a-chip integration. The recessed ring–disc electrodes array is an example of vertically aligned generator–collector electrode systems that have been extensively studied. In this geometry, the disc electrodes, acting as generators, are completely surrounded by the ring electrodes (acting as collector electrodes), leading to a very high collection efficiencies.

Very recently, Bohn et al. have proposed a novel redox-cycling system structure: the recessed Au nanoring–ring electrodes array (Au-NRRA), shown schematically in Figure 1. They experimentally demonstrated that the collection efficiency of this new configuration is ~100%. The Au-NRRA is derived from the recessed nanoring–disc electrodes array configuration, but the identical electrode geometry in the Au-NRRA helps to improve further the collection efficiency. Herein, a more detailed understanding of the main characteristics of the Au-NRRA is provided through numerical simulations using COMSOL Multiphysics. The model was first validated by comparing the results with experimental data. The results presented here provide valuable information for the future development of applications of Au-NRRA in several areas ranging from fundamental studies of electrochemical mechanisms to integrated lab-on-a-chip detection systems.

**EXPERIMENTAL SECTION**

**Chemicals and Instrumentation.** Potassium ferricyanide and potassium chloride were purchased from Caledon Laboratories. All solutions were prepared using ultrapure water (18.2 MΩ·cm) obtained from a NANO pure Diamond TM deionization system (Barnstead). Prior to measurements, the solution was purged with argon gas for 30 min. Electrochemical measurements were carried out using a Gamry Reference 600 potentiostats connected to each other. Data acquisition of the two potentiostats was synchronized using scripts made available by the manufacturer (Gamry Instruments, USA). A platinum wire was used as a pseudo-reference electrode. Another platinum wire served as a counter electrode. Notice that the experiments could have been performed using only one Pt wire. However, we chose to keep a four (or three)-electrode configuration to be consistent with the previous works in this area. All the experiments were performed after an equilibration time of 10 s and in a Faraday cage.

**Recessed Nanoring–Ring Microarray’s Geometry and Fabrication.** Figure 1a shows a schematic cross-sectional diagram of 6 × 6 Au-NRRA arranged in a square lattice. Each nanohole contains two nanoring electrodes that are electrically isolated and arranged vertically relative to each other. Nanohole structures in the array are formed by milling through a first insulating layer, recess depth, t (SiO₂ or Si₃N₄, 150 nm) and a first metal layer, upper ring electrode, h₁ (Au, 50 nm); down to a second insulating layer, insulating gap, g (SiO₂ or Si₃N₄, 150 nm) and a second metal layer, lower ring electrode, h₂ (Au, 50 nm), using FIB technique. The upper and lower ring heights (h₁ and h₂) and the gap thickness (g) could have all, in principle, been modified while maintaining the same array footprint. Here the heights of both lower and upper rings were the same, 50 nm. The details of the fabrication process are given in Supporting Information (SI) Figures S-1 and S-2.

**Simulations.** We have performed both 3D and 2D simulations on the 6 × 6 Au-NRRA operating in either single or dual mode, respectively. Simulations were carried out using a commercial finite-element software package (COMSOL Multiphysics ver. 5.2). The 2D simulations were run on our PC workstation with 32.0 GB RAM (Lenovo Thinkstation), and the 3D simulations were run on WestGrid and Compute Canada clusters. The details of the simulations are given in the SI file.
**RESULTS AND DISCUSSION**

**Electrochemical Investigation at Recessed Nanoring–Rings Microarray.** The experimental and simulated cyclic voltammetric curves for a $6 \times 6$ Au-NRRA ($r = 150$ nm; $g = l = 150$ nm) for both single and dual mode operations are shown in Figure 2a,b, respectively. The surface areas of both lower and upper ring electrodes were the same ($h_c = h_g = 50$ nm). In single mode, the lower rings were swept at 0.05 V s$^{-1}$ and the upper ring electrodes were considered as an insulator layer (see SI for the simulation details). This means that, in single mode operation, the cyclic voltammetry simulation was performed on a $6 \times 6$ nanorings array with 350 nm recess depth (see Figure S-4). In dual mode, the lower ring (generator) was swept at 0.05 V s$^{-1}$ while the potential of the upper ring electrodes was kept at 0.1 V (vs pseudo-Pt reference) in the experiment and at 0.3 V in the simulation.

![Figure 2](image-url)

*Figure 2.* Comparison of cyclic voltammograms for 20 mM potassium ferricyanide and 0.5 M KCl in a $6 \times 6$ Au-NRRA ($3.3 \mu m \times 3.3 \mu m$) operating in single mode (black curves) and redox-cycling mode (red curve, collector; blue curve, generator. (a) Experimental results; (b) simulated results. For single mode, the lower ring electrodes were swept at 0.05 V s$^{-1}$ while the upper ring electrodes remained at open circuit. For redox-cycling mode, the lower ring electrodes (the generator) were cycled at 0.05 V s$^{-1}$ while the potential of the upper ring electrodes was kept at 0.1 V (vs pseudo-Pt reference) in the experiment and at 0.3 V in the simulation.

![Figure 3](image-url)

*Figure 3.* Performance of the current characteristics of Au-NRRA calculated using COMSOL. (a) Dependence of the limiting current on the ring height ($h$) for holes of different radii. (b) Dependence of the limiting current density on $h$ for holes of different radii. The recessed depth, $l = 150$ nm, the insulating gap, $g = 150$ nm, the inter-electrode distance, 4$r$, and the scan rate, $v = 0.1$ V s$^{-1}$, were kept constant, in all the simulations. The height of the lower and upper ring electrodes were considered to be equal, $h_c = h_g$ for all these cases. The rest of the parameters are given in the text.
results in Figure 2 validates our approach. Notice that, at first glance, the amplification factor of the Au-NRRA configuration might seem a bit low for a redox-cycling system with such a high collection efficiency. This is because $A_f$ depends on the electrode geometry and scales with the electrode size.47 A clarification of these effects is provided as Supporting Information in the section “Notes on the amplification factor”.

Effect of Scaling of Electrode’s Dimensions on the Recessed Nanoring–Ring Electrodes Microarray Performance. The results from Figure 2 indicate that a computational investigation on the effect of geometric parameters in the performance of Au-NRRA should provide a description of the system that matches well with the experiments, while also allowing some insights into the transport mechanism. The geometry of the ring electrodes in Au-NRRAs is controlled via two parameters: height, $h$, and radius, $r$. The goal in this section is to use the numerical methods validated in Figure 2 to understand the effect of $h$ and $r$ on the performance of Au-NRRA. Simulations were performed for either constant height or constant radius conditions. The recessed depth, $l = 150$ nm, the insulating gap, $g = 150$ nm, inter-electrode distance, $4r$, and the scan rate, $v = 0.1$ V s$^{-1}$, were kept constant in all the simulations. In addition, the heights of the lower and upper ring electrodes were considered to be equal, $h_c = h_g$. Three different radii, 100, 150, and 200 nm, were considered. The current responses of the rings with different heights ($h = h_c = h_g$) of 25, 50, 75, and 100 nm in dual mode were investigated for each radius. The influence of the scaling of the electrode dimensions on redox-cycling response of Au-NRRA is summarized in Figure 3. The results in Figure 3 are shown in terms of both the limiting current ($i$) and current density ($j$).
Panels a and b of Figures 3 display simulated limiting current ($i_{\text{GR},\text{cyl}}$ (nA)) and limiting current density values ($i_{\text{GR},\text{rad}}$ (nA $\mu$m$^{-2}$)), from Au-NRRA in dual mode. The cyclic voltammograms and a summary of $i$ and $j$ values for different geometrical parameters are further shown as Supporting Information. As it can be seen in Figure 3a, upon increasing $h$, at a fixed ring radius, the limiting current does not vary remarkably. For example, for $r = 150$ nm, an increase in the ring height from 25 to 50 nm results in an increase of $\sim$10.4% in the limiting current. Moreover, scaling from $h = 50$ nm to $h = 75$ nm results in an increase of $\sim$3.9%, and varying from $h = 75$ nm to $h = 100$ nm results in a further increase of only $\sim$1.5%. In contrast to Figure 3a, Figure 3b shows a significant change in the limiting current density responses for Au-NRRA of constant ring radius upon varying the $h$ values. For example, for $r = 150$ nm, varying the ring height from 25 to 50 nm, from 50 to 75 nm, and from 75 to 100 nm results in decreases of the limiting current density magnitude of $\sim$44.8%, $\sim$30.7%, and $\sim$26.7%, respectively (variations for other values of $r$ are shown as SI). The current density on the generator decreased significantly with $h$ because the height does not have any sensible effect on the limiting current magnitudes. Particular attention to the concentration profiles next to the rings is required for the understanding of the behavior revealed in Figure 3. Figure 4 shows the effect of varying the ring height (25–100 nm) on the evolution of the concentration profile next to the generator electrode, at a constant ring radius, $r = 150$ nm. The concentration profile for other $r$ values is given in Figures S-8 and S-9. As it can be seen in Figure 4, the radial diffusion pattern next to the generator electrode weakens as the electrode height increases. As a result, a ring with a short height of 25 nm shows a relatively high limiting current compared to, for instance, a 100 nm high ring, due to the pronounced effect of the radial diffusion next to the generator electrode (compare Figure 4a,d). The height increase still leads to an overall increase in limiting current due to the effect of increasing the surface area of the electrodes. Hence, when the effect of the surface area is factored out, a large decrease in current density was observed for the 100 nm in height ring compared to a height of 25 nm, Figure 3b.

The results presented in Figure 3a,b also indicate that at a constant value of $h$ the magnitude of both $i$ and the $j$ increase with enlarging the hole radius. Figure 5 shows the variations in the shape of concentration profile at the vicinity of the generator electrode at the base of the hole for different $r$ values (100, 150, and 200 nm) at a fixed height of 50 nm. The concentration profile for other $h$ values is given in the SI. Obviously, the electroactive surface area available for the redox cycling increases with $r$. However, more importantly, the wider hole radius also amplifies the radial diffusion flux effect next to the generator electrode. Therefore, the increase in the limiting current due to ring enlargement has contributions from a combination of effects involving both an increase in surface area and the predominant radial diffusion near the generator electrode. The role of the radial diffusion contribution is seen in the increment in the limiting current density with enlarging the electrode radius in Figure 3b. In summary, the dependence of the current density on $h$ and $r$ is consistent with the shape of the diffusion profile within the ring–hole geometry. The efficient transport within the hole should introduce a degree of limitation on the amount of material potentially available to the generator during redox cycling. These results suggest that the width of the holes plays an important role in enhancing the redox-cycling performance of Au-NRRAs (for this particular inter-electrode gap). When the surface area is constant, the steady-state current (and the current density) during redox cycling decreases significantly as the inter-electrode gap distance ($g$) decreases (results presented in SI). Smaller values of $g$ favor fast transport between the electrodes, increasing the efficiency of the cycling process.

**Effect of Scan Rate on Recessed Nanoring–Ring Electrodes Microarray Performance.** It should be noted that an important characteristic of the redox-cycling systems (dual mode operation) is that the collector electrode, which is kept at a constant potential, shows a much smaller charging current in comparison to the generator electrode. This feature of redox-cycling systems allows fast scan cyclic voltammetry (CV) measurements to be used for monitoring electro-generated intermediates with very short lifetime and to study electrochemical reaction mechanisms. Therefore, one of the valuable futures of redox-cycling devices is their performance at high scan rates. For this main reason, we have studied the effect of the scan rate on the performance of the Au-NRRA.

Figure 6 compares simulated cyclic voltammogram curves for $6 \times 6$ Au-NRRA ($r = 150$ nm) in single and dual mode operation at various scan rates, ranging from 0.05 to 1000 V s$^{-1}$ (the calculations for Au-NRRAs of different radii and intergap distances are given in the Supporting Information). Here again, for single mode simulations, the potentials of the lower rings were swept between 0.3 and $-0.3$ V at different scan rates and...
the upper ring electrodes were considered as insulator layers. In dual mode, the lower ring (generator) potential was swept in the same way as in the single mode, while the upper ring potential (collector) was kept constant at 0.3 V. As it can be seen from Figure 6a, the cyclic voltammogram curves for both the generator and collector electrodes show a sigmoidal shape for all the scan rates investigated (between 0.05 and 1000 V s$^{-1}$), which confirms that valuable characteristic of the Au-NRRA. It should be noted that the current on the collector electrodes was nearly a mirror image of the generator response up to scan rates of 1 V s$^{-1}$. Consequently, the $\eta$ values were closer to unity in that range of scan rates (up to 1 V s$^{-1}$). A small decrease in the collector current was observed as the scan rate increased to 100 V s$^{-1}$, whereas the generator current magnitude remained practically constant. As a result, $\eta$ decreased to 97.1%. A scan rate of 1000 V s$^{-1}$ induced a quasi-steady-state wave at both generator and collector electrodes. Although the generator current magnitude remained similar to the values of lower scan rates, the magnitude of the current at the collector decreased even further ($\eta$ reached 90.86% in this case (1000 V s$^{-1}$)). The dependence of lower ring generator current on the scan rate was significantly different for single mode operation, as shown in Figure 6b. The current response of the array in single mode gradually shifted from steady-state waves (at scan rates up to 1 V s$^{-1}$) to quasi-steady-state waves (at the scan rates between 10 and 100 V s$^{-1}$) and to, finally, a peak-shaped wave at the highest scan rate (1000 V s$^{-1}$). The current magnitude of the generator electrode at single mode is almost constant up to a scan rate of 0.1 V s$^{-1}$ and then it gradually increases at higher scan rates. The diffusion layer from adjacent nanoelectrodes completely overlap in single mode operation over the range of scan rates investigated due to the relative small separation between the nanoholes on the array. Consequently, the whole array behaves like a single 3.3 $\mu$m $\times$ 3.3 $\mu$m microelectrode. The current response of the array at higher scan rates (>10 V s$^{-1}$) deviated from steady state because the shape of the diffusion layer over the whole array shifted from hemispherical to a mixed hemispherical and planar diffusion. At the fastest scan rate (1000 V s$^{-1}$), the planar diffusion toward the whole array completely dominates.

The values for $\eta$ and $A_f$ for different scan rates are summarized in Table 1. (Again, an important discussion on the seemingly low amplification factor of the Au-NRRA system is given in the SI.) As indicated in Table 1, the magnitude of $A_f$ decreases with the scan rate. This is because the magnitude of the generator current is practically independent of the scan rate in dual mode operation, whereas the current magnitude gradually increases with the scan rate at single mode.

| Table 1. Influence of the Scan Rate on the 6 × 6 Recessed Ring–Ring Array Performance* |
|---------------------------------|-------------|-------------|-------------|-------------|-------------|
| Scan rate (V s$^{-1}$) | $i_{cl}/nA$ | $i_{cl,ff}/nA$ | $i_{cl}/nA$ | $\eta$ (%) | $A_f$ |
| 0.05 | −3.7 | −13.08 | 13.06 | 99.85 | 3.5 |
| 0.1 | −3.7 | −13.08 | 13.06 | 99.85 | 3.5 |
| 1 | −3.8 | −13.09 | 13.04 | 99.62 | 3.4 |
| 10 | −4.06 | −13.09 | 12.94 | 98.85 | 3.2 |
| 100 | −4.88 | −13.11 | 12.73 | 97.1 | 2.7 |
| 1000 | −8.72 | −13.57 | 12.33 | 90.86 | 1.5 |

*The array characteristics were as follows: ring height ($h = 50$ nm); hole radius ($r = 150$).

**CONCLUSIONS**

The electrochemical responses of the gold nanoring–ring electrodes array were simulated using COMSOL. The simulations were first validated by comparing the computational results with experiments at both single and dual modes. The experiments were carried out using a 6 $\times$ 6 Au-NRRA (3.3 $\mu$m $\times$ 3.3 $\mu$m) fabricated on a metal/insulator/metal/insulator stack over a glass substrate. The nanopattern was created by FIB milling. In redox-cycling mode, the upper ring electrodes which were polarized at a constant potential acted as the collector electrodes and the lower ring electrodes at which the potential was swept acted as generator electrodes. With redox cycling the recessed nanoring–ring electrodes array showed a much higher limiting current compared to that of a recessed nanoring–ring electrodes array (without redox cycling). The Au-NRRA configuration showed a collection efficiency close to 100% at moderate scan rates. The high collection efficiency of this configuration is because the upper ring electrodes, the collector, constrain the depletion layer within the nanoholes and confine the mass transport inside the nanoholes. The generator electrode is completely surrounded by the collector electrode with the same geometry. In addition, both generator and collector are located in a nanohole and separated by a very small gap. Information on the influence of the scan rates and scaling of electrode dimensions on the redox-cycling behaviors of the Au-NRRAs was obtained through numerical simulations. Simulations on the effect of the scan rate on the performance of these devices showed a quasi-steady-state response in the redox-cycling mode even at 1000 V s$^{-1}$. This confirms that capability of Au-NRRA to monitor electrogenerated intermediates with very short lifetime and to study electrochemical reaction mechanisms. The effect of the electrode dimensions on the performance of Au-NRRA in redox-cycling mode revealed that the magnitude of the attainable limiting current depends strongly on the ring radius and intergap distance, while it is almost independent of the ring height variations (for the particular inter-electrode gap considered here). The information reported here should be useful for the design of recessed nanoring–ring arrays with improved redox-cycling performance for future applications.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.7b01943.

Notes on the fabrication process, simulation details, effect of varying the inter-electrode gap, amplification factor calculations, Z-contrast images, cyclic voltammograms, concentration profile images, and tables (PDF)

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**Notes**

The authors declare no competing financial interest.
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