Comparing the Electrochemical Response of Nanostructured Electrode Arrays

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Supporting Information

ABSTRACT: The electrochemical responses from periodic 6 × 6 arrays of recessed gold nanorings were compared to the 6 × 6 recessed gold nanodiscs arrays. The nanostructured arrays were fabricated by focused ion beam milling and their electrochemical response from a reversible redox pair was obtained. Three-dimensional cyclic voltammetry simulations using COMSOL were performed on 6 × 6 periodic arrays of both recessed nanodiscs and nanorings to elucidate the differences in mass transport between these geometries. Specific mass transport properties near the electroactive surface of the electrodes were elucidated by analyzing the calculated concentration profiles of the redox species. Relative contributions from radial diffusion regimes inside the nanoholes play an important role on the electrochemical response of the recessed nanorings. Arrays of nanodiscs are common in different types of applications, particularly in biosensors. The results presented here suggest that the performance and sensitivity of electrochemical nanosensors can be simply improved by implementing electrodes with a geometry which offer greater current density while keeping the overall footprint of the sensor element constant.

The size and geometry of an electrode strongly affect its electrochemical behavior. Decreasing the critical dimension of an electrode to less than 25 μm (microelectrode) greatly improves its performance relative to that of a regular-sized (e.g., millimeter-sized) conventional macroelectrode. The benefits gained from electrode miniaturization include enhanced mass transport rates, due to the predominance of the three-dimensional diffusion; reduced ohmic resistance; increased current densities; and enhanced signal-to-noise ratios. The combination of these characteristics greatly improves response time and sensitivity in analytical and biosensing applications. In addition, microelectrodes can be easily integrated into miniaturized devices that require low sample volumes for (bio)chemical analysis. The benefits gained from microelectrodes can be further amplified by entering the realm of nanoelectrodes (electrode critical dimension below 1 μm). The field of nanoelectrochemistry has flourished in the past few years, due to advances in fabrication methods for the mass-production of nanoelectrodes. Electroanalytical methods involving nanoelectrodes are faster and suitable for matrices with low conductivity. Nanoelectrodes can potentially be essential components of portable devices for extreme biosensing applications, such as single-molecule detection. However, a severe drawback to the widespread application of nanoelectrodes is their low output current. The current levels in nanoelectrochemistry are often in the pA-range, requiring specialized, low noise, electronic circuits for detection. This limitation can be overcome by utilizing an array of nanoelectrodes operating in parallel. The overall behavior of a nanoelectrode array depends on several factors, including the diffusion coefficient of the electroactive species, the electrode radius, the interelectrode spacing, the time scale of the experiment, the size of the whole array, and the electrode geometry. Research activity in the development of nanoelectrode arrays has been intense in the past few years. Most of the work focused on arrays of (either inlaid or recessed) nanodiscs. This is a relatively simple geometry and very common in the electrochemistry of micro/nanoelectrodes. However, other possible configurations for nanoelectrodes might provide advantages over a simple array of “recessed nanodisc electrodes” (r-NDE) in terms of electrochemical performance at the nanoscale.

Our research group has a vast experience on the application of arrays of nanoholes in gold films as surface plasmon resonance biosensors. The nanohole structures support the phenomenon of extraordinary optical transmission, which is an enhancement in the amount of light transmitted through the nanostructures at certain resonant wavelengths. Recently, we have transformed a regular array of nanoholes into arrays of “recessed nanoring electrodes” (r-NRE) by coating the top gold surface of the nanoholes array with a thin layer of an insulating material. As a result, the electroactive area remained confined as gold rings within the nanoholes. The nanorings were then coated with a thin layer of an electroconductive material, generating an array of polymer-modified nanoring electrodes. The optoelectronic properties of the polymer-modified

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nanorings array were then explored by electrochemically switching the optical transmission through the nanostuctures. They preliminary experiments suggested that arrays of r-NRE performed well as electrode elements, and since those structures can be fabricated in either large area or microarray format,

they have the potential to be applied in several types of bioanalytical devices. However, before embarking toward the development of applications, one might wonder how the electrochemical performance of a r-NRE array differs from that of one of the most common geometries, such as an array of r-NDE. In this work, a combination of experimental and numerical simulations was performed to compare the electrochemical characteristics of r-NRE and r-NDE. The results provide guidance to the electrochemical performance characteristics for both geometries.

**EXPERIMENTAL SECTION**

**Chemicals and Instrumentation.** Potassium ferricyanide and potassium chloride were obtained from Caledon Laboratories. All solutions were prepared using ultrapure water (18.2 MΩ cm) obtained from NANO pure Diamond TM deionization system. (Barnstead). Prior to measurements, the solution was deoxygenated by purging with argon gas for 30 min. Voltammetric experiments at r-NRE and r-NDE arrays were performed using a computer-controlled Autolab potentialstat-galvanostat (PGSTAT 30). For the experimental measurements’ details see the Supporting Information.

**Nanodiscs and Nanorings Electrode Arrays Fabrication.** The 6 × 6 r-NDE and r-NRE arrays were fabricated by focused ion beam (FIB) milling into 50 nm gold films on glass slides coated with Si3N4 (200 nm) insulating layer. The radius of the holes (r) were 150, 200, and 250 nm. The interelectrode distance between the nanoholes was kept as 4r as indicated in Figure 1. The sizes of the arrays were 2.3 μm × 2.2 μm, 3.3 μm × 3.3 μm, and 4.4 μm × 4.4 μm for 100 nm, 150 nm and 200 nm hole radius, respectively. Additional details on the fabrication are given in the Supporting Information.

**Nanodiscs and Nanorings Electrode Arrays Simulations.** All the cyclic voltammogram simulations of the 6 × 6 r-NRE and r-NDE microarrays were performed in three-dimensional domains, using finite element (FEM) software COMSOL Multiphysics version 5.2. The simulation of a simple reversible redox reaction with Butler–Volmer kinetics was considered. The details of the simulation parameters are given in the Supporting Information.

**RESULTS AND DISCUSSION**

**Influence of the Electrode Geometry on Voltammetric Response.** Figure 1 shows a comparison of the electrochemical response from a reversible process (ferricyanide reduction) between an array of r-NRE and an array of r-NDE. Both arrays had 6 × 6 elements and they were fabricated by focused ion beam (FIB) milling. Scanning electron micrographs of the arrays are shown as insets in Figure 1, together with three-dimensional cross-section schemes that represent the geometry of the arrays. The radius, r, of both ring and disc were 150 nm (nanohole’s radius) and both structures were supported in glass and coated with 200 nm insulating layer of Si3N4 (recess depth, h). The separation between the nanoelectrode elements for both arrays in Figure 1 was also identical and set to 600 nm, 4r. The ring electrode’s height, h, was 50 nm. Figure 1 shows that the steady-state reduction current density for the array of r-NRE (∼2.6 nA/μm²) was about 22% higher than that of observed for the array of r-NDE (∼ 2.1 nA/μm²). Although the absolute area of the r-NRE was 33% smaller than the r-NDE for the fabrication parameters used in Figure 1, both arrays occupied the same footprint. This indicates a potential advantage of the r-NRE, since its area can be controlled by adjusting the parameter h while keeping the radius of the hole and the distance between electrode elements constant.

In the experimental conditions of Figure 1 (scan rate 0.05 V s⁻¹), the diffusion layer that evolved from each nanohole electrode element is expected to overlap with the diffusion layer from neighboring elements. In the case of extreme overlap between the diffusion layers (which is expected in the case of Figure 1, due to the relatively slow scan rate and the small interelectrode distance), the whole array should behave as a single microelectrode with an area that corresponds to the entire size of the array. Since both arrays (nanodiscs and nanorings) were fabricated on the same geometrical area, 3.3 μm × 3.3 μm (the number of the electrode elements present in each array and the radius of the nanoholes were the same for both systems), the difference in the current density magnitude shown in Figure 1 should underlie different characteristics of mass-transport for each of the nanometric geometries. Finite element (FEM) calculations using COMSOL Multiphysics version 5.2 were performed in order to elucidate the mechanistic aspects of the mass transport toward the nanofeature elements in the arrays. There are intense simulation studies that address the electrochemical behavior of infinite arrays of microelectrodes with different geometries including inlaid and recessed microdiscs, porous, conical, and cylindrical microelectrodes. However, there are very few simulation studies on the electrochemical behavior of finite arrays of microdiscs, as well as regular and random nanodiscs arrays of microsized dimensions. There is no numerical study on the voltammetric response at the microsized array of nanoring electrodes. Moreover, reports on the comparison of the electrochemical responses of electrode arrays with different geometries in the nanoscale are also lacking, despite the fact that the effect of electrode geometry at the nanoscale is amplified. Although there are some comparative studies between (individual) microelectrodes of...
different geometries that demonstrate differences in their electrochemical behaviors. \(^{38,39}\) Here we performed simulations of cyclic voltammograms for \(6 \times 6\) r-NDE and r-NRE arrays in three-dimensional domains. A simple reversible redox reaction with Butler–Volmer kinetics was considered (see Supporting Information for details).

Figure 2 shows simulated voltammograms obtained for \(6 \times 6\) arrays of r-NDE and r-NRE. The nanohole radius \((r)\), recess depth \((l)\), interelectrode distance, were all set identical for both arrays and matched the experimental parameters in Figure 1. The height of the ring electrode \((h)\) was taken as 50 nm to comply with the experimental value (see the definition of the geometric parameters in Figure 1).

As it can be seen in Figure 2, the r-NRE array presents a larger steady-state current density than that of the r-NDE array for this particular set of geometrical parameters. The simulated current density magnitudes for both arrays in Figure 2 matches very well with the experimental values represented in Figure 1. Since all the simulation parameters and experimental conditions were similar, the observations from Figures 1 and 2 indicate that geometric effects contribute to the differences in output current density observed between the arrays.

Qualitatively, the diffusion layer should evolve quickly within each nanohole, reaches the hole opening, and then spreads over the nanohole with a 3D shape. \(^{17,40}\) As the diffusion profile of each adjacent nanohole overlaps, the overall shape of the concentration gradient profile and, consequently, the voltammetric response of the array, will depend on the size of the whole array. For a micrometer-sized array, the concentration profile over the entire array remains three-dimensional, regardless of the extent of the overlapping diffusion zones of the nanoelectrodes. \(^{15}\)

The radial diffusion pattern over the whole micrometer-sized array is responsible for the steady state voltammogram obtained for both r-NDE and r-NRE arrays in Figures 1 and 2. The calculated radial shape of the diffusion layers over the entire arrays are shown in 2D \((y−z\) plane) slice concentration profiles as insets in Figure 2. The 2D slice concentration profiles at the center of the nanoholes were taken from the first row in the arrays (see scheme in Supporting Information, Figure S-5).

2D slice concentration profiles of ferricyanide were taken at the potential, - 0.2 V, at which the steady-state current was established. 3D concentration profiles for both arrays are also shown in Figure S-6 (Supporting Information). The calculated radial diffusion pattern over the whole array is analogous for both r-NDE and r-NRE arrays (Figure 2). Supplemental animation files further demonstrate the dynamics of the concentration profiles evolution over both arrays for better visualization (Animation 1 shows 2D slices and Animation 2 shows 3D concentration gradient evolutions with time). The similar diffusion profile observed from the concentration gradient evolution of both arrays cannot account for differences in transport characteristics at each nanoelectrode element. Therefore, the transport properties at nanometric scale (inside the nanoholes) were further considered in order to find observable differences between the geometries. The geometry of the electrode must influence the supply of fresh redox species from the bulk to the electroactive area. The redox species obviously enters from the hole top and flows down toward the electroactive surface. In the case of the r-NDE, the flux to the electroactive surface (located at the base of the nanohole, see Figures 1 and S-6) is parallel to the hole length \((z\)-direction\). However, the mass flux to the r-NRE differs from r-NDE, as the electroactive surface is confined to the inner walls of the holes. Thus, the normal flux, in this case, is toward the inner walls of the hole, which is perpendicular to the hole length. This is verified by analyzing Figure 3, where the calculated concentration profiles across the diffusion layers inside the nanoholes of each array is shown. 2D \((y−z\) plane) slice concentration profiles at the center of the nanoholes are presented in Figure 3a,d. The calculated concentration profiles were obtained at the steady-state current at the same potential \((E = −0.2\) V\). Figure 3b and e show the close-up images of the concentration maps for a r-NDE and a r-NRE; \((c, f)\) concentration contour maps for a r-NDE and a r-NRE. All the parameters used in the simulations are the same as ones used in Figure 2. \(E = −0.2\) V (steady-state condition).

Figure 3 illustrates differences in the transport characteristics between a r-NRE compared to a r-NDE. Figure 3 shows that...
the mass transport properties within a single r-NRE and a single r-NDE can be broadly classified as "radial" and "planar diffusion", respectively. This difference in transport characteristics should contribute to the increased current density obtained by the nanorings array in comparison with the nanodiscs array (Figures 1 and 2). Figure 3e,f shows that the radial flux of molecules from the center-bottom of the hole toward the ring electroactive surface area enhances the mass transport of molecules from the bulk solution to the hole. Animation 3 shows the evolution of the concentration profiles within a single r-NRE and r-NDE at the same conditions as Figure 3 and helps to further illustrate the effect.

Figure 3a,d shows that the concentration profile (see the concentration scale bar in Figure 3), both within the holes and on the top opening of the holes, are dissimilar for each type of array. For instance, Figure 3d indicates that ~7 mM concentration of the oxidized species (ferricyanide) is expected to be inside the r-NRE hole, while for the r-NDE the same concentration is spread over the hole opening. This confirms that the radial flux of molecule to the r-NRE surface is more efficient in supplying fresh molecules from the bulk solution to the electroactive area in comparison with the flux of material to the r-NDE array (for the geometric parameters used in Figure 1).

**Influence of the Hole Radius and the Nanoring Height on the Current Density Magnitude.** The main conclusion from Figure 3 is that higher current densities for the r-NRE array compare to that of the r-NDE array can be achieved only when a radial diffusion contribution from the center toward the nanorings surface (within the nanoholes) dominates the transport. This implies that geometric parameters (r and h) that affect the nature of the diffusion layer geometry at the center of a r-NRE should have a strong influence on the magnitude of its current density.

Figure 4 shows simulated voltammograms obtained at different h-values. The scan rate and the hole radius were kept constant. The other parameters used in the simulations were the same as those used in Figure 2. Simulated voltammograms for other hole radiiuses are shown as Supporting Information (Figures S-7).

![Figure 4. Comparison of simulated cyclic voltammograms for 6 × 6 r-NDE and r-NRE arrays with different heights, 25, 50, 75, and 100 nm. The scan rate, v = 0.1 V s⁻¹, and hole radius, r = 150 nm, were kept constant. The rest of parameters used in the simulations were the same as those in Figure 2.](image)

Figure 4 shows that the highest steady-state current density magnitude is obtained from the r-NRE with h = 25 nm (the shortest ring height considered in Figure 4). The limiting current density for an array of r-NRE decreased as the ring height was increased. The values of the steady-state current densities from r-NRE arrays with h = 75 and 100 nm were less than that observed from an array of r-NDE with the same radius.

The behavior from Figure 4 can be explained by analyzing the diffusion profiles provided in Figure 5. The concentration profiles in Figure 5 were taken at the limiting current potential. Specifically, the close-up concentration profiles were calculated from the third nanohole on the first row of the array. Equivalent profiles for other r-values are shown in Figure S-8. Figure 5 confirms that the radial diffusion component dominates the transport in a nanoring element for small h-values. The radial nature of the flux geometry at the hole center decreases with increasing the ring height for constant values of scan rate and hole radius. As the ring height increases, the degree of the depletion of material from the center of the hole increased. This leads to an overlap of the radial diffusion layer at the center, which reduces the current density.

The concentration profiles in Figure 5 indicate some similarities between the general characteristics of the diffusion layer within the holes between the r-NRE with h = 75 and 100 nm (Figure S5d,e) and that of a r-NDE (Figure S5a). However, the r-NRE array with h = 75 and 100 nm presented lower current density magnitudes when compared to that of the r-NDE array. This is due to the height associated with the nanorings. Therefore, in the conditions of diffusion layer overlap at the center of the hole, a nanoring would be comparable to a deeper recessed nanodisc of the same radius. The current density for a recessed nanodisc decreases with the recessed depth.41 Similar transition between transport characteristics (as in Figure 5) was also observed when the height of the ring was kept constant, but the radius of the nanohole varied instead (Figure S-9). In summary, the effect of increasing the ring height (for a given radius), Figures 4 and S5, is the same as decreasing the radius for a constant ring height (Figures S-9).

The geometrical parameters, r and h, have a strong influence on the shape of the diffusion profile within the r-NRE. The interpaly between both parameters (also illustrated in Animation 4) suggests that optimization of the electrochemical performance of r-NRE microarrays requires analyses of the r/h ratio. Figure 6 shows a plot of the steady-state current density response, j, against r/h ratio for different nanohole diameters. The horizontal dashed lines correspond to the calculated j value for a r-NDE microarray with the indicated radius. The symbols in Figure 6 are experimental steady-state current (j values) obtained at the same electrochemical conditions as in Figure 1. The experimental values matched the calculated current densities (solid lines in Figure 6) within 5%. This matching with the experimental values for different geometrical parameters further validates the numerical approach.

Figure 6 reveals that, under steady-state conditions, the relative current density differences between the two microarrays, r-NRE and r-NDE, largely depends on the r/h ratio. This occurs because the extent of the radial diffusion within the hole center is controlled by the relative interplay between r and h. As the r/h ratio increases, the shape of the diffusion layer within the holes near the ring surface becomes more pronounced (Figures S5, S-8 and S-9). The shaded region in
Figure 5. Concentration distributions for species O within the hole next to the electrode surface for (a) a r-NDE and for r-NREs with different heights: (b) 25, (c) 50, (d) 75, and (e) 100 nm. The concentration profile images were taken from the third nanohole on the first row of the arrays (the emphasis is in the center of the bottom section of the hole surrounded by the ring). The hole radius \( r = 150 \text{ nm} \) and the scan rate \( 0.1 \text{ V s}^{-1} \) were the same for all these cases. (The concentration profiles for the r-NRE with different heights when the hole radius is \( r = 100 \) and 200 nm are shown in the Supporting Information, Figure S-8.)

![Figure 5](image)

Figure 6. Steady-state current density plotted against the \( r/h \) ratio for arrays of r-NREs. The solid lines were calculated using COMSOL. The horizontal dashed lines correspond to the calculated steady-state current density value of r-NDE arrays. The symbols correspond to \( j \) values obtained experimentally using the same electrochemical conditions as in Figure 1. The radii of each of the nanoholes in the microarrays are indicated. The shaded region highlights the condition where the steady-state currents from both r-NRE and r-NDE arrays are the same for a particular nanohole radius. The symbols in the shaded region are experimental results for r-NDEs. The scan rate \( r = 0.1 \text{ V s}^{-1} \) and interelectrode distance was \( 4r \) in all of the simulations.

![Figure 6](image)

Figure 6 shows that when the \( r/h \) ratio is about 2.4, the current density response of the r-NRE microarray will be the same as that of the r-NDE array with the same nanohole radius. The current density of the r-NRE will be higher/lower than that of a r-NDE when the \( r/h \) value is more/less than 2.4, for a constant nanohole radius (Figure 6). Notice that the geometrical area of a r-NRE will be equal to a r-NDE when the \( r/h \) ratio is equal to 2.

**Influence of the Scan Rate.** The size of the diffusion layer also depends on the time scale of the experiment, which in voltammetry it is dictated by the scan rate. Fast scan rates lead to smaller diffusion zones. At sufficiently high scan rates, the diffusion layer thickness becomes much smaller than the smallest dimension of the electrode. In this case, the planar diffusion to the microarray surface dominates the transport, and the current density turns proportional to the electrode surface area and becomes unaffected by the electrode geometry.\(^{38}\)

Figure 7 shows cyclic voltammograms for r-NRE and r-NDE microarrays at two scan rates (0.1 and 1000 V s\(^{-1}\)). Insets in Figure 7 present the 2D \((y-z)\) slice concentration profiles of species O for the first row of the microarray (remembering that all simulations were performed in the 3D domain). The concentration profiles were taken either at the steady-state potentials or at the peak potentials, depending on the shape of the voltammetric wave. The simulated voltammograms for other scan rates are presented as Supporting Information (Figure S-10 and Table S-1).

An immediate observation from Figure 7 is that both the geometry of the concentration profile over the whole microarrays and the voltammogram wave shapes are similar for the r-NREs and r-NDEs. The shape of the diffusion layer over the whole microarrays always presents a radial component within the r-NRE, independently of the scan rates (\( r/h \) ratio = 3 in Figure 7). Figure 7 shows that the current density differences between the two nanohole geometries become less important as the scan rate increases. At slow and intermediate scan rates, a radial diffusion layer dominates over the whole array, increasing the efficiency of the mass transport. Accordingly, a greater difference in current density magnitudes between r-NRE and r-NDE is observed (Figure 7a). The 3D diffusion layer over the whole array amplifies the effect of the radial diffusion toward the nanorings surface within the nanoholes. The efficient transport at low scan rates leads to a voltammogram with a sigmoidal waveform in Figure 7a. The transport characteristics move toward a mixed hemispherical and planar geometry and finally to a planar geometry at large values of \( v \). These changes in transport characteristics are reflected in the voltammogram waveforms. For instance, a peak-shaped voltammogram, indicating the dominance of planar diffusion, is shown in Figure 7b. The current density from r-NRE microarrays are still slightly higher than that of the r-NDE array even at a scan rate of 1000 V s\(^{-1}\). The small difference between the peak currents values of the r-NRE and r-NDE arrays is consistent with the differences in their diffusion layer inside the holes. These can also be visualized in Animation 5, where 2D slices concentration profiles time evolution over the whole arrays and the corresponding voltammogram at various scan rate are shown.

The comparison of the electrochemical behavior of r-NREs and r-NDEs microarrays presented so far should provide guidance on possible implementation of devices based on those geometries. One of the advantages of the r-NRE is that the electrochemical characteristics for a given nanohole radius can be tuned by adjusting the \( h \) value. This can provide
opportunities to improve the electrochemical response while maintaining the footprint of the microarray. For instance, Figure S-11 shows arrays of r-NRE (r/h = 3) and r-NDE of the same radius, but with distinct electrochemical responses. In a multiarray device, according to Figure S-11, the arrays of r-NRE could be placed ~2 μm closer together than arrays of r-NDE (Figure S-11 and Table S-2) and still provide independent electrochemical response. This property has obvious advantages on the design of addressable multiple electrochemical sensors in a miniaturized footprint.

**CONCLUSIONS**

A comparison of the electrochemical characteristics of microarrays of r-NDEs and r-NREs was carried out. The experimental results were confirmed by three-dimensional mathematical modeling. The effect of geometrical parameters, such as nanohole radius and ring height on the output current densities of the microarrays with different geometries, r-NRE and r-NDE, was revealed. The fundamental differences between the electrochemical responses of the r-NRE and r-NDE arrays have been clarified by considering the mass transport properties within the nanoholes. In the case of the r-NRE, the characteristic mass transport inside an individual hole is controlled by the r/h ratio. In principle, when the r/h ratio is higher than 2.4, the shape of the diffusion layer inside the nanohole is virtually radial, and a higher steady state current density is obtained for the r-NRE microarray in comparison to the r-NDE microarray (with the same microarray dimension and identical hole radius). Note that the radial diffusion geometry near the r-NRE surface (inside the nanoholes) increases with the r/h ratio. This leads to an increasing in the percentage difference between the steady-state current density responses of the r-NRE and r-NDE microarrays. On the other hand, it has been shown that when the r/h ratio is lower than 2.4 the shape of the concentration field within the r-NRE is virtually planar, similar to that of a r-NDE array. However, the current density of the r-NRE array, in this case, is lower than that of the r-NDE array. This is due to the extra height associated with the r-NRE. The nanoring electrode, in this case, would be comparable to a deeper recessed nanodiscs electrode with the same radius. Numerical simulations on the effect of the scan rate on the output current densities responses of the nanoholes microarrays were performed and the shapes of the voltammograms at different experimental time scales were predicted. Finally, this work provided guidance toward the potential implementation of practical electrochemical devices and sensors based on r-NRE microarrays.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.7b00932.

Notes on the fabrication and simulation details; additional concentration profile images and Z-contrast images and tables as noted in the text (PDF).

Animation 1. 2D slices concentration profiles evolution over the whole arrays of nanorings and nanodiscs with time (AVI).

Animation 2. 3D concentration profiles evolution of the entire nanorings and nanodiscs arrays with time (AVI).

Animation 3. The evolution of the concentration profile within a single nanoring and nanodisc electrode as being discussed in Figure 3a,d (AVI).

Animation 4. The evolution of the concentration profiles within the single nanoring and nanodisc electrode by varying the hole radius and ring height being discussed in Figures 5, 6, S-8, and S-9 (AVI).

Animation 5. 2D slices concentration profiles evolution over the whole arrays of nanorings and nanodiscs with time and corresponding voltammogram response by varying the scan rate (AVI).

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**Notes**

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**REFERENCES**