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Finely Tuning Metallic Nanogap Size with Electrodeposition by Utilizing High-Frequency Impedance in Feedback**

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Nanomaterials and molecules have shown quite remarkable features for nanoscale devices when they are organized in fine structures either by top-down techniques or bottom-up approaches.[1–3] Making metallic pairs with gap sizes commensurate with the objects of interest so that such system can interact with the outside is one of the key issues that remains a challenge. The desired distance between electrodes ranges from less than 1 nm up to more than 100 nm for different systems involving small molecules,[4] nanoparticles,[5] nanotubes,[1a] and biomolecules such as DNA chains.[2d]

Conventional top-down techniques such as electron-beam lithography still suffers from a disadvantage in terms of yield when the feature size approaches 10 nm or below. However, recent reports have shown very promising results on the shrinkage of the gap size of a predefined pattern by electrodeposition with an active feedback loop. Compared with other techniques, such as break junction, which mechanically tears a narrow metallic wire,[6] and electromigration, which splits a very thin metallic layer by current-induced migration,[7] the electrochemical method is arguably more versatile with a controllable gap range.[8]

The feedback signal of such electrochemical systems normally utilizes a dc voltage or ac voltage of very low frequency (< 10 Hz)[9,10] to detect the occurrence of electron tunneling through the gap during metal deposition, or uses one of the electrodes as the reference to sense the sharp potential drop when the electrodes grow within the electrical double layer.[8] The electrochemical process is stopped when the feedback signal shows significant change, which results in a gap size normally around 1 nm in the tunneling region in the first case, or below 10 nm for the latter. These systems show the controllability of such a feedback design, but they also pose several problems, such as a very narrow range of available gap size or an asymmetric deposition behavior. These limitations can be mainly attributed to the low frequency of the feedback signal, electrodes playing different roles during deposition, or the features that are needed to arbitrarily separate the ac signal from the dc deposition current.

In the present study we used a very different system design, which showed very interesting frequency dependency on the final gap size in a previous study.[11] Herein we investigate this behavior in detail with improved electrode geometry[12] and demonstrate that a gap size larger than 10 nm can be obtained reproducibly by using a high-frequency feedback signal. We will discuss the mechanism of the prominent impedance change over a complete deposition process by reference to the amplitude and phase-shift data, and show that the gap size can be further tuned down to around 1 nm simply by controlling the subsequent deposition time. This method is unique in that it indicates the distinctive behavior of the high-frequency impedance in such a nanoscale electrochemical system, and it provides a very flexible and common way to fabricate nanogaps for various applications.

We first prepared an initial metallic electrode pair which was over 200 nm apart. The gap was then narrowed by controlled electrodeposition. A sharp tip-against-tip geometry of the initial electrodes was found to be more favorable than a flat-top configuration for a reproducible feedback signal and a good final shape.[10,12,13] This geometry was achieved in two steps: First, a metal bar of length 50 μm and width 5 μm was fabricated by using a conventional photolithography technique, which was followed by metal evaporation (15 nm Ti covered by 85 nm Au) and lift-off. The bar was then carved in the middle by a focused ion beam to form two sharp tips with a distance ranging from 200 to 500 nm (Figure 1a). A small amount of SiO_2 under the metal in this area was also etched away to make sure that the tips were isolated. The sample was then immersed in concentrated HNO_3 for 30 minutes and washed with sufficient Milli-Q water to remove the residue Ga^{3+} ions that became doped during the course of the ion bombardment.

A schematic diagram of the feedback system is shown in Figure 1b.[11] Briefly, both electrodes of the gap were used as cathodes to symmetrically deposit metal, Au in our experiments. The unique symmetric design ensures that the ac signal travels only in the symmetric circuit loop, while the faradic current can be recorded independently on the electrochemical workstation. The ac voltage (V_s) at one of the electrodes was analyzed by a two-phase lock-in amplifier and its amplitude (V_m) was used as the feedback signal. This ac voltage has a very simple relationship to the impedance of the gap,[11] and shows a prominent decay when the gap distance is close enough.

Figure 1c gives the typical V_m–t curves for a complete deposition process using different ac frequencies. The curves are composed of three stages: 1) the sudden decay in the first few seconds of the Au deposition, which is attributed to the charging process of the double layer; 2) a plateau before the

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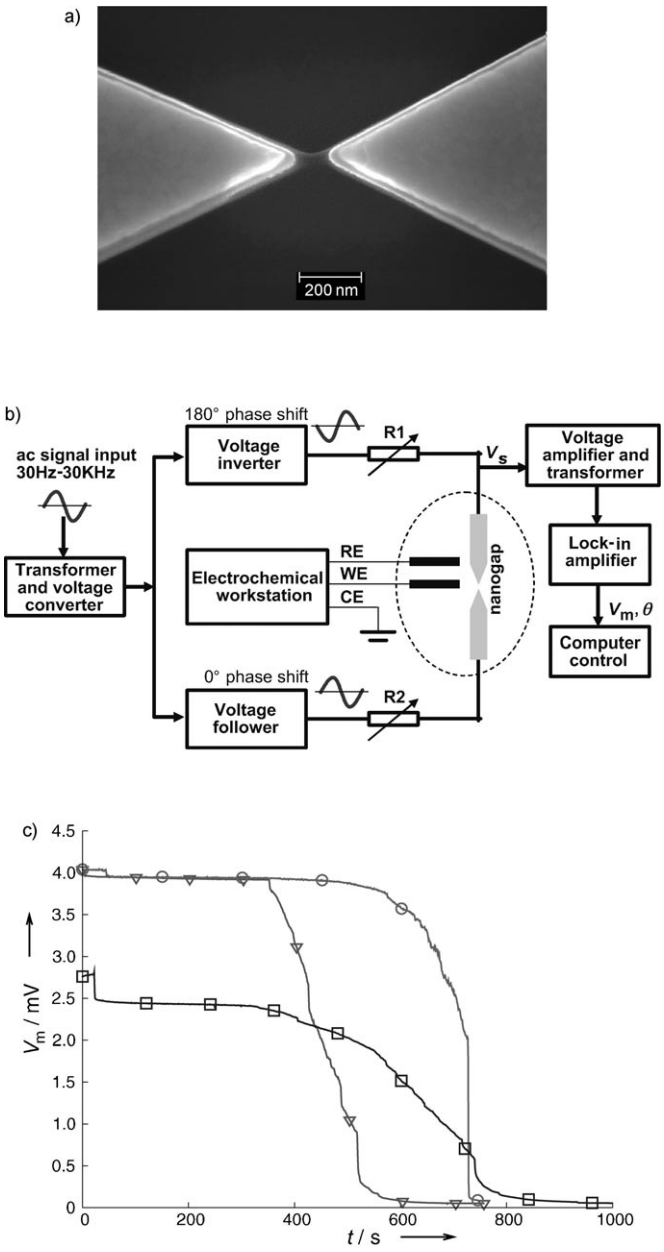

Figure 1. a) SEM image of the initial electrode pair. b) Schematic diagram of the electrodeposition system. The parts in the circle were immersed in solution. R1 and R2 were both set to 1 KΩ. c) The time evolution of V_m for different ac frequencies in a complete deposition process. ▽: 70 Hz, ○: 300 Hz, □: 3 KHz.

gap distance enters the critical region; and 3) a prominent decrease as the electrodes grow close enough and finally down to zero when a metallic contact is established.

A computer program was used to record the V_m signal and to detect the beginning of stage 3.[11] In other words, when the program detected an accelerated decrease in the value of V_m after the plateau (stage 2), it would take action—either stopping the deposition or doing so after a programmed period of time. We define the interval of time between the actual inflexion of the curve and the point at which the program reacted as Δt. The algorithm for such detection means we normally get a minimum Δt value of around seven seconds.

Three samples prepared at 3 KHz are presented in Figure 2. These samples showed consistent Δt values of around seven seconds (Figure 2a), which is a measure of the stability of the program algorithm and is consistent with a gap distance of around 30 nm (Figure 2b). It should be noted that the different initial gap distances of these samples did not show any critical effect on the final gap size. These results demonstrate persuasively the reproducibility of the system.[14]

Current mechanisms for the change in the feedback signal involve electron tunneling and the electrical double layer. The tunneling region in a vacuum is known to be only a few angstroms, while in solution it may be slightly larger because of the screening effect of ions.[15,16] Furthermore, the thickness of the electrical double layer is very sensitive to the ion strength in solution, but can be considered to be less than 1 nm in the buffer solution used in our experiments.[17] So our results here reach far beyond these regions, and imply quite a different story.

The first evidence of the mechanism lies in the different patterns of the third stages of the V_m–t curves shown in Figure 1c. At low frequencies, such as 70 and 300 Hz, the curves showed clear discrete behavior, which, when converted into conductance between the electrodes, gave steps at multiples of quantum conductance.[14] As for the 3 KHz case, the value of V_m decreased smoothly down to zero. The quantum conductance behavior clearly proved that the decrease in the feedback signal at low ac frequency reflected primarily the tunneling event and the quantum contact between the two electrodes. This is in good agreement with other reported results.[9] However, the capacitive reactance was actively involved at high ac frequency.

We can easily calculate the resistance and capacitive reactance from the amplitude and phase-shift data that were recorded simultaneously. Figure 3a and c give the raw data at a frequency of 300 Hz and 3 KHz, respectively. Similar to the amplitude signal, the phase-shift signal also showed a steady state followed by a remarkable increase.[18] Figure 3b gives the calculated resistance and capacitive reactance at 300 Hz on using an equivalent circuit of a resistor and a capacitor in parallel. Figure 3d shows the calculated resistance and capacitive reactance for 3 KHz obtained using an equivalent circuit of a resistor in series with a capacitor.

It can be seen from Figure 3b that the change of resistance and capacitive reactance was composed of two parts. In Part I only the resistance was decreasing while the capacitive reactance remained almost constant, while in Part II the capacitive reactance showed a radical increase, which is because the equivalent circuit was no longer valid in this region, since a quantum contact was formed. This effect was evidenced by the steps in the enlarged R–t curves of this region of the graph (inset of Figure 3b). The controlling program always stopped the deposition in Part I, where the change of resistance dominated. In sharp contrast, the resistance and capacitive reactance at 3 KHz decreased together to zero, as shown in Figure 3d.

The surface area of the electrodes and the frequency can be considered as constant within this region, so the media

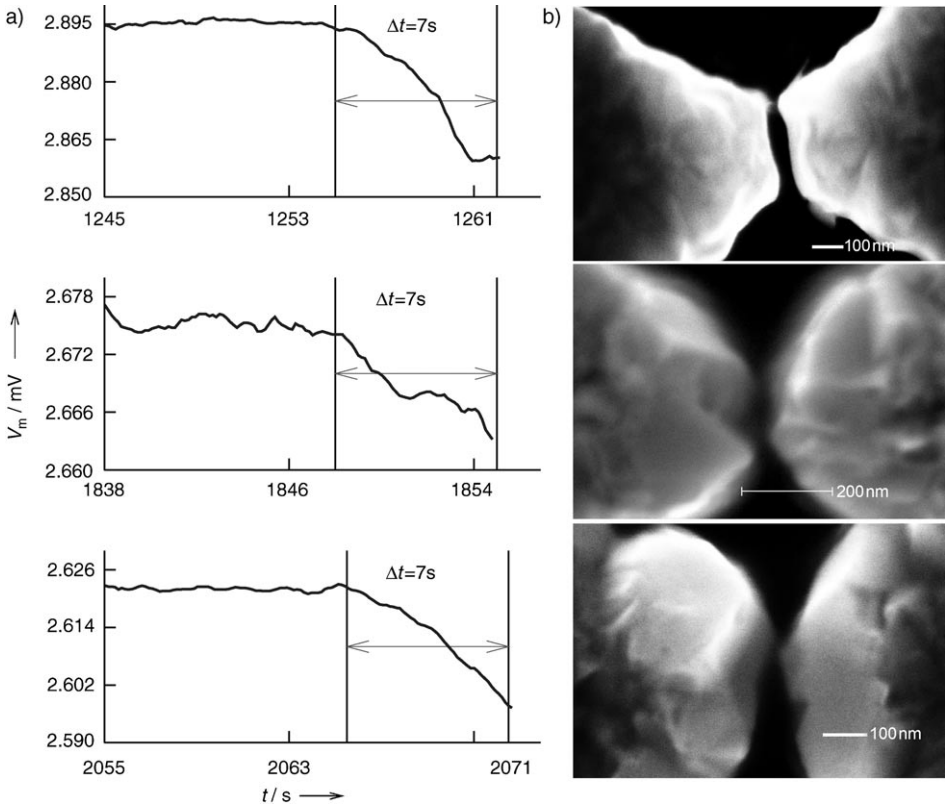

Figure 2. a) The V_m–t curves of three samples prepared at 3 KHz, only the last part is shown. The controlling program stopped the deposition at the last point. Δt is defined as the interval between the inflexion of the curve and the last point. b) The SEM images of the resulting gap in the three samples prepared as in (a), with a gap distance of 27, 35, and 25 nm, respectively.

between the electrodes could be the real cause of the behavior at 3 KHz. Considering the fact that there was an electric field of $10^5\,V\,m^{-1}$ between the electrodes (established by the feedback ac signal), the distribution of ions could be seriously perturbed, that is, the ions could be pushed and pulled according to the ac frequency between the electrodes. The solvent molecules could also be highly polarized, which will affect the dielectric constant.

In short, there will be a detectable change in the impedance for a frequency at which the capacitive reactance plays a dominant role, namely, when the nanogap shrinks to the extent that makes the electric field strong enough. This change is mainly affected by the field strength and the media between the electrodes, and thus is relatively stable. The frequency of the ac feedback signal can tune the ratio of the capacitive reactance, and the amplitude controls the strength of the electric field. The gap distance can be easily controlled by carefully tuning these two parameters.

Since the break point of the high-frequency feedback signal at which the gap distance was still relatively large can be detected very reproducibly, and the electrodeposition in the constant current mode evolved slowly and steadily, the gap size can be further developed by simply controlling the subsequent deposition time. For a frequency of 3 KHz, the deposition was stopped at $\Delta t = 9$, 25, 42, and 62 s on four samples, and the gap size was found to decrease from 26 nm to 16 nm, to 7 nm, and finally to around 1 nm, respectively (Figure 4). A simple analysis of these data showed a very good linear relationship between the final distance and the time, from which a deposition rate of $0.5\,nm\,s^{-1}$ can be calculated. In comparison, for a frequency of 300 Hz, gap sizes remained around or below 1 nm for $\Delta t = 7$ s and $\Delta t = 15$ s, which could not be measured directly by SEM (Figure 5). This result also indicated that only a very small portion of the deposited metal atoms helped to decrease the distance when the gap was less than 1 nm. This set of data is very clear proof of the important role that the high-frequency impedance plays in controlling the gap distance over a wider range.

The feedback signal at low frequencies could also establish an electric field strong enough to affect the movement of the ions between the electrodes. However, because the capacitive reactance was insignificant in the total impedance, it could not be observed. Furthermore, at a sufficiently high frequency, the electric field would change its direction before the ions could finish their movement across the short distance within a half cycle, which would cause them to oscillate between the electrodes.[19] This dynamic behavior could not be observed in our system because the surface area of the electrodes was large, and the impedance at such high frequencies was practically zero. The frequency range of the system could be expanded, and more information could be revealed by using a mask to minimize the surface area.

In summary, we have demonstrated that the high-frequency impedance of a pair of nanoscale electrodes can be greatly affected by a strong electric field between them. Utilization of this impedance change in the feedback loop enables nanogaps of 30 nm to be formed very reproducibly at a frequency of 3 KHz by an electrodeposition system. This distance is affected by the frequency and the amplitude of the ac signal, and the gap can be further finely tuned to around 1 nm by simply controlling the subsequent deposition time. This feedback system is stable and flexible, as well as providing a new strategy to prepare wide ranges of nanogaps for various applications. Furthermore, this method can also be used to study the impedance of a confined, nanoscale electrochemical system that is either in equilibrium or dynamic, for example, with a redox reaction proceeding on the surface. The dynamic behavior of molecules of special interest, such as DNA chains, proteins, or molecules with binding groups, could also be revealed with this system.

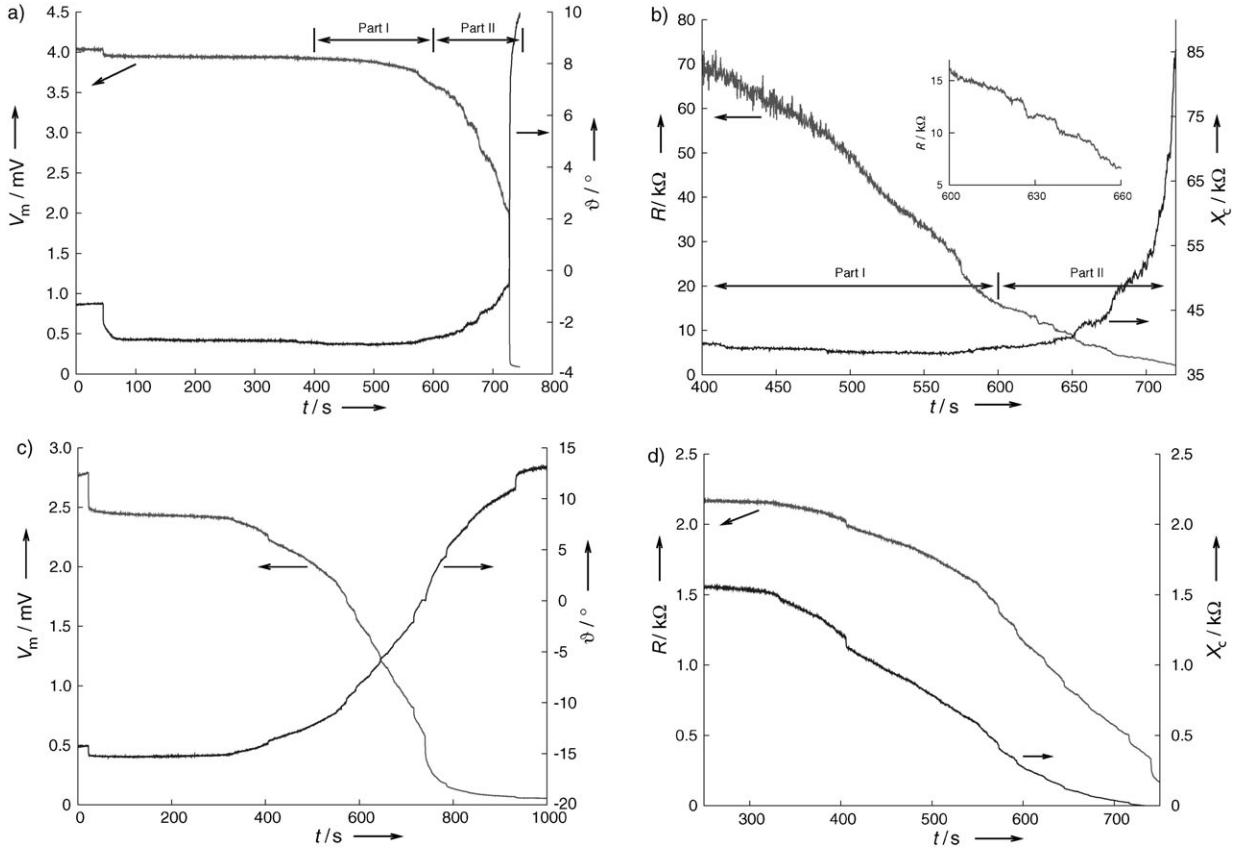

Figure 3. a) The amplitude (V_m) and phase-shift (θ) data versus time collected in a complete deposition at 300 Hz. b) Calculated resistance and capacitive reactance data according to (a) using an equivalent circuit of a resistor and a capacitor in parallel. Inset: enlarged *R*–*t* curve of Part II. c) The amplitude (V_m) and phase-shift (θ) data versus time collected in a complete deposition at 3 KHz. d) Calculated resistance and capacitive reactance data according to (c) using an equivalent circuit of a resistor and a capacitor in series.

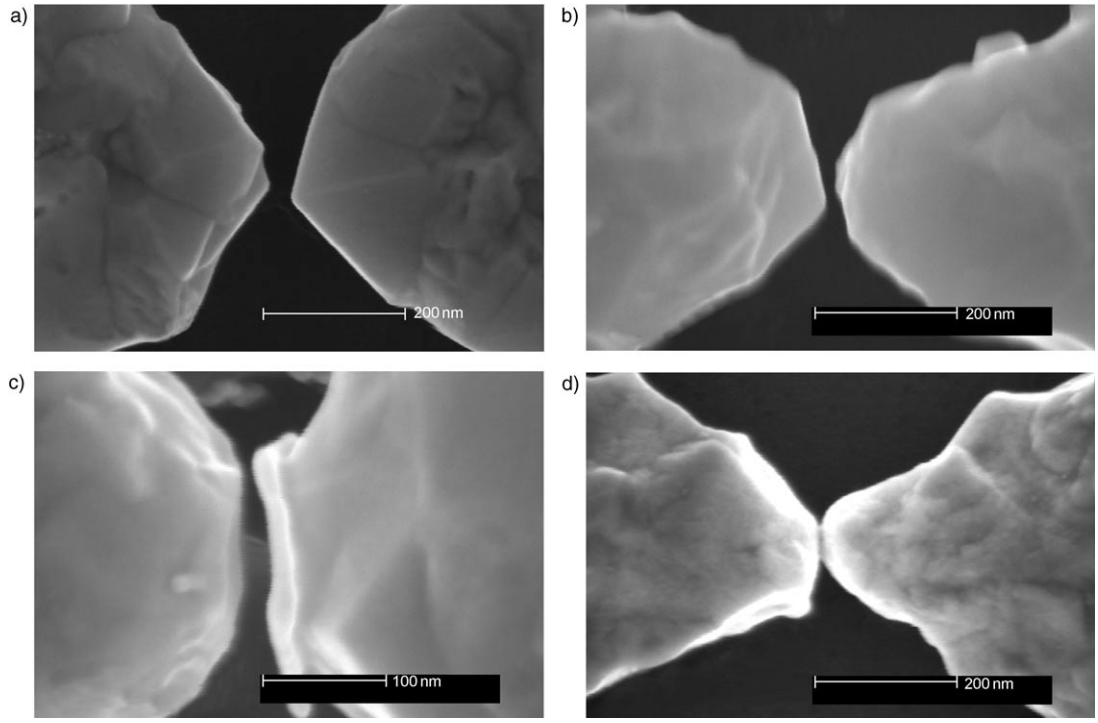

Figure 4. SEM images of the samples prepared at 3 KHz with different Δt values: a) $\Delta t = 9$ s, $d = 26$ nm; b) $\Delta t = 25$ s, $d = 16$ nm; c) $\Delta t = 42$ s, $d = 7$ nm; d) $\Delta t = 62$ s, $d = \approx 1$ nm.

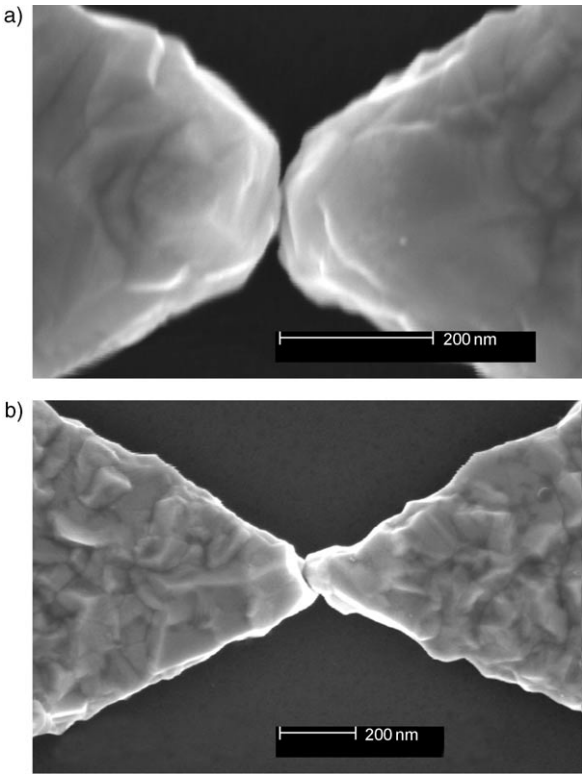

Figure 5. SEM images of the samples prepared at 300 Hz with different Δt values: a) $\Delta t = 7$ s, $d < 1$ nm; b) $\Delta t = 15$ s, $d < 1$ nm.

Experimental Section

The dc deposition was achieved with a commercial electrochemical station (CHI660B), and the current density was constant at 0.3 mA cm^{-2}. The electrolyte solution consisted of 0.1 M $KAu(CN)_2$ and 0.1 M potassium citrate buffer (pH 5.45). All solutions were prepared with analytic grade reagents and Milli-Q water (resistance: 18 MΩ). The electrochemical cell was elaborately designed to keep a constant electrode area exposed in the solution; in this study, the surface area was 0.30 ± 0.05 mm^2, as measured by an optical microscope.

Both electrodes of the gap were used as cathodes. A symmetric ac circuit composed of two 1 KΩ resistors and two ac sources with a phase difference of 180° was connected to them. The frequency could be adjusted from 30 Hz to 30 KHz, which resulted in different gap sizes ranging from less than 1 nm to 70 nm. The amplitude of the sources was normally set to 4 mV. The ac signals were monitored with a two-phase lock-in amplifier (Model 5206, EG&G Princeton Applied Research). In cases when we needed to record both amplitude and phase-shift data, a Keithley 4200 semiconductor characterization system was programmed for multichannel measurements. Otherwise a Keithley 6517a electrometer was used to collect real-time data. The electrodes with a nanogap separation after electrodeposition were imaged by scanning electron microscopy (SEM, XL30S-FEG, 15 kV).

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[18] When the amplitude of the input signal becomes very small, the phase-shift output of the lock-in amplifier used stays at a relatively constant value of around 10°. Thus, when the amplitude has approached zero the last portion of the phase-shift data should be considered as inaccurate and invalid for calculation of the impedance.
[19] Consider, for example, the SO_4^{2-} ion with a mobility of 8.27×10^{-8} m^2 s^{-1} V^{-1} in a electric field of 10^5 V m^{-1}. It will take 3.6×10^{-6} s for the ion to get through a 30 nm gap, which corresponds to a frequency of 551 KHz. In real systems, this frequency could be significantly lower because of the absorption of ions as well as the changes of the solution viscosity under the high electric field.

