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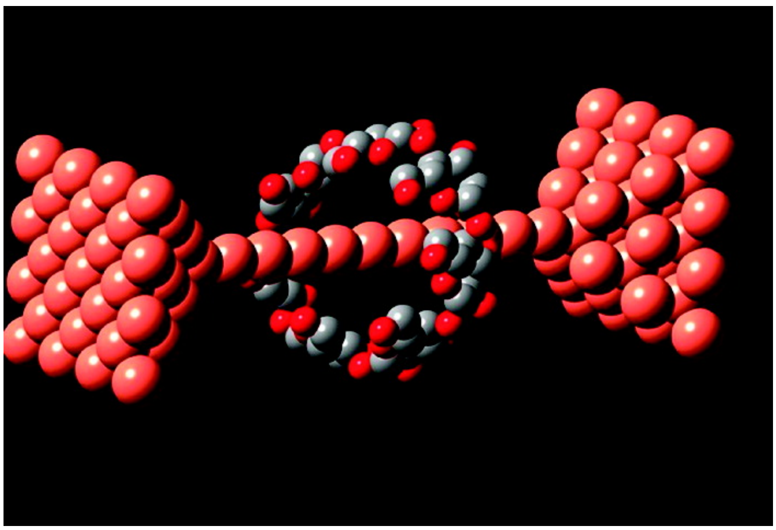

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Atomic Contacts via Electrochemistry in Water/Cyclodextrin Media: A Step Toward Protected Atomic Contacts

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Abstract: Atomic contacts are nanoscience devices proposed for applications such as single-atom switches in nanoelectronic circuits or one-molecule sensing devices. The conductance of such contacts varies in a stepwise fashion with a tendency to quantize near integer multiples of the conductance quantum (G_0) but can also deviate significantly from integer values upon molecular adsorption. However, for sensing applications it is first necessary to coat the contact permanently to avoid nonspecific adsorption. Here, we show that marked differences are observed between atomic contacts generated in water, and in water/β-CD. In this latter medium, atomic contacts with unusual properties can be generated. They have below 1 G_0 conductance, low conductance fluctuation with time, and appear to be protected or partially protected from salicylate external molecular probes. Such contacts are not obtained in water, in water/glucose, or when β-CD is added after 1 G_0 contacts have been generated in water. These results indicate specific adsorption of β-cyclodextrin on the atomic contacts and are compatible with the formation of encapsulated atomic contacts. However, direct independent structural evidence is still needed to confirm or infirm this interpretation.

Introduction

Electrochemistry has proved useful for generating metallic nanowires between two electrodes.[1−4] When the diameter of the wire is comparable to the electron Fermi wavelength, the phenomenon of conductance quantization occurs.[5−7] The narrowest portion of the wire consists of only a few atoms and controls the conductance of the entire macroscopic system. One can, in such a case, speak of atomic contact or of quantum wires. The conductance of an atomic contact is given by the Landauer formula $G = (2e^2/h)\sum_{i=1}^{N} T_i$, in which N is the number of conductive channels, T_i the transmission coefficient of channel i, and $G_0 = 2e^2/h$ the quantum of conductance. For several metals at room temperature (platinum, gold, copper, silver), the transmission coefficient is close to unity, and, thus, steps in the conductance close to an integer value of G_0 have been demonstrated.[8,9] However, experimental and theoretical evidence shows that T_i may differ significantly from 1, so each quantum step may not be exactly 1 G_0. Indeed, T_i depends on the valence of the metal,[10] on the presence of localized scattering centers and on boundary scattering.[11] An atomic contact with quantized conductance shifted from an integer value of G_0 is thus theoretically possible[11] and often observed experimentally.[12−15] In particular, molecular adsorption on an atomic contact has proved capable of changing T_i and yielding a noninteger conductance value.[16−21] For instance, the study of the adsorption of mercaptopropionic acid, 2,2′-bipyridine and dopamine onto atomically thin copper nanowires has shown that upon molecular adsorption the quantized conductance decreases to a fractional value. The decrease was found to be as high as 50% for the thinnest nanowires whose conductance is at the lowest quantum

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step. The adsorbance-induced conductance changes depend on the binding strengths of the molecules, which decrease in the order: mercaptopropionic acid, 2,2′-bipyridine, and dopamine.[17] Similar effects were reported upon anionic adsorption.[18,19] If one considers adsorbed molecules as individual local scatterers, these observations fully agree with the theoretical calculations.[11] This conductance variation upon molecular adsorption has been proposed as the basis for chemical sensor applications. However, no specificity has yet been demonstrated because all of the molecules surrounding the contact may adsorb or leave the contact at any time, causing fluctuations in the conductance versus time curve. To achieve specificity, it is first necessary to coat the contact permanently with receptor molecules. With such a configuration, the binding of a target molecule to the receptor molecules may cause a specific change in the conductance of the atomic contacts, and single target molecule recognition may be transducted. Other applications for atomic contacts as single-atom switches in nanoelectronic circuits have been proposed.[16,22]

In this work, we study the electrochemical generation of copper atomic contacts in water/β-cyclodextrin media. We show that in this medium two types of atomic contacts are obtained. The first is shown to be similar to atomic contacts generated in water. The second has unusual properties, demonstrating strong, permanent, and specific β-cyclodextrin (β-CD) adsorption. Moreover, these contacts are protected against external molecular probes. Given the particular shape of β-CD, these results can be explained by assuming that encapsulated atomic contacts are obtained.

Experimental Section

Copper was used as starting material because it is known to give atomic contacts easily using electrochemistry.[2] Atomic contacts were generated using the self-terminated method,[3] with an external resistance of 10 kΩ. Insulated copper wires 50 μm in diameter were glued onto a microscope slide and cut with a surgical knife. This setup makes it possible to generate a clean gap of around 20 μm between the two copper electrodes. A drop of the electrolytic media is then deposited, and a bias is applied between the two electrodes. The electrolytic medium is MilliQ water, MilliQ water + 10^{-4} M β-CD, or MilliQ water + 7.10^{-4} M glucose. Glucose and β-CD were provided by Aldrich and used as received.

With our setup, copper growth is dendritic, and many copper wires of various diameters (they do not have a well defined lateral dimension; the size variation along the length of the wire is ill defined) are generated but only one of them is responsible for the contact between the two electrodes. TEM and scanning probe techniques are unlikely to locate this particular wire and cannot provide good evidence for atomic contact formation. As a consequence, we will have to rely on transport measurements, like most groups working on such systems.[1,2,4,10,12,15−22]

The conductance versus time curves and the *I*/*V* characteristics were recorded using a Keitley 6487 picoamperometer and an acquisition card connected to a personal computer. *Synchrony* software was used for displaying the results and analyzing the rms noise of the conductance versus time curves. For *I*/*V* characteristics, a ±1V potential sweep was applied to the atomic contact plus the 10 kΩ external resistor, which yields to a smaller window for the effective potential applied to the atomic contact. No hysteresis in the *I*/*V* curves was observed.

For each medium, 120 atomic contacts were generated and studied. The conductance versus time curve for each contact was recorded during 400 s. We have only focused and used "stabilized conductance", defined as the conductance obtained generally at the end of the 400 s of the experiment duration and stable enough to show a well defined plateau (or several well defined plateaus) of the conductance value during at least 20 s (with small fluctuations around this value). In some cases, the conductance appeared stable in a time window during at least 20 s but became unstable with large fluctuations at the end of the 400 s experiment time. In such cases, the stabilized conductance observed in the plateau was used to build up the histograms. In doing so, we capture events that may not be stable enough for a long period but remain significant of a particular configuration of the contact. The rms fluctuations were determined on the whole conductance versus time curve and are thus a measure of the contact stability. Note that no transient conductance and no selected data were used is the study. More precisely, we have disregarded the results obtained through the measurements of the initial conductance of the contacts, defined as the average conductance recorded during the first 2 s after contact has been reached. Note also that we did not include in the statistics experiments that did not yield a contact between the two electrodes. This sometime occurs when the copper wires glued onto the microscope slide move when they are cut with the surgical knife.

To construct the histograms, we divided each quantum steps into three intervals, one of them centered on an integer value of G_0. Between 0 and 1.2 G_0 we used intervals of [1.2 to 0.8 G_0], [0.8 to 0.6 G_0], and [0.6 to 0.2 G_0] and each recorded stabilized conductance was attributed to one of these intervals and considered as a single point at 1 G_0, 0.7 G_0, or 0.4 G_0 values. A smoothing function (spline function in the *Origin* software) was then used to reach the final form of the histograms. By using these quite large intervals, we avoid small variations of the conductance around 1 G_0 being abusively attributed to molecular absorption.

Results

Preparation of Copper Atomic Contacts in Water. We first tested the self-terminated method, introduced by Tao et al.[3] with an external resistance of 10 kΩ to generate atomic contacts in various electrolytes. The electrolytic media were 10^{-2} M $CuSO_4$/10^{-2} M H_2SO_4, H_2SO_4 at various concentrations down to 10^{-6} M, and MilliQ water. When the bias is applied, copper dissolves at the anode, copper(II) is generated, diffuses into the micronic gap, and deposits at the cathode. During this first step, the current is controlled by the electrochemical process occurring at the microelectrodes. Typical current recorded is about 100−500 nA (depending on the electrolyte used) and the *I*/*V* characteristic, before contact has occurred, shows sigmoid waves usual for electrochemistry on microelectrodes (using the i_{lim} recorded in 10^{-2} M $CuSO_4$/10^{-2} M H_2SO_4 makes it possible to estimate a diameter around 80 μm for the microelectrodes obtained through the copper wire cutting procedure. This value is close to the initial diameter of the copper wire). Copper deposition at the cathode is not uniform and occurs preferentially on small local probes of the surface. As a consequence, the distance between the electrodes decreases and after a certain time they come into contact. In many electrolytes, and with various biases or external resistances, the contact is macroscopic and its resistance is close to zero. For instance, contact formation in 10^{-2} M $CuSO_4$/10^{-2} M H_2SO_4 or in 10^{-2} M H_2SO_4 occurred easily but yielded only macroscopic contacts with above 10 G_0 conductance. Decreasing the H_2SO_4 concentration yielded contacts with smaller conductance and 10^{-6} M H_2SO_4 gave contacts that could be considered as atomic. To our surprise, MilliQ water, a bias of 1.2 V, and an external resistance of 10 kΩ gave the best results.[23] Using this unconventional media gave atomic contacts easily. Curve a of Figure 1 shows a typical curve recorded in MilliQ water. In this case, the conductance of the contact is very close to 1 G_0 and remains stable for the

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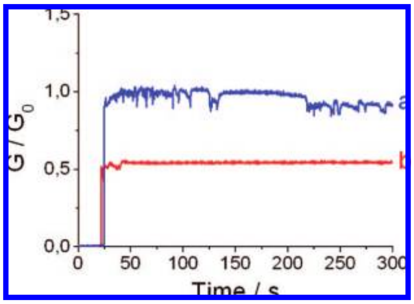

Figure 1. Conductance vs time during the electrochemical process for contacts generated in: a) water and b) water + 10^{-4} M β-CD.

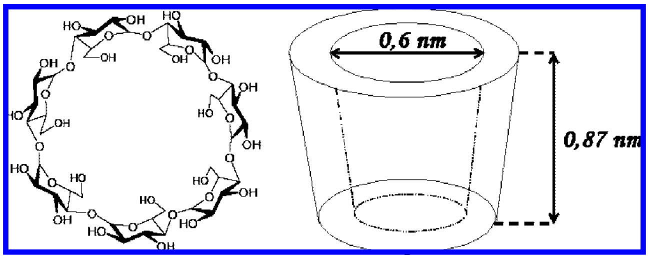

Figure 2. Chemical structure and general form of β-cyclodextrin.

600 s of the experiment. Note also that steps near interger values of G_0 are sometimes observed (below)

Preparation of Copper Atomic Contacts in Water/β-CD. Cyclodextrins are naturally occurring molecular tubes composed of several α-1,4-linked glucopyranose units (Figure 2). The rim-to-rim tube length is 0.87 nm but this dimension varies with the conformation, and cyclodextrins often pack more closely than this in the solid state through hydrogen-bonding interactions to form channel structures.[24] They have a hydrophilic external surface and a hydrophobic cavity, 0.47, 0.60, and 0.75 nm in diameter for α, β, and γ cyclodextrin, respectively. As a consequence, CDs form inclusion complexes with a wide variety of organic guests in aqueous solution. In molecular electronics, they have been used to generate encapsulated molecular wires.[25−29]

Copper(II) is known to interact with CD. A 2:1 stoichiometric complex [30,31] in neutral and alkaline media has been reported

(23) It is quite surprising that atomic contacts can be obtained without any supporting electrolyte. The intrinsic solution conductivity and potential distribution in the microgap is therefore at the mercy of dissolved gases and contamination (thanks to one of the referees for this comment). Nevertheless, it is with this unconventional electrolyte that we obtain the best reproducibility using the self-terminated method. We believe that the slow and smooth interpenetration of the large diffuse layers of the two electrodes getting closer is a key to understanding this effect. We are currently working on this particular observation (we believe also that contamination is at the origin of the few below 1 G_0 atomic contacts generated in water that are sometimes observed).

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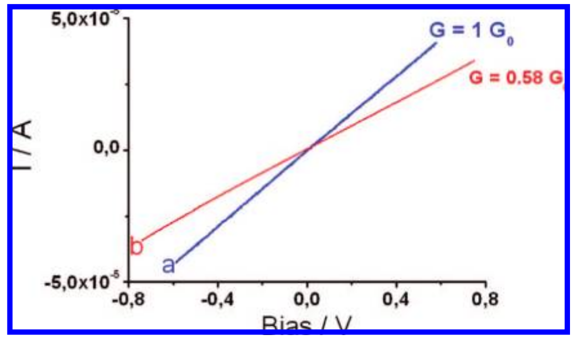

Figure 3. *I*/*V* curves for contacts generated in: a) water, b) water + 10^{-4} M β-CD.

in which two copper(II) atoms bridge the hydrophilic upper rim of CD and are thus located at the center of the tube just above the cavity. A 1:1 complex in which copper(II) is present almost in the center, inside the cavity,[32] has also been characterized using ^{1}H NMR spin−lattice relaxation time measurements. Recently, the crystal structures of molecular complexes between β-CD and $CuCl_2$ were reported.[33] The copper ion is axially coordinated with hydroxy groups of adjacent β-CD molecules, giving a 1D β-CD/$CuCl_2$ array. The geometry of these complexes may induce a template effect in copper(II) reduction processes.

When the solution contains 10^{-4} M β-CD, it is very difficult to obtain a contact between the two electrodes using the same bias as in water (1.2 V). Indeed, the current drops to 50 nA and the time before connection is considerably increased. This clearly shows that β-CD has a marked effect on the electrochemical process and suggests that copper(II) binds with β-CD, in agreement with the reported complexes.[29−32] However, increasing the bias to 1.6 V makes it possible to generate an atomic contact. Curve b of Figure 1 shows the typical curve recorded in water/β-CD. In this case, the conductance of the contact is close to 0.5 G_0, much less than expected (1 G_0) for a one-atom contact, and is much less noisy.

Characterization of the Copper Atomic Contacts Generated in Water and in Water/β-CD. The contacts generated in this study (after a stabilized conductance is reached) were characterized using potential gradients from −1 to +1 V at a sweep rate of 100 mV s^{-1}. Figure 3 shows *I*/*V* curves of the contact in the various electrolytic media. The stable ohmic behavior between −1 and +1 V indicates that a metallic regime has been reached. The slopes of these two curves are in agreement with the measured stabilized conductance during atomic contact formation.

The examples given above are not selected curves. They have been reproduced many times, and many experiments in water have been compared with the same number of experiments in water/β-cyclodextrin. Figure 4 shows the histograms of the stabilized conductance in the two different media. The general shapes of these two curves are completely different. In MilliQ water, the conductance histogram reveals well-defined peaks at integer multiples of G_0 and more than 62% of the contacts have conductances of 1 or 2 G_0. These results are in agreement with those obtained by many other groups. On the contrary, in water/β-CD, 60% of the atomic contacts show conductances below or equal to 1 G_0 and, among this type, 66% are below

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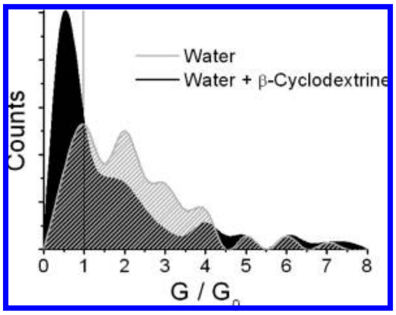

Figure 4. Histograms of stabilized conductances in water and in water/β-CD.

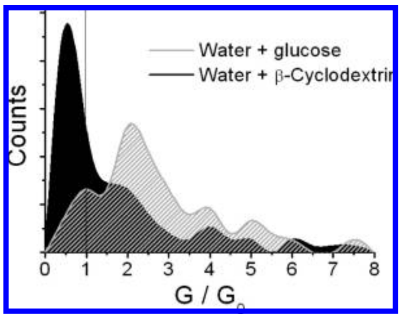

Figure 5. Histograms of stabilized conductances in water/glucose and in water/β-CD.

0.75 G_0, which is much less than in water (with 1.2 V bias). These appreciable changes are in agreement with molecular adsorption on an atomic contact, which is known to decrease the conductance.[16−20] This effect has been attributed to the scattering of the conduction electrons in the nanowire by the adsorbates[11] and appears to be related to the adsorption strength. The results observed in this work constitute another example of such effects and clearly demonstrate that β-CD is adsorbed on the quantum wire when contact occurs and remains on the contact for a long time.

Preparation of Atomic Contacts in Water/Glucose. To check if this molecular adsorption is specific to β-CD or if the difference in bias could induce the differences observed in the conductance of the atomic contact generated in water and in water/β-CD, control experiments were performed in water/glucose. Glucose has similar functional groups to β-CD and could adsorb on the quantum wire with similar strength. The same number of atomic contacts was generated in water/7 10^{-4}M glucose using the same 1.6 V bias as for water/β-CD. Figure 5 compares the histograms obtained in water/glucose and water/β-CD. Glucose and β-CD do not give similar results. In water/glucose, the conductance of the most frequently generated atomic contact is around 2 G_0, the peaks in the conductance histogram broaden and only 5% of the contacts exhibit stabilized conductance below 1 G_0. On the contrary, in water/β-CD, most of contacts reach stable values below 1 G_0, and 33% have stabilized conductance below 0.75 G_0. Furthermore, the contacts generated in water/glucose appear to be much less stable (as judged by the noise in the conductance versus time curves (Supporting Information, SI1) than in water/β-CD.

Therefore, the differences between atomic contacts generated in water and in water/β-CD cannot be attributed to the differences in the bias used. Moreover, the effect of β-CD on the formation of the contact is not similar to that of glucose, even though these two molecules have similar functional groups. These experiments prove the specific role of β-CD and confirm that it is adsorbed on the quantum wire when contact occurs and remains on the contact for a long time.

Discussion and Control Experiments. The occurrence of atomic contacts with below 1 G_0 conductance, observed when they are generated in water/β-CD and never or rarely seen in water or in water/glucose, is due to β-CD adsorption. Parts a and b of Figure 6 show two plausible situations. In the first one, the metallic nanowire is encapsulated by a β-CD molecule. Given the shape of β-CD (molecular tube), it is plausible that metal electroreduction in this medium yields an insulated atomic contact, just as electropolymerization of small conjugated oligomers is known to yield insulated molecular wires.[24−28] In the second one, β-CD adsorption takes place without any encapsulation, and the atomic contact is not threaded in the β-CD cavity.

To discriminate between these two plausible situations several experiments were performed.

First, atomic contacts were generated in MilliQ water or in water/glucose, and then β-CD was introduced into the solution. Encapsulation of the atomic wire by cyclodextrin, as depicted in part a of Figure 6, is not possible unless the contact breaks after its formation. Figure 7 shows the effect of injecting β-CD into an atomic contact generated in water. No significant change in the conductance is observed. Similar results were obtained for atomic contacts generated in water/glucose (not shown). Experiments were repeated 30 times on 1 G_0 contacts: none showed any significant change in conductance. This shows that β-CD has to be present during generation of the wire to obtain below 1 G_0 conductance; added subsequently it has no effect.

Second, other experiments were performed with sulfonated calix-4-arene and calix-6-arene. These molecules have also a cavity and might give similar results but, in fact, no stabilized atomic contacts were obtained (Supporting Information, SI2). Furthermore, the size of the cyclodextrin was changed. There is a small difference in the histograms of the stabilized conductance when α-, β-, and γ-CD are used but contacts with below 1 G_0 stabilized conductance are also obtained with the other CDs (Supporting Information, SI3). This means that the results are cyclodextrin specific but are not very sensitive to the size of the cyclodextrin even though important differences are observed in the histograms of the conductance a few seconds after the contact has been generated (not shown).

Third, we constructed several copper atomic contacts in water, water/glucose, and in water/β-CD and studied the effect of sodium salicylate. Sodium salicylate is known to passivate copper very efficiently through the formation of a very thin film of copper(II) salicylate.[34] If copper(II) salicylate is incorporated between copper atoms of atomic contacts generated in water, this will lead to the breakdown of the contact and the loss of ohmic behavior. However, if the contact is insulated by cyclodextrin, as depicted in part a of Figure 6, this breakdown could be slowed down or the atomic contact might not see sodium salicylate and would retain ohmic behavior with a below 1 G_0 conductance. For these experiments, the contacts generated in water/β-CD were divided into two types. Type I contacts do not show strong β-CD adsorption effects and have above 1 G_0 conductance. In the second type (type II), below 1 G_0 conductance is observed showing strong β-CD adsorption effects. Figure 8 shows the effect of sodium salicylate on contacts

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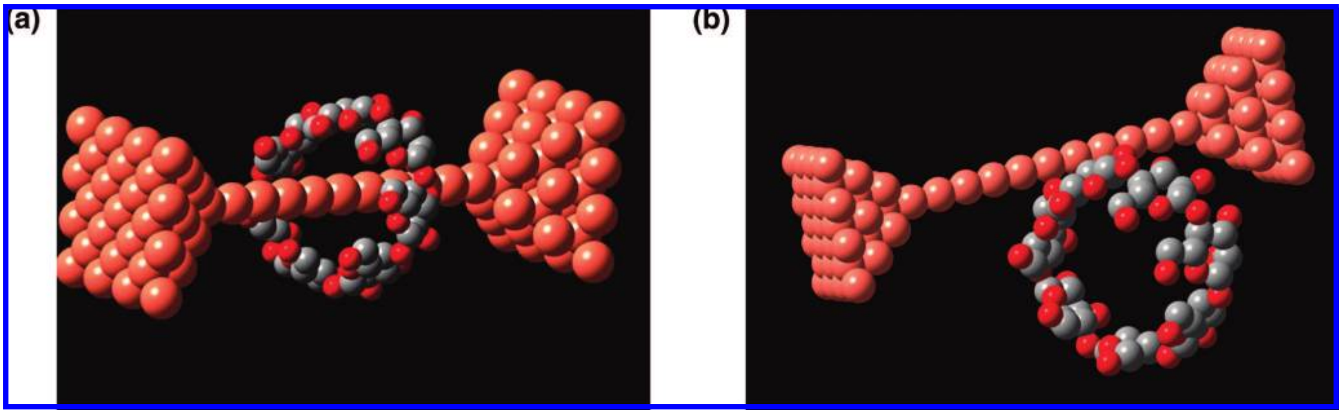

Figure 6. a) Metallic atomic contact encapsulated by one β-cyclodextrin. (Note that the numbers of copper atoms and β-CDs involved are unknown), b) metallic atomic contact with β-CD adsorption.

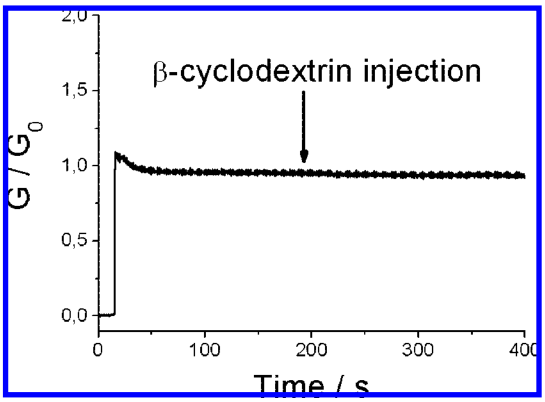

Figure 7. Effect of β-CD on an atomic contact generated in water.

generated in water (part a of Figure 8) and in water/β-CD (part b of Figure 8) for type II contacts. A few seconds after salicylate addition, contacts generated in water break down (the same result is obtained in water/glucose, Supporting Information, SI4), whereas type II contacts resist much longer, stay at a low conductance value, and retain their ohmic behavior. This behavior is reproducible and eventually the contact breaks. In contrast, type I atomic contacts generated in water/β-CD appear to be salicylate-sensitive and behave like those generated in MilliQ water (they break a few seconds after salicylate addition and lose their ohmic behavior), which indicates that they are not protected against salicylate.[35] This clearly suggests that the two types of atomic contacts obtained in water/β-CD are different and that those showing a below 1 G_0 conductance are partially protected from added molecules. The slight increase in conductance observed after adding salicylate (part b of Figure 8) may be attributed to its adsorption on cyclodextrin, reducing the strength of adsorption on the copper contact.

Finally, because salicylate seems to be able to discriminate between two types of atomic contacts generated in water/β-CD, we have analyzed the noise recorded in the conductance versus time curves (Figure 2) of these two types of contact and on atomic contacts generated in water or in water/glucose. Table 1 shows the results obtained.

We find that among atomic contacts generated in water, 82% have a conductance fluctuation above 0.03 G_0 (18% below 0.03 G_0). Type I atomic contacts generated in water/β-CD display the same fluctuation (86% above 0.03 G_0). In marked contrast, 78% of type II contacts generated in water/β-CD show fluctuation below 0.03 G_0. Control experiments with glucose confirm that this medium does not give atomic contacts similar to those generated in water/β-CD despite having similar functional groups. Furthermore, there is a strong correlation between the conductance noise versus time curves and the sensitivity toward salicylate of atomic contacts generated in water/β-CD. Type II contacts showing low conductance fluctuations are partially protected against salicylate probes, whereas type I contacts are not protected and exhibit marked conductance fluctuations. This confirms that two different types of atomic contacts are generated in this medium and that type II contacts have a set of unusual properties (below 1 G_0 conductance, partially insulated from added molecules, low conductance fluctuations), which are compatible with their encapsulation. Note also that the average rms noise has been taken on the whole conductance versus time curve, during the 400 s of the experiments (the initial time for calculating average rms noise is that when contact has been reached). It is therefore a measure of the stability of the contact in the various electrolytes. Type II contacts generated in water/β-CD are thus much more stable than contacts generated in the other media.

In the following part, we will focus on type II contacts. Some of them show steps at fractional values of G_0 (0.1 G_0 for the lowest), as can be seen in part b of Figure 9. For atomic contacts generated in water or in water/glucose, when steps are seen in the conductance versus time curves (part a of Figure 9), they are close to an integer value of G_0. Such up-and-down fluctuations of the conductance, with well defined steps, are generally attributed to surface reconstruction. In the present case (part b of Figure 9), steps, which are only a fraction of G_0, clearly indicate strong and specific CD adsorption. It also suggests that the narrowest portion of the wire, which controls the conductance of the entire macroscopic system, may consist of a few atoms (and not of one atom) with an effective transmission coefficient of the contact significantly different from unity.

Conclusion

Marked differences are observed between atomic contacts generated in water, water/glucose, and water/β-CD. Atomic contacts generated in water/β-CD using 1.6 V bias with the self-terminated method show specific adsorption effects on the conductance, and a type of contact with unusual properties (below 1

(35) Note also that 1 G_0 atomic contacts generated in water and then exposed to cyclodextrins and finally to salicylate always break a few seconds after salicylate injection. This shows that β-CD has to be present during generation of the contact to obtain protection against salicylate; added subsequently it does not protect the contact.

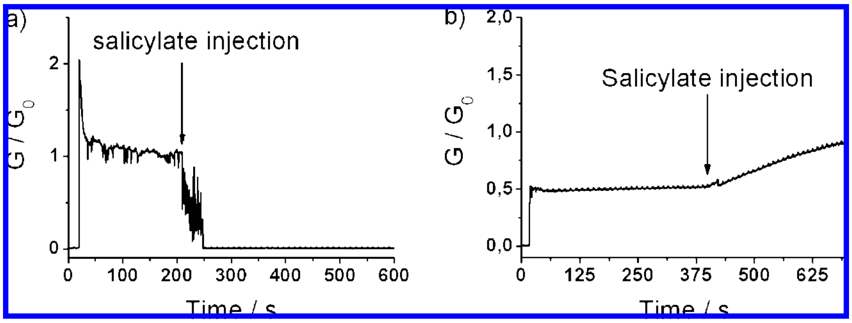

Figure 8. Effect of sodium salicylate on: a) atomic contact generated in water, b) atomic contact generated in water/β-CD.

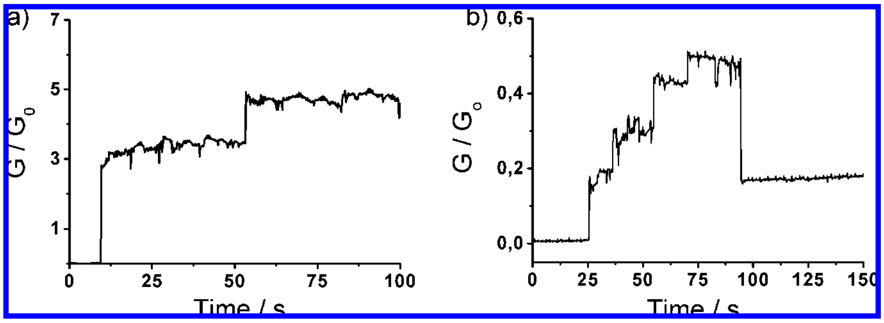

Figure 9. Conductance steps after contact formation: a) in water, b) in water + 10^{-4} M β-CD.

Table 1. Proportion of Atomic Contacts with Low and High Conductance rms Noise and Average Noise Recorded in the Conductance versus Time Curves for Contacts Generated in Water, Water/Glucose, or Water/β-CD (for Type I and Type II Contacts)

	water	water/glucose	water/β-CD	
			Type I $G > 1\ G_0$	Type II $G < 1\ G_0$
proportion of atomic contacts with conductance rms noise <30 mG_0 (%)	18	8	14	78
proportion of atomic contacts with conductance rms noise >30 mG_0 (%)	82	92	86	22
average noise <rms> mG_0	171	178	182	27

G_0 conductance and reduced conductance fluctuation with time) is frequently obtained. Such a type is not generated in water using a lower bias (1.2 V) or in water/glucose using the same bias (1.6 V). Addition of cyclodextrin to the electrolytic medium, after 1 G_0 contacts have been generated in water, does not lead to significant conductance decrease; this type of atomic contact can only be generated when cyclodextrin is added prior to contact formation. Moreover, sodium salicylate causes breakdown of atomic contacts generated in water, whereas those in water/β-CD, showing a below 1 G_0 conductance and reduced conductance fluctuation, are only slightly affected and appear to be partially insulated from this external molecular probe. On the other hand, noisy above 1 G_0 contacts generated in water/β-CD behave toward salicylate like those generated in water. Therefore, below 1 G_0 conductance, conductance fluctuation with time and protection of the atomic contact against salicylate are correlated. The observed effects clearly demonstrate that protected or partially protected atomic contacts can be fabricated. Moreover, the particular shape of β-CD, the fact that copper(II) is transported in such media in copper(II)/cyclodextrin complexes with favorable geometry, and the occurrence of this type of atomic contact with a set of unusual properties suggest that some of the contacts generated are encapsulated by β-CD. However, direct independent structural evidence (such as TEM or STM characterization) is still needed to confirm or infirm this interpretation, which remains speculative because it relies only on transport measurements as performed by most groups working with such systems.[1,2,4,10,12,15−22] Indeed, the indirect connection between an observed conductance and a structural model makes it difficult to rule out other less interesting conclusions. That CD protects the copper wire is experimentally demonstrated. That CD surrounds the copper wire is plausible, based on the experimental observations, but remains far from unequivocal.

Such a system may nevertheless prove extremely useful for sensing applications. We anticipate that our results could be a starting point for sophisticated sensing devices. For example, the grafting of specific recognition sites onto cyclodextrin would be relevant for such developments.

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