Open Carbon Nanopipettes as Resistive-Pulse Sensors, Rectification Sensors, and Electrochemical Nanoprobes

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Supporting Information

ABSTRACT: Nanometer-sized glass and quartz pipettes have been widely used as a core of chemical sensors, patch clamps, and scanning probe microscope tips. Many of those applications require the control of the surface charge and chemical state of the inner pipette wall. Both objectives can be attained by coating the inner wall of a quartz pipette with a nanometer-thick layer of carbon. In this letter, we demonstrate the possibility of using open carbon nanopipettes (CNP) produced by chemical vapor deposition as resistive-pulse sensors, rectification sensors, and electrochemical nanoprobes. By applying a potential to the carbon layer, one can change the surface charge and electrical double-layer at the pipette wall, which, in turn, affect the ion current rectification and adsorption/desorption processes essential for resistive-pulse sensors. CNPs can also be used as versatile electrochemical probes such as asymmetric bipolar nanoelectrodes and dual electrodes based on simultaneous recording of the ion current through the pipette and the current produced by oxidation/reduction of molecules at the carbon nanoring.

Nanometer-sized pipettes pulled from borosilicate or quartz capillaries have been widely employed in analytical chemistry,1 nanoelectrochemistry,2 and scanning probe microscopies.3 Nanopipettes are easy to fabricate using a laser pipette puller. A very small orifice radius (e.g., a ≤ 10 nm4) makes nanopipettes useful for studies of charge transfer kinetics at the liquid/liquid interface,4,5 and sensing applications based on current rectification6–8 or resistive-pulse measurement.9–11 The outer diameter of the pipette can also be very small because the wall thickness at the tip is comparable to or smaller than the orifice radius.1–3 With their small physical size and needlelike geometry, nanopipettes are excellent tips for scanning electrochemical microscopy (SECM)3a,d,12–14 and scanning ion-conductance microscopy (SICM).3b,14,15

Many applications of nanopipettes require the control of the surface charge and chemical state of the inner wall. The inner pipette wall can be silanized,12b,c,16 chemically modified using various reagents,17 or functionalized by deposition of proteins,18a and polymers.18b,c,19 These labor-intense methods are plagued by partial pipette blocking and contamination by chemical residues from the reagents.2,4–5b Surface modification of very small (e.g., 1–5 nm radius) pipettes is especially difficult.4b Here we explore a different approach to controlling the pipette properties by coating its inner surface with a nanometer-thick layer of carbon. The potential of the carbon film can be varied by applying voltage between it and the reference electrode, thus changing the surface charge and the electrical double-layer at the pipette wall. In this way, one can control the gating properties of the pipette as well as the electroosmotic flow inside its tapered shaft.

The methodology for chemical vapor deposition (CVD) inside pulled quartz pipettes has been developed previously20 and used to fabricate carbon nanopipettes (CNP) with an open path in the middle21 as well as carbon electrodes with a nanocavity (“nanosampler”)22a and platinized nanosensors.22b Somewhat similar procedures were used to fabricate multifunctional carbon electrodes, including platinum disk/carbon ring and carbon ring/nanopore probes.23 CNPs have been employed for intracellular injections, electrical measurements, and electrophysiology.24 Here we focus on electrochemical and sensor aspects of CNPs.

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MATERIALS AND METHODS

A complete description of materials, instrumentation, and procedures is available in the Supporting Information.

RESULTS AND DISCUSSION

Current Rectification and Resistive-Pulse Sensing. The setup employed in these experiments is shown schematically in Figure 1A. The CNP is filled with (typically aqueous) electrolyte solution and immersed in external solution with either the same or different composition. The outer solution contains one reference electrode (ref 1), while the internal reference (ref 2) is placed in the solution-filled tip of a plastic pipette tightly fitted to the back of the CNP. The carbon layer can either be connected to the potentiostat as a working electrode or floating at an open circuit potential. The ion current through the CNP orifice can be induced by applying voltage between ref 2 and ref 1 (\(V = \text{potential of ref 2} - \text{potential of ref 1}\)). Similarly to quartz pipettes and nanopores,1 essentially linear current–voltage (\(i-V\)) curves were obtained with relatively large CNPs (e.g., \(a = 650\) nm; Figure 1B), while smaller carbon pipettes (\(a = 43\) nm; Figure 1C) showed significant current rectification indicative of the negatively charged carbon surface.

The rectification exhibited by small CNPs is more pronounced than that observed previously with similarly sized quartz pipettes and nanopores,1 with relatively large CNPs (e.g., \(a = 650\) nm; Figure 1B), while smaller carbon pipettes (\(a = 43\) nm; Figure 1C) showed essentially linear \(i-V\) curves because of the much lower charge density (Figure S2 in Supporting Information).

The current rectification is expected to become more pronounced with the increasingly negative surface charge, i.e., when a significant negative potential is applied to the carbon layer. This effect can be seen in Figure 2. When the carbon layer was biased at the open circuit potential (\(-110\) mV vs the internal reference electrode; red curve) or a slightly more negative potential (e.g., \(-200\) mV; black curve) only minor current rectification was observed using a relatively large CNP (\(a \approx 240\) nm). The rectification increased markedly with increasingly negative carbon bias (e.g., \(-500\) mV; purple curve). In contrast, when the carbon surface was biased positively (e.g., \(+500\) mV; orange curve), the rectification disappeared completely and the corresponding \(i-V\) curve became linear. Applying even more positive bias to observe reverse current rectification was not possible with our experimental setup because of the high anodic current flowing at the large carbon surface under such conditions.

The possibility of reversibly changing the surface charge of the inner pipette wall suggests that a CNP can be used as a versatile resistive-pulse sensor whose response can be tuned to detect a specific analyte. The feasibility of resistive-pulse sensing with CNPs is shown in Figure 3 that presents typical current–time recordings obtained in a buffer solution and in the presence of 10 nm Au nanoparticles with covalently attached monoclonal primary antihuman PSA antibodies and prostate specific antigen (AuNP-antibody-PSA).26a The 40–60 nm radii of these NPs26b make them a convenient model for our proof-of-concept experiments. Unlike a background trace (A) obtained with no nanoparticles added to the external solution, a number of pulses with the current changes much larger than the noise level can be seen in trace B. Similarly to resistive-pulse recordings obtained for the same negatively charged carbon surface.
charged AuNP-antibody-PSA using quartz pipettes. Current blockages were observed only when a positive potential was applied to ref 2 with respect to ref 1. However, CNP’s properties as a resistive-pulse sensor are markedly different from those of a quartz pipette. For instance, the voltage applied in Figure 3 was only +100 mV, while a much higher voltage (e.g., +600 mV) was required to detect the same nanoparticles using a quartz nanopipette.

Bipolar Nanoelectrodes. One should notice that there are two parallel pathways for the current flow through a CNP with the carbon electrode floating (i.e., not connected to the potentiostat). In addition to the ion current discussed above, electronic current can flow in the conductive carbon layer (Figure 4A). The relative magnitudes of the ionic and electronic components of the total current flowing between the two reference electrodes are determined by the resistance associated with each pathway, as shown by the equivalent circuit in Figure 4B. The resistance to the ion current depends on the solution conductivity and the inside geometry of the pipette; the latter is largely defined by the orifice radius (a) and the tip angle (θ). Both parameters are controlled by pipette pulling and CVD and can be determined by voltammetry and TEM (for details, see the Supporting Information). R_{ionic} increases with decreasing a, θ, and the ionic strength of solution. An i−V curve obtained with a not very small CNP normally is retraceable, and its shape is independent of the potential sweep direction (Figure 2), indicating that ion current is the main source of signal. The i−V curves obtained with smaller pipettes show significant hysteresis due to the contribution of the double-layer charging current flowing at the large carbon/solution interface (Figure S3 in the Supporting Information).

The ion pathway can be completely eliminated by not filling a CNP with the liquid phase, so that only the back portion of the carbon layer and its nanometer-sized tip are exposed to solution (Figure 4A). Two cyclic voltammograms obtained in this configuration by sweeping the voltage applied between two reference electrodes (Figure 4C) are very similar to the curves measured at similarly sized electrodes, which can be made by completely filling the pipette orifice with carbon. A wide polarization window (>2 V) can be seen in the black curve obtained with no electroactive species added to the external solution, and a nearly perfect steady-state voltammo-gram was recorded after adding 1 mM ferrocenedimethanol (red curve). In these experiments, the carbon layer was not connected to a potentiostat and behaved as an asymmetric bipolar electrode with the large (~mm^2) surface area on the back of the CNP and a microscopic ring-shaped tip. The shape of the voltammogram suggests that both the ohmic resistance of the carbon film and the electron-transfer resistance at the macroscopic end of the pipette are negligibly small. The electron transfer between the back portion of the CNP and the solution is sufficiently fast not to affect the voltammetric response despite the absence of added redox mediator in that solution because the exposed surface area of carbon is many orders of magnitude larger than that of the pipette tip. The picoamp-range current at such a large surface can be produced by double layer charging and/or oxidation/reduction of impurities.

The voltammogram in Figure 4C is essentially retraceable, suggesting that the size of the carbon/solution interface did not change on the experimental time scale. However, it was noticed previously that aqueous solution can gradually advance into the carbon pipette shaft. The effect of the carbon potential on this process (electrowetting) has yet to be investigated.

Dual Electrochemical Probes. The ion current flowing between two reference electrodes and oxidation/reduction current of electroactive molecules at the carbon nanoring exposed to the external solution can be recorded independently. The voltammograms shown in Figure 5 were obtained using a CNP filled with an organic solvent (benzonitrile) immiscible with water and immersed in aqueous solution containing 10 mM of Ru(NH3)_6Cl_3, 0.1 M KCl, and 0.5 mM NaPF_6. The steady-state voltammograms of PF_6^- transfer across the liquid/liquid interface (Figure 5A) and reduction of Ru(NH3)_6Cl_3 at the carbon nanoring (Figure 5B) were recorded by scanning the voltage applied between the internal and external reference electrodes and the carbon electrode potential, respectively. The good quality ion-transfer and electron-transfer voltammograms in Figure 5 suggest that both signals can be measured independently without significant interference.

Dual electrochemical nanoprobe, consisting of an open glass pipette and a solid electrode have been fabricated previously by pulling theta-tubing or depositing a conductive layer on the outer pipette wall and coating it with the insulating film. The
advantages of CNPs include a small size (potentially, just a few nanometers diameter), complete electrical insulation of the carbon side surface without any additional coating, and axisymmetric geometry with the concentric liquid/liquid and carbon/solution interfaces. These features suggest that CNPs can be employed as SECM tips for high-resolution simultaneous imaging of surface topography and reactivity. Another potential application is for generation/collection experiments that can be useful for studying mechanisms of multistep electrochemical processes.

**CONCLUSIONS**

In conclusion, we have shown that a carbon nanopipette produced by coating the inside of the pulled quartz capillary with a nanometer-thick carbon layer can be employed for a wide range of electrochemical and sensing applications. The extent of ion current rectification in a CNP depends on the potential applied to carbon, which determines the surface charge and electrical double-layer at the pipette wall. Thus, a CNP can work as a tunable resistive-pulse sensor whose properties can be adjusted to detect a specific analyte. The ability to vary the charge on the carbon surface can be useful for changing the translocation time of charged analytes, e.g., slowing down the translocation of DNA to facilitate its sequencing. Another potential application is to control the electroosmotic flow inside the pipette tapered shaft and study its effects on the ion current. These include the intriguing “electroosmotic flow separation” that can cause ion current to increase when an SICM probe approaches an insulating surface.

The attainable diameter of a CNP tip is <20 nm because both the pipette orifice and the carbon layer are inside a prepulled quartz pipette. Such a small physical size makes CNPs potentially useful for local electrochemical and resistive-pulse measurements. The CNP tip can also support a nanometer-sized liquid/liquid interface. The two signals, ion-transfer current across the liquid/liquid interface and electron-transfer current at the carbon nanoring, have been monitored independently, suggesting the suitability of a CNP as a dual-mode SECM probe for high-resolution topography and reactivity imaging.

REFERENCES


