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# Controlling the Conductance of Atomically Thin Metal Wires with Electrochemical Potential

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***Abstract:*** We report on the study of quantum transport in atomically thin Au wires suspended between two Au electrodes by modulating the electrochemical potential of the wires in various electrolytes. The potential modulation induces a conductance modulation with a phase shift that is always ~180°, meaning that an increase in the potential always causes a decrease in the conductance. The amplitude of the induced conductance modulation, however, depends on several parameters. First, it depends on the atomic configurations of the individual wires. Second, the relative amplitude, defined as the ratio of the conductance modulation amplitude to the conductance, decreases as the diameter of the wire increases. Third, it depends on whether anion adsorption is present. In the absence of anion adsorption, it is $\sim 0.55G_0$ ($G_0 = 2e^2/h$) per V of potential modulation, for a wire with conductance quantized near $1G_0$. This double layer charging-induced conductance modulation can be attributed to a change in the effective diameter of the wire. In the presence of anion adsorption, the amplitude is much larger (e.g., $\sim 1.6G_0/V$ when $I^-$ adsorption takes place) and correlates well with the strength of the adsorption, which is due to the scattering of conduction electrons by the adsorbed anions.

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## Introduction

Nanostructured materials and devices are interesting not only because they promise various new applications, but also because they exhibit novel quantum phenomena. Many quantum phenomena were originally discovered in semiconductor devices often under high vacuum and low-temperature conditions. Extension of the studies to liquid environment at room temperature offers us exciting opportunities to study chemical and electrochemical processes at the nanometer scale. An important example is single electron charging phenomenon in nanoparticles or quantum dots.[1−3] Recent studies of the phenomenon at room temperature[4] and in the electrochemical environment[5−7] have provided new insight into electron-transfer chemistry and may lead to applications such as molecular switches[8] and chemical sensors.[9] The present paper is aimed at another quantum phenomenon, conductance quantization in metallic nanowires. This phenomenon has been demonstrated in electrolytes,[10−12] but several basic questions remain to be addressed: Will a change in the electrochemical potential of a nanowire change the quantized conductance? If yes, by how much, and what is the mechanism? The goal of the present work is to address these questions. Because electrochemical potential controls various electrochemical processes, answers to these questions will allow us to study the processes taking place on a nanowire via monitoring the conductance of the nanowire. The ability to change the conductance of a nanowire with a third electrode in a fashion of transistor is also directly relevant to devices applications.

The phenomenon of conductance quantization occurs in a semiconductor or metal wire connected between two macroscopic electrodes when the following two conditions are satisfied. First, the wire must be shorter than the electron mean free path so that electrons transport ballistically along the wire. Second, the wire diameter must be comparable to the electron wavelength to allow electrons to form standing waves (quantum modes) in the transverse direction of the wire. When the two conditions are met, the conductance of the system, defined as the ratio of the current ($I$) to the voltage ($V$), is[13]

$$G \equiv \frac{I}{V} = G_0 \sum_{n=1}^{N} T_n \qquad (1)$$

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where $G_0 = 2e^2/h$, and $N$ is the number of quantum modes in the wire. For an ideal wire, the transmission probability is $T_n \approx 1$, and the conductance is quantized and given by $G = NG_0$, where $N$, the number of quantum modes, is determined by the diameter of the wire.

This interesting phenomenon was first clearly observed in experiments in semiconductor devices, where the electron mean free path is many micrometers, and the electron wavelength is ~40 nm, much larger than the atomic scale.[14,15] The relative large wavelength made it possible to fabricate the required nanowires using conventional nanofabrication techniques, but it leads to a small energy difference between the quantum modes, which means a pronounced conductance quantization in the semiconductor devices only at liquid helium temperature. For a typical metal (e.g., Au), the electron wavelength is only a few angstroms, so it does not require low temperature to observe the phenomenon, but the wires must be atomically thin. To date, two general methods have been developed to fabricate atomically thin metal wires that exhibit the conductance quantization. One is a mechanical approach, which forms a nanowire by separating two electrodes from contact.[16−18] During the separation, a metal neck is formed between the two electrodes and then stretched into an atomically thin wire with quantized conductance before completely broken. The second method, developed by us recently, is to electrochemically fabricate the nanowires.[10,19] Recent transmission electron microscopy has directly confirmed that a metal wire with quantized conductance consists of a string of a few metal atoms.[20,21] We note that the metallic nanowires described here are also sometimes called quantum wires or quantum point contacts.

In a semiconductor nanowire or quantum point contact, the width and the electron density of the nanowire can be controlled flexibly with gate electrodes. This flexibility, unfortunately, does not exist for metallic nanowires in a vacuum or in air. In electrolytes, however, we can control the electrochemical potential of a metallic nanowire in a fashion similar to the gate voltage. By controlling the electrochemical potential, it is possible to control the conductance of the wire via controlling various electrochemical processes taking place on the wire. We observed recently an interesting fractional conductance quantization at very negative potentials by analyzing conductance histograms (occurrence of conductance at various conductance steps).[11] Because the peaks due to conductance quantization in the histogram are rather broad, we were not able to determine the dependence of the quantized conductance on the electrochemical potential. The histogram-based analysis also prohibited us from measuring electrochemical effects on the conductance of each nanowire. In this work, we have accurately determined the potential-induced conductance change in each of the individual nanowires using an AC technique and studied both the double layer charging and the anion adsorption effects by performing the AC measurement in electrolytes containing various anions.

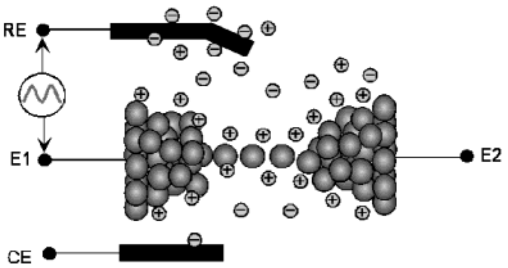

***Figure 1.*** Schematic drawing of the experimental setup. An atomically thin Au wire is suspended between two Au electrodes (a substrate and a STM tip). The electrochemical potentials of the two electrodes, $E1$ and $E2$, are controlled relative to a reference electrodes (Ag wire) with a bipotentiostat. The bias voltage across the wire is $E1 - E2$, which is fixed at 40 mV during the experiment.

## Experimental Section

We created atomically thin Au wires by pulling a Au STM (scanning tunneling microscope) tip out of contact with a Au substrate using a piezoelectric transducer in two ways (Figure 1). The first one pulled each wire by manually controlling the voltage applied to the piezoelectric transducer. During the pulling process, we monitored the conductance of the wire continuously. When the conductance was stabilized at a desired quantum step, we froze the pulling and studied electrochemical effects by varying the electrochemical potential of the wire. Although the wires lacked long-term stability, they frequently lasted for many seconds, long enough for the measurements. To obtain good statistics, we used a second method to quickly and repeatedly form a large number of wires with a feedback control. The feedback loop started by driving the STM tip into contact with the substrate at a rate of 40 nm/s. Once the contact was fully established as the conductance between the tip and the substrate reached a preset value (i.e., $4G_0$), the feedback loop activated the piezoelectric transducer to pull the STM tip out of the contact. During the pulling process, nanowires with different conductance (diameters) were formed, and the same procedure was repeated over 1000 times.

To accurately determine the electrochemical potential-induced conductance change, we modulated the electrochemical potential around various preset DC values and measured the amplitude and phase shift of the induced conductance modulation. This AC technique removed various noises including mechanical drift effects in a similar way to a lock-in amplifier. The conductance of the nanowire was monitored with a digital oscilloscope (DL708, Yokogawa Co.) by simultaneously recording the current ($I$) with a modified STM preamplifier and the bias voltage ($V = 40$ mV). Although the bias voltage was preset at 40 mV, small fluctuations from the preset value could affect the measured conductance, so it is important to use the actual recorded bias voltage to determine the conductance using formula $G = I/V$.

We performed the measurements using a Teflon cell mounted inside of a glass chamber flashed with $N_2$. Before each experiment, the cell was cleaned by boiling it in Piranha solution (98% $H_2SO_4$:30% $H_2O_2$ = 3:1, v/v), and then was thoroughly sonicated in 18 MΩ water three times (Nanopure system fed with campus distilled water). (Caution: piranha solution reacts violently with most organic materials and must be handled with extreme care.) We controlled the electrochemical potential of the nanowire with a homemade bipotentiostat using a Pt wire as a counter electrode and a Ag wire as a quasi reference electrode. The quasi reference electrode was calibrated against the more widely used Ag/AgCl reference electrode before and after each experiment, and all of the potentials quoted in this work are in terms of the Ag/AgCl scale. The use of a quasi reference introduced an error of ~0.1 V in the quoted potentials. The STM tip was made of 0.25 mm gold wire (99.999%) and coated with Apiezon wax to reduce ionic

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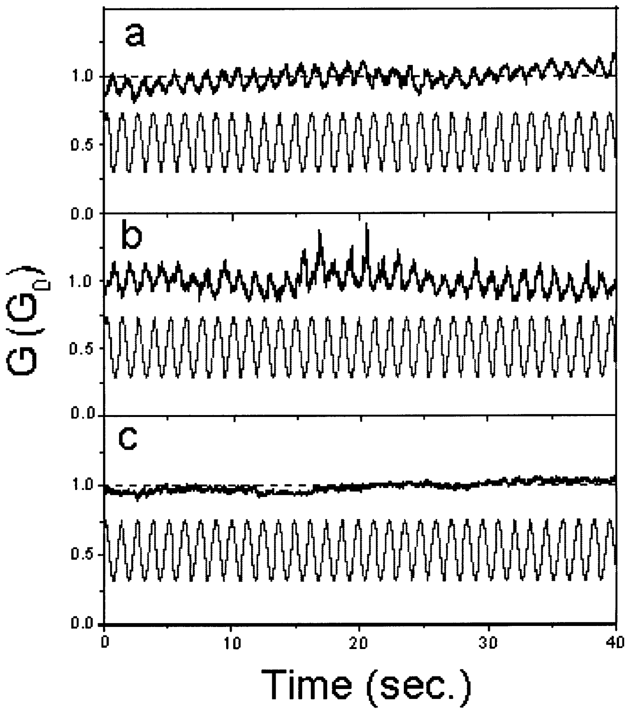

***Figure 2.*** Typical traces of electrochemical potential modulation-induced conductance changes (black line) for Au wires with conductance quantized near $1G_0$ in 0.5 M $NaClO_4$. The three traces (a, b, and c) were recorded for three wires in the same experiment, which show a large dependence of the conductance modulation on the specific atomic configuration of each wire. The amplitude and frequency of the electrochemical potential modulation (grey line) are 0.1 V and 0.85 Hz, respectively. The phase difference between the induced conductance modulation and applied electrochemical potential modulation is about 180°.

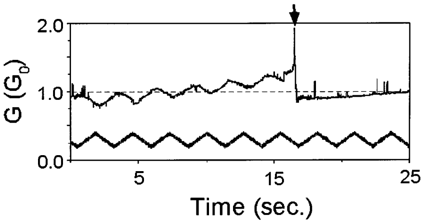

***Figure 3.*** An abrupt change in the induced conductance modulation (black line) due to a sudden switch in the atomic configuration of a nanowire in 0.5 M $NaClO_4$. The amplitude and frequency of the electrochemical potential modulation (grey line) are 0.1 V and 0.4 Hz, respectively.

conduction and polarization. The leakage current due to ionic conduction and polarization was on the order of pA, much smaller than 3 $\mu$A, the current that corresponds to the lowest conductance quantum step. The substrate was a Au film evaporated on mica in a UHV chamber. We used 0.5 M $NaClO_4$ (99.99%), 0.1 M $KClO_4$ (99.5%), and 0.5 M NaF (99.99%) as electrolytes to study double layer charging effects and 0.01 M NaCl (99.999%), NaBr (99.99%), and NaI (99.99%) in 0.5 M NaF supporting electrolyte to study anion adsorption effects. These anions are known to adsorb onto Au electrode with strengths varying from very weak to very strong in the order of $F^- < Cl^- < Br^- < I^-$.

## Results and Discussion

**Double Layer Charging.** We studied double layer charging effects on the conductance quantization using $NaClO_4$, $KClO_4$, and NaF solutions as electrolytes because the cations and the anions in these electrolytes adsorb weakly onto Au surfaces within the studied potential window. We first formed a nanowire with conductance stabilized at a certain quantum step while holding the electrochemical potential (DC level) of the nanowire at a given value. We then modulated the electrochemical potential (AC) and monitored a consequent change in the conductance. Figure 2 shows several typical measurements on nanowires with conductance quantized near $1G_0$ in 0.5 M $NaClO_4$. An electrochemical potential modulation does, in general, induce a modulation in the conductance, but the amplitude of the induced conductance modulation varies from one nanowire to another. For a 0.05 V (amplitude) potential modulation, although the typical induced conductance modulation is about 3% (Figure 2a), it can vary from ~0% (Figure 2c) to ~10% (Figure 2b). These nanowires were formed consecutively within seconds in the same experiment, so the observed variations in the conductance modulation are unlikely due to changes in experimental conditions, such as contaminations and leakage current. The large variation in the conductance modulation rules out the possibility of electronic coupling between the conductance measurement and potential control circuits as the cause of the observed conductance modulation because such coupling should not vary from one nanowire to another. We note that electronic coupling could, in principle, affect measured conductance via either the current or the bias voltage. Our STM tip is well insulated so that both faradic and polarization currents are many orders of magnitude smaller than the transport current through the nanowires. The coupling of the AC modulation into the bias voltage was also found to be negligibly small.

We have often observed abrupt changes in the conductance modulation amplitude when a nanowire is held at a fixed quantum step. For example, Figure 3 shows the conductance modulation of a nanowire with conductance near $1G_0$ as a result of an electrochemical potential modulation. During the measurement, the conductance has a tendency to drift to a larger value. At a certain point (marked by an arrow), the amplitude of the conductance modulation drops to zero suddenly as the conductance jumps to a lower value. Abrupt changes in the conductance of the metallic nanowires have been previously observed and found to be due to the rearrangements of the atoms in the nanowires from one configuration to another.[22] Thus the sudden change in the conductance modulation is associated with a change in the atomic configuration of the nanowire. Recent high-resolution transmission electron microscopy has directly observed that Au nanowires with similar conductance can have different atomic configurations.[23] On the basis of these facts, we believe that the variation in the amplitude of the induced conductance modulation reflects different atomic configurations of the nanowires (although with similar conductance). Despite the variation in the amplitude, the phase shift between the induced conductance modulation and the applied electrochemical potential modulation is always close to 180°, meaning that an increase in the electrochemical potential always results in a decrease in the conductance.

The dependence of the induced conductance modulation on the atomic configuration of the nanowire demands a statistical analysis of a large number of nanowires with different configurations. To meet this demand, we used the second method described in the previous section to quickly (~20 min) form over ~1000 nanowires with conductance quantized at various values (Figure 4a). We used a computer routine to automatically

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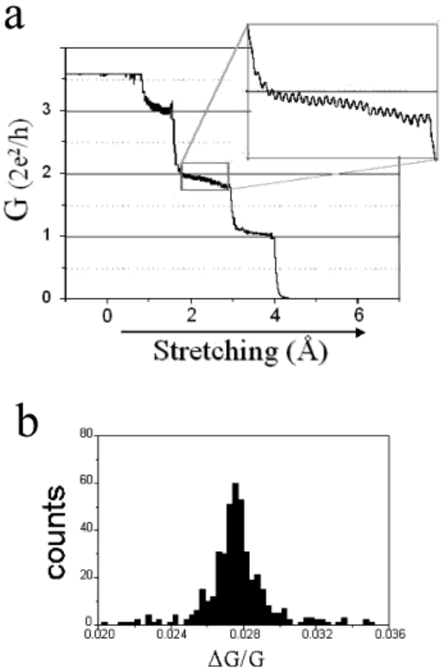

*Figure 4.* (a) A typical conductance trace of a nanowire during stretching. The stepwise change in the conductance is due to conductance quantization, and the small modulation superimposed on the conductance steps is due to a 0.05 V (amplitude) electrochemical potential modulation. The insert shows more clearly the induced conductance modulation. (b) Histogram of the conductance modulation amplitude ($\Delta G/G$) for nanowires with conductance near $1G_0$. The histogram was constructed from 1000 conductance traces such as the one shown in (a).

find all of the conductance steps and determine the amplitude of the conductance modulation at each of the steps. A histogram was constructed from such measurements to show the occurrence of various conductance modulation amplitudes for nanowires with conductance between $0.95G_0$ and $1.05G_0$ (Figure 4b). The amplitude varies over a certain range, but the histogram shows a well-defined peak, so the average conductance modulation gives a good representative description of a large ensemble of nanowires. For simplicity purpose, we use a dimensionless quantity, $\Delta G/G$, where $\Delta G$ is the average amplitude of the conductance modulation, and $G$ is the conductance of a nanowire, to describe the relative amount of the conductance modulation. For nanowires with the potentials held at 0 V in 0.5 M $NaClO_4$, $\Delta G/G$, as a result of a 0.05 V modulation in the electrochemical potential, is about 0.028.

We have studied $\Delta G/G$ as a function of the amplitude and frequency of the electrochemical potential modulation. Within the tested potential range (0−0.3 V), $\Delta G/G$ increases linearly with the amplitude of the applied electrochemical potential modulation (Figure 5). When increasing the potential modulation above 0.3 V, the conductance frequently jumps to a different step as the nanowires switch atomic configurations for the reason we will discuss later. The conductance modulation ($\Delta G/G$) is independent of the frequency of the electrochemical potential modulation up to 2 kHz. The upper bound of the frequency is limited by the frequency bandwidth of the system.

We have determined $\Delta G/G$ for nanowires at various conductance steps (Figure 6). For comparison, we have also plotted the conductance histogram in the figure, which shows three peaks near the first three integer multiples of $G_0$ due to conductance quantization. Although the peaks are pronounced, they are quite broad, meaning that the quantization is not as ideal as the prediction of eq 1. $\Delta G/G$ decreases as the conductance increases, and a broad dip near $1G_0$ is also apparent. Although the broad dip is not as pronounced as the $1G_0$ peak in the conductance histogram, it has been repeatedly observed (see also Figure 7a and Figure 8a). The dependences of $\Delta G/G$

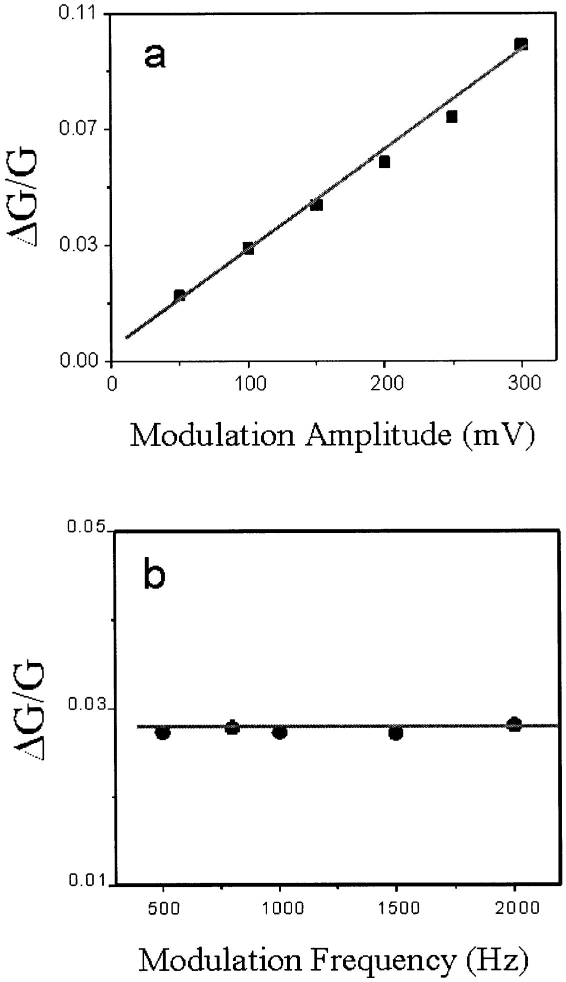

*Figure 5.* Dependence of electrochemical potential-induced conductance modulation on the amplitude (a) and frequency (b) of the applied electrochemical potential modulation. The data were taken in 0.5 M $NaClO_4$, but similar behaviors were also observed in other electrolytes.

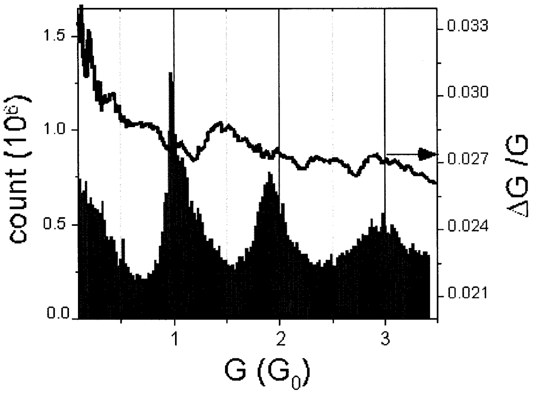

*Figure 6.* Conductance histogram (vertical lines) and induced conductance change (solid black line) versus $G$. The data were extracted from 1500 individual conductance traces in 0.5 M $NaClO_4$ at 0.4 V. The amplitude of the applied electrochemical potential modulation is 0.05 V, and the frequency is 1 kHz.

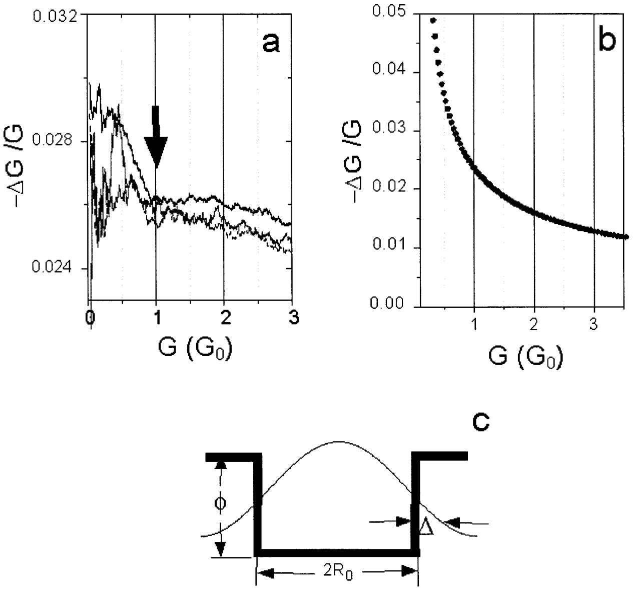

***Figure 7.*** (a) $\Delta G/G$ as a function of $G$ in three s electrolytes, 0.5 M NaF, 0.05 M $KClO_4$, and 0.5 M $NaClO_4$ at $-0.1$ V. The amplitude of the applied electrochemical potential modulation is 0.05 V, and the frequency is 1 kHz. (b) A model calculation of $\Delta G/G$ as a function of $G$ (see text for details). (c) A model picture shows the electron density profile in the transverse direction of a nanowire. The long detail outside of the square potential barrier is due to electron "spill out" into the electrolyte with an amount given by eq 2.

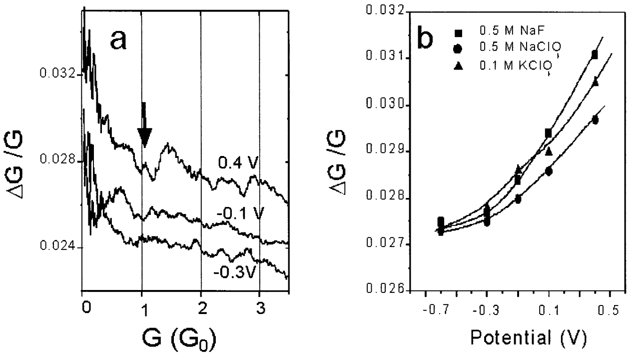

***Figure 8.*** (a) $\Delta G/G$ versus $G$ at different electrochemical potentials in 0.5 M $NaClO_4$. A broad dip near $1G_0$ is marked with an arrow. The amplitude of the applied electrochemical potential modulation is 0.05 V, and the frequency is 1 kHz. (b) The dependence of $\Delta G/G$ versus electrochemical potential for nanowires with conductance near $1G_0$.

on the conductance of the nanowire in $NaClO_4$, $KClO_4$, and NaF are nearly identical (Figure 7a), indicating a common origin in the potential-induced conductance modulation.

What is the mechanism of the electrochemical potential-induced conductance modulation? In the double layer charging regime, electrochemical potential can induce several possible changes, such as electron density, surface stress, and work function, which might be responsible for the observed conductance change. First, let us consider the possible change in the electron density in the nanowires. For a bulk Au electrode, changing the electrochemical potential by 1 V from PZC (potential of zero charge) can induce a surface charge density of 0.1$e$ per atom. This would correspond to a large change in the electron density of an atomically thin wire because every atom in the wire is a surface atom. However, because the atomically thin wires in our system are connected to macroscopic electrodes, a redistribution of electrons in the electrodes and the wire is expected to offset at least part of the electron density change in the nanowire region. While an exact distribution of electrons at equilibrium is determined by the electrochemical potentials of the nanowire and the macroscopic electrodes, a uniform electron density distribution has been assumed in several theoretical calculations that are in good agreement with experiments.[24−26]

Electrochemical potential can induce a large surface stress that can change the conductance of the nanowire via a change in the structure of the nanowire. For Au electrodes, a 0.1 V potential causes a surface stress change of ~0.05 N/m,[27,28] corresponding to a force change of ~0.015 nN per atom. Because the spring constant of an atomically thin wire has been determined to be ~30 nN/nm,[22] the force will result in an interatomic spacing change of $10^{-4}$ nm. To test if such a spacing change is enough to change the conductance of the nanowires, we measured the conductance while stretching/pushing the nanowires with the piezoelectric transducer and found the conductance changes insignificantly only if the stretching/pushing amplitude reached ~0.1 nm. So for a 0.05 V (amplitude) modulation in the electrochemical potential, the induced surface stress is not enough to explain the observed conductance change. However, increasing the amplitude of the potential modulation (to, e.g., 1 V), we frequently observe abrupt changes in the conductance, as shown in Figure 3. These abrupt changes are likely due to the stress-induced changes in the atomic configurations of the nanowires.

We now turn to the potential-induced change in the work function. It has been shown that the work function of a metal, $\phi$, is related to the applied electrochemical potential, according to $\phi = \phi_0 + eE$,[29] where $\phi_0$ is the work function at PZC, and $E$ is the electrochemical potential. The change in the work function can affect the conductance of the nanowire on the basis of the following considerations. For a finite work function, electrons in the metal nanowire spill out into the vacuum (electrolyte) region (Figure 7c), so the effective radius of the nanowire should be greater by an amount of the electron spill-out, given by[30]

$$\Delta(E) = \frac{\hbar}{\sqrt{2m(\phi_0 + eE)}} \tag{2}$$

where $h$ is the Planck constant, and $m$ and $e$ are the electron (effective) mass and charge, respectively.

Consequently, the change in the effective radius ($\delta R$) of the nanowire due to a modulation in the electrochemical potential ($\delta E$) is

$$\delta R = -\frac{1}{2}\frac{\hbar}{\sqrt{2m(\phi_0 + eE)}}\frac{e\delta E}{\phi_0 + eE} \tag{3}$$

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According to the expression, an increase in the electrochemical potential reduces the effective radius and thus the conductance of the nanowire, which explains the 180° phase shift between the observed conductance modulation and the applied electrochemical potential modulation. For the sake of simplicity, we can estimate the amplitude of the induced conductance change due to this mechanism using a semiclassical expression for the conductance of a metallic point contact[31]

$$G = G_0\left(\frac{\pi^2 R^2}{{\lambda_F}^2} - \frac{\pi R}{\lambda_F}\right) \qquad (4)$$

where $\lambda_F$ is the Fermi wavelength of the electrons. This formula is applicable only if the wavelength is small as compared to the dimension of the nanowire, so it does not describe the stepwise change of the conductance as a function of the diameter of the nanowire. However, it provides a correct description of the overall envelope shape of the conductance versus diameter plot. Because $\lambda_F$ is determined by the electron density of the nanowire, which is not expected to depend strongly on the potential as we have discussed earlier, we can easily determine the conductance modulation with eqs 3 and 4. The calculation requires only one unknown parameter, $\phi_0$, the work function of Au in electrolytes at PZC. While the work function of Au in electrolytes has been determined by STM, the experimental value often varies over a quite large range,[32−35] and it is also known to underestimate the actual work function due to tip−substrate interactions.[36] Thus we used $\phi_0 \approx 2$ eV, determined from the ab initio calculation using effective one-electron potentials and molecular dynamic simulations of the water molecules by Schmickler.[37] The calculated $\Delta G/G$ versus $G$ using eqs 2 and 3 is plotted in Figure 7b, which shows that the model gives not only the correct order of magnitude but also the dependence of the conductance modulation on $G$. We note that although the calculated $\Delta G/G$ depends on the value of $\phi_0$, the simple model gives the correct order of magnitude even if $\phi_0$ is allowed to vary over a large range.

As we have already pointed out, the above semiclassical theory does not include electron quantization in the transverse direction of the nanowires. For a two-dimensional wire, the quantization (standing waves) condition is $W = n(\lambda_F/2)$, where $W$ is the width of the wire, and $n$ is an integer that equals the number of standing waves. When the width varies between $n(\lambda_F/2)$ and $(n + 1)(\lambda_F/2)$, the conductance remains at the $n$th quantum step because the number of standing waves in the transverse direction does not change. This argument applies also to three-dimensional metallic nanowires in our experiment, except that the quantization condition is given by the roots of Mathieu function.[38] Thus if the electrochemical potential-induced change in the effective diameter of the nanowire does not result in a change in the number of standing waves, the conductance will not change, and we expect a dip $\Delta G/G$ near the $nG_0$. We did observe evidence of a dip near $1G_0$, but it is severely broadened. A large broadening of the peaks in the conductance histogram is also observed (see Figure 6), which shows that the ideal conductance quantization predicted by the simple model is never observed in metallic nanowires due to various factors, such as defects and variations of the atomic configurations. These factors may also be the reason for the broadened dips observed here. We remark that, according to the above model, electrochemical potential changes the conductance via changing the effective diameter of a metallic nanowire, which resembles the effect of the split gate voltage in the semiconductor nanowires.

**Potential Dependence.** We have measured the potential-induced conductance modulation ($\Delta G/G$) by holding the DC electrochemical potential at various values (Figure 8a). $\Delta G/G$ versus $G$ plots have a similar shape for all of the potentials, but the plot shifts upward as the potential increases. The dependence of $\Delta G/G$ on the electrochemical potential for nanowires with conductance quantized near $1G_0$ has been determined for nanowires in different electrolytes (Figure 8b). Despite small deviations between different electrolytes, there is an ~10% increase in $\Delta G/G$ as the potential increases from −0.5 to +0.5 V. This observation is not expected according to eq 2. In fact, eq 2 says that the change in the effective radius ($\delta R$) for a given potential modulation ($\delta E$) should decrease as the potential ($E$) increases (the denominators of eq 2 increase), which should lead to a slight decrease, rather than observed increase, in $\Delta G/G$. We attribute the apparent discrepancy to the adsorption of anions (including possible trace amounts of $Cl^-$, etc., in the electrolytes) at high potentials. Surface conductance of metal films has been measured as a function of electrochemical potential in electrolytes, such as KF and $KPF_6$, which shows a similar dependence on the electrochemical potential and has been explained in terms of electron scattering by the weakly adsorbed anions.[39−41] To test if anion adsorption can indeed give rise to the observed increase $\Delta G/G$, we have performed the measurement in electrolytes containing anions with different adsorption strengths to Au electrodes.

**Anion Adsorption.** When anion adsorption takes place on nanowires, the first question that we encounter is the following: Is the conductance of the nanowire still quantized? To answer this question, we determined the conductance histograms of nanowires formed in electrolytes containing different anions at various electrochemical potentials. The results for 0.01 M NaBr + 0.5 M NaF are shown in Figure 9. At low potentials, peaks near the integer multiples of $G_0$ are well defined. This is expected because no strong anion adsorption takes place on Au surfaces at these potentials. We note also a peak near ~$0.5G_0$, a phenomenon that we have previously observed.[11,12] As the potential increases, the adsorption increases, and the peaks in the conductance histogram broaden. In NaBr solution, the peaks smear out completely at ~0.4 V. The evolutions of the conductance histograms for nanowires in NaCl and NaI electrolytes are similar except that the smearing-out is more pronounced in NaI and less in NaCl, which correlates with the adsorption strengths of the anions.

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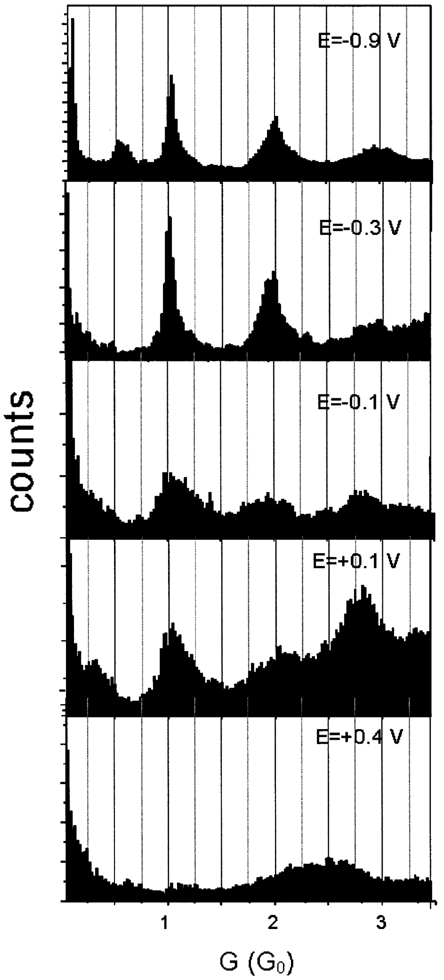

***Figure 9.*** Conductance histograms of nanowires formed in 0.01 M NaBr + 0.5 M NaF at various electrochemical potentials.

We have extracted $\Delta G/G$ versus $G$ in 0.5 M NaF, 0.01 M NaCl + 0.5 M NaF, 0.01 M NaBr + 0.5 M NaF, and 0.01 M NaI + 0.5 M NaF at various potentials (Figure 10). At low potentials, $\Delta G/G$ versus $G$ plots for all of the electrolytes nearly overlap with each other. They are also similar to the plots for nanowires in $NaClO_4$ and $KClO_4$ electrolytes, which is consistent with the fact that no anion adsorption takes place at very negative potentials (Figure 10a). The potential-induced conductance modulation in the low potential regime is solely determined by the double layer charging effect that we have discussed earlier. Increasing the potential, $\Delta G/G$ increases for all of the electrolytes, but the amount of the increase differs dramatically from one anion to another (Figure 10b). To illustrate the trend more clearly, we plotted $\Delta G/G$ as a function of potential for nanowires with a conductance near $1G_0$ (Figure 10c). In 0.5 M NaF, the change is only ~10% from −0.7 to +0.8 V. In sharp contrast, the change in 0.01 M NaI + 0.5 M NaF is as large as ~300%! The amount of change varies in the order of $F^- < Cl^- < Br^- < I^-$, in good agreement with adsorption strengths of these anions. A decrease in the conductance of classical metal thin films due to anion adsorption has been observed in electrolytes containing $F^-$, $Cl^-$, $Br^-$, and $I^-$.[39−44]

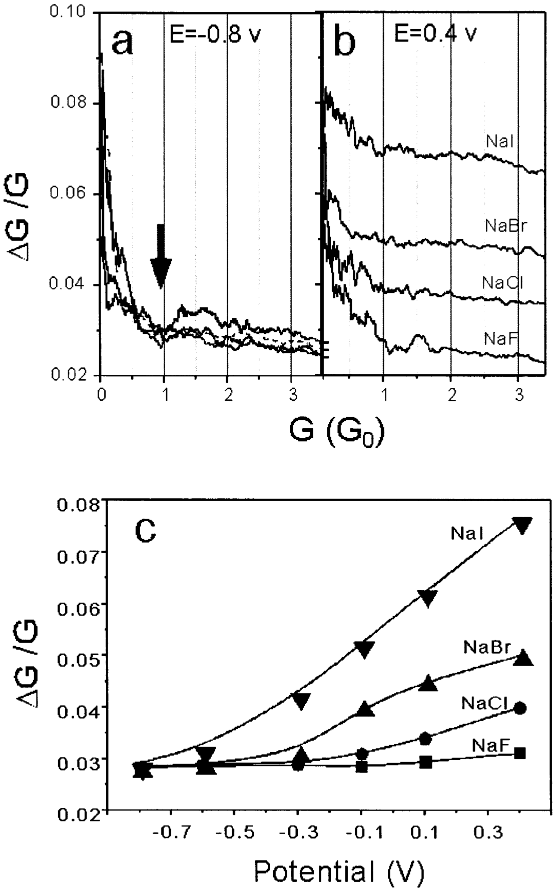

***Figure 10.*** $\Delta G/G$ versus $G$ at −0.8 V (a) and +0.4 V (b) for nanowires in 0.5 M NaF, 0.01 M NaCl + 0.5 M NaF, 0.01 M NaBr + 0.5 M NaF, and 0.01 M NaI + 0.5 M NaI. (c) The dependence of $\Delta G/G$ versus electrochemical potential for nanowires with conductance near $1G_0$ in the above four electrolytes. The amplitude of the applied electrochemical potential modulation is 0.05 V, and the frequency is 1 kHz.

The systematic dependence of the induced conductance change on the anion adsorption strength at high potentials leads us to believe that the anion adsorption does play a role in the potential-induced conductance change.

One possible mechanism for the anion adsorption-induced conductance change is the scattering of conduction electrons in the nanowires by the adsorbed anions on the surfaces of the nanowires.[45,46] The scattering is expected because the electrons spill out of the metal into the double layer where the anions reside. For classical conductors, the scattering of electrons by adsorbates[47−49] in terms of the density of states of the adsorbates near the Fermi level of the metal has been developed.[50] It has been pointed out that the degree of the scattering is correlated with the electrosorption valency of the adsorbates.[51] A quantitative relation between the conductance change and electrosorption valency[52] based on Persson's model seems possible.[43,44] For atomic-size wires, a calculation based on a simple delta-function type of scattering centers has been performed which shows a

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decrease in the conductance that is qualitatively similar to the classical wires.[53] A recent molecular dynamics simulation has found that an adsorbate molecule can insert itself into an atomically thin metal wire, which demonstrates the importance of including individual atoms for a complete description of the adsorbate−metal wire interaction.[54] While we have identified the scattering of conduction electrons by adsorbed ions as the main contribution for the measured conductance change, other mechanisms, such as shift in PZC upon specific anionic adsorption, may also have a contribution (as suggested by the referee). Further studies will be needed for a complete understanding of the anionic adsorption onto atomic-scale wires.

## Summary

We have studied quantum transport in atomic-scale Au wires suspended between a STM tip and a substrate as a function of electrochemical potential of the wires. To accurately determine the potential effects, we have measured conductance changes by modulating the electrochemical potential of the wires. In the absence of specific adsorption (the double layer charging regime), the potential modulation induces a conductance modulation. The phase shift of the conductance modulation is always about 180°, but the amplitude depends on the atomic configuration of the wire. A statistical analysis of over 1000 wires shows that the amplitudes in most wires with conductance quantized near $1G_0$ (the thinnest wires) are about $0.55G_0$ per V. The effect decreases as the diameters of the wires increase. We attribute the potential-induced conductance modulation to a change in the effective diameters of the wires, in a fashion similar to the split gate control in the semiconductor quantum wires. A simple model calculation based on this picture explains the phase and the amplitude of the conductance modulation as well as the dependence of the conductance modulation on the diameter of the wire.

We have also studied the role of anion adsorption in quantum transport using electrolytes containing anions with different adsorption strengths to Au surfaces. At very negative potentials, no substantial anion adsorption takes place, and the induced conductance modulations are similar for all of the electrolytes. Increasing the potential, the conductance modulation increases as anions adsorb on the wires. The dependence of the conductance change on the potential correlates well with the adsorption strengths of the anions, in the order of $F^- < Cl^- < Br^- < I^-$. The significant reduction of the conductance of the atomic-scale Au wires upon anion adsorption is attributed to the scattering of the conduction electrons in the wires by the adsorbed anions.

This work shows that electrochemical processes taking place on the surface of an atomic-scale metal wire can be studied by measuring the conductance of the wire, which allows us to examine concepts developed for bulk electrodes to the atomic-scale electrodes. The observed conductance change in the presence of anions reflects the adsorption of a single or a few ions onto the wire, which may lead to a method to detect and study the adsorption of single ions.

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**Supporting Information Available:** Partial dependence of conductance histogram (jpeg). This material is available free of charge via the Internet at http://pubs.acs.org.

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