Molecular Sensing Based on Metal Quantum Wire in Solution

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Stable gold and silver quantum wires with atomic-scale were successfully fabricated with an electrochemical method in solution and the molecular adsorption onto the quantum wires were studied. The conductance of gold quantum wires showed a decrease upon exposure to definite concentration of dopamine solution and the conductance of silver quantum wires showed an increase upon exposure to ascorbic acid solution. Different sensor mechanisms were proposed with the two kinds metal quantum wire. Because the quantized conductance is determined by a few atoms at the narrowest portion of each quantum wire, adsorption of a molecule onto the portion is enough to change the conductance, which may be used for chemical sensors.

Keywords: Quantum wire, Quantum conductance, Molecular sensing, Gold, Silver.

INTRODUCTION

The nanoscale world is exciting not only because it exhibits many novel phenomena but also because it leads to many new applications in the fields of surface science, nano- and molecular electronics and chemical and biological sensors¹⁻³. Over the past few years, fundamental theoretical and experimental studies have proved the quantum conductance phenomenon of atomic-sized metal point contacts^{4,5}. Electrical conductance through thin metal wires in an atomic scale can be expressed by $G = G_0 \sum_{i=1}^N T_i$, where $G_0 = 2e^2/h \approx 1/(12.9 \text{ K}\Omega)$. T_i is the transmission coefficient and, for many metals at small contacts, the value is close to 1, thus the conductance changes in steps of the order of G_0 , the quantum conductance. The current passing through the quantum wire is ballistic and the last plateau is generally assumed to correspond to a single-atom contact.

In recent years, the fabrication of miniaturized sensors using novel nanostructured materials and the realization of molecular level detection have been active topics^{6,7}. In this paper, we describe a molecular detection method based on the conductance quantization in metallic quantum wires. Because the few atoms of the metal quantum wire dictate the conductance of the entire wire, adsorption of even a single molecule onto them may drastically change the conductance, which is the basis of molecular detection explored in this paper.

EXPERIMENTAL

The experimental setup was the same with our previous work^{8,9}, in which the main part was a home-made electro-

chemical system which had different function with different programmed control. A function generation was used as bias voltage supply. The electrochemical cell was made of an Ag/AgCl reference electrode, a platinum slice counter electrode and a metal wire that served as a working electrode onto which the metal was etched or deposited. All chemicals used were of analytical reagent grade. All solutions were prepared with deionized water (18.2 M Ω cm).

Gold quantum wire preparation: First, a thin gold wire (25 μm in diameter, 99.999 % purity) was supported on the glass slide and coated with insulating glue which served as an insulation layer to reduce electrochemical leakage current except for a small region ($< 1 \mu\text{m}$) exposed to the etching solution of 0.5 mol/L KCl. An alternate current voltage (15 mV, 10 Hz) for monitoring and a direct current voltage (0.95 V) for etching were applied simultaneously. When the alternate current monitor current decreased abruptly, the program will automatically cut off the direct current etching voltage and a small gap was formed. Then the solution was added a few drops of 0.02 mol/L $\text{H}[\text{AuCl}_4]$ solution. By controlling the deposition potential, the Au ions were deposited back to the wire. The initial electrodes width was large and the alternate current monitor current was very low due to ion conductivity, then with the ongoing deposition process, the alternate current monitor current increased sharply due to tunnel conductivity. Fig. 1 showed a time evolution of the current across the electrodes during electrochemical deposition process. The stepwise increase of current was clearly observed under a time resolution of 200 ms, as shown in the Fig. 1. These plateaus of current indicated that the contact between the two electrodes consisted

Fig. 1. Typical monitor current *versus* time curve during the Au ions deposition process. The stepwise changes could be observed

of a few Au atoms and are formed layer by layer in an atomic scale. These procedures mentioned above showed by carefully controlling the potential, the electrochemical etching/deposition process could be controlled so slowly that removal/deposition of a single atom could be observed. When the alternate current monitor current reached the preset current value, the programmed switch turned the dissolution/deposition off by cutting off the electrochemical dissolution/deposition current that flow between one of electrodes and the counter electrode and an Au quantum wire could be obtained. Then the formed Au quantum wire would be transferred into pure water.

Silver quantum wire preparation: The fabrication method of Ag quantum wire was similar with the fabrication method of Au quantum wire. First, a thin Ag wire (50 μm in diameter, 99.999 % purity) was supported on the glass slide and coated with insulating glue except for a small region exposed to the etching solution of 10 mmol/L KNO_3 . An alternate current voltage (15 mV, 10 Hz) for monitoring and a direct current voltage (0.36 V) for etching were applied simultaneously. When the small gap was formed, the solution was added a few drops of 10 mmol/L AgNO_3 solution. By controlling the deposition potential, the Ag ions were deposited back to the wire. Fig. 2 showed a time evolution of the current across the electrodes during electrochemical deposition process. When the alternate current monitor current reached

Fig. 2. Typical monitor current *versus* time curve during the Ag ions deposition process. The stepwise changes could be observed

the preset current value, the programmed switch turned the dissolution/deposition off and an Ag quantum wire could be obtained. Then the formed Ag quantum wire would be transferred into pure water.

Interactions of metal quantum wire with sample molecules: The metal quantum wire was prepared in a pure water environment. A two-electrode system was used for conductance measurements at a bias of 10 mV. Once a steady baseline had been obtained, a sample solution of a certain concentration (about 0.3 mL) was added to the solution (about 3 mL) with an injector and the subsequent current change was recorded with a programmed computer (current *versus* time plots).

RESULTS AND DISCUSSION

Molecule sensing with Au quantum wire: The dopamine molecule was chosen due to its weak adsorption onto the Au electrode with Au-N bond. Fig. 3 showed the change of current with time upon the introduction of 1 mmol/L dopamine solution. The current decreased dramatically (about 50 %) and then stabilized at a lower value. Adding another drop of dopamine solution caused no further change, which indicates no further adsorption once the quantum wire was covered with the molecules. The above experiments were reproducible. As shown in Fig. 3, the conductance quantization is sensitive to molecular adsorption. The possible mechanism of the adsorbate-induced conductance change is due to the scattering of the conduction electrons by the adsorbates as the electrons impinge on the surface, which is consistent with the previous study^{10,11}. Since the quantum wire consists of only a few atoms, which dictate the conductance of the entire wire, adsorption of even a single molecule onto them may drastically change the conductance. Based on the above argument, we expect that the atomically thin quantum wires give the highest sensitivity.

Fig. 3. Response of the current *versus* time for Au quantum wire when added dopamine solution

Molecule sensing with Ag quantum wire: Fig. 4 showed the change of current with time upon the introduction of 1 mmol/L ascorbic acid solution. The current increased gradually and then stabilized at a higher value. No further change would be found with more ascorbic acid solution added into the cell, which is the same as Au quantum wire mentioned above. Based on the previous study¹², we proposed the existence of Ag ions on the surface structure of Ag quantum wires. This was based on the two considerations as follows. First, the Ag quantum

Fig. 4. Response of the current versus time for Ag quantum wire when added ascorbic acid solution

wire with quantum conductance was composed of a few atoms in its cross section and each atom almost belonged to a surface atom, so the surface atoms would show highly mismatched states. Second, the surface atoms were easy to be oxidized due to the high surface energy in the existence of oxygen in the aqueous solutions. According to the previous study¹³, the ascorbic acid is chemical reduced reagents and used widely to prepare Ag nanoparticles. So the current change might be attributed to a reason that the surface Ag ions were reduced into Ag atoms to increase the conductance.

Conclusion

In this work, we have systematically studied the interactions between two kinds of metal quantum wires and sample molecules in an aqueous environment. The conductance of Au quantum wires showed a decrease upon exposure to definite concentration of dopamine solution and the conductance of Ag quantum wires showed an increase upon exposure to ascorbic acid solution. Different sensor mechanisms proposed with the two kinds of metal quantum wire might be due to different nature of the two kinds of metal. As we have known, the Ag is more active than Au, which resulted in the easier oxidation of Ag than Au in solution and lead to different surface structure of

the two kinds of quantum wire. The dependence of the conductance on molecule adsorption may be used for chemical sensor applications. The present work has shown that the metal quantum wire sensor has high sensitivity and fast response time. The ultimate specificity for molecular identification depends on the mechanism for the adsorbate-induced changes in the conductance, which is not yet fully understood. We will continue to make an effort to solve these problems.

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