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Short Communication

Study of the Electrochemical Preparation of Atom-Scale Iron Quantum Wire Controlled by an External Resistor

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In the present work, the stable atom-scale iron quantum wire was electrochemically prepared and characterized successfully by a homemade electrochemically controlled system. By adjusting the resistance of the external resistor, the atom-scale iron wire with preset conductance would be obtained. When scanned with low bias, the iron quantum wires showed the linear ohmic relationship for the current-voltage curve. With an external resistor control, the diameter, aspect ratio can be easily tailored, so it was a simple and controllable method. In addition, with a pure water environment of the preparation, the method had a less interference of other ions and was more suitable for sensor study of the quantum wire. The work was greatly significant for material science, molecular electronics, chemical and biological sensing.

Keywords: iron; atom-scale; magnetic materials; electrochemistry; quantum wire

1. INTRODUCTION

Today, nanostructured materials have drawn much attention because of their distinctive chemical and physical characteristics in contrast to their bulk materials and potential utilization in many fields, such as surface science [1,2], nanoelectronics [3,4] chemical and biological sensors, etc [5,6]. Over the last decades, the quantum conductance behavior of atom-sized metal junctions has been verified with much theoretical and experimental research [7,8]. For many metals, the electrical conductance passing through the atom-scale metal junction corresponds with the formula $G=NG_0$, where N is an integer, G_0 is called the quantum conductance and the value is approximately equal to 1/(12.9 kΩ). Thus the electrical conductance shows an integral multiple of G_0, and the last terrace of $1G_0$ is generally reckoned to conform to a single-atom junction [9]. Due to the quantized behavior of the conductance, this atom-sized metal wire (junction) is also called a metal quantum wire. Due to the width of the metal junction reaching the same order of magnitude with the Fermi wavelength, it will have many unique properties different from bulk materials, such as mechanical, electrical, magnetic and surface properties.

In recent years, metal quantum wires have received increasing research interest because of their potential applications in many fields [10-12]. But the synthesis and precise control of atom-scale nanostructures is challenging in materials science. There are a few strategies proposed for the fabrication, such as mechanically controllable break junction (MCBJ) [13], scanning tunneling microscopy (STM) [14] and electrochemical methods [15-17], etc. Within the numerous methods of fabrication, the electrochemical method is simple and controllable. By finely controlling the electrochemical potential, single atom etching/deposition can be achieved. Today, one-dimensional magnetic nanomaterials have been extensively studied not only for attractive magnetic properties but also for their potential applications in ultrahigh-density magnetic storage devices [18,19], chemical and biological sensors [20,21], microwave materials and microelectromechanical systems [22,23]. Among them, the iron based nanostructures not only reveal the best magnetic properties, but also attract the research attention in biomedical applications due to their extensive promise in medical diagnosis and treatment coming from their high saturation magnetization and excellent biocompatibility [24-26]. To our knowledge, there are few reports for iron quantum wire fabrication [27].

2. EXPERIMENTAL

The experimental device studied here was similar to that previous work reported by our group [28,29], where the central section was a homemade electrochemically controlled system. With the present experiment, the main difference of the setup was that the alternating current (AC) signal generator was not necessary for the AC monitoring. Unlike the previously described method of direct electrochemical etching and deposition [27], the present method is much simpler. An automatically terminated electrochemical experimental scheme was taken for iron quantum wire preparation [30]. Briefly, the ends of a thin piece of iron wire (1cm in length, 100 μm in width, 99.999% purity) were connected closely with the conductive part of two thin insulated wires and laid on the glass flake (2cm in length, 1cm in width) which was cut from slide. The whole iron wire and the two contacts were insulated with a thin layer of AB glue (main ingredients: epoxy) and attached closely on the glass substrate. Then the middle part of the iron wire was cut by a blade to form two iron electrodes with small gap between them on the glass flake, which was followed the immersion of the whole part into a glass-made electrochemical cell with only ultra pure water in it. The homemade three-electrode electrochemically controlled system was converted into a two-electrode scheme by the connection together of the reference and counter electrodes. The obtained two iron electrodes, the pure water between them and a resistance (R) was placed successively to consist of a voltage distribution circuit, then with the two-electrode control system, both ends of the circuit was put a voltage of about 1 V (Fig. 1). When the value of the resistance changed, the atom-scale iron junction with different conductance was made.

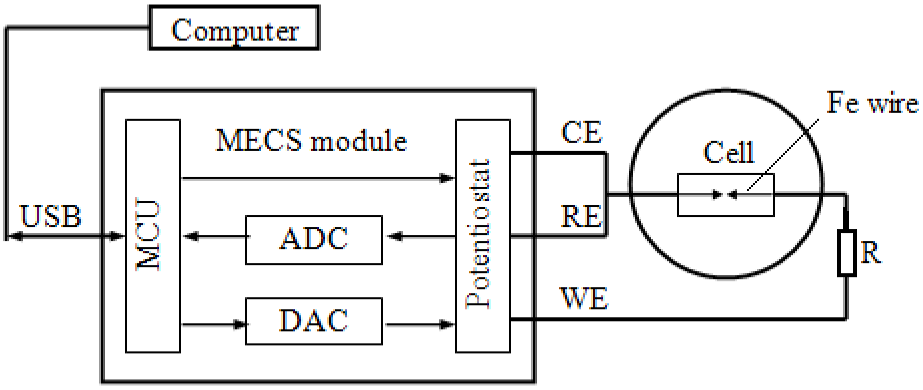

Figure 1. Schematic drawing of the atom-scale iron junction preparation system with two-electrode electrochemically controlled system. The abbreviations of MECS, MCU, ADC, DAC, CE, RE, WE represent respectively micro-electrochemistry control system, micro-controller unit, analog to digital converter, digital to analog converter, counter electrode, reference electrode, working electrode.

3. RESULTS AND DISCUSSION

3.1. Iron quantum wire preparation

When the bias was initially applied to the open circuit, because the gap between the two iron electrodes was wide, the resistance was also very large, which resulted in the effect of the whole bias was used to etch iron from one electrode (anode) and to deposit the iron ions to the other electrode (cathode). The gap width would decrease gradually due to the etching process taking place on the whole surface of the anode and the corroded iron ions depositing on the pointed end of the cathode due to the electric field orientation [31]. With the ongoing process, when the gap width between the two iron electrodes reached the threshold distance, tunneling occurred and the current which was exponential with the gap width enlarged dramatically, which resulted in the gap resistance decreasing accordingly. Consequently, the bias applied between the two iron electrodes reduced automatically as well, which slowed the electrochemical etching/deposition effect rapidly. Finally, after forming a junction, the current stabilized at a definite value, which showed the process was terminated (Fig. 2a). Although the current in the end could be stable for a long time, occasionally abrupt fluctuations up and down would be observed (inset of fig. 2a), which might be due to the rearrangement of the iron atoms. According to the definite current value, the conductance of the prepared iron junctions could be calculated. Theoretically, the resistance of the quantum wire should be equal to the external resistor due to the divided voltage. With our experiment, the relationship between theoretical conductance value and the measured value was studied. The result showed these two values were substantially equal (Fig. 2b). It could be seen that the atom-scale iron point contact with preset conductance could be fabricated by changing the resistance.

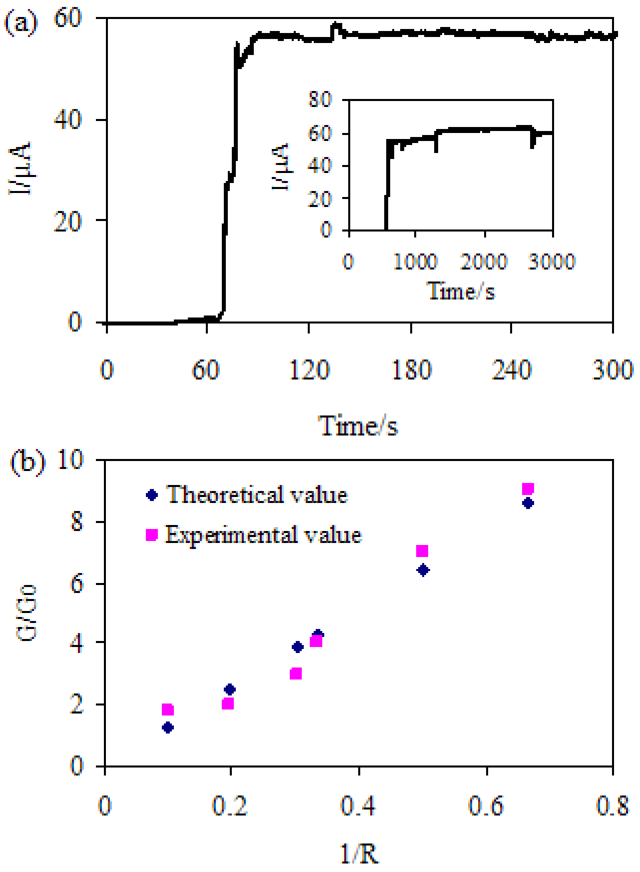

Figure 2. (a) The typical current changing when the bias was applied to the open circuit (V = 0.7 V, R = 6 kΩ). The calculated conductance of the formed iron quantum wire was $2G_0$. The inset showed that sometimes the current will fluctuate up and down, which might be due to the atomic rearrangement. (b) The contrast of the conductance between the theoretical value and the measured experimental value with different resistance of external resistor.

It was necessary to discuss the reproducibility of the present experiment. Although in most cases, for the prepared atom-scale iron junctions, the conductance showed good agreement with the principle mentioned above, the deviating more or less the theoretical value for it would be observed occasionally. The possible reason was when the sample reached the atomic level, the experimental details would not always conform to the macroscopically designed parameters [32], which was also observed by another group [33].

3.2. Iron quantum wire characterization

Due to the limitation of the resolution, scanning electron microscopy (SEM) was difficult to give a clear and intuitive image for the prepared atom-scale iron junctions. As a result, like the majority of groups working on such systems [34,35], the electrical transport measurements were used for quantum wire characterization.

In the same way, with no external resistor, the two-electrode electrochemically controlled system was used to test the changing current with the scanning voltage for the atom-scale iron quantum wire. With a low bias scanning, the linear ohmic feature of the current-voltage (I-V) curve was always demonstrated for the fabricated iron junction with the definite conductance, which was in accordance with previous results for different quantum wires studied by other group [36,37]. The scanned results of the fabricated iron junction with high bias were also studied. With the bias increasing at a speed of 10mV/s, failure was observed at a critical point (inset of fig. 3a), indicating that the atom-scale junction was broken. This might be attributed to the function of electromigration, a phenomenon that had been used formerly to prepare the nanogap electrodes [38]. Fig. 3b showed the prepared iron atom-scale junction could remain stable for some time.

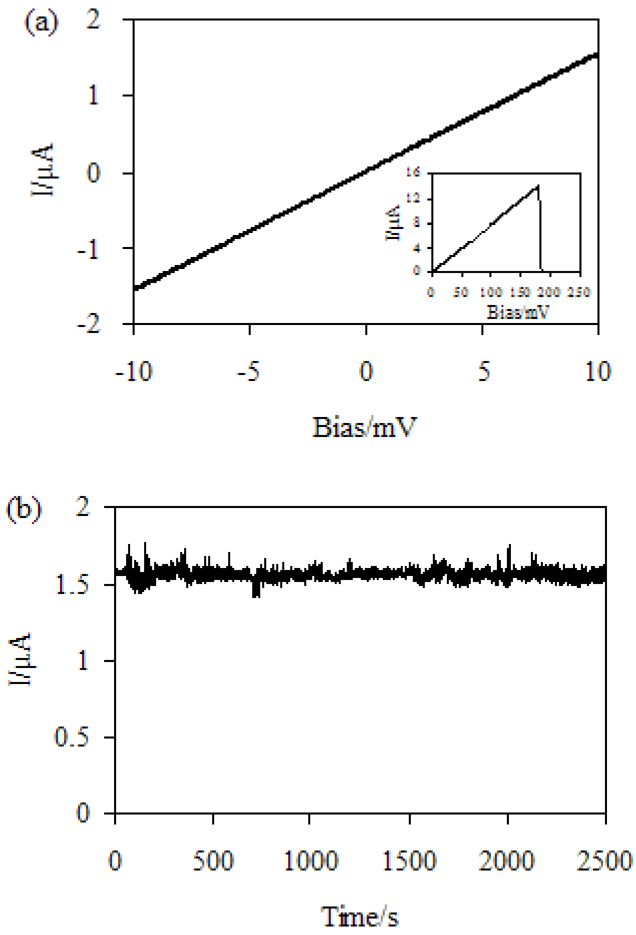

Figure 3. (a) The representative current-voltage curve of the atom-scale iron junction in pure water when the bias changed from -10mV to 10mV at a rate of 1mV/s ($2G_0$). The inset showed the iron junction collapsed with a higher bias ($2G_0$). (b) Change of current of the iron quantum wire with the time in a pure water environment ($2G_0$).

4. CONCLUSIONS

In this work, the electrochemical preparation of stable atom-scale iron junction with a homemade electrochemically controlled system was described. The conductance of the fabricated iron junctions could be adjusted by changing the resistance of the external resistor. The two-electrode electrochemically controlled system was used to characterize the fabricated iron junctions. With low bias, the I-V curve of the prepared iron junctions showed the linear ohmic characteristics and with high bias, the electromigration phenomenon was observed. In the end, the stability of the atom-scale contacts was evaluated. The work was very meaningful for material science, nanoelectronics, surface chemistry and sensing.

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