Asian Journal of Chemistry; Vol. 25, No. 9 (2013), 4773-4775

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14095

Electrical Studies of Fe_2O_3 Nanocrystal Using Nanogap Electrodes Prepared by Electrochemical Method

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(*Received*: 23 May 2012; *Accepted*: 6 March 2013) AJC-13068

The gold nanogap electrodes were successfully fabricated with a two-step electrochemical method in solution by a home-made electrochemically controlled system. By careful controlling the etching/deposition process, stepwise conductance behaviour could be clearly observed. The formed gold nanogap electrodes were used to study the electrical properties of single Fe_2O_3 nanocrystal. The current-voltage characteristics of these devices exhibited a Coulomb staircase at room temperature. This work is possible to be adapted to the study of a host of nanocrystals made by solution chemistry and is of great significance for molecular and nano electronics.

Key Words: Au, Nanogap electrodes, Fe_2O_3, Coulomb blockade.

INTRODUCTION

Nanoscience and technology have attracted a tremendous amount of interest not only because materials and devices exhibit many novel quantum phenomena but also because they lead to many new applications[1-3]. During the past decades, the study on electrical transport through nanocrystals, molecules, nanotubes and nanowires displayed many novel quantum phenomena and the study on the electrical characterization of individual molecules and nanocrystals has received considerable attention in the scientific and engineering communities[4,5]. Because the electron density in metals is very high, single electron transistors based on metallic nanoparticles can be much smaller in size than semiconducting transistors, which is believed to be one of the candidates to replace complementary metal oxide semiconductor field effect transistor. Furthermore, electron transport through these chemical nanostructures is strongly affected by electron-electron repulsion and energy level quantization and transport experiments can provide detailed insight into the electron dynamics. The ability to make electrical devices based on individual molecule and nanocrystal is technologically relevant as well because it allows the fabrication of new types of devices whose function is defined by the chemical identity of the components[6].

In this full paper, the gold nanogap electrodes were fabricated electrochemically and the electrical transport properties of the tunneling device with Fe_2O_3 metal-oxide semiconductor nano-particles were studied by current-voltage measurements.

EXPERIMENTAL

The experimental setup was the same with our previous work[7,8], a function generation was used as bias voltage supply. The electrochemical cell was made of an Ag/AgCl reference electrode (RE), a platinum slice counter electrode (CE) and a gold wire that served as a working electrode onto which the metal was etched or deposited. The main part of the setup was a homemade micro electrochemistry system (MECS) which had different function with different programmed control. USB2.0 protocol was employed in this system, so it could exchange data between PC with a rate up to 480 Mbit per second. A 20 bit digital to analog converter (DAC) was used in this system. Using a special calculating method, this system could measure AC and DC current simultaneously. So it could automatically switch to a preset potential during the dissolution and deposition process when the AC or DC current reached a preset threshold. All chemicals used were of analytical reagent grade. All solutions were prepared with deionized water (18.2 MΩ.cm).

Nanogap electrodes preparation: Fabrication consisted of two major steps. The initial electrodes were fabricated following a method similar to that described previously for Cu quantum wire fabrication[9]. A benefit of using this approach was that compared with other electrochemical method[10], it had no a photo- or electro-beam lithography process and could be carried out at ambient conditions without the use of sophisticated equipment. Especially, the electrode insulation which was to reduce the faraday current was easy to control. Details

of the electrode fabrication were as follows. First, a thin Au wire (25 μm in diameter, 99.999 % purity) was winded to the metal ends of two thin insulation metal conducting wires which were connected with external circuit and was put onto a glass slide with minimal mechanical stress. Then we coated the whole wire with AB glue which served as an insulation layer to reduce electrochemical leakage current (< 50 pA at a bias of 10 mV). The Au wire was then cut with a razor blade to expose a minimum area at which the metal wire could be in contact with an electrolyte solution. This process could be monitored using a multimeter. The glass slide was then immersed into an electrochemical cell for electrochemical etching. The excitation AC bias was 15 mV with a frequency of 10 Hz. Low frequencies for monitoring AC voltage were necessary to avoid shorting of the AC current by the capacitive part of the impedance of the electrolytic bath and preserve sufficient measurement sensitivity. The low AC bias voltage was to minimize the electrochemical process between the two electrodes. The electrolyte solution was 0.5 M KCl and the DC etching voltage was 0.95 V. When the AC monitor current decreased abruptly, the program will automatically cut off the DC etching voltage and a small gap was formed. With the second step, when the thin Au wire was completely breakdown, a few drops of 0.02 mol/L $HAuCl_4$ solution were added into the cell to ensure having enough Au ions to be deposited. By controlling the deposition potential, the Au ions were deposited back to the wire. When the AC 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. As a result, the Au nanogap electrodes could be obtained.

Electrical characterization of Fe_2O_3 nanocrystal: The Fe_2O_3 hydrosol was synthesized by using hydrolysis method reported by previous literatures[11,12]. The potentiostat was changed into two-electrode system by shorting the counter and reference electrode and the two-electrode system was used to characterize the electrical behaviour of the Fe_2O_3 nanocrystal. The samples were prepared by placing a drop of Fe_2O_3 hydrosol on the nanogap electrodes. The I-V characteristic of the Au nanogap electrodes was measured at room temperature.

RESULTS AND DISCUSSION

Nanogap electrodes preparation: The initial gap width between the two electrodes by the first step of electrochemical etching was large due to the mechanical stress coming from the metal itself and the insulating materials[7,8], so the further electrochemical deposition was needed. With the second step, in the beginning, the AC monitor current was very low due to ion conductivity and then with the ongoing deposition process, the AC monitor current increased sharply due to tunnel conductivity. Fig. 1 showed a time evolution of the conductance across the electrodes during electrochemical deposition (a) and subsequent etching process (b). The quantum conductance increase and decrease were clearly observed under a time resolution of 200 min as shown in the Fig. 1. These conductance plateaus indicated that the contact between the two

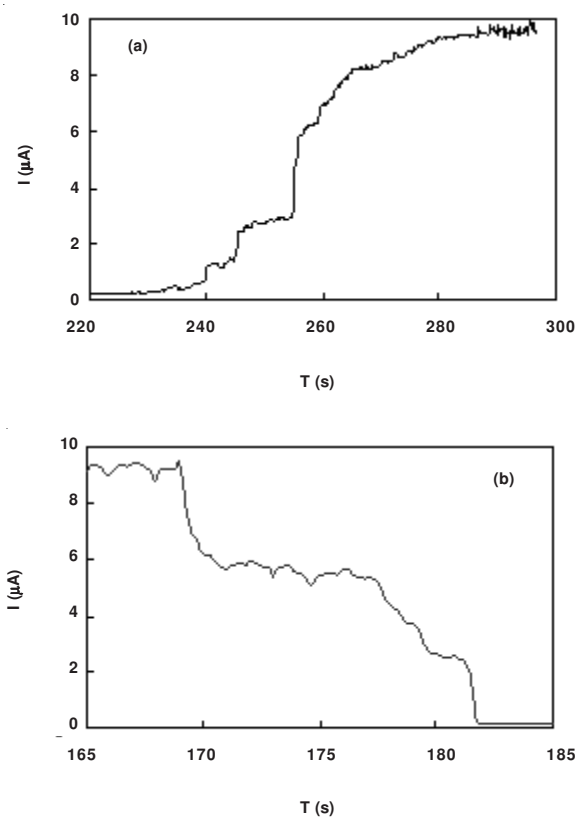

Fig. 1. Typical monitor current *versus* time curve during the electrochemical deposition (a) and etching (b) process. The stepwise changes could be observed

electrodes consisted 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. Therefore, when the AC 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. As a result, the Au nanogap electrodes could be obtained. Then the formed Au nanogap electrodes must be transferred into pure water in order to avoid the interference of other ions. It must be mentioned that the behaviour of the monitor current as a function of electrode separation is worth to comment. It has been speculated that the large current flowing between the electrodes at small separation is due to direct electron tunneling, enhanced by the presence of ions in the electrolyte. However, it seems unlikely that a considerable contribution to the current can originate from direct tunneling for separations exceeding 5 nm. The precise mechanism requires further investigations, which was similar with previous literature[13].

Electrical characterization of Fe_2O_3 nanocrystal: The I-V characteristic of the Au nanogap electrodes (without Fe_2O_3 colloidal nano-particles) measured at room temperature was shown in the Fig. 2a. The insulating characteristic of the nanogap electrodes was held in the voltage range of ± 2 V and the increase of the current due to applying high electrical field was not observed in this range. By depositing the Au nano-

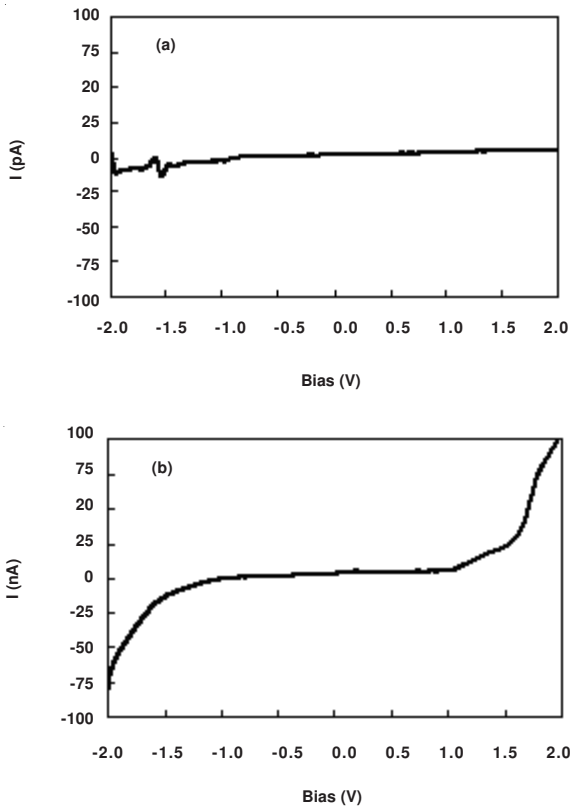

Fig. 2. Typical room-temperature I -V characteristics with pure water (a) and a 5 nm cluster trapped (b) between Au electrodes

particles on the nano-gap electrodes, the I-V characteristics were dramatically changed. Fig. 2b showed the I-V curve measured at room temperature on a 5 nm cluster. It exhibited a pronounced nonlinearity. The current suppression observed was consistent with Coulomb blockade through the cluster.

Conclusion

In this work, the Au nanogap electrodes were successfully fabricated with a two-step electrochemical method in solution by a home-made electrochemically controlled system. To demonstrate the applicability of the fabricated nanogap electrodes to the electron transport studies of nano-sized objects, we measured the electrical characteristics of Fe_2O_3 colloidal nano-particles. The Coulomb blockade phenomenon was observed at room temperature. The significance of the study on the electron transport of nanostructures comes not only from underlying basic physics in low-dimensional systems, but also from its possible applications for future nanoelectronic devices.

ACKNOWLEDGEMENTS

The work was supported by the Hebei Provincial Natural Science Foundation of China (No. B2011201101), Medical Engineering Cross Foundation of Hebei University (No. BM201108), Medical Discipline Construction Foundation of Hebei University (No. 2012A1003) and Training Programs of Innovation and Entrepreneurship for Undergraduates of Hebei University (No. 2012085).

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