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Carbon Nanotube Clamped Metal Atomic Chain: Fabrication, Structure and Property

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1. Introduction

Metal atomic chain (MAC) is an ultimate one-dimensional structure with unique physical properties, such as quantized conductance, colossal magnetic anisotropy and quantized magnetoresistance. Therefore, MACs show great potential as possible components of nanoscale electronic and spintronic devices. However, MACs are usually suspended between two macro-scale metallic electrodes, hence obvious technical barriers exist in the inter-connection and integration of MACs. In this presentation, we report a carbon nanotube (CNT)-clamped MAC [1], where CNTs play the role of electrical leads for electrodes. This nanostructure is prepared by in situ machining a metal filled CNT, including peeling off carbon shells by spatially and elementally selective electron beam irradiation and further elongating the exposed metal nanorod under TEM. The microstructure and formation process of this CNT-clamped MAC are explored by both TEM observations and theoretical simulations. First-principles calculations indicate that strong covalent bonds are formed between the CNT and MAC. The electrical transport property of the CNT-clamped MAC was experimentally measured, and quantized conductance was observed. The strategy we proposed is effective in fabricating a variety of MACs and in situ connecting these MACs with CNTs, thus it may find potential applications in the assembly of nano/sub-nano devices.

2. Results and discussion

A Fe-filled CNT sample was prepared by floating catalyst chemical vapour deposition (FCCVD) using ferrocene as catalyst precursor and acetylene as carbon source. The outer and inner diameters of the CNT are about 25 nm and 10 nm, respectively. The filled Fe nanorod is single crystalline and body-center cubic (bcc) structured. When electron beam (with a current density of 100-300 A/cm^2) was focused on the carbon shells surrounding the Fe nanorod, the CNT walls were removed element- and site-selectively. And then the exposed Fe nanorod was further deformed and thinned, under strong electron irradiation. When the diameter of the Fe nanorod was reduced to ~6 nm (Figs. 1a, b), the intensity of the electron beam was decreased to a level normally used for TEM observations (10-30 A/cm^2). The Fe nanorod was elongated and thinned spontaneously, possibly due to the strain existing in the TEM sample. Atomic steps are observed during the thinning process as marked by arrows in Figs. 1c and 1d. Fig. 1g shows that a Fe nanorod contains only 3 layers of Fe atoms, and a single-atom wide Fe AC is finally formed in Fig. 1h. This single-atom wide Fe AC is composed of 5 atoms with 3 atoms suspended, as schematically shown in Fig. 1i. The inter-atom distance at the center of the Fe AC is about 2.2 Å.

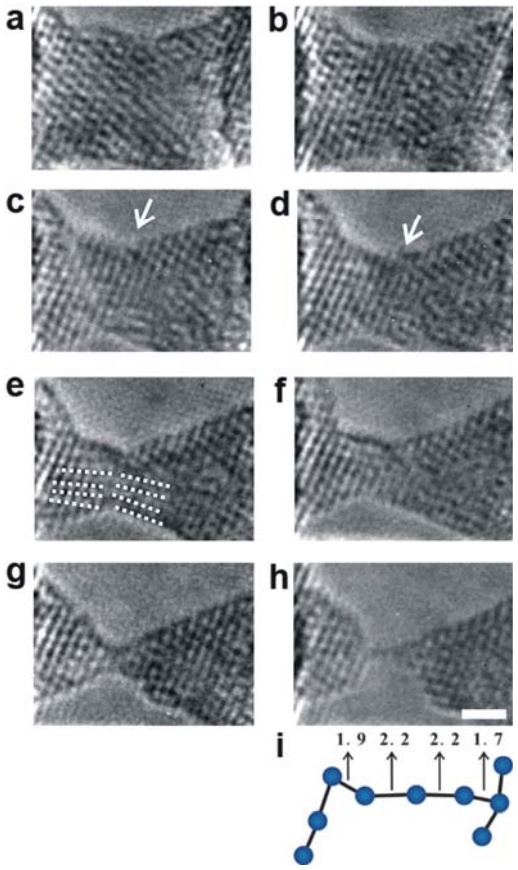

Fig. 1 Formation of a single-atom wide Fe AC. a-h, High resolution TEM images showing the formation process of the Fe AC. Atomic steps can be observed at the surface (marked by arrows in (c) and (d)). Distortion along (110) is marked with dotted lines in e. The scale bar is 2 nm. i, Schematic drawing of the Fe AC shown in (h), the projected inter-atom distances are marked in Å. [1]

First-principles calculation is effective in investigating the formation mechanism and physical properties of MACs. We used this method to simulate the formation process of Fe ACs and to explore the electronic structure of CNT-clamped Fe ACs.Our simulations start from a Fe nanorod oriented along [110] direction, based on the results of the above HRTEM characterizations. This nanorod is elongated gradually along the axis direction with a step of 0.4 Å. Along with the elongation, the center atoms in the second and fourth layer extrude out. Then, the nanorod shows obvious distortion perpendicular to the [110] direction, consistent with the experimentally observed slip of Fe (110) planes. The nanorod is elongated continuously and an AC emerges. The AC is stretched further as the elongation continues, and finally a single-atom wide Fe AC composed of 4 atoms formsbefore rupture. The inter-atom distances of the Fe AC were calculated to be 2.27 Å, 2.24 Å and 2.30 Å, which are larger than the inter-plane distance of bulk Fe(110) plane, coinciding well with the TEM observations.

Having realized the connection of CNT and Fe AC, we further investigated the electronic conductance of the obtained CNT-clamped Fe AC *in situ* by using a TEM-STM holder. An Fe filled CNT is suspended between a gold STM tip and a gold wire. Then, strong electron beam is used to peel off the carbon shells and to thin the exposed Fe nanorod of the Fe filled CNT. When the diameter of the Fe nanorod reaches several nanometers, the electron beam is reduced to a level for normal TEM observations and a tensile force is applied by retracting the STM tip gently with a speed ~ 0.1 nm/s to form an Fe AC. Electrical conductance is measured at a constant bias of 12 mV simultaneously, along with the elongation, thinning and rupture of the Fe AC, with a recorded curve of conductance versus time. The conductance decreases in a stepwise way, and the conductance plateaus are found to be near integral multiples of 0.5 G_0 (conductance quantum, which is $2e^2/h \sim (13k\Omega)^{-1}$). The last plateau is about 2 G_0, because the Fe nanorod ruptured before single-atom wide AC formed. Then, we re-connected the ruptured Fe nanorod and stretched it more slowly. In this case, stepwise-decreasing plateaus were also recorded, and the last plateau is around 0.5 G_0. The conductance can be interpreted with the Landauer formula ($G=G_0 \Sigma T_i$, where $G_0=2e^2/h$, T_i is the transmission probability for the ith conductance channel). For ferromagnetic metals, the conductance peaks are around integral multiples of 0.5 G_0, rather than G_0 for non-magnetic metals such as gold and alkali metals, due to the lack of spin degeneracy. Therefore, the conductance plateaus in our work can be interpreted as quantized conductance of ferromagnetic metal (Fe), and the conductance steps are ascribed to structural rearrangements during elongation. The plateaus are not always at the integral multiples of 0.5 G_0, which was also found previously for other metals, and this can be understood because the transmission probability is not always one for one conductance channel. The plateaus last at a time scale of several seconds, therefore the current dependence on bias voltage (I-V characteristic) could be measured when suspending the elongation process. When the contact is about 0.75 nm in width, corresponding to 3 to 4 Fe atomic layers, the I-V curve is almost linear within the measurement voltage range (-0.5 to 0.5 V), with a calculated conductance of about 1.5 G_0. Previous studies have shown that contamination of gas adsorption may lead to nonlinear behavior for metal nanocontacts, so the linear behavior observed in this study indicates that the conductance is Ohmic and the contact is clean. The above results show that after the connection and assembly with CNT, the MACs could well retain their unique electrical transport properties, such as quantized conductance.

In addition to the CNT-clamped Fe AC, we also applied the above fabrication philosophy to other metals and alloys. For example, Pt-filled CNTs and Fe-Ni alloy-filled CNTs were produced by an anodic aluminium oxide (AAO) template and chlorine-promoted FCCVD method, respectively. CNT-clamped Pt and Fe-Ni alloy ACs were successfully fabricated by an approach similar to the fabrication of the Fe AC as described above. DFT calculations also confirmed that both the Pt and Co ACs can form strong connection with CNTs. Therefore, a variety of metals are applicable for the fabrication of CNT-clamped MACs.

3. Conclusions

To sum up, we design and fabricate CNT-clamped MACs, which can provide a general approach for the inter-connection and integration of MACs with CNTs. The formation process of CNT-clamped MACs was explored by both *in situ* TEM observations and first-principles calculations. Electronic structure calculations indicate that strong covalent bonds are formed at the CNT/MAC interface. The intriguing properties of Fe ACs, such as half-metallicity and quantized conductance, are retained after the combination of Fe ACs and CNTs. The strategy we proposed is effective in fabricating a variety of MACs and *in situ* connecting these MACs with CNTs, thus it may find potential applications in the assembly of nano/sub-nano devices.

References

[1] D. M. Tang, L. C. Yin, F. Li, C. Liu, W. J. Yu, P. X. Hou, B. Wu, Y. H. Lee, X. L. Ma, H. M. Cheng, Carbon nanotube-clamped metal atomic chain, Proc National Acad Sci USA **107** (2010) 9055.