Atomic Structure and Electronic Properties of Single-Wall MoS_2 Nanotubes

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Abstract. Using atomically-resolved scanning tunneling microscopy and spectroscopy, we probe the structure and the electronic properties of sub-nanometer MoS_2 single wall nanotubes (SWNT) at room temperature. We find that, the nanotubes condense uniformly in ropes with achiral atomic structure and conical ends. Scanning tunneling spectroscopy measurements indicate a semiconducting behavior that is slightly dependent on their structural parameters. The contrast of atomic scale topographic and current STM images reveal the details of the lattice structure which allow us to identify clearly the locations of both atoms on the tube surface. By using AFM as a manipulating tool, we are able to transport or distort single MoS_2 nanotubes. We will show how to artificially produce kinks, draw a circle, and write letters or numbers from MoS_2 SWNT using AFM techniques.

INTRODUCTION

Research on carbon fullerenes and nanotubes has led to many important results that are extremely useful for applications in nanoelectronics. These remarkable achievements stem from their small dimensions coupled with structural and electronic properties. The driving mechanism of such novel structures is the instabilities in nano-graphene sheet, which favor the formation fullerenes like structure than the planar geometry. By analogy, it was suggested that nanoscopic planar sheets of layered dichalcogenides are unstable, and may transform under proper conditions, into tubular structures[1]. Just 1 year after the discovery of CNT, Tenne et al[1] have reported in 1992 the formation of tube-like structures, of diameter 20 nm, from layered dichalcogenides. It has been argued that smaller diameters (especially single wall MoS_2) are unstable to be realized. In 2001 Remskar et al[2] have reported a sub-nanometer MoS_2 nanotubes by using an efficient synthesis route involving C_{60}. Similar to CNT, these unique structures are expected to enjoy many interesting properties owing to their small dimensions. Here we report on the structure and electronic properties of these nanotubes using scanning tunneling microscope operated at room temperature. Results show that most of the nanotubes are achiral structure (armchair or zigzag) with diameters as small as 0.8 nm. Generally speaking the electronic properties show semiconducting properties with a gap of about 0.9 eV. We

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will also demonstrate manipulations of these nanotubes to write characters, numbers, or artificially produce kinks using AFM techniques.

EXPERIMENTAL DETAILS

The nanotubes are grown by an iodine transport method using C_{60} as a growth promotor. C_{60} in propotion of 5 wt.% is added to MoS_2 powder. The transport reaction was running for a few days at 1010 K in an evacuated silica ampoule at a pressure of 10^{-2} Pa and with a temperature gradient of 6 K/cm. The grown material is subsequently washed with toluene to remove residual C_{60}. A mat of the generated soot was sonicated in ethyl alcohol for a few minutes prior to being cast onto a highly oriented pyrolytic graphite (HOPG) substrate for STM measurements. We have carried out STM measurements using a Digital Instruments Nanoscope IIIa instrument equipped with customized vibration isolation, operated at room temperature. High quality images revealing the atomic structure of SWCNT-IMJs, were obtained by recording the distance between the Pt-Ir tip and the substrate at constant current, with the STM operated at a typical tunnel current of 300 pA and a bias voltage of 10 mV. The images presented here have not been processed in any way. Scanning tunneling spectroscopy (STS) measurements were performed by interrupting the lateral scans, as well as the feed-back loop, and measuring the current (I) as a function of the tip-sample voltage (V) at a fixed tip-sample distance. A combination of STM and STS measurements on individual nanotubes allowed us to investigate both their structural and electronic properties.

RESULTS AND DISCUSSIONS

In figure 1 we show a large-scale (1 μm^2) scan of MoS_2 nanotubes. Ropes are clearly visible everywhere in the entire image.

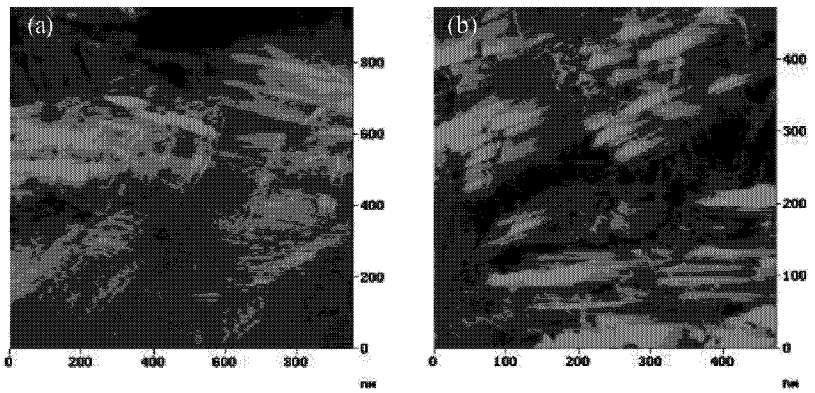

FIGURE 1. STM images in constant current mode show MoS_2 nanotubes bundles. We have only observed ropes with no other structures which is quite unique to these types of nanotubes.

Unlike nanotubes of carbon we haven't observe any kind of nanoparticles. In fact scanning different areas reveals similar details with no other type of structures (like flaks, adsorbates, ..etc.). In general tubes are condense in ropes with average rope size is 20 nm and rarely found as individual tubes. Based on our STM analysis we find that the average tube diameter around 1.7 nm, although smaller (0.8 nm) diameters are also found.

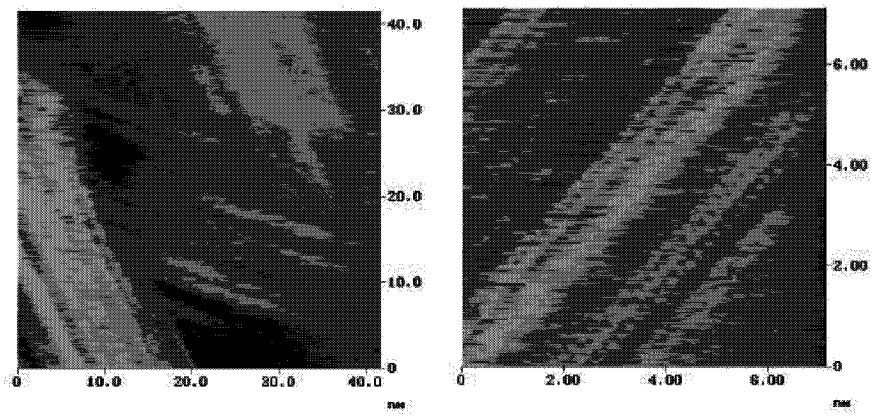

FIGURE 2. A close view on MoS_2 nanotube ropes. In (a) the ends appear more conical than round. The diameter of a single tube can be as small as 0.81 nm, figure 2(b). The atomic features on this image is due to sulfur atoms; the S-S distance is about 0.31 nm.

More details on individual nanotubes within a single rope are illustrated in figure 2. The tubes ends appear conical rather than round. Sharp ends are quite useful for applications; for example as field emitters or perhaps tips for high-resolution microscopy. We have also observed tubes with sub-nanometer diameters (0.81 nm); see figure 2(b) which are consistent with previous report using transmission electron microscopy[2]. Unlike small diameter CNT which can only exist in a host lattice, 0.8 nm diameter MoS_2 nanotubes are stable even in ambient conditions. It is indeed quite remarkable to see shell three atoms can be have such extremely narrow diameter.

Based on density-functional tight-binding calculations, it was concluded that large diameters MoS_2 nanotubes are semiconducting with direct or indirect band gap depending on their structural parameters[3]. Small diameters MoS_2 nanotubes, however, were expected to be metallic due to size effect. We have employed STS technique on single tubes in order to explore the electronic properties of MoS_2 nanotubes. Results are shown in figure (3) which displays a relation between tunneling current and bias voltage taken at room temperature. The I-V curves shows a semiconducting behavior as the current increases gradually only after certain threshold voltage. Different curves correspond to different locations on the nanotube wall. The value of the semiconducting gap is about 0.9 eV. This value is quite reasonable if one would like to study the transport properties of single MoS_2. We have tested several nanotubes,

and found that the semiconducting behavior almost independent on the nanotubes structures.

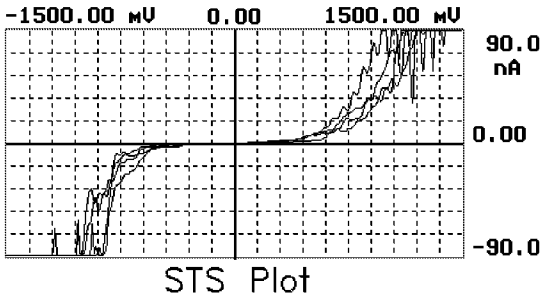

FIGURE 3. I-V spectroscopy on small diameters MoS_2 nanotubes shows semiconducting behavior.

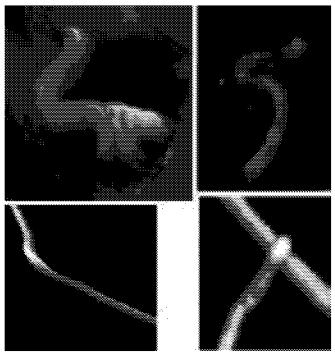

FIGURE 4. AFM manipulations of MoS_2 nanotubes demonstrates there flexibility; numbers 4 and 5 are written using the same bundle. The diameter of the rope is 4 nm.

Finally we show an example of MoS_2 nanotubes manipulations using AFM in dynamical force mode. Figure 4 shows a set of snapshots where a small single rope (diameter 4 nm) was deformed as AFM tip is mechanically pushing it along the substrate.

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