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Nature and electronic properties of Y-junctions in CNTs and N-doped CNTs obtained by the pyrolysis of organometallic precursors

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Abstract

Carbon nanotubes (CNTs) and N-doped CNTs with Y-junctions have been prepared by the pyrolysis of nickelocene–thiophene and nickel phthalocyanine–thiophene mixtures, respectively, the latter being reported for the first time. The junctions are free from the presence of sulfur and contain only carbon or carbon and nitrogen. The electronic properties of the junction nanotubes have been investigated by scanning tunneling microscopy. Tunneling conductance measurements reveal rectifying behavior with regions of coulomb blockade, the effect being much larger in the N-doped junction nanotubes.

1. Introduction

Y-junction carbon nanotubes are considered to be of potential use in the upcoming field of nanoelectronics. In this context, methods that can deliver junction nanotubes of high purity and in good yields are of importance. Satishkumar et al. [1] reported the synthesis of Y-junction nanotubes by the pyrolysis of metallocenes in the presence of thiophene and other sulfur-containing organic compounds. The junctions were later prepared by the pyrolysis of methane over Co supported on MgO by Li et al. [2]. Pyrolysis of organometallics such as metallocenes and metal phthalocyanines in the presence of thiophene, however, appears to be a reliable and efficient route to the junction nanotubes [3,4]. An important aspect of the junction nanotubes relates to the structure and chemical composition of the junction itself, these factors having a bearing on the electronic properties. In the case of the junction nanotubes prepared by the pyrolysis of organometallics in the presence of organosulphur compounds, it becomes necessary to establish whether sulfur atoms are incorporated at the junctions, considering the high propensity of sulfur to form rings. If sulfur is absent in the junction region, it would imply the presence of five-, seven- or eight-membered rings required to bring about necessary curvature to form a junction [5]. In this context, the disposition of the graphene layers around the junction is a relevant aspect. Since metal nanoparticles are necessary for the formation of the nanotubes, it is of interest to understand their role as well. We have investigated the Y-junction carbon nanotubes prepared by the pyrolysis of nickelocene–thiophene and nickel phthalocyanine–thiophene by transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) to throw light on the nature of the Y-junctions.

There have been a few reports on the electronic properties of junction nanotubes [1,6–10]. Rao and coworkers [1] carried out scanning tunneling spectroscopy (STS) measurements on Y-junction carbon nanotubes (CNTs)

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and reported that the junction acts as a diode. A theoretical study of the electron transport properties of doped nanotubes has shown that a doped nanotube with donor atoms on one side and acceptor atoms on the other, can function as a nanodiode [8]. Negative differential resistance behavior predicted for intramolecularly doped carbon nanotube junctions [9] was subsequently observed experimentally in the case of K-doped SWNTs [10]. We have carried out a detailed study of the Y-junctions both in CNTs and in N-doped CNTs by scanning tunneling microscopy (STM). The results show that the Y-junctions, particularly in the N-doped carbon nanotubes, possess rectification behavior. This is the first study of its kind on doped carbon nanotube junctions.

2. Experimental

Y-junction carbon nanotubes were prepared by the pyrolysis of nickelocene–thiophene employing the experimental set-up described earlier [1]. Pyrolysis of nickel phthalocyanine–thiophene mixtures was carried out to obtain N-doped carbon nanotubes with Y-junctions.

The nanotubes were examined with a JEOL JEM-3010 transmission electron microscope (TEM) operating at 300 kV and also with a JEM 4000 EX microscope (Fa. JEOL, Japan) with an accelerating voltage of 400 kV and a LaB_6 cathode. EELS chemical mapping was performed with a energy-filtering microscope (Zeiss 912 Omega, acceleration Voltage, 125 keV and LaB_6 cathode). Electron energy loss spectra were recorded with a Gatan imaging filter system attached to the JEOL microscope and fitted with a CCD camera. X-ray diffraction (XRD) patterns were recorded using a Seifert instrument with Cu Kα radiation.

The carbon nanotube junctions were investigated by tunneling conductance measurements. Highly oriented pyrolytic graphite (HOPG) was used as the substrate. Freshly cleaved HOPG substrates were prepared by peeling the upper layers with an adhesive tape. The nanotubes were then taken as a suspension in an organic solvent (typically CCl_4 and ethanol was used) sonicated for 30 min, after which a drop was deposited onto the substrate. The substrate was left in air but covered, for a period of 12 h for drying. Imaging and spectroscopy were carried out using Au tips prepared by electrochemical etching. The STM and STS studies were carried out at room temperature (using a Omicron Vakumphysik STS) operated in air. Atomically resolved images of HOPG were used for internal calibration. Current–voltage (I–V) data were collected in the spectroscopy mode with the feedback loop turned off (maximum current, 50 nA). Tunneling conductance measurements were carried out by positioning the tip atop a Y-junction (the point of contact between the three arms) as well as on the individual arms. The I–V data from the clean areas of the HOPG substrate were collected repeatedly as reference to ensure the reliability of the measurements.

3. Results and discussion

3.1. Y-junction CNTs

TEM images of the products of pyrolysis of nickelocene–thiophene mixtures show the presence of highly crystalline Y-junction carbon nanotubes with well-formed arms (Fig. 1a). The images also reveal certain

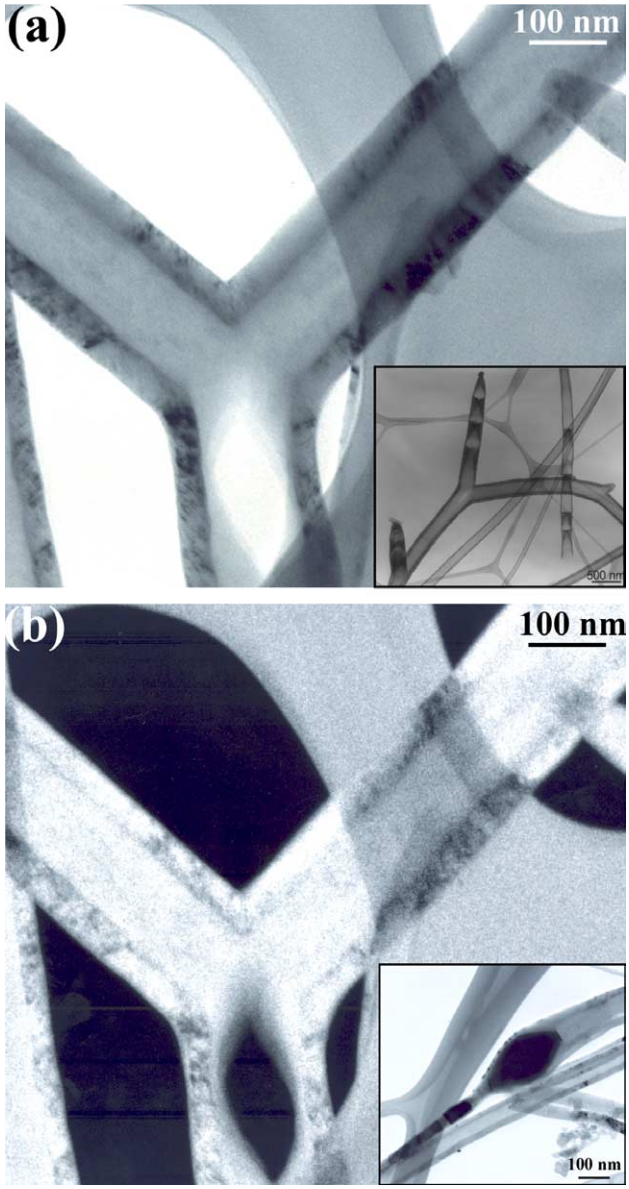

Fig. 1. (a) TEM image of a Y-junction carbon nanotube obtained by the pyrolysis of nickelocene–thiophene mixture. The inset in (a) shows asparagus tips in the Y-junction nanotube. (b) EELS mapping of carbon in the Y-junction carbon nanotube. The inset in (b) shows the TEM image of a Ni nanoparticle inside a carbon nanotube.

unusual nanotube structures such as asparagus-like branches and bamboo structures (see the inset of the Fig. 1a). We show the EELS chemical mapping for carbon in Fig. 1b to demonstrate how the nanotube is made entirely of carbon. We failed to observe any sulfur in the junction region. We have examined the nickel nanoparticles produced in situ by the pyrolysis of the nickelocene–thiophene mixtures. The TEM image of a Ni-nanoparticle is shown in the inset of Fig. 1b. EELS mapping showed the presence of a considerable amount of sulfur, close to 25%, in the nanoparticle. The XRD pattern of the Ni nanoparticles after the reaction with thiophene showed characteristic reflections of rhombohedral Ni_3S_2 with unit cell dimensions of $a = 5.75$ Å and $c = 7.13$ Å (JCPDS file: 44-1418). The sulfur from the thiophene is entirely removed by the nickel particles leaving the thiophene–carbon fragment which could form five-, or seven-membered carbon rings by adding on to different carbon centers in the nascent graphene sheets. Traces of S, in the nanotubes, if at all present, could not be detected at all by EELS or EDX.

The nanotube shown in Fig. 1a was examined by normal-incidence selected area electron diffraction (SAED) with the electron beam perpendicular to the junction. The diffraction pattern of one of the arms close to the junction (Fig. 2a), shows a set of arcs corresponding to four (0 0 2) maxima. Similar diffraction patterns were obtained from the other two arms next to the junction, suggesting that the graphene layers close to the junction are well-graphitized and are possibly slanted with some curvature. The electron diffraction pattern of the center shown in Fig. 2b reveals streaks of arcs corresponding to the (0 0 2) maxima arising from the three sets of graphitic planes in the three arms close to the junction [11–14]. The intensity distribution is not uniform in the arcs due to the complex nature of the orientation of the graphitic planes at the junction. In Figs. 2c,d, we show the schematic representations of the likely disposition of the graphene sheets around a Y-junction. The structure in Fig. 2c has gradual bends around the junction which can arise due the presence of five- and seven-membered carbon rings in the graphene sheets. It is also possible to have a junction with different fishbone-like orientations of the graphene sheets. From the observations depicted in Figs. 2a,b, it seems likely that the bends at the junctions may not be entirely continuous but instead consist of short straight segments arising from a fishbone-type stacking as in Fig. 2d.

Typical results from the STM measurements on the Y-junction carbon nanotubes are shown in Fig. 3. The image in Fig. 3a shows nanotubes with multiple junctions named J_A, J_B, J_C and J_D, where J_A and J_C are terminal junctions and J_B and J_D are junctions in the middle segments of the nanotubes. A high resolution image of junction J_A, given in the inset, suggests the possible presence of five and eight-membered rings near the

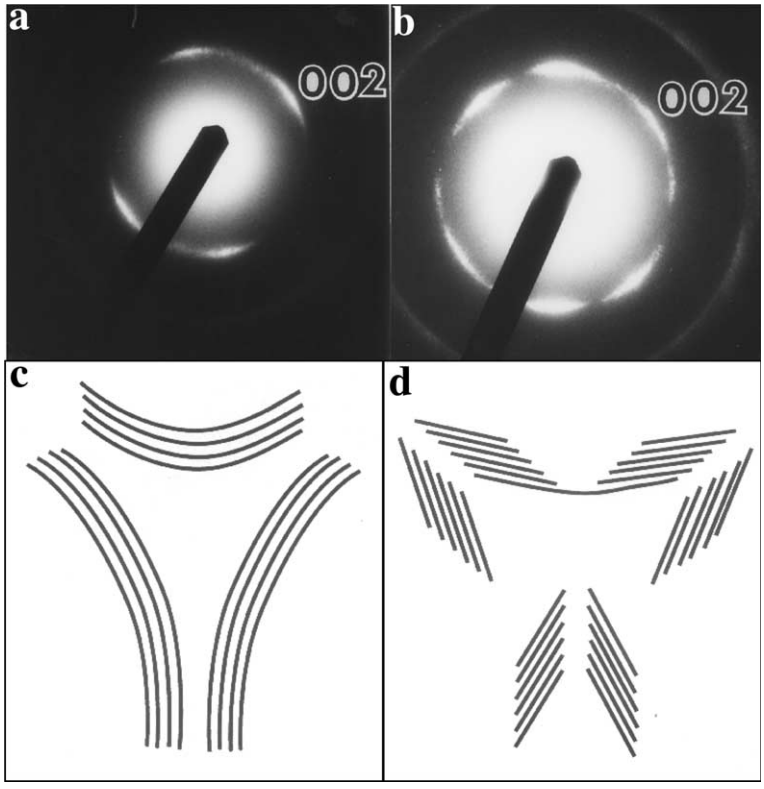

Fig. 2. Selected area electron diffraction (SAED) patterns of the Y-junction carbon nanotubes: (a) of the arms and (b) of the junction region. (c) and (d) Schematic drawings showing different ways of stacking of the graphene sheets in the Y-junction carbon nanotubes.

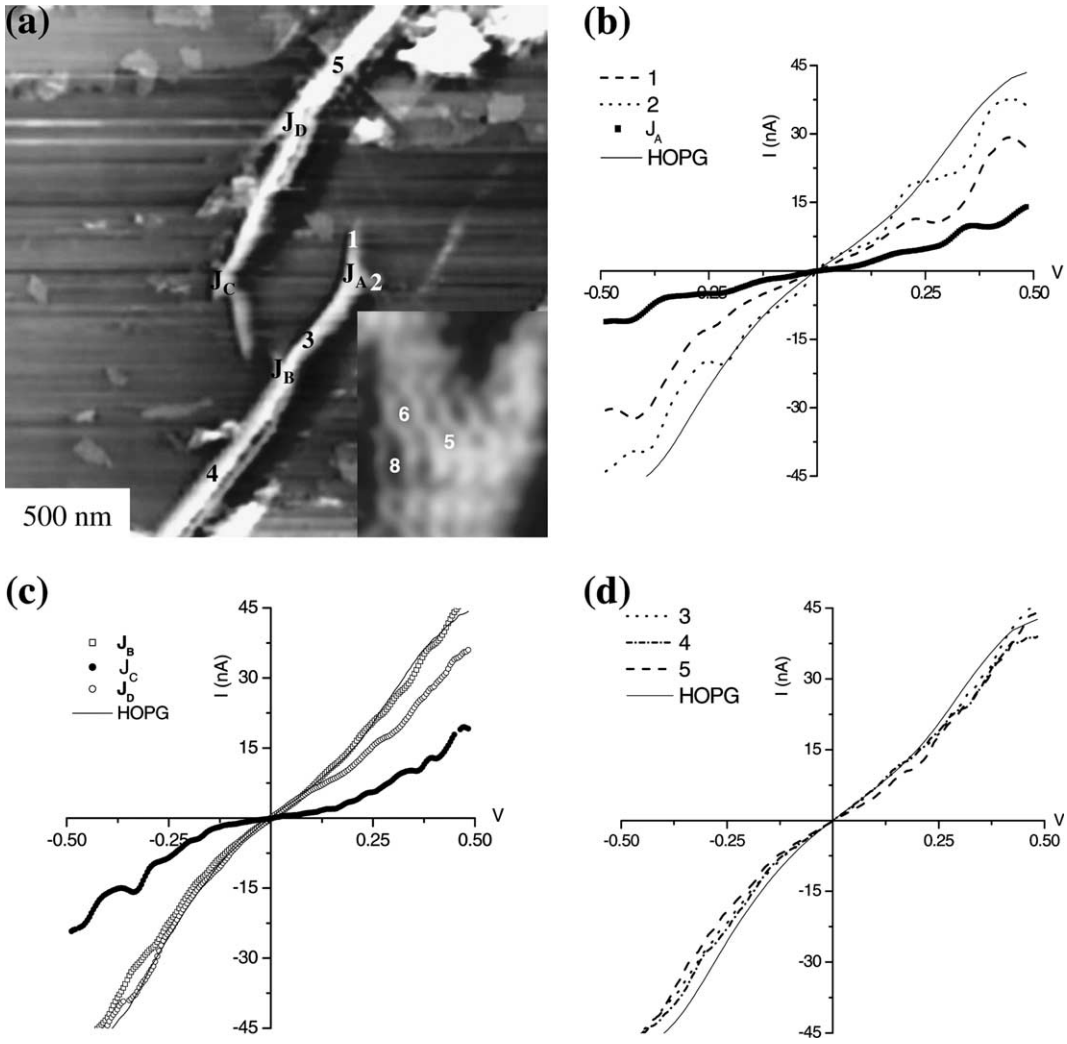

Fig. 3. (a) STM image of undoped carbon nanotubes with multiple junctions. Inset gives a close-up image revealing a five-membered ring (pentagon), and a eight-membered ring (octagon) at the junction region along with many six-membered rings (hexagons) as marked in the figure. (b)–(d) I–V data from the regions marked in (a).

junction region along with the six-membered rings. This is in accordance with the understanding of the structure of junctions in carbon nanotubes, wherein the introduction of five-, seven- or eight-membered rings in an otherwise hexagonal framework is responsible for formation of the junctions. The I–V data collected by positioning the tip over junction J_A exhibits an overall reduction in the current as compared to the HOPG substrate, with steps in the current at ±0.2 and ±0.4 V (Fig. 3b), perhaps due to incremental charging. The low current flat region enclosed by the first step (±0.2 V) corresponds to coulomb blockade at the junction. The curve is also somewhat asymmetric with a rectification ratio (which is the ratio of the forward and reverse currents at a given bias) of 1.3 at ±0.5 V. The data collected from the side arms 1 and 2 showed an overall increase in the current with prominent jumps at similar bias values. The terminal junction J_C exhibits a rectifying behavior similar to J_A (see Fig. 3c) while the interior junctions J_B and J_D show I–V characteristics comparable to those of the graphite substrate. This is also true of the regions – 3, 4, 5 (Fig. 3d) along the length of the tubes, a behavior characteristic of metallic nanotubes. What is noteworthy is the rectification behavior of the terminal junctions J_A and J_C.

3.2. N-doped Y-junction CNTs

We could obtain good yields of N-doped Y-junction carbon nanotubes by the pyrolysis of nickel–phthalocyanine mixture. These nanotubes have rounded tips and uneven arms (Fig. 4a). Chemical mapping of the tubes revealed a small amount of nitrogen but there was no sulfur in the junction region. Thus, the EEL spectrum (Fig. 4b) shows characteristic edges at 284 and 400 eV corresponding to the K-shell ionization of carbon and nitrogen, respectively. The nitrogen signal is a doublet due to π^* and σ^* levels, thereby indicating that the nitro-

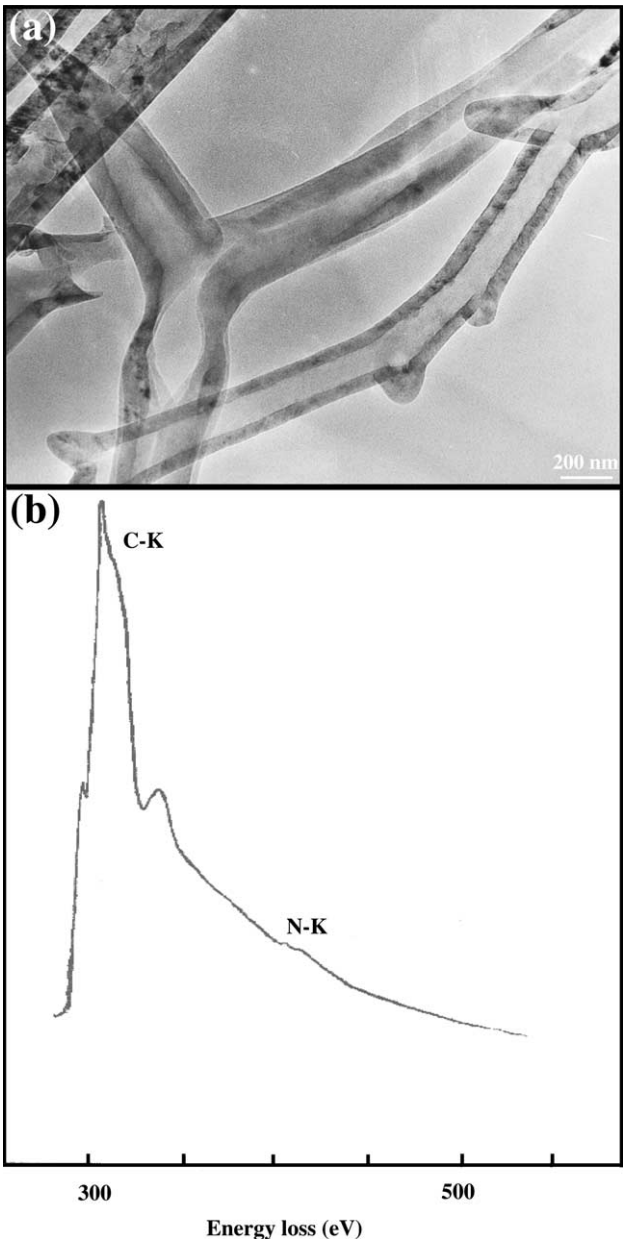

Fig. 4. (a) TEM image of N-doped Y-junction carbon nanotubes prepared by the pyrolysis of a Ni–phthalocyanine–thiophene mixture. (b) EEL spectrum showing the presence of doped nitrogen.

gen is present substitutionally in the graphene sheet. Based on the EEL spectrum, the average composition of the nanotubes is estimated to be $C_{45\pm5}N$ [15,16].

We have carried out tunneling conductance measurements on a large number of N-doped Y-junction carbon nanotubes. The junction (J_A) in Fig. 5a exhibits a rectification behavior with distinct change of slope in the I–V data at −1.5 and +1 V. A high value of rectification ratio of 4.75 is obtained for bias voltages of ±1.5 V. Coulomb blockade is easily identifiable in the bias range, −0.4 to +0.6 V. The arms of the tube, however, are devoid of blockade but exhibit varied behavior. The arm-1 shows distinct features at ±0.4 V. In the case of arm-2, similar

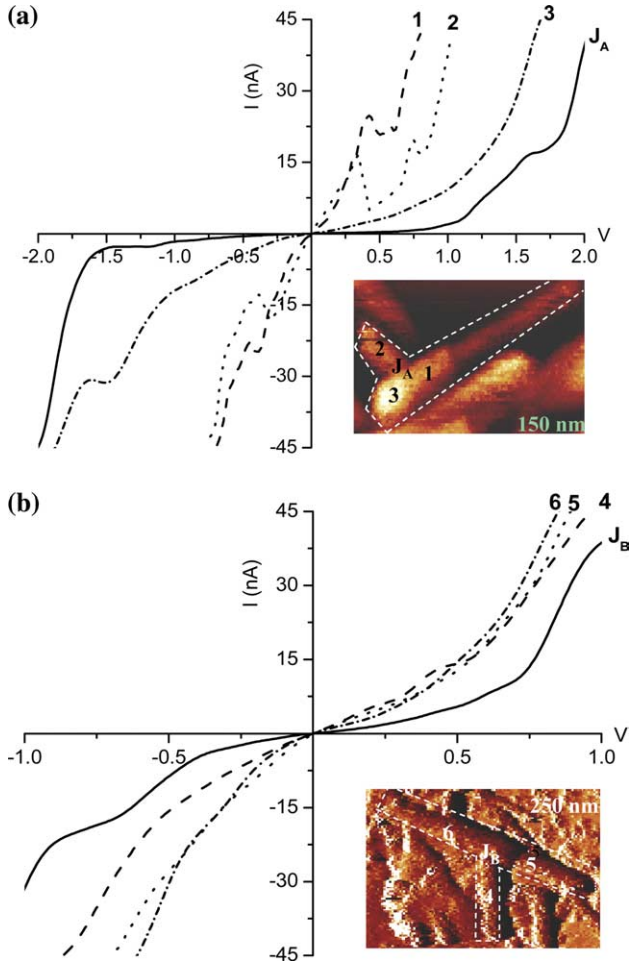

Fig. 5. I–V data of N-doped Y-junction carbon nanotubes shown along with the STM images. The regions where the I–V data were collected are marked with numbers.

features are seen at a slightly lower bias of ±0.3 V. It also exhibits an additional feature in the positive bias region at 0.75 V. The I–V data for arm-3 shows a feature around −1.5 V. While the distinct spectroscopic features corresponding to regions with negative differential resistance would arise from charging or other effects, the occurrence of a wide blockade region at the tube junction is noteworthy. Fig. 5b shows a nanotube with junction J_B, bearing a low-current flat region in the I–V data, from −0.4 to +0.75 V, indicative of a rectification behavior, similar to J_A shown in Fig. 5a. The rectification ratio in this case is 1.21 at ±1.0 V. The I–V curves from the arms (regions 4, 5 and 6) are somewhat asymmetric across zero bias, but do not exhibit any blockade.

4. Conclusions

In conclusion, Y-junction carbon nanotubes prepared by the pyrolysis of nickelocene–thiophene and nickel phthalocyanine–thiophene mixtures do not contain

sulfur at the junction but consist entirely of carbon or carbon and nitrogen, suggesting the presence of five-, seven-, or eight-membered rings at the junction. STM investigations show that rectification behavior at the junction is a fairly general feature, although it is more prominent in the N-doped CNTs. In addition, some of the junction nanotubes show coulomb blockade and features of NDR (negative differential resistance) as well.

Acknowledgments

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