

# Atomic force microscope manipulation of multiwalled and single walled carbon nanotubes with reflux and ultrasonic treatments

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**Abstract** We are reporting the atomic force microscope (AFM) nanomanipulation of ultrasonically dispersed and reflux-oxidized multiwalled carbon nanotubes (MWCNT) and single walled carbon nanotubes (SWCNT) by controlling the AFM tip with a NanoManipulator on a silicon substrate. The structure and the morphology of the carbon nanotubes (CNT) were confirmed with AFM interfaced with NanoManipulator and transmission electron microscope. The modifying parameter, which controls the force exerted by AFM tip, was set to be 0.5 nA in each case (0.5 nA = 20 nN). Bending was observed in ultrasonically dispersed MWCNTs, whereas, cutting was observed for reflux-oxidized MWCNTs along with the lateral movements. Similar observations were found for SWCNTs with sharp cuts and lateral displacements. The results show that CNTs deform by combining bending and distortion when subjected to large mechanical forces exerted by the tip of

the AFM. The magnitude of the force, required to deform the reflux-oxidized CNTs is less than that for the ultrasonically dispersed CNTs, for both MWCNTs and SWCNTs.

**Keywords** CNTs · AFM · Nanomanipulation · Functionalization · Bending

## Introduction

Nanomanipulation plays an important role in nanodevice designing, nanofabrication, and exploring the secrets of nano world, and thus becomes a starting point to research future nano-machine. In this arena carbon nanotubes (CNT) have produced plethora of applications in nanofabrication, and atomic force microscope (AFM) has been used as manipulating media in recent times for fabrication of nanodevices and biological samples (Bhushan et al. 2008; Carpick and Salmeron 1997; Guthold et al. 1999, 2000). Scanning-probe microscopy especially AFM (Binnig et al. 1986) is an indispensable tool for nanofabrication.

Since their discovery, CNTs have attracted substantial attention due to their unique physicochemical, mechanical, and optoelectronic properties (Iijima 1991) making them potential candidates for a myriad of industrial applications (Bachtold et al. 2001; Saito et al. 1998). Despite their positive attributes, the hydrophobic character of the graphene sidewalls coupled with strong van der Waals interactions between the individual tubes cause pristine CNTs to assemble as bundles, rendering them water insoluble and inappropriate for any practical application. Therefore, functionalization of CNTs is an essential prerequisite to proceed toward their application in any field and subsequently realize their practical potential. While

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studying the manipulation at nanoscale, sliding friction and tribological behavior play an eminent role (Carpick and Salmeron 1997; Meyer 2002; Persson 2000). Some pioneer work on manipulation of CNTs (Falvo et al. 1998, 1999; Hertel et al. 1998) by using a force stylus to feel the CNTs on a surface is available in the literature. Evidences are available for the possibility of cutting of bamboo shaped CNTs (Jang et al. 2005) with tip force application. At nanoscale, the CNTs stick to the surface of substrate and behave like claws of gecko (Yurdumakan et al. 2005). The AFM tip can be used to apply the force on the entangled CNTs to study the interactions between AFM tip and CNTs to measure the elastic and adhesive properties (Decossas et al. 2001). Their high-tensile strength, flexural rigidity, and high-aspect ratio make them potentially interesting materials for strong fibers, tips in scanning-probe microscopy for high resolution, and mechanical non-invasiveness (Qian et al. 2002; Yu 2004; Yu et al. 2001, 2000; Wilson and Macpherson 2009). The fabrication of carbon-nanotube/metal connections to establish electrical contacts to the outside world and to perform electrical measurements remains a major challenge. Nanomanipulation is the technique which can be helpful in this area. It can help in fabricating single electron transistor (SET) including nano-electromechanical systems (NEMS) and micro-electromechanical systems (MEMS) (Ahlskog et al. 2000; Thelander et al. 2001; Artukovic et al. 2005). In a more general sense, nanomanipulation includes different kinds of changes to the matter at nano-level such as: carving, indenting, oxidizing, etc. The AFM can be utilized not only as a sensor for imaging the topography of a sample, but, also as a robot for manipulation at the nanoscale. Due to its high resolution and its flexibility against different type of samples and ambient conditions, the AFM is applicable for a variety of nanomanipulation tasks. The possible applications range from the fabrication, preparation or modification of nanoscale devices and structures to the characterization, and handling of biological samples, i.e., dissection of DNA, etc. (Fotiadis et al. 2002; Hansma et al. 1992).

The novelty of our experiment is the comparative study of oxidized and dispersed single walled carbon nanotubes (SWCNT) and multiwalled carbon nanotubes (MWCNT) by controlling the AFM tip by NanoManipulator. It was observed that oxidation enhances the chance of any physical deformation during the application of force with the AFM tip. We have used the AFM in non-contact mode for imaging and in contact mode during the manipulation. We have not encountered any such comparison in the literature showing that oxidation reduces the amount of force required for the physical deformation of CNTs when deformed with AFM tip, with comparative studies on SWCNTs and MWCNTs.

## Experimental

### Sample preparation

The CNTs synthesized by arc-discharge method were obtained from Amorphous Materials Inc., USA. The  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  were purchased from Loba Chemie, India. All the chemicals were used without any further purification. The MWCNTs of length 0.5–2  $\mu\text{m}$  with diameter  $10 \pm 2$  nm and SWCNTs having similar lengths, i.e., 0.5–2  $\mu\text{m}$  with diameter  $2 \pm 0.5$  nm were used in the experiment.

For the oxidation of both kinds of the CNTs, a suspension was prepared by adding 5 mg of pristine CNT materials in the acid mixture ( $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ ) in ratio 3:1 in total acid volume of 20 ml. The resulting mixture was refluxed for 1 h at 80 °C. The resultant dispersion was centrifuged and washed with deionized water and acetone, and dried under vacuum. A similar amount of CNTs was sonicated in acid mixture with the same volume for 1 h in a sonicator at a frequency of 40 kHz. 0.5 mg of each type of reflux-oxidized and ultrasonicated CNTs were dispersed in 10 ml of water separately and the resultant suspension was dispensed on silicon substrate. The substrate was fixed on a stub for AFM imaging and manipulation. The AFM manipulations were performed in ambient conditions by employing an advanced operator interface called the NanoManipulator. This system provides the ability to perform complex manipulations, as well as transparent switching between low force non-contact AFM for imaging and contact AFM for manipulation. During each manipulation, the calibrated lateral force is monitored as a measure of the CNT substrate friction. The modifying parameter was set to be 0.5 nA in each case (0.5 nA = 20 nN).

The manipulation studies were performed by AFM (tip diameter 50 nm) from Veeco (Veeco Instruments Inc., USA) interfaced with nanohand-Phantom (SensAble Technologies, USA) controlled with NanoManipulator (3rd Tech. Inc., USA). The transmission electron microscope (TEM) images were obtained from FEI Tecnai G2 model transmission electron microscope (FEI, USA). Fourier transform infrared (FTIR) spectra were recorded using Perkin Elmer instrument (Perkin Elmer, USA). Ultrasonication studies were performed by using ultrasonic cleaner (frequency 40 kHz) from Raj Analytical Services, India. Analysis of nanotube lengths was performed using the image analysis software (Image J, National Institutes of Health, USA).

## Results and discussion

### TEM and AFM analysis

The TEM samples were prepared by sonicating 1 mg of oxidized MWCNTs in 10 ml of water for 30 min. A drop

of the sonicated dispersion was put onto a carbon coated copper grid and allowed to dry for few minutes. For AFM analysis, a drop of dispersion was poured on a cleaned silicon substrate and kept for drying before analysis. The images of CNTs obtained from TEM (Fig. 1a, b) and AFM (Fig. 1c, d) are shown in Fig. 1.

The images show rope like shapes of the CNTs with the outer diameter of MWCNTs around  $10 \pm 5$  nm and varied length ranging between 0.5–1.5  $\mu\text{m}$ , whereas, SWCNTs has diameter  $2 \pm 0.5$  nm with length in range of 0.5–1.5  $\mu\text{m}$ .

#### FTIR studies

The pure and oxidized CNTs samples were mixed with KBr prior to the analysis to make a pellet. FTIR spectra were recorded using Perkin Elmer instrument (Perkin Elmer) in the  $4,000\text{--}400\text{ cm}^{-1}$  range as shown in Fig. 2.

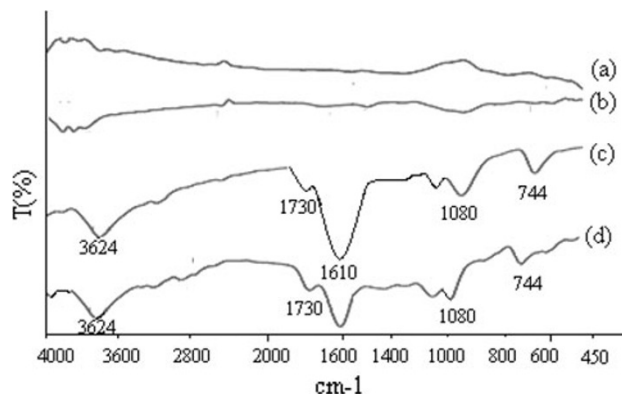
The peaks observed at  $1,610\text{--}1,730\text{ cm}^{-1}$  confirms the presence of carboxylic groups, i.e., the oxidation of the CNT samples. Peak at  $3,624\text{ cm}^{-1}$  depicts the carboxylic acid O–H stretch. Peak at  $1,080\text{ cm}^{-1}$  may be attributed to the C–O stretch, whereas, peak at  $744\text{ cm}^{-1}$  may be to the C–H bond.

#### AFM manipulation of ultrasonically dispersed CNTs: bending and deformation

##### MWCNTs

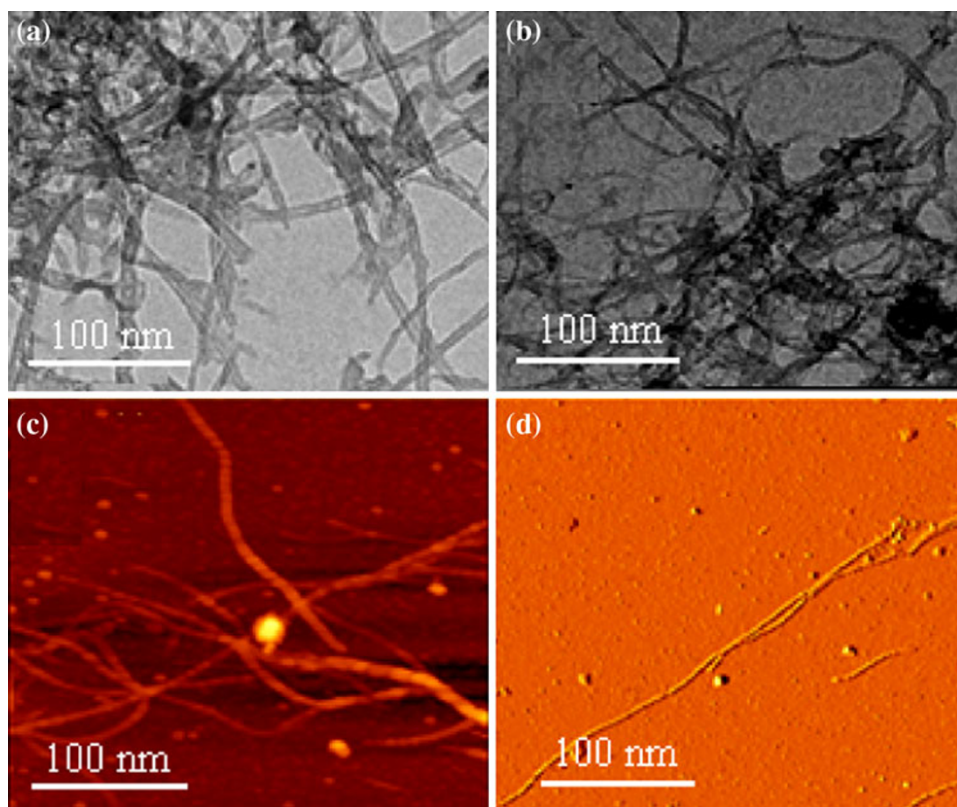
The AFM interfaced NanoManipulator image of the oxidized MWCNTs on the silicon substrate is shown in Fig. 3.

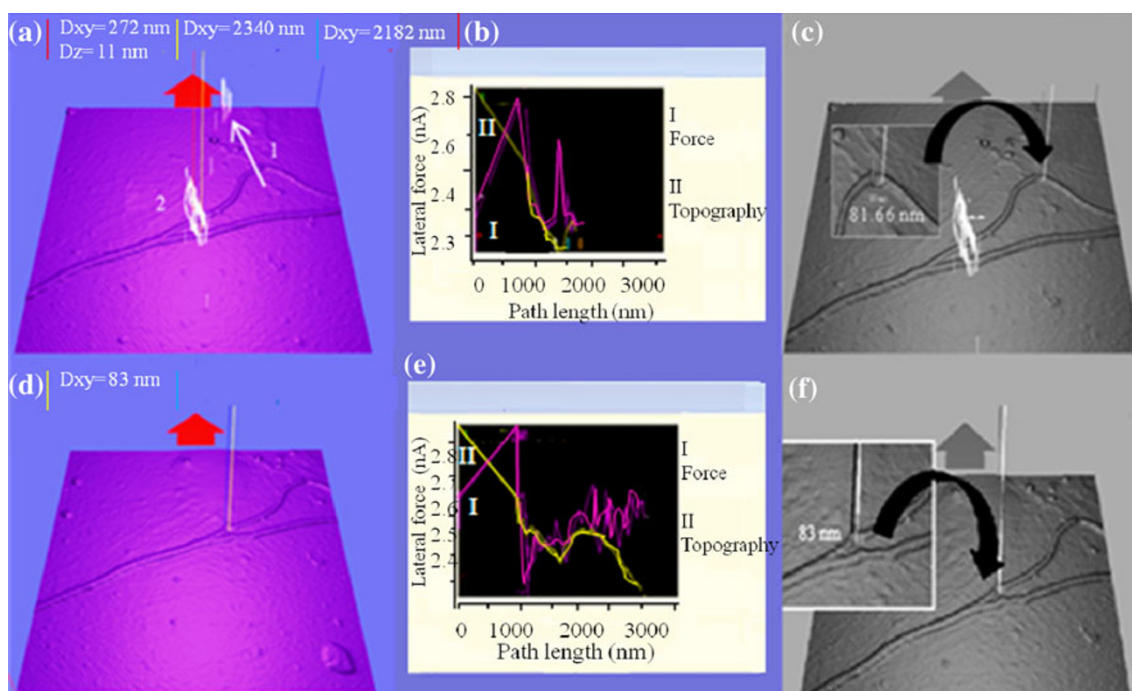
A force of 112 nN (i.e., 2.8 nA) was applied on two portions of MWCNT, marked as 1 and 2 as shown in Fig. 3a. The variation of force and path length moved by the tip is shown in Fig. 3b. From Fig. 3b it is clear that as



**Fig. 2** FTIR spectra of the **a** pristine MWCNTs, **b** pristine SWCNTs, **c** oxidized MWCNTs, and **d** oxidized MWCNTs

**Fig. 1** TEM images of the oxidized CNTs: **a** MWCNTs, **b** SWCNTs; AFM images: **c** MWCNTs, **d** SWCNTs





**Fig. 3** AFM interfaced NanoManipulator image: **a** MWCNTs on substrate with *white arrow* showing the direction of force, **b** force versus morphology plot *part I*, **c** the deformation produced (*inset*: enlarged view), **d** force on two simultaneous MWCNTs at *part II*; the

deformation width is shown by *blue and yellow line*, **e** Force versus topography plot, and **f** resultant CNT deformation (*inset*: enlarged view). *Colored lines* show the gap as mentioned

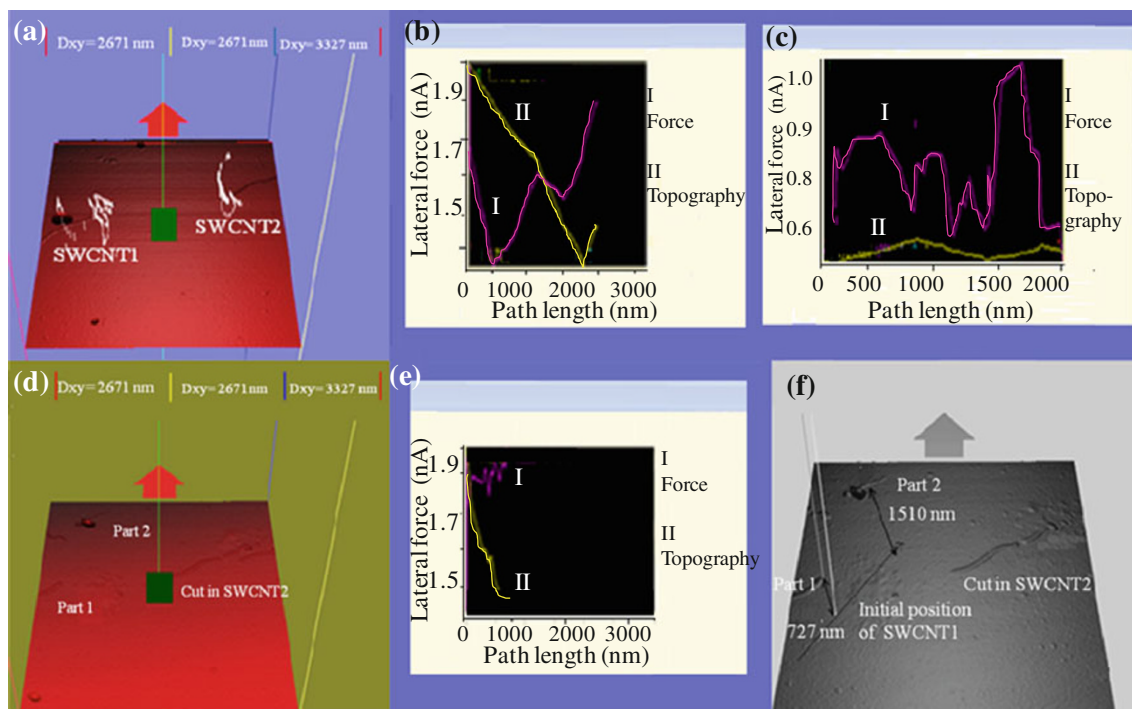
the tip touches the CNT, the amount of force required to deform is increased and the curve rises. It may be ascribed due to the fact that when the tip touches the CNT more force is required to push it and after crossing the CNT there is decrease in the topography line as the tip has pierced through the CNT piercing it into two halves. The piercing gap of 81.66 nm was produced in MWCNTs. The after piercing ripples in the force line are due to the dragging of the tip on the surface as clear from the image. The magnified deformed MWCNT at part I and force applied on part II are shown in Fig. 3c (*inset* as enlarged view) and the measured gap is shown with blue and yellow line in Fig. 3d. The resultant plot in Fig. 3e shows that topography and force lines follow the same profiles as in the previous case. In this case only a slight bending deformation was produced instead of cutting in single CNT case. Then the tip drags on the surface of the substrate and small peaks in the force peaks can be seen in the Fig 3. The resultant CNT image shows bending deformation of around 83 nm that was produced (*inset*: enlarged view Fig. 3f). In both the cases the amount of force required to deform the MWCNTs is nearly 112 nN. The results obtained here contradict with those observed by Falvo et al. (Falvo et al. 2000), on bending and buckling of CNTs, where they have concluded that some strains can be produced in CNTs without separating the CNTs on mica.

#### SWCNTs

The AFM image of ultrasonicated SWCNTs dispersed on silicon substrate is shown in Fig. 4. Figure 4a shows the AFM interfaced NanoManipulator with two CNTs, marked as SWCNT1 and SWCNT2.

The force was applied on SWCNT1 at middle point as indicated by white marks, which cuts it into two parts which are marked as part 1 and part 2. During application of force on SWCNT1, it was dragged to a distance of 727 nm and then the SWCNT1 was cut. It may be ascribed to the fact that in the first attempt no pinning center or obstruction was encountered to drag SWCNT1 up to distance of 727 nm and when it was encountered and obstructed from the opposite end it resulted in a cut in the SWCNT1. The force was also applied on the part 2 of the SWCNT1. The resulting force displaced the part 2 to a distance of around 1510 nm from the initial position (Fig. 4a, f). This portion was just displaced and no deformation was observed, but lateral displacement was observed in this portion after being segregated from the part 1. Figure 4b and c shows force versus displacement plots for the corresponding portions i.e., for forces on SWCNT1 and part 2. From Fig. 4c, it is clear that force required for displacing SWCNT is about 40 nN (i.e., 1 nA) which is less than the force required to cut the SWCNT1.





**Fig. 4** AFM interfaced NanoManipulator images of **a** SWCNTs with two white marks indicating application of force, **b** force versus path length plot for SWCNT1, **c** force versus path length plot for

segregated *part II*, **d** displaced CNT portions, **e** force versus path length plot for SWCNT2, and **f** final view after the application of the force with demonstration

The force was also applied on the SWCNT2 as shown in Fig. 4d. The corresponding force and topography plot is shown in Fig. 4e. In this case, only cutting was observed with no displacement. It may be ascribed due to the fact that SWCNT2 may be pegged by amorphous carbon particles or impurities on substrate acting as pinning centers, resulting a cut in the nanotube. However, the results observed by Falvo et al. (1997) have shown rolling mechanism for MWCNTs with the range of 100 nN on HOPG substrates. But, Singjai et al. (2002) have predicted that cutting is produced in MWCNTs at force greater than 40 nN at voltage set parameter of 2.0 V.

### Manipulation of oxidized CNTs: cutting and lateral displacement

#### Oxidized MWCNTs

The AFM interfaced NanoManipulator images of oxidized MWCNTs are shown in Fig. 5.

Some dot like structures can be seen in Fig. 5; these might be amorphous carbon particles. The force applied is in the direction as indicated by white marks in Fig. 5a. The corresponding force versus displacement is shown in Fig. 5b. From the plot it is indicated that as the force is applied on the SWCNT it is ruptured into two halves,

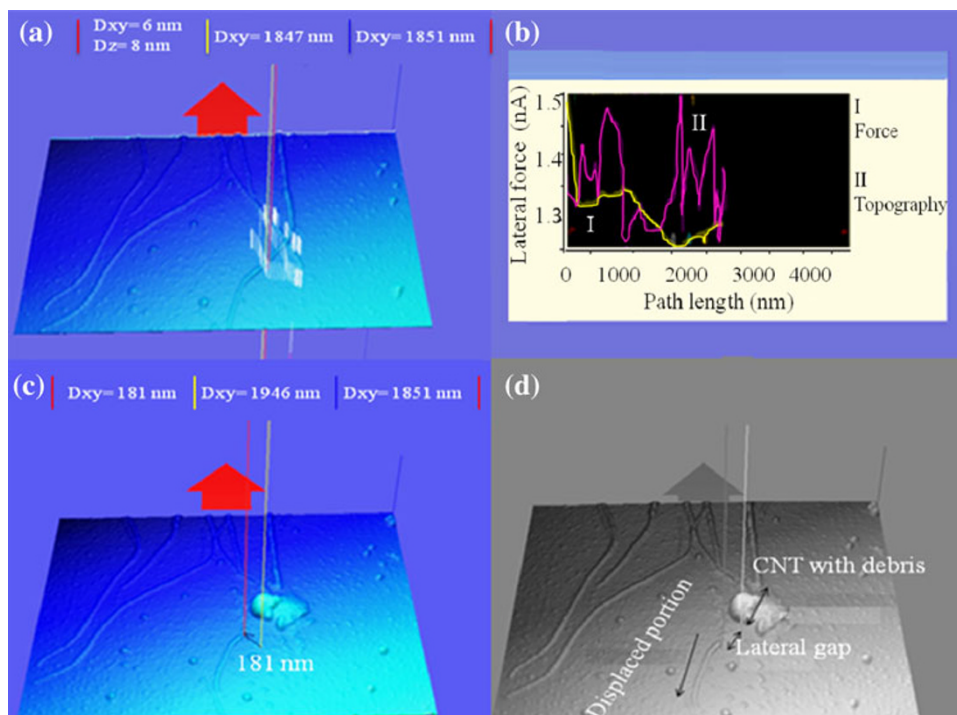
producing a cut with gap of 101 nm shown by red and yellow lines in Fig. 5c. It was observed that the segregated right part is displaced toward the direction of application of force during the cutting of CNTs. The CNT was also found to be displaced in the direction indicated by the arrow mark in Fig. 5d. It may be ascribed to the reason that when CNTs are oxidized, they are shortened in their lengths and some carbon particles may be produced, which may act as pinning centers or impurities on the substrate that supports the cutting of CNTs during the application of force by the tip which results in the lateral movement of the CNTs. Similar pinning centers were used by Decossas et al. (2003) to produce the displacement of CNTs on nanostructured surface. The lateral motion of the CNT is confirmed as AFM tip diameter which is around 50 nm. It was also observed that the maximum amount of force required to cut the oxidized MWCNTs is 60 nN (1.5 nA), which is less than that observed in case of ultrasonically dispersed MWCNTs.

#### Oxidized SWCNTs

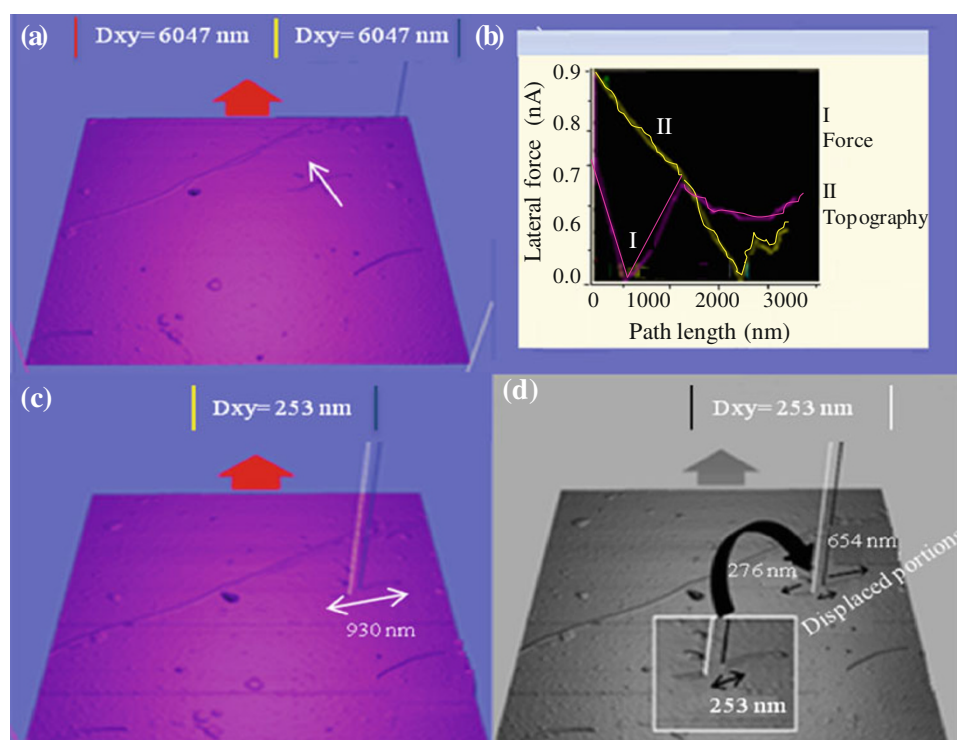
The AFM interfaced NanoManipulator images of oxidized SWCNTs are shown in Fig. 6.

In this case a force was applied on the oxidized SWCNTs as indicated by the arrow in Fig. 6a. The corresponding force versus topography is shown in Fig. 6b indicating the interaction of tip and the MWCNTs. It was

**Fig. 5** Nanomanipulation of oxidized MWCNTs: **a** direction of application of force, **b** force versus displacement plot, and **c, d** final images after application of force showing the cut and lateral displacement (scales are shown by colored lines)



**Fig. 6** Nanomanipulation of oxidized SWCNTs: **a** functionalized CNTs arrow indicating the application of force, **b** force versus displacement plot, and **c, d** show final images after application of force showing the cut and lateral displacement



observed that the tip pierced SWCNT into two halves as shown in Fig. 6c producing a gap of 253 nm as shown with help of blue and yellow line. The oxidized SWCNTs were also found laterally displaced as illustrated in Fig. 6 with respect to the reference points on the substrate, but the displacement is more in case of the oxidized SWCNTs.

The mechanism has been shown in Fig. 6d. In this case the original length of the SWCNT is 930 nm. After the application of force, the SWCNT was segregated into two parts having lengths 654 and 276 nm, which results in the lateral displacement of 253 nm. Also, the magnitude of force required to cut the oxidized SWCNTs is 36 nN

(i.e., 0.9 nA), which is again less than ultrasonically dispersed counterpart.

## Conclusion

In this experiment we have demonstrated a nanoscale manipulation of two kinds of CNTs with single walled and multiwalled morphology using a contact force mode AFM interfaced with NanoManipulator. The diameter of the CNTs was confirmed by TEM and AFM images. The oxidation of CNTs was confirmed by the presence of carboxylic groups using FTIR analysis. It was observed that the acidic treatment given to the CNTs under ultrasonication and refluxed oxidations make them to behave differently when force is applied. Ultrasonically dispersed MWCNTs showed bending deformations at a force of 112 nN, the corresponding SWCNTs showed cutting deformations and sliding displacement by applying a force of 30 and 40 nN force application, whereas in reflux-oxidized case these values are 60 and 36 nN for MWCNTs and SWCNTs, respectively. In case of oxidized CNTs, both the types intimated cutting and some lateral movement with lesser amount of force as required for these deformations. The observations were similar in some cases and contradicting with those available in the literature. However, we assumed that lateral movement may be due to the amorphous carbon or debris on substrate acting as pinning centers produced during oxidation of CNTs, and there could be different parameters, which can influence the results while manipulating the nanomaterials at nanoscale with AFM tip.

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