Preparation of graphene nanoribbons (GNRs) from twisted structure carbon nanotubes using unzipping technique

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Abstract. This work deals with the preparation of graphene nano ribbons (GNRs), which are small bars or strips of graphene with narrow range width less than 50 nm and one atom thick sheet (approximately 140 Å). This material has many applications in electronics, polymer composite, contrast agent bio-imaging and others. This material was prepared from twisted structure of carbon nanotubes CNTs using oxidation process by acids and breaking down by high frequency ultrasonicication (sonochemical unzipping). Pre-prepared twisted CNTs were characterized by scanning electron microscope (HRSEM) before treatment. The size, morphology, crystallinity of prepared graphene nanoribbons was also investigated using transmission electron microscope, high resolution transmission electron microscope, and X-ray diffraction and particle size analyzer. The results showed of formation of GNRs with narrow width as lower than 29 nm and uniform sizes. X-ray diffraction reveals Bragg reflections corresponding to the lattice planes (002), (100), (101), (004), and (110) matched with hexagonal system of graphite.

Keywords: Twisted carbon nanotubes; graphene nanoribbons; sonochemical unzipping

1. Introduction
Graphene and single-layered graphite are considered as great promise two-dimensional material [1]. Unique crystallinity and excellent electronic properties candidate them for the nanofabricated devices [2]. Graphene with narrow width (below 50 nm) is considered as a zero or one dimension nanomaterials depending on size, on other word is considered a graphene nanoribbons [3,4]. Numerous approaches are found to synthesis graphene nanoribbons. Lithographic, CVD and unzipping are the main ones. Lithography approach gives GNRs with disordered edges. Nanoribbons with smooth edges could be obtaining s via chemical vapor deposition process near 950 °C, whereas carbon nanotubes unzipping technique gives GNRs with wide range of widths depending on CNTs (diameter, length, structure, defects…etc) and technique parameters (energy, time, acidity, applied forces, etc) [5]. Although numerous papers was published using CNTs unzipping technique has, twisted CNTs cutting is unreported. It had been developed a sonochemical approach to prepare GNRs with width range less than 30 nm. In this study, GNRs are derived by sonochemical unzipping of twisted carbon nanotubes. It had been produced a yield of nanoribbons using oxidation process to cut side walls of multiwalled carbon nanotube from defects region. This technique depends on the damaging of covalent bond in localized regions of twisted CNT walls by acids and high power ultrasonicication (probe disrupter). These regions are crystallographic defects called Stone-Wales defects which responsible of helicity of twisted CNT [6]. Stone-Wales defects are pentagon and heptagon carbon network defects instead of hexagon in graphite sheet [7, 8, 9,10]. These defects act as anode in corrosion process, so the acid would corrode the CNTs side walls localized in
high potential energy area of unsaturated covalent bonds resulting narrow slices of graphene from individual CNT.

2. Experimental work

2.1 Unzipping Technique
Twisted MWCNTs was pre-prepared by chemical vapor deposition. As (0.1 g) of pre-prepared twisted CNTs were dispersed in concentrated acids mixture: sulfuric acid H$_2$SO$_4$ and nitric acid HNO$_3$ (3:1) using high frequency ultrasonication technique (Ultrasonicator probe type; BRANSON model, 400 Watt) for (3 hr) to produce graphene nanoribbons GNRs. The obtained colloidal was washed several times with deionized water, filtered and then dried at (100 °C for 48 h).

2.2 Characterization of graphene nanoribbons GNRs
Twisted CNTs were characterized by high resolution scanning electron microscope before treatment (HRSEM, Hitachi S-4700, accelerating voltage 0.5-30 kV, and resolution of 1.5 nm). The used accelerating voltage was 10 kV. Transmission Electron Microscope (TEM, JEOL 1400 model, accelerating voltage 40–120 kV), was used to characterize the GNRs. High Resolution Transmission Electron Microscope was also used (HRTEM, Tecnai G2F30 twin, FEI) with point resolution 0.24 nm, magnification reaches to 800 kX, acceleration voltages (100, 200 and 300) kV. X-Ray diffraction type (Rigaku-Model UltimaIV, Cu/K-alpha target, 1.54059Å d-Spacing, 40 kV Voltage, 44 mA current) was used to characterize GNRs structure. Particle size analyzer was also utilized to investigate the size and distribution of GNRs, the device would recognize only GNRs width, because the GNRs thickness is lower than laser wavelength. Few milliliters of washed GNRs was ultrasonicated in ethanol and then analyzed directly by (Brookhaven Nano Brook 90 plus, USA) to determine particle size and distribution.

3. Results and Discussion
Figure 1 shows the SEM image of twisted CNTs before unzipping. It has outer diameter about 50 nm. Figure 2 and 3 show the TEM images of GNRs after CNT’s unzipping by acids and ultrasonication at different magnification. It could be observe that GNRs width varies from (10-25) nm with uniform shape distribution. The variety of width belongs to many reasons:
1. Which walls are derived from, because the outer diameter is about 50 nm but the inner diameter is smaller that makes the obtained GNR is less in width and so on.
2. Different sizes of twisted CNTs because it obtained from CVD approach.
3. Stone-Wales defects exist in different density in each tube.
4. Sonochemical parameters.
Figure 1: HRSEM image of the pre-prepared twisted structure CNT.

Figure 2: TEM image of the prepared graphene nanoribbons GNRs at low magnification.

Figure 3: TEM image of the prepared graphene nanoribbons GNRs at higher magnification.

Figure 4: HRTEM image of the prepared graphene nanoribbons GNRs.
Figure 4 shows the HRTEM image of GNRs. HRTEM image of the ribbons revealed the presence of hexagonal patterns of carbon atoms structure.

Figure 5 shows the XRD pattern of graphene nanoribbons structure. The results showed highly crystalline of nanoribbons as graphite-like structure, with strong Bragg's reflections at planes (002), (100), (101), (004), and (110). These results are in good agreement with JCPDS 2011 International Centre for Diffraction Data, card No. (01-0640).

Figure 6 shows the particle size and distribution of graphene nanoribbons. The relationship between particle size and fraction % reveal that particle average size is about 29 nm, and 93% of ribbons are in width below than 50 nm.

4. Conclusion
Preparation of graphene nanoribbons using unzipping technique of twisted structure of CNTs is so fast, simple, low cost, and medium skill requirement. GNRs were obtained from twisted CNTs using unzipping approach. Sonochemical unzipping approach is considered easy, economic and efficient to prepare 100% yield of GNRs generated from the energy concentration regions (Stone-Wales defects) in twisted CNTs. In this study, the derived graphene nanoribbons could be classified as a zero dimension nanomaterials due to size. These results lead to applying GNRs products in electronics fields, biology, composite materials and other applications where large quantities of nanoribbons are needed.

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