

# CONVERSION OF REDUCED GRAPHENE OXIDE INTO MULTI-WALLED CARBON NANOTUBES

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**Abstract:** We report the green, simple microwave-assisted approach for catalytic conversion of reduced graphene oxide (rGO) into multi-walled carbon nanotubes (MWCNTs) in presence of conducting polymer poly aniline (PANI) and Indium tin oxide (ITO) powder as catalytic agent. Rod like MWCNTs with inner hollow bamboo-shaped structures were obtained. The observed MWCNTs have length 6025 nm and outer diameter 150 nm. The UV-Visible absorption spectrum of MWCNTs shows bands at 236 and 254 nm which results from the  $\pi$ -plasmon excitation. In photoluminescence (PL) spectra, MWCNTs shows emission bands at 439 and 659 nm when excited at 325 nm. Infra-red spectroscopy and electrochemical studies were performed for the MWCNTs. The morphology of the MWCNTs were characterized by using X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) techniques.

**Keywords:** multi-walled carbon nanotubes; graphene oxide; poly aniline; microwave-assisted

## 1. Introduction:

Graphene is a two dimensional single layer of carbon atom and one carbon atom –thick planer  $sp^2$  hybridization carbon atom which arrange in a hexagonal structure. It has unique and remarkable mechanical, thermal, optical and electronic properties. Also graphene have a zero band gap and act as a semimetal. Carbon nanotubes (CNTs) are usually considered as the rolled up graphene sheets with a co-axis and with less dragging bonds and defects than carbon black. CNTs can be divided essentially in three categories: Single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs) and MWCNTs. CNTs have a wide variety of applications such as field emission displays, fuel cells, electronic devices, catalysis, to prepare modified electrodes etc. [1,2,3,4].

## 2. Experimental:

### 2.1. Materials and instrumentals:

Graphite pencil was collected from local market. Sulphuric acid ( $H_2SO_4$ , 98%), Potassium permanganate ( $KMnO_4$ , 99%), Hydrogen peroxide ( $H_2O_2$ , 30%) and Sodium nitrate ( $NaNO_3$ ) were purchased from Merck. UV-Visible spectroscopy measurements were carried out on double beam UV-1800 Shimadzu UV - Spectrophotometer. Photoluminescence spectroscopy measurements were carried out on Hitachi F-2500 Fluorescence Spectrophotometer (Xenon lamp light source). The FT-IR spectra were recorded using Affinity-I Shimadzu Spectrophotometer. Cyclic voltammetry were recorded using BAS-100 Electrochemical Analyzer. XRD measurements were performed using a Philips X' PERT PRO instrument operating of a voltage 40 KV and a current of 30 mA with a  $CuK\alpha$  radiation. HR-TEM image were obtained by using TEM-JEM-2100, 200KV, Jeol. Surface area measurements of rGO nanosheets were performed using Micrometrics Tri Star Surface Area and Porosity Analyser.

### 2.2. Exfoliation of Graphene Oxide:

GO was exfoliated from graphite via modified Hummer's method [5,6,7].

### 2.3. Synthesis of rGO:

GO sheets were chemically reduced as follows: To 25 ml yellow-brown GO suspension (0.05g/5ml) in de-ionized water, 15  $\mu$ l hydrazine hydrate (80%) and 10 ml sodium dodecyl sulphate (SDS 1%) as dispersing agent

were added. The resulting mixture was rigorously stirred and then sonicated for 30 minutes. A stable black coloured rGO nanosheets dispersions so obtained were centrifuged at 10000 RPM for 10 minutes. Washed the black coloured rGO with water for 3-4 times to remove SDS, hydrate residues and excess hydrazine and then allowed to dry in the oven at 60°C for 4hrs[8,9,10,11].

The BET surface area of the resulting rGO was measured to be  $89.642 \pm 11.110 \text{ m}^2 \text{ g}^{-1}$ .

#### 2.4. Synthesis of MWCTNs by microwave-assisted method:

0.5g rGO was physically mixed with conducting PANI and ITO-powder in the ratios 3:1:0.5 respectively. (PANI=Aniline+dil.HCl+ Ammonium per-sulfate(APS) at 0-5°C, APS:Aniline=1:1). The mixture of rGO-PANI-ITO was rigorously stirred for 1 hour with 5 ml de-ionized water and there after sonicated for 30 minutes. The conducting mixture was microwave irradiated in air at 720 Watt for 1 minute. On microwave irradiation the aqueous suspension of the conducting rGO-PANI-ITO mixture is heated to very high temperature upto 1100°C, where PANI decomposes to hydrocarbons over ITO catalysts. The rGO nanosheets at very high temperature in presence PANI and ITO catalysts converted into rolled up graphene sheets with a co-axis which is termed as CNTs. The reason for utilizing the conducting polymers such as PANI is that, PANI can be heated to very high temperature in a very short time and as well as PANI acts as heating and carbon sources towards the growth of CNTs through microwave-assisted approach[12]. Since ITO powder have high thermal conductivity, acts as the heating layer as well as catalytic agent[13,14,15,16].

### 3. Results and discussions:

#### 3.1. UV-Visible spectra of GO, rGO and MWCNTs:

UV-Visible spectra of GO, rGO and MWCNTs are shown in **Figure 1a, b and C**. Dispersion of GO in water shows absorption bands at 224nm corresponding to  $\pi-\pi^*$  transition of aromatic C=C skeleton. A broad shoulder at ~300nm corresponding to  $n-\pi^*$  transitions of C=O bonds for the carboxylic acid functionalities of GO. On reduction of GO using hydrazine hydrate, shifts the band 224nm to 234nm due to the restoration of conjugation that was distorted in GO. Furthermore, disappearance of shoulder at ~300nm accounting for the C=O bond that appeared in GO confirms the deoxygenation process and removal of carboxylic acid. MWCNTs shows absorption bands at 236 and 256nm corresponding to  $\pi$ -plasmon resonance bands.

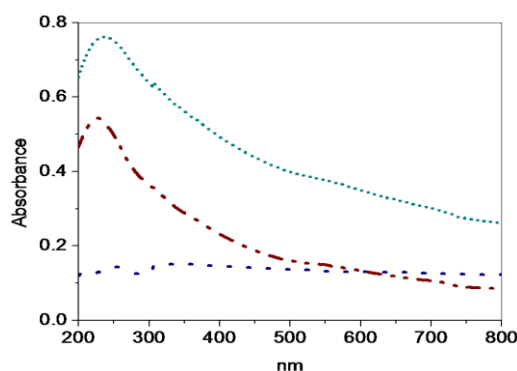
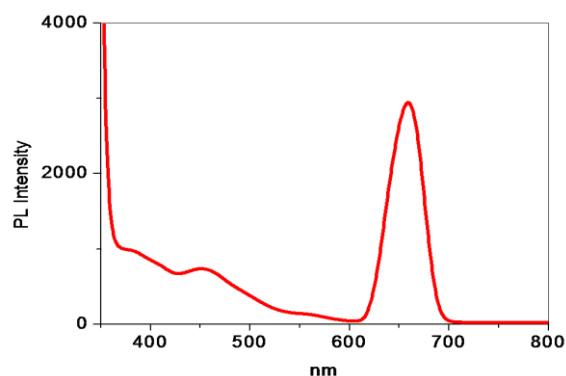


Figure 1: UV-Visible spectra of (a) . . . . MWCNTs, (b) \_ \_ \_ GO and (c) ..... rGO dispersed in DMSO/H2O.

#### 3.2. Photoluminescence spectra of MWCNTs:

On excitation at 325nm MWCNTs shows emission band at 439nm. The origin of this PL is due to the existence of extensive conjugated electronic structure and excitation energy trapping associated with defects in the MWCNTs (**Figure 2**).



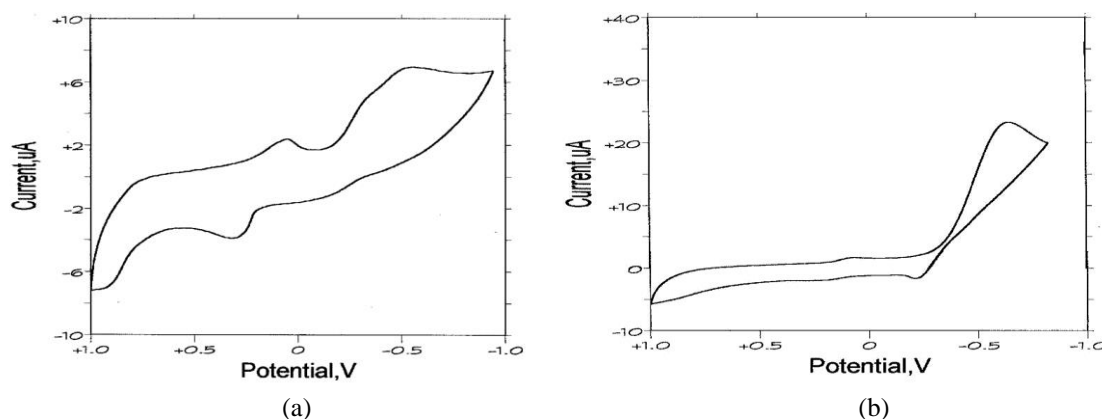
**Figure 2:** PL spectra of MWCNTs dispersed in DMSO/H<sub>2</sub>O.

### 3.3. FT-IR of MWCNTs:

MWCNTs exhibits C=O stretching vibration (carbonyl of carboxyl groups) at  $1743\text{cm}^{-1}$ . C-H asymmetric and symmetric stretching vibrations at  $2870\text{-}2959\text{cm}^{-1}$ ; C=C stretching mode vibration at  $1519\text{cm}^{-1}$  originates from the graphene plane of CNTs back-bone; C-C stretching vibrations at  $1466$  and  $1157\text{cm}^{-1}$  were observed for CNTs.

### 3.4. Electrochemical studies of rGO and MWCNTs:

The cyclic voltammogram for rGO and MWCNTs are shown in the **Figure 3a and b**. The cyclic voltammogram of rGO shows cathodic peak potential  $E_{pc} = +0.057\text{V}$  and anodic peak potential  $E_{pa} = +0.312\text{V}$  corresponding to the reduction and oxidation of the rGO carboxyl groups respectively. The rGO cyclic voltammogram also shows a cathodic peak potential  $E_{pc} = -0.568\text{V}$  corresponding to the reduction of C-O bond of rGO. The MWCNTs cyclic voltammogram shows a cathodic peak potential  $E_{pc} = +0.068\text{V}$  and an anodic peak potential  $E_{pa} = +0.268\text{V}$  corresponding to the reduction and oxidation of the MWCNTs carboxyl groups respectively. The cathodic peak potential  $E_{pc} = -0.648\text{V}$  corresponding to the reduction of C-O bond of CNTs. The reduction and oxidation peak currents of the MWCNTs carboxyl groups were significantly smaller than rGO. This confirms that the oxygen functional groups are almost removed in MWCNTs.



**Figure 3:** (a) Cyclic voltammogram of rGO in DMSO/Acetonitrile; (b) Cyclic voltammogram of MWCNTs in DMSO/Acetonitrile. Supporting electrolyte: Tetrabutyl ammonium perchlorate; Working electrode: Glassy carbon electrode; Reference electrode: Ag-AgCl electrode; Scan rate 0.05 Volt/ Second.

### 3.5. XRD studies:

The XRD of MWCNTs was recorded in order to confirm the formation of MWCTs (**Figure 4**). The XRD of MWCNTs shows  $2\theta=25.74^\circ$  [ $d(002)=3.39$  nm] and  $2\theta=42.2^\circ$  corresponding to  $d(100)$  reflection –atoms. The peak at  $42.2^\circ$  is due to the turbostratic nature of the MWCNTs[17].

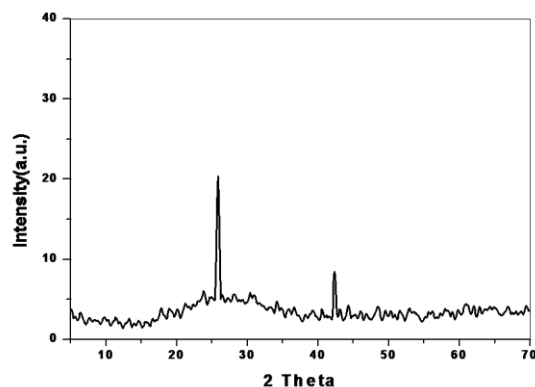


Figure 4: XRD of MWCNT.

### 3.6. FE-SEM and HR-TEM analysis:

The Scanning Electron Microscopy(SEM) and Transmission Electron Microscopy(TEM) were used to observe the morphology changes before and after conversion. The FE-SEM image was obtained for rGO before conversion into MWCNTs is shown in the **Figure 5a**. As shown in the FE-SEM image (**Figure 5b**) a long CNT tube with inner hollow bamboo-shaped, closed at both ends by semi spherical caps that could be joined together to form fullerene were obtained. From the FE-SEM image (**Figure 5b**) it is clearly observable that the tubular structure of MWCNTs were lying on the graphene surface and most of the residual ITO used in catalysis remain on the graphene surface.

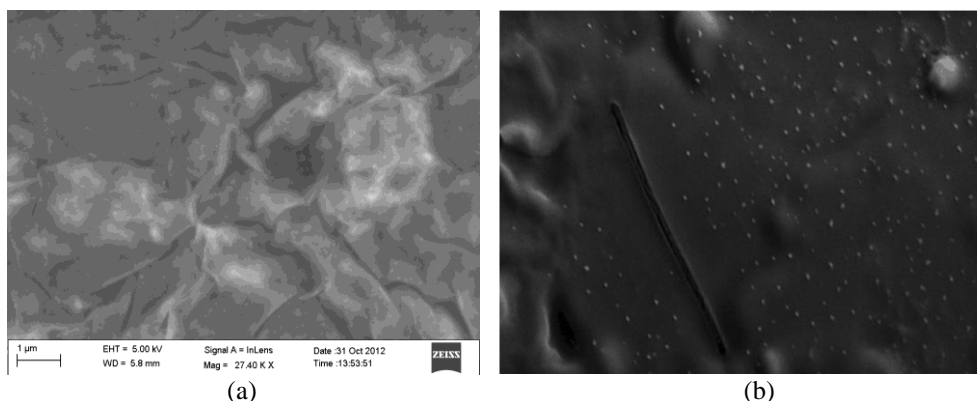
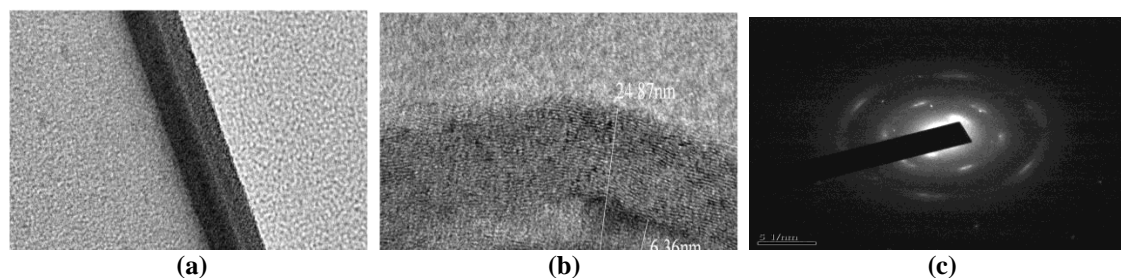


Figure 5: FE-SEM image of (a) rGO; (b) MWCNTs. MWCNTs length=6025nm; outer diameter=150nm.

The HR-TEM images of MWCNTs are shown in the **Figure 6a, b and c**. The HR-TEM image of MWCNTs is a poorly crystalline exhibiting numerous imperfections. The line scan reveals a rather poor crystalline caused by the presence of wide peaks. This is a characteristics of defective CNTs exhibiting distorted layers that form the concentric nanotubes. The selected area electron diffraction(SAED) patterns shows that graphitic (002) and (004) reflections are present in MWCNTs.



**Figure 6:** HR-TEM images of (a) MWCNTs (outer diameter ranges 21.3 to 24.87 nm). (b) MWCNTs with 38 inter layers. Inter layer distance 0.285 nm, outer diameter 24.87 nm and inner hollow diameter 6.36 nm. (c) SAED patterns of MWCNTs.

#### 4. Conclusions:

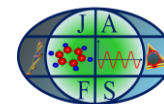
We have described simple microwave-assisted approach for catalytic conversion of rGO into MWCNTs in air at room temperature within few seconds. This microwave-assisted approach is low cost, ultrafast, high efficiency for sustainable catalytic conversion of rGO into MWCNTs. The MWCNTs synthesized by this approach can be used as biosensing as well as catalytic applications.

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