

## High temperature acidic oxidation of multiwalled Carbon nanotubes and synthesis of Graphene quantum dots

Neelam Kushwaha; Jagjiwan Mittal<sup>\*</sup>; Shifa Pandey; Robin Kumar

Amity Institute of Nanotechnology, Amity University Uttar Pradesh, Noida, Uttar Pradesh, India

Received 20 September 2017; revised 10 January 2018; accepted 01 February 2018; available online 04 February 2018

### Abstract

The acid oxidation of carbon nanotube generally results in opening the close ends of the nanotube and to make surface modifications. Herewith, Multiwall carbon nanotubes (MWCNTs) were oxidized in acids at high temperature experimental conditions which led to the formation of graphene quantum dots (GQDs). High resolution transmission electron microscope (HRTEM), energy dispersive X-ray spectroscopy (EDS), IR Infrared study showed the formation of 5-10 nm diameter GQDs and their crystalline structure having the inter-planar distance of 2.40 Å and 2.14 Å were confirmed by the electron diffraction. The UV visible spectroscopy showed the lowest exciton peak at 4eV. Photoluminescence (PL) studies showed the Photoluminescence peak in visible range which is independent of excitation wavelengths. A mechanism for the formation of highly crystalline graphene quantum dots during the high temperature acid oxidation of MWCNTs is proposed in the paper.

**Keywords:** Carbon nanotubes; Electron microscopy; Graphene quantum dots; Oxidation; Photoluminescence; UV visible spectroscopy.

### How to cite this article

Kushwaha N, Mittal J, Pandey Sh, Kumar R. High temperature acidic oxidation of multiwalled carbon nanotubes and synthesis of graphene quantum dots. *Int. J. Nano Dimens.*, 2018; 9 (2): 191-197.

### INTRODUCTION

Extraordinary electronic and mechanical properties of carbon nanotubes (CNTs) make them highly suitable for the applications in nanodevices [1- 8]. Although Single wall carbon nanotubes (SWCNTs) have been of particular interest owing to their small diameter and well-defined properties, multiwall carbon nanotubes (MWCNTs) are becoming more and more attractive due to their relatively low production costs and availability in large quantities than SWCNTs. MWCNTs resemble to graphite owing to their larger diameter and reduced strain while SWCNTs samples contain a mixture of semiconducting and metallic tubes [9-10]. CNTs show poor solubility in water due to agglomeration in bundles or other aggregates and are therefore difficult to handle [11-13]. To enhance their solubility, CNTs have been functionalized by different methods [14-17]. The easiest way to covalently attach chemical groups (e.g. carboxylic groups) is by oxidation. Pristine MWCNTs are oxidized by treating with oxidizing agents such as  $\text{HNO}_3/\text{H}_2\text{SO}_4$ ,  $\text{CO}_2$  and  $\text{O}_2$  which results in the

opening of closed ends [18-22]. Further, it creates defective sites in the wall structure, resulting in the formation of carbonyl, carboxyl and/or alcoholic groups on the surface of the nanotubes [20]. In addition, a controlled oxidation in air provides a simple purification method for the removal of disordered carbon from carbon nanotube samples [23, 24]. During acid oxidation, the carbon-carbon bonded network of the graphitic layers is broken, which allow the introduction of oxygen in the form of carboxyl, phenolic and lactone groups, [25] which have been extensively exploited for further chemical functionalization [26]. However, very few studies have been undertaken on the excess oxidation on the carbon nanotubes [27]. It is reported that over-oxidation may occur causing the carbon nanotube to break up into fragments, which are known as carbonaceous fragments [28]. Heating in  $\text{O}_2$  atmosphere > 400 °C results in the complete elimination of nanotubes. Higginbotham et.al [29] synthesized graphene nano-ribbons by over oxidation of multiwall nanotubes using acidic mixtures. However, fewer studies are undertaken

\* Corresponding Author Email: [jmittal@amity.edu](mailto:jmittal@amity.edu)

on the study of acidic oxidations of carbon nanotubes at high temperatures (~ 350 °C).

In the present study, we investigated the high temperature acidic oxidations of MWCNTs which led to the formation of graphene quantum dots. Graphene quantum dots found to use for applications in different areas [30-32]. Detailed study of the treatment to MWNTs along with the proposed mechanism for their transformation to GQD is discussed in the paper.

### EXPERIMENTAL

Multiwall carbon nanotubes (MWCNTs) were obtained from Applied science Inc. (ASI) having an average outer diameter of 100 nm. 50Mg of MWCNTs were refluxed with a mixture (3:1) of concentrated HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> for 24 hours at 100 °C. The solution was heated at 350 °C (above the boiling point of H<sub>2</sub>SO<sub>4</sub> 337°C) in a furnace for 1 hr. The acid oxidized solid residue was extracted by centrifuge and filtration. Structural investigations of residue material were carried out by high resolution transmission microscope (HRTEM) and X-ray energy dispersive spectroscopy (EDX). The crystallinity of oxidized material was analyzed using electron diffraction (ED). Fourier transform infrared (FTIR) spectroscopy was done to study the functional groups present on the oxidized material.

Further Photoluminescence spectrometer was used to study the luminescence properties. UV-Visible spectroscopy was done for band gap estimation of the material.

### RESULTS AND DISCUSSIONS

#### HRTEM study

HRTEM micrograph shows in Fig. 1a closed MWCNT of 100-nm in diameter and 20 nm thick graphene walls with an empty core of 60 nm. Crystalline nature of the nanotube wall is demonstrated by two bright spots in opposite directions for (002) and (004) crystal planes and a bright circle belongs to (110) plane of graphite in the ED [Fig. 1(b)].

The acid oxidized residue material was characterized by AFM and HRTEM in Fig. 1c and Fig 1e. The AFM micrograph shows the formation of carbon nanoparticles (CNP) of 50-100 nm. Whereas HRTEM study in Fig. 1e shows that the synthesized material is a cluster of many small particles. High magnification study of the cluster (Fig.1f) discloses the existence of various spherical dots of the diameters between 5-9 nm. No nanotube was observed in the final product which indicates that all MWCNTs are transformed during the treatment and its carbon is either oxidized or converted into carbon dots (CDs.).

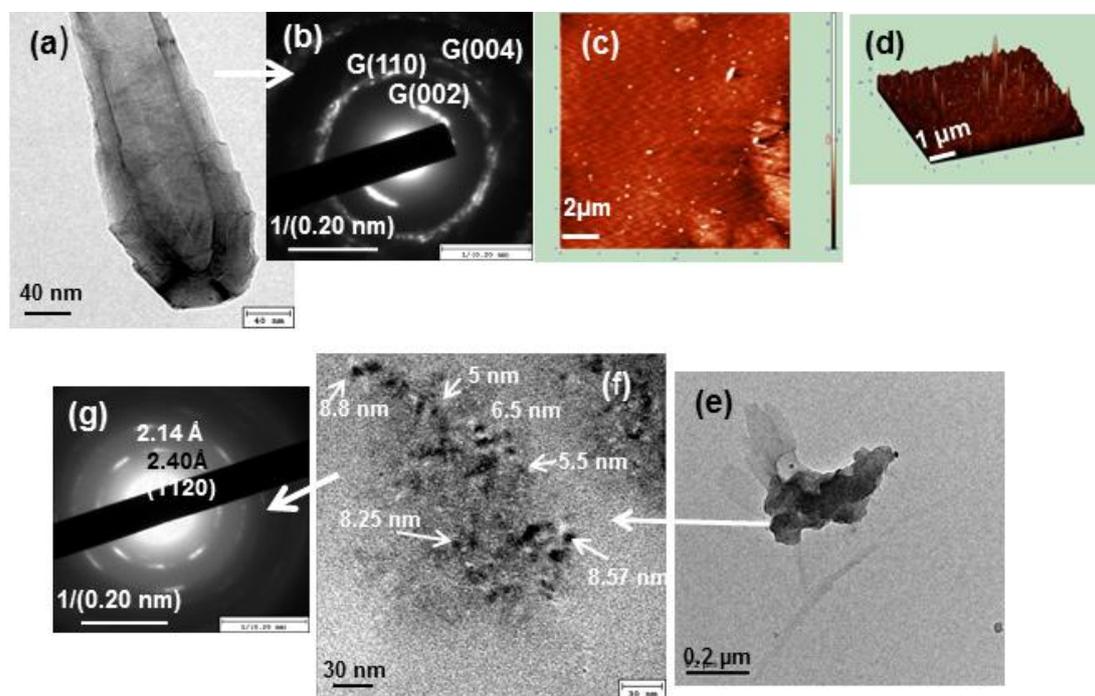


Fig. 1: HRTEM micrographs showing (a & b) Pristine MWCNT and its electron diffraction, (c& d) AFM micrographs of quantum dots and its three dimensional study, HRTEM micrographs showing (e) low magnification view of over-oxidized carbon nanotubes, (f) graphene quantum dots of different diameters and their (g) electron diffraction.

*Crystal plane and elemental analysis*

To analyse the formed carbon dots the Electron diffraction, Inverse Fast Fourier Transform (IFFT) and Fast Fourier Transform FFT was performed. The ED study in Fig. 1g of CD reveals the existence of two crystal planes of 2.40 Å and 2.14 Å. Crystal plane analysis of one spherical dot in Fig. 2a and in Fig. 2b demonstrates the existence of the two of planes with inter-planner distances of 2.14 Å and 2.40 Å. Interestingly, these two crystal planes aggregate at separate places in a dot. The presence of these two crystal planes is further confirmed by Fast Fourier Transform (FFT) analysis in Fig. 2b and Fig. 2c.

The inter-planner distance of 2.40 Å is due to (1120) lattice fringes of graphene. Inverse FFT of the spot in Fig. 2d exhibits the regularity in spacing between these planes with little defects which indicates the formation of highly crystalline Graphene Quantum dots [33] and inter-planer

distance 2.14 Å is due to in plane lattice spacing in graphene. Inverse FFT (IFFT) in Fig. 2e illustrates the formation of the hexagonal structure by the carbon atoms in graphene dots. Further, tabulated EDX studies of the Graphene quantum dots in Fig. 2h reveals the existence of carbon and oxygen in the particles in the ratio of 73 : 27. Interestingly, no traces of sulphur or nitrogen are observed in the samples. This shows all the sulphur and nitrogen are completely removed during heating at high temperature and leads to the formation of highly crystalline quantum dots.

*FTIR spectroscopy*

FTIR of pristine MWCNTs in Fig. 3a displays broad and low intensity infrared signals at 400-650 cm<sup>-1</sup> and 3448 cm<sup>-1</sup>. Low wave number near 1500 cm<sup>-1</sup> signals show the presence of highly graphitized structure in nanotubes [34] while the other band at higher wave numbers reveals the presence of

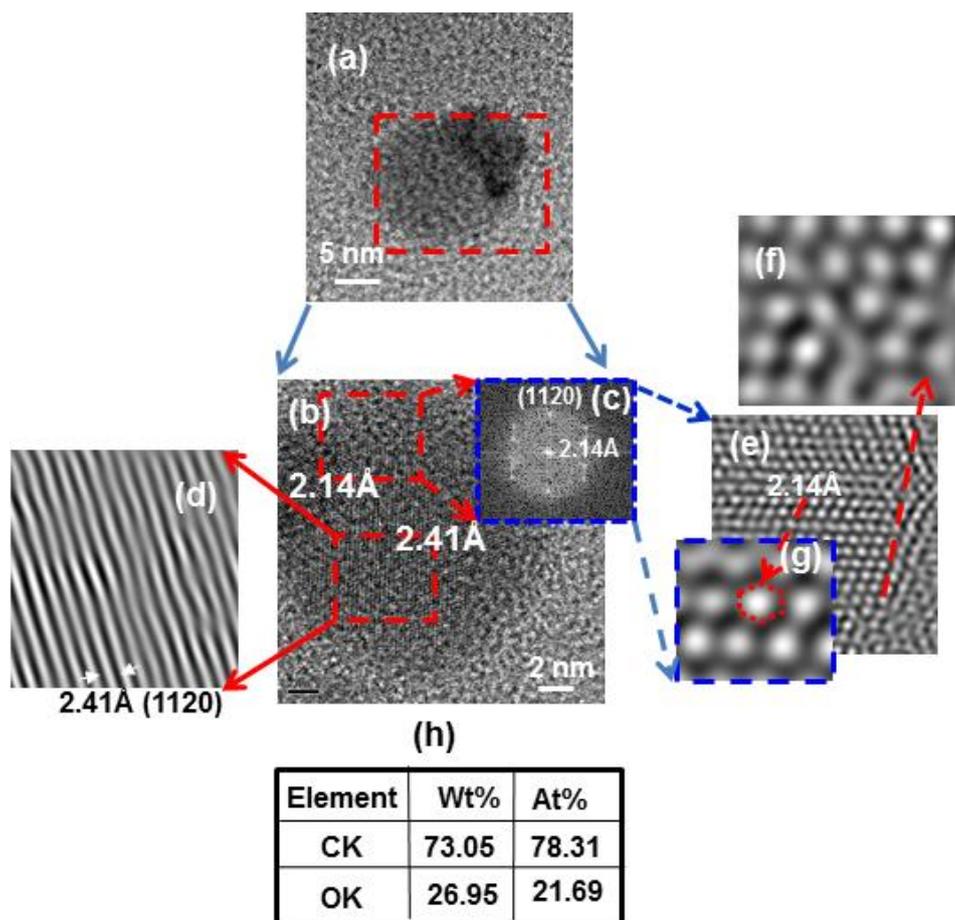


Fig. 2: HRTEM micrographs showing (a) graphene quantum dot, (b) crystal planes in GQD in (c), FFT of a portion of GQD (a) IFFT of another portion in (b), (e) IFFT of 2.14Å spot in (c), (f & g) two different hexagonal structures in (e), (h) atomic concentrations of carbon and oxygen in GQD.



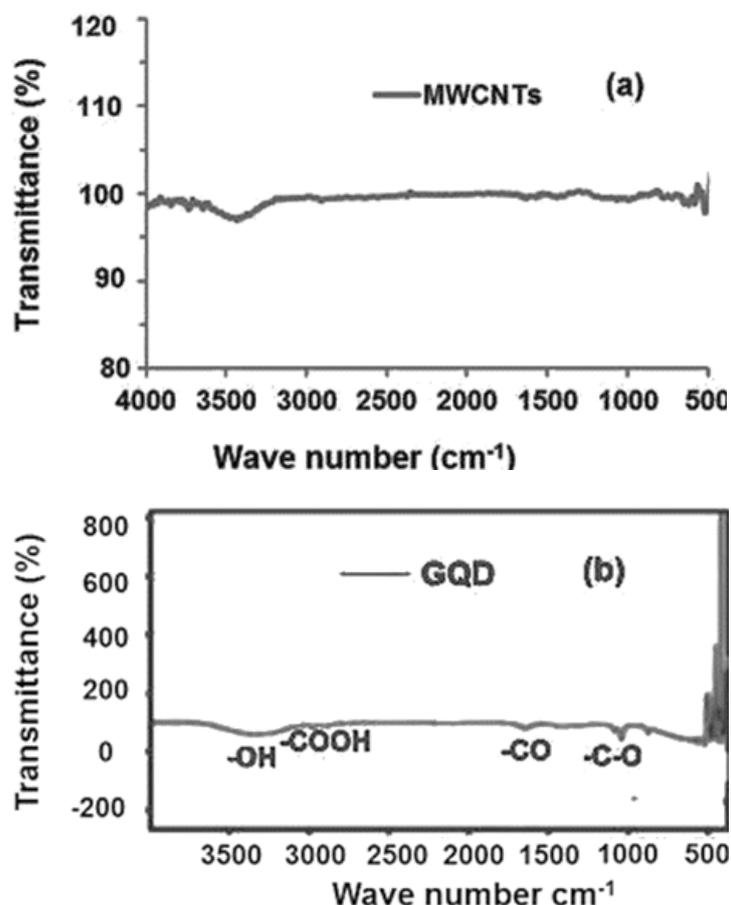


Fig. 3: FTIR of (a) Multiwalled carbon nanotubes (b) graphene quantum dots.

absorbed water. In contrast, a band at  $1650\text{ cm}^{-1}$  owing to the existence of carbonyl groups is present in the GQDs (Fig. 3b) [35]. A small peak at  $2975\text{ cm}^{-1}$  and broad band at  $3363\text{ cm}^{-1}$  show the presence of carboxylic and OH groups in the GQDs [36]. Two peaks at  $1086\text{ cm}^{-1}$  and  $1043\text{ cm}^{-1}$  and one peak  $878\text{ cm}^{-1}$  show the existence of C-O groups in the various chemical surrounding [35-37]. Presence of these groups in graphene quantum dots is further confirmed by the peaks of the substituted aromatic ring at  $550\text{ cm}^{-1}$ . As observed in EDX studies, no -NO and -SO groups are observed in the IR spectra of graphene quantum dots. This shows that the high temperature acid treatment removes the -NO and -SO groups.

#### UV Visible and Photoluminescence spectroscopy

Fig. 4a shows the UV-visible absorption spectrum of Graphene quantum dots (GQDs) in water in the range 200-500 nm [38]. The UV-visible spectrum of the GQDs shows a band with the peak at 300.5 nm. Using this, we define the lowest exciton absorption peak position of the

GQDs. To measure it, we fit a parabola curve over the experimental curve and by subtraction of the parabola curve from the experimental curve, a Gaussian curve is obtained. The peak value of Gaussian curve shows the value of lowest exciton absorption peak which is  $\sim 4.0\text{ eV}$ . The absorption by the GQDs typically shows strong optical absorption in the UV region, with a tail extending into the visible region which is attributed to the  $n-\pi^*$  transition of C=O bands or other connected groups. The transition is centered at  $\sim 300\text{ nm}$  due to the trapping of excited state energy by the surface states results in strong emission [39-41].

Fig. 4b shows the photoluminescence (PL) spectra of GQDs in water for different excitation wavelengths of 300 nm, 320nm and 340 nm [38]. The high intensity broad luminescence peak observed at 486 nm showed nearly no shift in position with the change of excitation wavelength, however, the intensity of the peak slightly increased. Unlike most reported GQDs, the emission wavelength of the GQD synthesized by over-oxidation is independent of the excitation

wavelength. Usually, excitation-dependent PL behaviours of Carbon quantum dots reflect the effect resulting from the particles of different sizes in the sample and a distribution of different surface states [42].

Therefore, the excitation-independent PL behaviour suggests the formation of uniform size GQDs ranges from 5 to 9 nm. It is reasonable that the PL of the GQDs should be attributed to the radiative recombination of electrons and holes trapped on the surface. The broadening of the PL peak defines the role of surface atoms and attached groups on the surface of small size GQDs. These GQDs have different kinds of surface states (presence of oxygen, COOH, OH and the carbonyl group) corresponding to the relatively wide distribution of different energy levels to generate a broad absorption band.

*Proposed mechanism of high temperature acidic oxidation of MWCNTs and GQD synthesis*

On the basis of, HRTEM, PL and FTIR results, a pictorial view of the proposed mechanism for

high temperature oxidation process of MWCNTs and formation of GQD is depicted in Fig. 5. During the oxidation of MWCNTs at high temperature with  $\text{HNO}_3/\text{H}_2\text{SO}_4$  the nanotubes are opened up by removing their tip [43]. Carbon atoms at the tip are easily oxidized due to higher strain in the C-C bonds compared to carbon atoms at the wall of MWCNTs [43]. Besides of removing tip, acid reagents also oxidizes the graphene layer of the surface wall of the carbon nanotubes as shown in Fig. 5a. This results in the formation of carbonyl, carboxylic, sulphur oxide and nitro groups at the surface of MWCNTs [44]. With the increase in reaction time, underneath graphene layers of the surface wall are oxidized. This leads to the bending, buckling and folding of nanotubes (Fig. 5b) [27]. During heating at the high temperature  $> 350\text{ }^\circ\text{C}$ , the formation of acid vapors oxidizes these nanoparticles. In this process, functional groups like NO, CO, COOH, SO, CO etc. removed in the form of  $\text{CO}_2$ ,  $\text{NO}_2$  and  $\text{SO}_2$  gases. This leads to burst the tube and resulting into small size highly crystalline particles (GQDs).

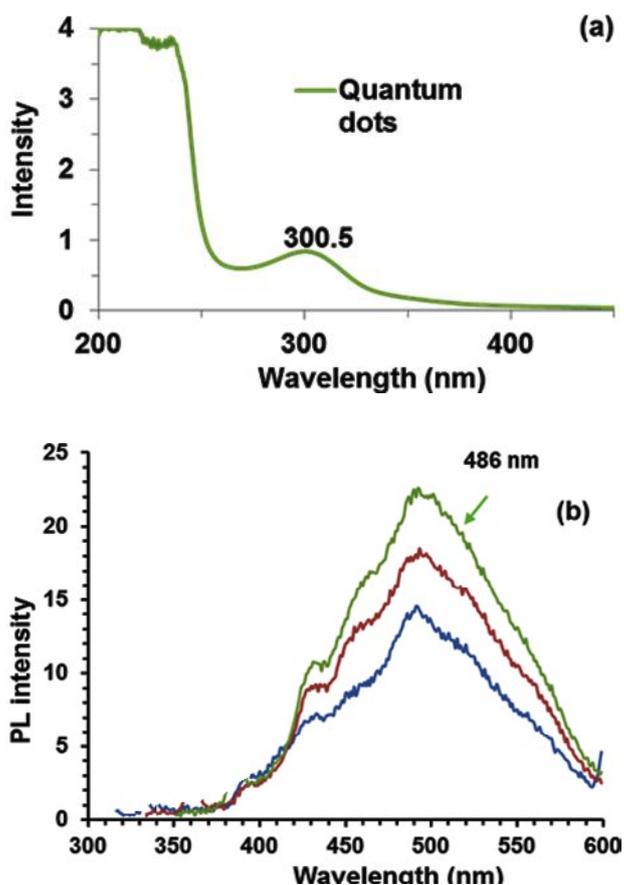


Fig. 4: (a) UV spectra of quantum dots showing the peak at 300.5 nm.(b) Photoluminescence (PL) spectrum of quantum dots at different excitation wavelengths.

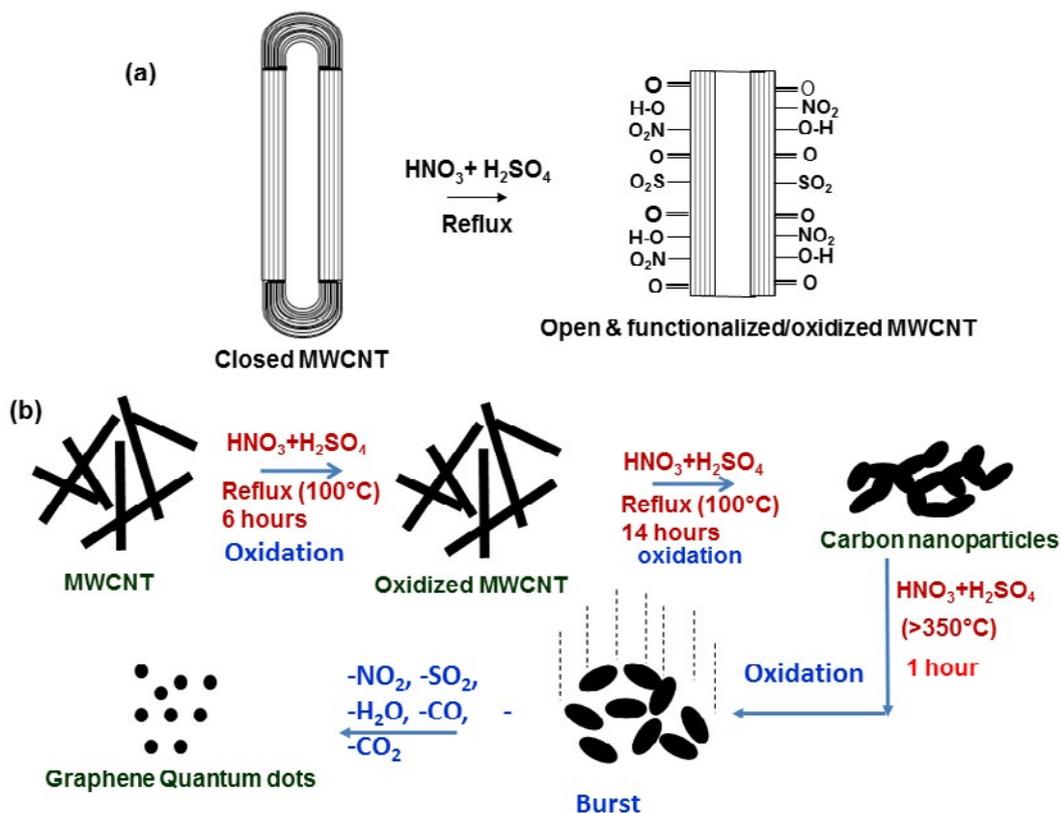


Fig. 5: Proposed mechanism for the formation of graphene quantum dots (GQDs) from high temperature acidic oxidation of multiwalled carbon nanotubes (MWCNTs).

## CONCLUSIONS

Oxidation of carbon nanotubes using the mixture of acid above the boiling temperature of  $\text{H}_2\text{SO}_4$  was studied which results in the formation of crystalline graphene quantum dots having the diameter of 5-10 nm. Work demonstrates that the high temperature oxidation of MWCNT in strong acids at high temperature does not result in the complete diminishing of the carbon nanotubes or carbon atoms but forms other products such as GQDs. This will lead to the oxidation study of carbon nanotubes using other oxidizing agents at higher temperatures. Graphitic structure in quantum dots is due to the highly graphitic crystal structure of multiwall carbon nanotubes.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

## REFERENCES

- [1] Dai H., Hafner J. H., Rinzler A. G., Colbert D. T., Smalley R. E., (1996), Nanotubes as nanoprobe in scanning probe microscopy. *Nature*. 384: 147-152.
- [2] Tans S. J., Verschueren A. R., Dekker C., (1998), Room-temperature transistor based on a single carbon nanotube. *Nature*. 393: 49-55.
- [3] Mittal N., Jain S., Mittal J., (2015), Application of electron energy loss spectroscopy for single wall carbon nanotubes-review. *J. Appl. Spect.* 82: 1-12.
- [4] Mittal J., Lin K. L., (2011), The formation of electric circuits with carbon nanotubes and copper using tin solder. *Carbon*. 49: 4385-4391.
- [5] Mittal J., Lin, K. L., (2017), Bulk thermal conductivity studies of Sn/SnO coated and filled multiwalled carbon nanotubes for thermal interface material. *Fullerenes, Nanotubes Carbon Nanostruct.* 25: 301-305.
- [6] Mittal J., Lin K. L., (2017), Carbon nanotube-based interconnections. *J. Mater. Sci.* 52: 643-662.
- [7] Garmaroudi F. S., Vahdati R. A. R., (2010), Functionalized CNTs for delivery of therapeutics. *Int. J. Nano Dimens.* 1: 89-102.
- [8] Moosa A. A., Ibrahim M., Salloom R. F., (2014), Synthesis and purification of Carbon nanotubes. *Int. J. Nano Dimens.* 5: 97-104.

- [9] Jorio A., Saito R., Dresselhaus G., Dresselhaus M. S., (2004), Determination of nanotubes properties by Raman spectroscopy. *Philos. Trans. R. Soc. London Ser. A*. 362: 2311-2336.
- [10] Reich S., Thomsen C., (2004), Raman spectroscopy of graphite. *Philos. Trans. R. Soc. London A: Mathem. Phys. Eng. Sci.* 362: 2271-2288.
- [11] Sandler J., Shaffer M. S. P., Prasse T., Bauhofer W., Schulte K., Windle A. H., (1999), Development of a dispersion process for carbon nanotubes in an epoxy matrix and the resulting electrical properties. *Polymer*. 40: 5967-5971.
- [12] Baskaran D., Mays J. W., Bratcher M. S., (2005), Noncovalent and nonspecific molecular interactions of polymers with multiwalled carbon nanotubes. *Chem. Mater.* 17: 3389-3397.
- [13] Zhang M., Su L., Mao L., (2006), Surfactant functionalization of carbon nanotubes (CNTs) for layer-by-layer assembling of CNT multi-layer films and fabrication of gold nanoparticle/CNT nanohybrid. *Carbon*. 44: 276-283.
- [14] Garg A., Sinnott S. B., (1998), Effect of chemical functionalization on the mechanical properties of carbon nanotubes. *Chem. Phys. Lett.* 295: 273-278.
- [15] Kuzmany H., Kukovec A., Simon F., Holzweber M., Kramberger C., Pichler T., (2004), Functionalization of carbon nanotubes. *Synth. Metals*. 141: 113-122.
- [16] Zhao W., Song C., Pehrsson P. E., (2002), Water-soluble and optically pH-sensitive single-walled carbon nanotubes from surface modification. *J. Am. Chem. Soc.* 124: 12418-12419.
- [17] Unger E., Graham A., Kreupl F., Liebau M., Hoenlein, W., (2002), Electrochemical functionalization of multi-walled carbon nanotubes for solvation and purification. *Curr. Appl. Phys.* 2: 107-111.
- [18] Porro S., Musso S., Vinante M., Vanzetti L., Anderle M., Trotta F., Tagliaferro A., (2007), Purification of carbon nanotubes grown by thermal CVD. *Physica E: Low-dimens. Syst. Nanostruct.* 37: 58-61
- [19] Rosca I. D., Watari F., Uo M., Akasaka T., (2005), Oxidation of multiwalled carbon nanotubes by nitric acid. *Carbon*. 43: 3124-3131.
- [20] Tsang S. C., Harris P. J. F., Green M. L. H., (1993), Thinning and opening of carbon nanotubes by oxidation using carbon dioxide. *Nature*. 362: 520-522.
- [21] Ajayan P. M., Ebbesen T. W., Ichihashi T., Iijima S., Tanigaki K., Hiura H., (1993), Opening carbon nanotubes with oxygen and implications for filling. *Nature*. 362: 522-525.
- [22] Hiura H., Ebbesen T. W., Tanigaki K., (1995), Opening and purification of carbon nanotubes in high yields. *Adv. Mater.* 7: 275-276.
- [23] Ebbesen T. W., Ajayan P. M., Tanigaki K., (1994), Purification of nanotubes. *Nature*. 367: 519-519.
- [24] Tsang S. C., Chen Y. K., Harris P. J., Green M. L., (1994), A simple chemical method of opening and filling carbon nanotubes. *Nature*. 372: 159-162.
- [25] Shaffer M., Fan X., Windle A. H., (1998), Dispersion and packing of carbon nanotubes. *Carbon*. 36: 1603-1612.
- [26] Sun Y. P., Fu K., Lin Y., Huang W., (2002), Functionalized carbon nanotubes: Properties and applications. *Acc. Chem. Res.* 35: 1096-1104.
- [27] Mittal J., Kushwaha N., (2015), Over-oxidation of multiwalled carbon nanotubes and formation of fluorescent carbon nanoparticles. *Mater. Lett.* 146: 37-40.
- [28] Bergeret C., Cousseau J., Fernandez V., Mevellec J. Y., Lefrant S., (2008), Spectroscopic evidence of carbon nanotubes' metallic character loss induced by covalent functionalization via nitric acid purification. *J. Phys. Chem. C*. 112: 16411-16416.
- [29] Higginbotham A. L., Kosynkin D. V., Sinitiskii A., Sun Z., Tour J. M., (2010), Lower-defect graphene oxide nanoribbons from multiwalled carbon nanotubes. *ACS Nano* 4: 2059-2069.
- [30] Wang L., Li W., Wu B., Li Z., Pan D., Wu M., (2017), Room-temperature synthesis of graphene quantum dots via electron-beam irradiation and their application in cell imaging. *Chem. Eng. J.* 309: 374-380.
- [31] Wang L., Li W., Wu B., Li Z., Wang S., Liu Y., Pan D., Wu, M., (2016), Facile synthesis of fluorescent graphene quantum dots from coffee grounds for bioimaging and sensing. *Chem. Eng. J.* 300: 75-82.
- [32] Wang L., Wu B., Li W., Li Z., Zhan J., Geng B., Wang S., Pan D., Wu M., (2017), Industrial production of ultra-stable sulfonated graphene quantum dots for Golgi apparatus imaging. *J. Mater. Chem. B*. 5: 5355-5361.
- [33] Peng J., Gao W., Gupta B. K., Liu Z., Romero-Aburto R., Ge L., Vithayathil S. A., (2012), Graphene quantum dots derived from carbon fibers. *Nano Lett.* 12: 844-849.
- [34] Tucureanu V., Matei A., Avram A. M., (2016), FTIR spectroscopy for Carbon family study. *Critical Rev. Anal. Chem.* 46: 502-520.
- [35] Stobinski L., Lesiak B., Kövér L., Tóth J., Biniak S., Trykowski G., Judek J., (2010), Multiwall carbon nanotubes purification and oxidation by nitric acid studied by the FTIR and electron spectroscopy methods. *J. Alloys Comps.* 501: 77-84.
- [36] Rajabi M, Moradi O., Mazlomifar A., (2015), Adsorption of methyl orange dye from Water solutions by Carboxylate group functionalized multi-walled Carbon nanotubes. *Int. J. Nano Dimens.* 6: 227-240.
- [37] Abdi Z., Sedaghat S., (2016), Synthesis and characterization of functionalized single-walled Carbon nanotube/Chitosan/ Polyaniline nanocomposite. *Int. J. Nano Dimens.* 7: 25-32.
- [38] Cullum B. M., Tuan Vo-Dinh., (2014), Preparation of liquid and solid samples: Wiley-VCH.
- [39] Wang X., Cao L., Yang S. T., Lu F., Meziani M. J., Tian L., Sun Y. P., (2010), Bandgap-Like strong fluorescence in functionalized Carbon nanoparticles. *Angew. Chem.* 122: 5438-5442.
- [40] Anilkumar P., Wang X., Cao L., Sahu S., Liu J. H., Wang P., Sun Y. P., (2011), Toward quantitatively fluorescent carbon-based "quantum" dots. *Nanoscale*. 3: 2023-2027.
- [41] Sun Y. P., Wang X., Lu F., Cao L., Meziani M. J., Luo P. G., Veca L. M., (2008), Doped carbon nanoparticles as a new platform for highly photoluminescent dots. *J. Phys. Chem. C*. 112: 18295-18298.
- [42] Zhu S., Shao J., Song Y., Zhao X., Du J., Wang L., Yang B., (2015), Investigating the surface state of graphene quantum dots. *Nanoscale*. 7: 7927-7933.
- [43] Zhao N., He C., Li J., Jiang Z., Li Y., (2006), Study on purification and tip-opening of CNTs fabricated by CVD. *Mater. Res. Bull.* 41: 2204-2209.
- [44] Kundu S., Wang Y., Xia W., Muhler M., (2008), Thermal stability and reducibility of oxygen-containing functional groups on multiwalled carbon nanotube surfaces: A quantitative high-resolution XPS and TPD/TPR study. *J. Phys. Chem. C*. 112: 16869-16878.