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Transformation of hydrocarbon soot to graphenic carbon nanostructures

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ABSTRACT

Graphenic carbon nanostructures were synthesized from different precursors of petroleum and agricultural origin by oxidative scissoring. In the present study soot, an environmental pollutant is converted to a value-added product by facile synthesis techniques. The physicochemical changes of the nanostructures are investigated by means of XRD, AFM, FTIR, Raman spectroscopy, XPS analyses SEM-EDS and TEM analysis. XRD analysis confirms the formation of few layer oxidized carbon nanostructures with smaller lateral dimensions. Raman spectra reveal the existence of graphenic layer with a fewer defect. AFM and SEM analyses reveal the formation of stacked tiny fragments of graphenic carbon lamellae. XPS and IR analyses confirm the incorporation of oxygen functionalities into the carbon backbone.

Keywords: *Hydrocarbon soot; graphenic carbon; kerosene; camphor; liquid paraffin*

1. INTRODUCTION

Nano-sized carbon materials have always fascinated researchers and persist fascinating them due to their distinctive features. These materials are generally prepared through chemical vapor deposition, laser ablation or electrooxidation. However, off late, carbon nanoparticles have been synthesized by simple oxidation of candle soot, natural gas soot and paraffin oil soot [1]. The burning of fuels results in a carbonaceous mass termed as soot. Soot particles nucleate and begin to grow, thereby polymerizing, when the conditions for combustion are rightly met. Although soot is reported to possess performed carbon nanostructures, it, however, is an undesirable combustion product that poses peril to human health and environment [2]. Bearing this in mind, the present work aims at chemically transforming the so-called pollutant soot to graphenic carbon nanostructures.

Graphenic carbon materials are carbonaceous solids that basically comprise elemental carbon bonded through sp^2 -hybridization. These materials include the 2D as well as 3D forms of carbon whose structures depend on graphene layers as the conceptual structural unit [3]. From the very first isolation of graphene, the awareness of fundamental physicochemical properties of graphenic carbons has developed considerably. With their heterogeneous structure and morphology, the sp^2 -hybridized carbon materials have tremendous application materials science. Research on synthesis, properties and application of sp^2 -based carbon materials are a matter of intense pursuit [4-11].

The topology of graphenic lattice structures are pivotal and dictate their physical, chemical and electronic properties. For precise topological control, it is always better to employ precursor with nanostructured carbon embedded in it [5]. As mentioned earlier, soot possesses preformed carbon nanoparticles. In this context, kerosene, camphor and liquid paraffin were chosen as hydrocarbon precursors and their respective soot nanostructures were chemically modified to graphenic carbon nanostructures. Kerosene is a cheap, abundant, widely used domestic and industrial fuel. Camphor is a botanical hydrocarbon possessing antimicrobial and therapeutic properties. Liquid paraffin is a highly refined mineral oil widely used in cosmetics and for medical purposes. Due to their ease of availability, low cost, abundance and peculiar properties, these materials were chosen as precursor materials. They were converted to their respective soot nanostructures by means of flame combustion. The soot nanostructures were then treated by modified Hummers’ method to form graphenic carbon nanostructures.

2. EXPERIMENTAL SECTION

Kerosene, camphor and liquid paraffin were subjected to carbonization by means of flame combustion. The respective carbonized hydrocarbon end products were termed as HS1, HS2 and HS3 while pristine graphite was commercially procured and was termed HS4. HS1, HS2, HS3 and HS4 were subjected to Hummers’ treatment, described elsewhere [11]. The obtained products were designated as GCN1, GCN2, GCN3 and GCN4 graphenic carbon nanostructures.

X-ray diffractograms of the samples were obtained using a Bruker AXS D8 Advance X-ray diffractometer. Raman measurements were performed at a wavelength of 514.5 nm using Horiba LABAM-HR spectrometer. The compositional analysis of the samples was carried out using X-ray photoelectron spectroscope (XPS Omicron ESCA probe with monochromatic (Al) X-radiation). The AFM images were obtained using a Nano Surf Easy Scan2 AFM machine. The SEM-EDS micrographs of the samples were recorded by means of JSM-6360 A (JEOL) system. TEM analyses of the samples were done using a JEOL JEM-2100 model.

3. RESULTS SECTION

The comparative study of XRD profiles of the nanostructures synthesized is presented along with that of graphite in Fig. 1 (a-b). The diffraction peak at ~25° is due to reflection from (002) plane, exhibiting the presence of carbon structures with short range ordering comprising mainly graphene flakes of small lateral size, spaced close to that of graphite [6]. Reflections observed at ~44° and ~54° correspond to (101) and (004) planes of graphite [7]. The lateral size (L_a), stacking height (L_c), inter-planar distance (d), number of aromatic lamellae (N), number of carbon atoms per aromatic lamellae (n) and degree of graphitization (G) for the carbon nanostructures formed are presented in Table 1.

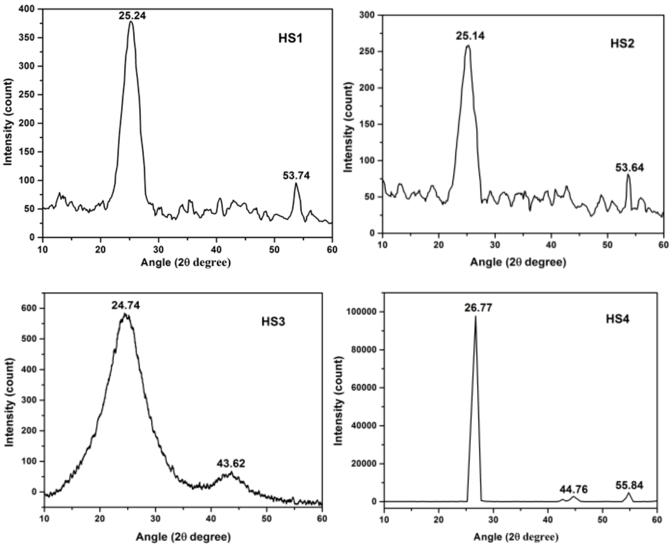


Fig. 1.a. XRD patterns of Carbonized samples (HS1, HS2 and HS3 along with HS4).

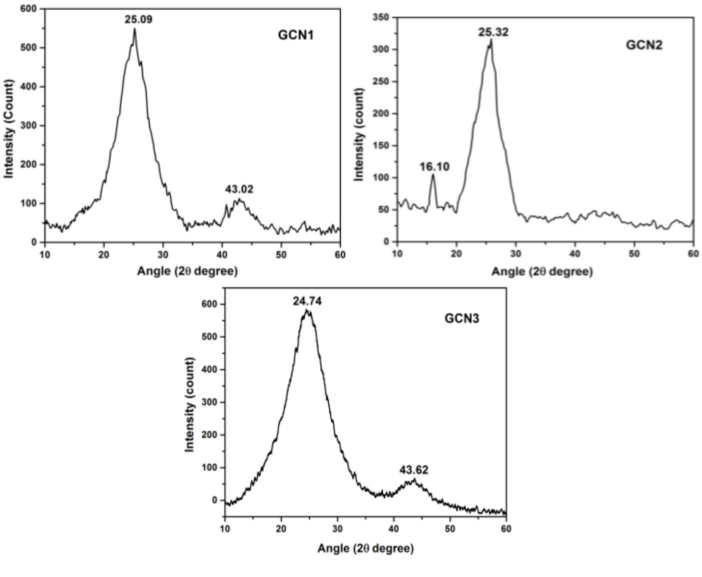


Fig. 1.b. XRD patterns of graphitic nanostructure (GCN1, GCN2 and GCN3).

The structural parameters are calculated using the modified Scherrer equation [6-9]. The values of L_a and L_c ranges from 7.33 nm to 2.10 nm and 3.10 to 2.28 respectively indicating that these nanostructures possess nano dimension and very few layers of graphene (less than 10). The degree of graphitization (carbonization) is found to be more than 70% in all the samples, confirming their three-dimensional crystalline ordering [9].

The graphitic carbon nanostructures were then treated by modified Hummers' technique to further scissor the graphene layers. XRD spectra of the nano graphenic carbon structures formed (Fig. 1.b) exhibit slightly broadened peaks at ~25° which can be attributed to the incorporation of oxygen functionalities to the carbon matrix and tiny size of the graphenic fragments [10]. The peak at ~ 44° is due to the presence of graphitic carbon. A small peak is observed at ~6° because of sulfonation, as a result of treatment by means of sulfuric acid [11]. The d_{002}-spacing of the lamellae is found to be increased in all the samples as a result of incorporation of chemical functionalities above and below the graphene planes (refer Table 1). The low value of L_a in all these cases indicates the formation of graphenic carbon nanostructures [12].

Table 1. Structural Parameters of the Samples elucidated from XRD analysis and intensity of defect peak to graphitic peak (from Raman analysis)

Sample	d_{002} [nm]	L_a [nm]	L_c [nm]	N	n	G (%)	I_D/I_G
HS1	0.337	6.48	2.71	9	25	73	0.82
HS2	0.336	7.33	2.76	9	25	93	0.95
HS3	0.337	2.69	2.28	8	20	80	0.97
GCN1	0.342	3.02	2.90	9	25	-	0.91
GCN2	0.341	4.14	3.10	10	32	-	0.98

XPS Analysis. C1s XPS spectra of the graphenic carbon nanostructures (Fig. 2) clearly indicate that they have been functionalized by oxygen moieties forming four different species namely, the sp^2 Carbon (~284 eV), C in C-O bonds, C bonded to O as epoxy/hydroxyl (~286 eV), Carbonyl C, (i-e) C=O of alcohols/ phenols/ether (~287.1 eV) and the carboxylate C, O-C=O (~288.7.0 eV). O1s was seen in all the samples at a binding energy of ~ 532 eV as it arises from C=O (~531.2 eV), C (=O)-(OH) (~531.3 eV) and C-O (~533 eV) [10, 13,14]. The XPS results are well corroborated by the FTIR spectra which shows the presence of all the carbonyl, carboxyl, epoxy and hydroxyl functional groups in it [15].

Raman Analysis. Raman spectra of original precursor (Fig. 3) show two broad and strongly overlapping D and G bands at around 1347 cm^{-1} and 1583 cm^{-1} respectively, similar to that of turbostratic graphitic nanocarbon. The D-band occurs as a result of defects and also due to a broken symmetry of basal plane of the graphitic carbon atoms [16]. These defects might be induced during the nucleation and growth of carbon nanostructures in the flame combustion synthesis process. The G-band corresponds to the E_g vibrational mode of sp^2 hybridized carbon atoms in both the rings and chain structures [17].

A broad 2D band is also observed at around 2750 cm^{-1} implying layered graphitic structure. HS4 possesses narrow D, G and 2D bands at 1353 cm^{-1}, 1579 cm^{-1} and 2715 cm^{-1} respectively. Raman spectra of GCN1, GCN2 and GCN4 (Fig. 4b) have D and G bands centered at around 1351 cm^{-1} and 1590

cm^{-1} respectively, shifted towards higher wavenumbers compared to initial untreated samples.

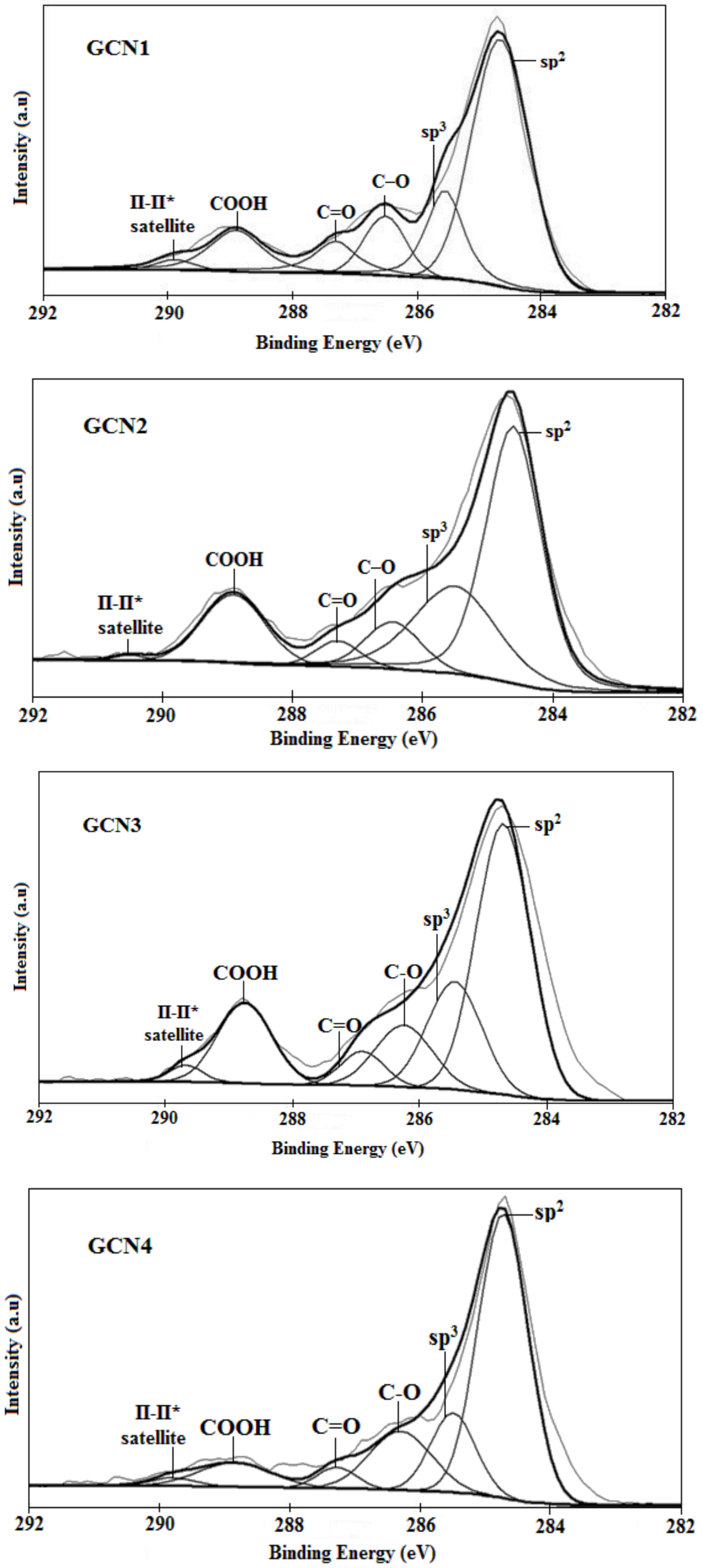


Fig. 2(a-d). Deconvoluted C1s XPS spectra of GCN1, GCN2, GCN3 and GCN4.

This might be either due to the transformation of graphitic carbon crystals to graphenic carbon lamallae or because of the reason that isolated carbon double bonds resonate at frequencies greater than the graphitic G band or due to chemical functionalities [18, 19]. The 2D region consists of bumps, implying the presence of few graphene layers. In case of GCN3, the Raman spectrum doesn't show discrete bands due to the interference of Raman signal by the fluorescence of the graphenic carbon dots excited by 514 nm laser. In Raman spectra, the relative D to G band intensity (I_D/I_G) is associated with the size and physical and/or chemical defects present in the crystallographic plane of the characteristic graphene sheets [20, 21]. All the samples possess I_D/I_G close to 1 due to inherent and induced defects (Table 1).

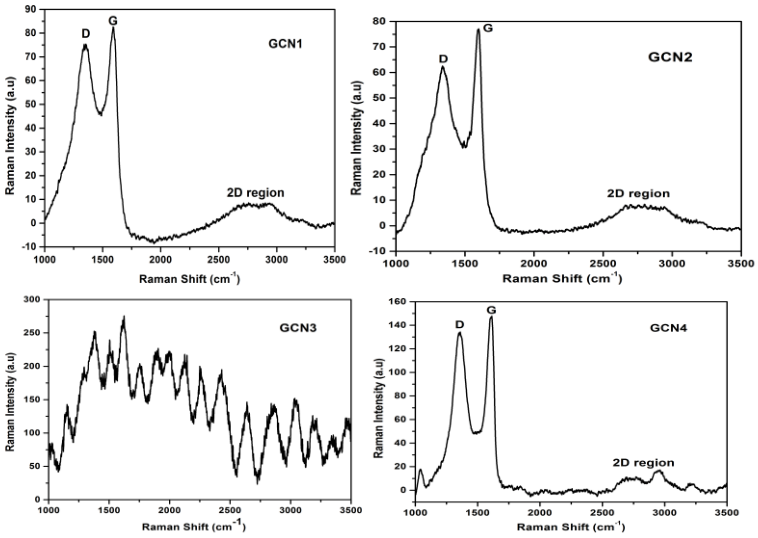
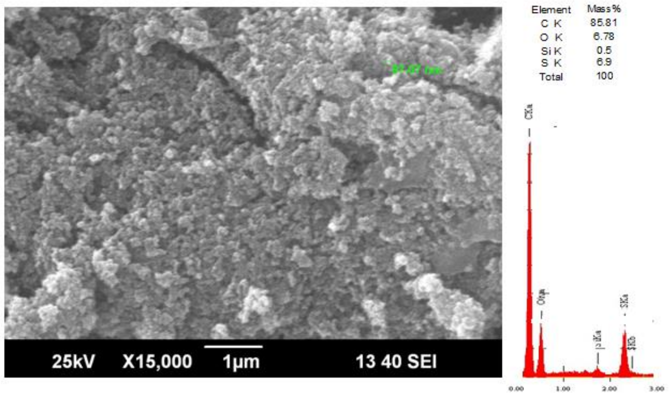


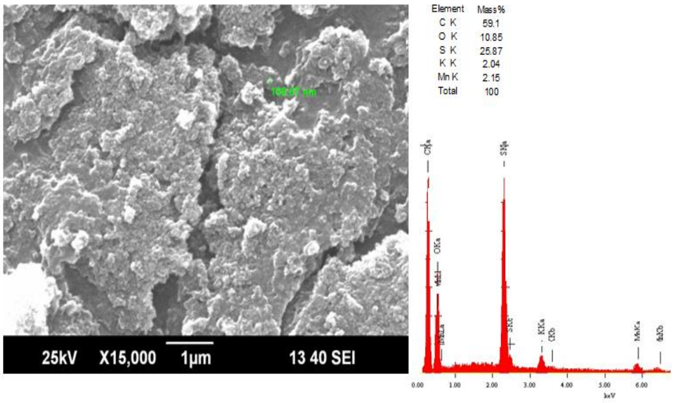
Fig. 3. Raman spectra of graphenic structure (GCN1, GCN2, GCN3 and GCN4).

Scanning Electron Microscopy. The SEM micrographs of the synthesized carbon nanostructures reveal non-uniform agglomerated nano spherules and layer formation (Fig. 4.a-c). Agglomeration is by virtue of Π- Π interactions and Van der Waal's forces between the graphene layers. It is also due to ionic and hydrogen-bonding [22]. HS4 possesses stacked graphene flakes with a range of lateral dimensions. The sample GCN1 and GCN2 (Fig. 5a-c) exhibit layers of interlinked nanospheres. GCN3 displays comparatively larger surface area graphene lamellae (not shown) while GCN4 shows wrinkled graphene nanosheets. SEM image of the untreated samples appears as agglomerated spheroids with irregularities with their diameter in nanoscale range (not shown). With Hummers treatment, the development of layered structure is observed on the surface.



Element	Mass%
C K	85.81
O K	6.78
Si K	0.5
S K	6.9
Total	100

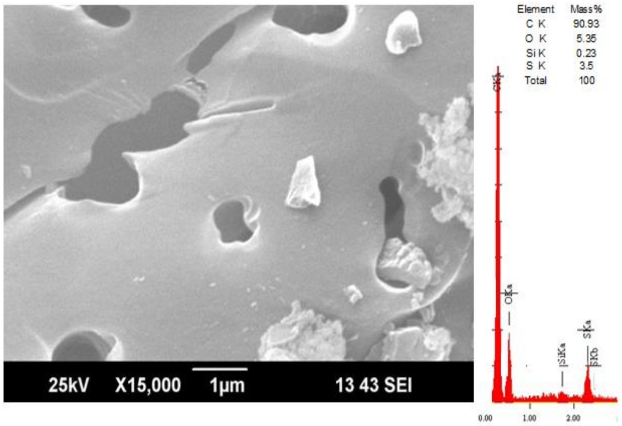
Fig. 4.a. SEM image of nanostructure in GCN1 sample.



Element	Mass%
C K	59.1
O K	10.85
S K	25.87
K K	2.04
Mn K	2.15
Total	100

Fig. 4.b. SEM image of nanostructure in GCN2 sample.

In the case of GCN2 sample, the nanosphere is open up and a layered structure is formed and confirming the graphitization and is in support with (of) the result of Raman and XRD analysis.



Element	Mass%
C K	90.93
O K	5.35
Si K	0.23
S K	3.5
Total	100

Fig. 4.c. SEM image of nanostructure in GCN4 sample.

In the micrograph of the sample after Hummer's treatment, the formation of layer structure with different areas is observed. This layer structure implies that with oxidative-reduction treatment, the structure is transformed into graphite like flakes. The EDS analysis shows only the presence of carbon and little amount of oxygen in the untreated sample (HS1, HS2, HS3 & HS4) (Table 2). But upon oxidation-reduction process, oxygen groups are incorporated in the microstructure with other elements like, Mn, Si, S and K possibly from the chemicals used for the Hummers method [22-24].

Table 2. Elemental analysis of the product by EDS

Sample	Carbon [Mass %]	Oxygen [Mass %]	Manganese [Mass %]	Potassium [Mass %]	Sulfur [Mass %]	Silica [Mass %]
HS1	99.18	0.62	….	…	…	…..
GCN1	85.81	6.78	-	-	6.90	0.50
HS2	99.51	0.49	….	….	….	….
GCN2	59.10	10.85	2.15	2.04	25.87	-
HS3	98.73	1.27	…	…	…	…
GCN3	46.94	13.93	3.48	3.2	32.44	-
HS4	100	…	….	….	…	….
GCN4	90.93	5.35	…	….	3.50	0.23

AFM Analysis. AFM images (Fig. 5) of GCN1 portray coagulated, distorted graphenic carbon spheroids. The surface height profile shows a variation of about 10.6 nm. GCN2 exhibits distributed agglomerated carbon spherules. The surface profile is about 10-45 nm. GCN3 shows the formation of heterogeneous graphenic platelets resembling graphene quantum dots. The height profile confirms the formation of nanostructure in the treated sample [10].

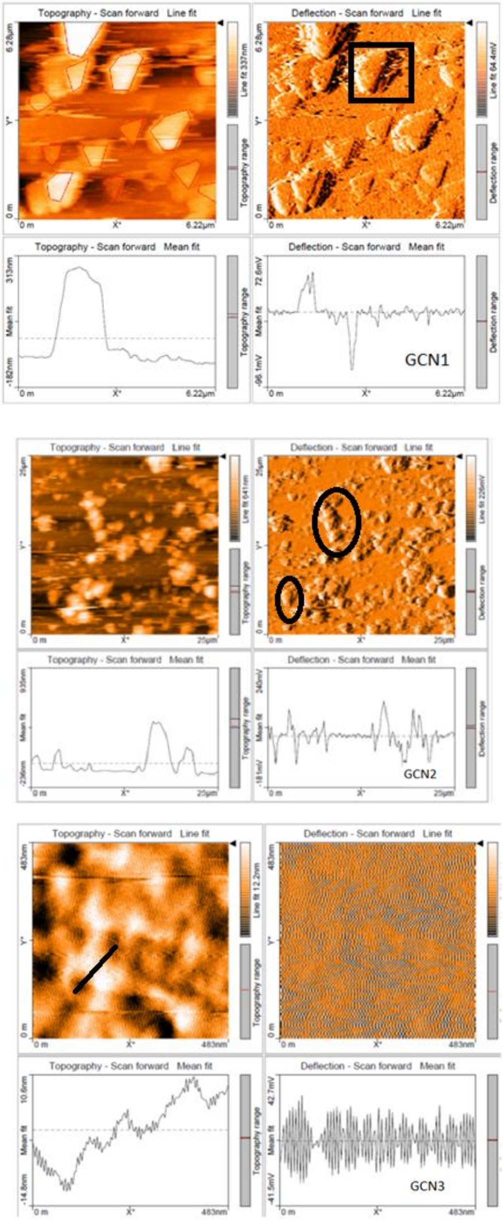


Fig. 5(a-c). AFM images of nanostructure in the synthesized products (GCN1, GCN2 and GCN3) (Height profile of the particle is presented. Highlighted area shows the formation of graphene nanostructure).

A typical AFM image of the obtained graphene is presented in Fig. 4 (a-c). The crosss section height profile analysis indicates that GCN2 samples indicates the formation of multilayes. The height profile confirms that the graphene layer formed is wrinkled or folded.

TEM Analysis. TEM micrographs (Fig 6 a&b) reveal nearly spherical aggregates of graphene fragments, forming interconnected chain-like structures. The nanohorn aggregates are robust and cannot be separated into individual components. The distortion in the tubular structure of the shortened, bumpy nanohorns, seen in the TEM image, could be as a result of a trade-off between the van der Waals force of interaction between the adjacent nanohorns and the stiffness of the individual horns, which depends on the diameter of the tubule (Fig. 6.b) [10,11]. Fig. 6 (b) depicts TEM images of graphene sample GCN3 prepared by modified Hummer's method. Small particles with diameter in the range 3-10 nm range along with globular structure are found in the TEM image. The recorded SAED pattern concentric rings which are diffused, which indicates the short range ordering of carbon layers in the sample.

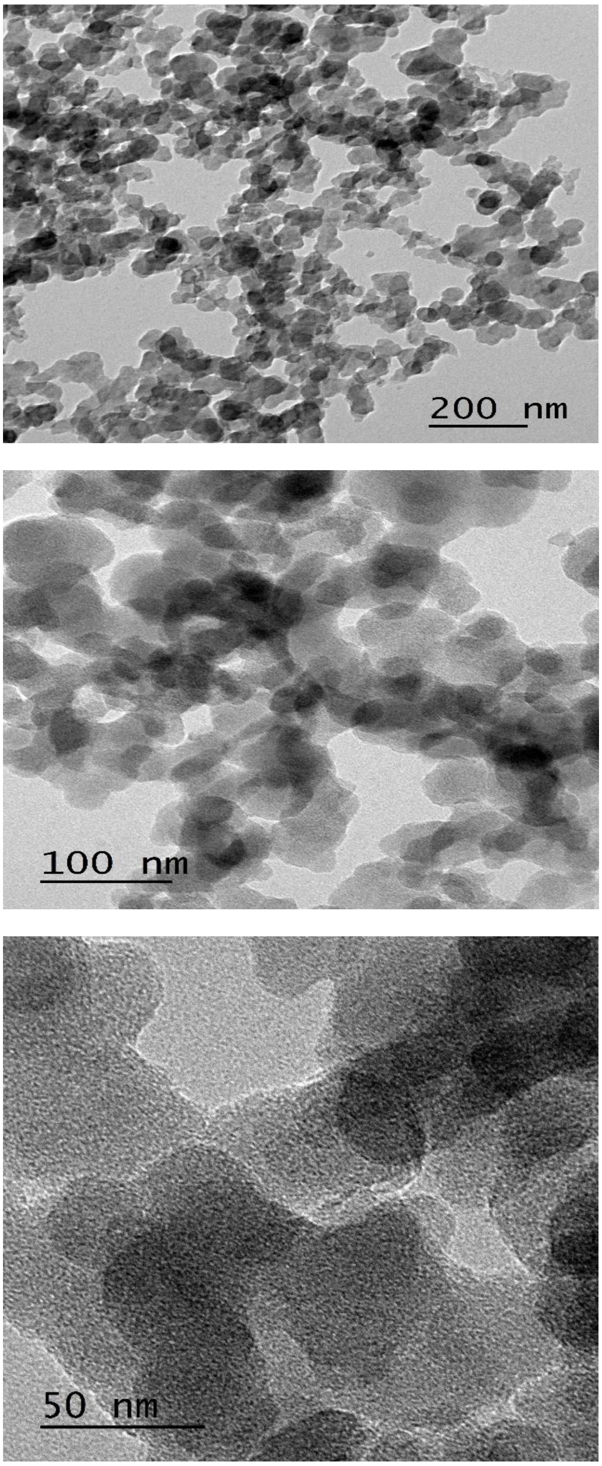


Fig. 6.a. TEM images of graphene obtained (GCN1).

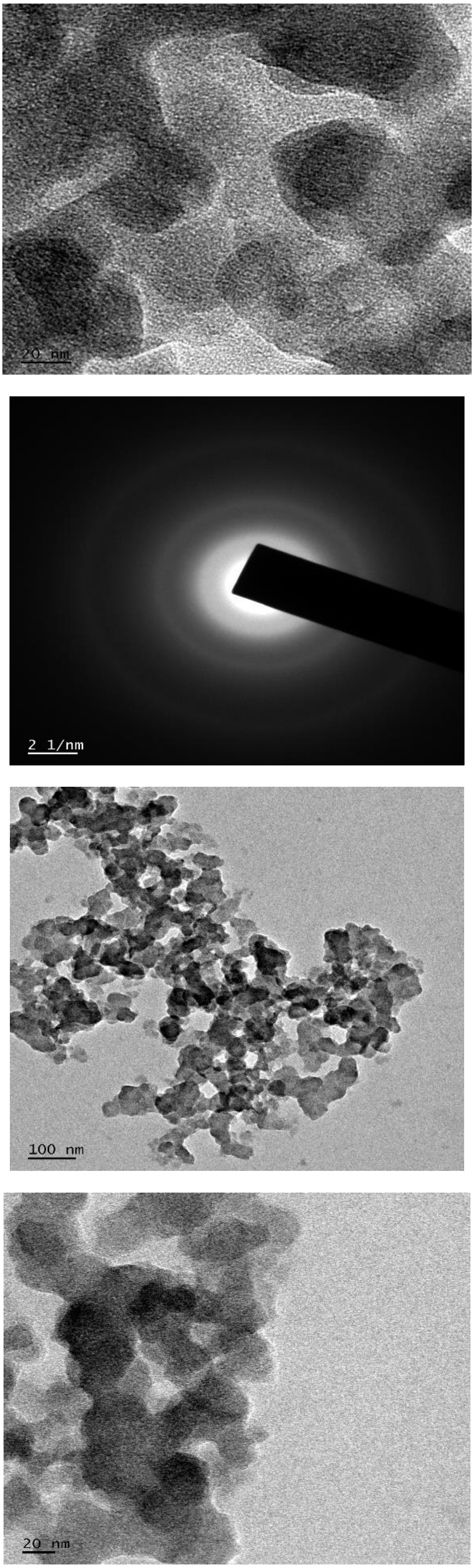


Fig. 6.b. TEM images of graphene obtained (GCN3).

4. CONCLUSIONS

Graphenic carbon nanostructures were synthesized from plentiful hydrocarbon sources like kerosene, camphor, and liquid paraffin by means of a facile and economical chemical treatment. XRD patterns of the samples revealed the formation of sp^2 hybridized few layer graphenic carbon nanostructures with very small lateral size. Raman spectral analysis unveiled that the samples possessed fewer disorder and defects. AFM and SEM images of GCN1 and GCN2 displayed aggregated nano graphenic spherules similar to carbon dots while GCN3 and GCN4 showed platelets of lamellar graphenic carbon, resembling graphene quantum dots. Small particles with diameter in the range 3-10 nm range along with globular structure are found in the TEM image. Hence, soot particles that are environmental pollutants were successfully modified to graphenic carbon nanostructures decorated with oxygen moieties. These nanostructures render ease of functionalization for graphene based composites and could, therefore, find a variety of applications ranging from electronics to biomedicine.

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