

Facile synthesis of preformed mixed nano-carbon structure from low rank coal

MANOJ B. *, ASHLIN M. RAJ, GEORGE THOMAS CHIRAYIL

Department of Physics, Christ University, Bangalore, 560029, Karnataka, India

Coal is a natural energy resource which is mainly used for energy production via combustion. Coal has nanocrystals embedded in it, formed during the coalification process, and is an ideal precursor for nano-carbon dots and diamonds. Herein, we report a facile top-down method to synthesise nanodots and diamonds of the size of 5 nm to 10 nm from three different types of coal by simple chemical leaching. TEM analysis revealed the formation of a mixture of carbon dots, graphene layers, and quantum dots in bituminous coal and sub-bituminous coal. Raman analysis confirmed the existence of synthesized nano-diamond and nano-carbon mixed phase with defects associated with it. It is concluded that graphene quantum dots, nano-diamonds, graphene sheets and carbon dots present in coal can be extracted by simple chemical treatment. These structures can be tuned to photoluminescent material for various optoelectronic applications or energy harvesting devices like super capacitors.

Keywords: *tertiary coal; Gondwana coal; carbon nanodots; graphene layers; quantum dots; nano-diamonds; mixed structure*

1. Introduction

Coal is an abundant solid fuel, which provides most of the energy for living and economic advancement of any nation. With the industrial revolution, coal has turned out to be a vital energy source across the globe. Besides as an energy source, it is utilized as an important and vital reserve for the manufacturing of chemicals such as creosote oil, naphthalene, phenol and benzene [1–5]. With the discovery of carbon nanomaterials, scientific research on coal based products have received ever increasing attention [6–8]. The carbon crystallites in coal are easy to displace by oxidation, resulting in nanometre-sized graphene layers with amorphous carbon addends on the edges. Coal can be turned into glowing quantum dots or fluorescent carbon nanoparticles which have a wide utility in biomedicine, and the imaging of cells and tissues. Graphene nanostructures have been synthesised from anthracite coal and coke by the methods of simple wet-chemistry and the advantages of these structures of coal to form sp^2 nanostructures have been stated [8, 9]. Coals of different ages have

been varying their chemical compositions and possess various ranks. It has also been reported that the yield of graphene quantum dots (GQDs) is highly dependent on the rank of coal [7–12]. In addition to the effective use as an energy source, coals are potential precursors for nanocrystalline carbon dots, if bond hybridization is controlled in a suitable way. The main hindrance in the wide utilization of coal is its inherent mineral matter. Removal of these inherent minerals is essential for the value improvement of any low quality coals.

Herein we report a facile method to synthesize mixed phase nanometre-sized diamond and carbon dots from sub-bituminous coal, bituminous coal and lignite. In this investigation we also report a comprehensive study of nanostructures in coal by collecting the information obtained by using advanced characterization tools.

2. Materials and methods

2.1. Materials and pre-treatment

Tertiary Indian coal from Neyveli, India (Lignite), Gondwana coal from Godavari deposit (sub-bituminous coal) and coal from Damodar Valley (Bihar-High volatile bituminous coal) were chosen

*E-mail: manoj.b@christuniversity.in

as the main material owing to the different ranks and wide availability. Available coal in a lump was treated with EDTA (ethylene-diamine tetra-acetic acid) (0.1 N solution from Spectrum Reagents and Chemicals Pvt. Ltd.) for one day to loosen the minerals present and was then used for synthesis.

2.2. Synthesis method

A lump of pre-treated sample (2 g) and hydrofluoric acid (50 mL) (40 % from RFCL Ltd.) were refluxed in a polypropylene beaker and left undisturbed for 2 hours. This mixture was ultrasonicated at low power (42 kHz) in water for exfoliation and for dispersion of nanoparticles for 30 minutes and left undisturbed to settle down. The mixture was cleaned several times with double distilled water and centrifuged at a speed of 5000 rpm to remove non exfoliated coal and other agents. The residue was dried in a vacuum oven at 110 °C for 8 hours until a dry powder of the sample was obtained. The same procedure was adopted to chemically treat all the samples (lignite-L1H, sub-bituminous coal-G1H and bituminous coal-B1H). The obtained product was subjected to various characterizations. X-ray powder diffraction (XRD) patterns were obtained using a Bruker AXS D8 Advance X-ray spectrometer. Raman spectra were measured using Lab RAM HR spectrometer (excitation wavelength of 532 nm). SEM micrographs and EDS spectra were recorded with GEMINI ULTRA 55 high resolution microscope. The TEM micrographs of the samples were recorded by means of JEM-2100 (JOEL) system.

3. Results and discussion

3.1. Physicochemical characterization of the samples

Results of proximate and elemental analysis of the demineralized coal samples are presented in Table 1. The fixed carbon (FC) content in G1H sample has changed from 45.66 wt.% to 68.89 wt.%, with a reduction of volatile matter (VM) from 36.90 wt.% to 24.26 wt.%. The ash in bituminous coal (B1H) was reduced from 12.87 wt.% to 0.1 wt.% accompanied by an increase of 16 wt.% in fixed

carbon content. The elemental analysis results reveal that in G1H and B1H sample, carbon and oxygen are the major constituents with hydrogen and nitrogen as minor elements. Sulphur is also present in a small amount in all the three samples. In the L1H sample, the oxygen and volatile matter content is found to be higher than in the other two samples. The content of ash is reduced to 0.1 wt.% with HF leaching of bituminous coal.

3.2. X-ray diffraction analysis

The structural parameters of the samples were elucidated by the modified Scherer formula as reported in the literature [1, 12, 13]. The X-ray profile analysis of the samples showed two peaks at 2θ : $\sim 18.29^\circ$ and 24.85° originated from the γ -band and the π -band (Fig. 1). The π -band results from the aromatic ring while the γ -band is due to the aliphatic content. The diffraction profile shows broadening of the peak in the 20° to 26° region mainly due to the existence of carbon nanocrystallites. The narrow peak at 26° in lignite is due to the minerals present in the coal, mainly in the form of quartz or silicates. In the G1H and B1H samples, a peak originating from the hexagonal lattice structure of the carbon atom is noticed at $\sim 42^\circ$. This peak is not observed in the L1H sample.

The structural parameters of the nanostructured carbon from all the three coal types are presented in Table 2. The stacking height is found to be ranging from 1.40 nm to 3.40 nm due to the piling of graphene layers in the coal. In case of lignite (L1H), multilayer (about 10 layers) stacking as that in graphite is observed, while in case of sub-bituminous coal (G1H), formation of few layer (5) graphene is noticed. In case of bituminous coal (B1H), the layer formation takes place between that of few layers graphene and stacked graphite. The X-ray analysis confirms the formation of stacked graphene layers in the coal. The stacking height increases with a decrease in coal rank, while the number of aromatic lamellae shows a reverse trend, with an increase in the rank. Upon chemical synthesis, the high rank coals are converted to few layer graphene oxide while lignite shows the structure of graphite with wrinkles.

Table 1. Elemental analysis of chemically leached coal.

Sample	Fixed carbon [wt.%]	Volatile matter [wt.%]	Ash [wt.%]	Moisture [wt.%]	C [wt.%]	H [wt.%]	N [wt.%]	O [wt.%]	S [wt.%]
G1H	68.89	24.26	3.06	3.79	77.21	4.00	1.57	16.64	0.28
B1H	56.96	35.22	0.10	7.72	72.88	4.68	1.75	21.37	0.58
L1H	32.62	43.38	9.53	14.48	35.86	2.61	3.83	56.6	1.10

Table 2. Structural parameters of chemically leached coal.

Sample	Stacking height L_c [nm]	Number of layers	Coal rank	d_{002} [nm]	I_D/I_G	$I_D/I_{D'}$
G1H	1.40	5.00	2.48	0.35	0.54	3.40
B1H	2.27	7.00	1.51	0.35	0.58	3.16
L1H	3.40	10.0	0.77	0.35	0.63	6.80

3.3. Raman analysis

Raman spectra of the nanocarbon from the coal are presented in Fig. 2. Raman spectrum of graphite comprises strong peaks at 1580 cm^{-1} and 2700 cm^{-1} named as G band and 2D band (a second order of D band), respectively. The G band arises due to tin plane optical phonon modes. G mode has E_{2g} symmetry which does not require the presence of six-fold rings, hence, it occurs at all sp^2 sites [13–15]. The 2D band originates from the double resonance process and hence, appears to be dispersing in nature. In addition to these bands, a D band is noticed at 1350 cm^{-1} which arises due to the proximity of defect or diamond like structure [2–4]. The sp^3 carbon network shows characteristic Raman features, prominently at 1148 cm^{-1} and secondary peaks at 1274 cm^{-1} and 1307 cm^{-1} (owing to tetrahedral amorphous carbon-ta-C) for sub-bituminous coal [13]. Earlier studies assigned this band to hexagonal diamond, nanocrystalline diamond or sp^3 rich carbon structures. There are also studies which have designated the origin of this band to the sp^2 - sp^3 mixed structure [13, 14]. The 2 D region is broad and bumpy with numerous high intensity absorption peaks for the G1H and B1H samples. This indicates the formation of wrinkled graphene layers of about 4 to 5 layers. However, the L1H sample shows no such characteristic peak in the 2D region and behaves like bulk graphite.

The G band in the Raman spectrum shows the presence of sp^2 carbon network. As the layer thickness increases, the position of this band shifts to lower energy resulting in softening of the bonds with addition of graphene layers.

Other than the G and 2D peaks, D and D' peaks are also observed in the spectrum and are attributed to defect-induced Raman features which are inactive in highly crystalline carbon. The intensity ratio (I_D/I_G) of the D and G band is widely used for characterizing the defect quantity in graphitic materials and is found to be 0.54 for sub-bituminous coal, 0.58 for bituminous coal and 0.63 for lignite. This reveals the presence of graphitic nano-carbon with fewer defects. The intensity ratio ($I_D/I_{D'}$) gives the information about the nature and concentration of defects. D' peak has generally low intensity compared to D peak (which usually appears as a small shoulder of G peak). This ratio was found to be 3.40 for sub-bituminous coal due to boundary-like defects, 3.16 for bituminous coal indicating boundary-like defects and 6.8 for lignite, attributed to vacancy-like defects [15–18].

3.4. Scanning electron microscopic and energy dispersive X-ray spectroscopic analysis

The SEM micrograph of B1H (Fig. 3a) shows agglomeration of nanospheres and carbon dots. The SEM confirms the presence of mixed

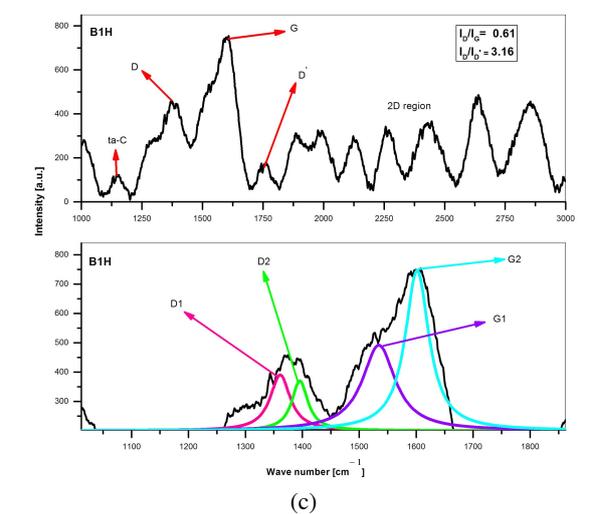
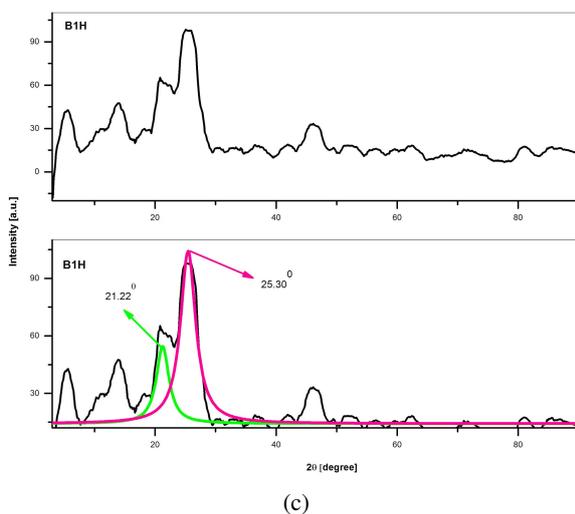
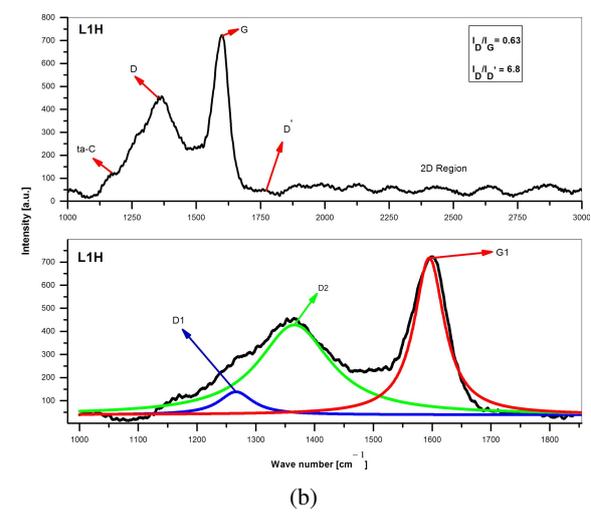
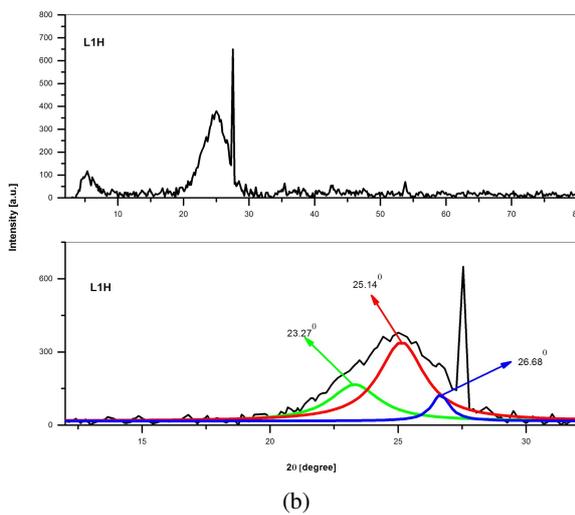
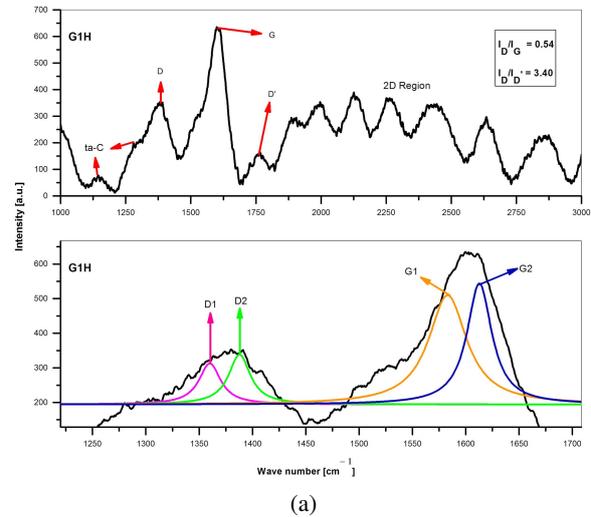
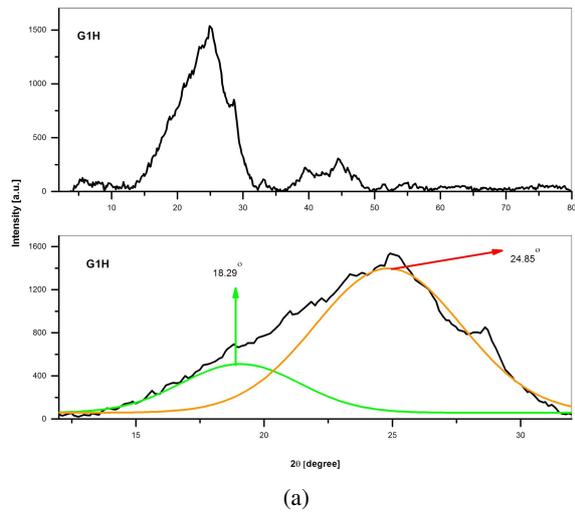


Fig. 1. XRD spectra of nanostructures of (a) sub-bituminous coal (G1H), (b) lignite (L1H), (c) bituminous coal (B1H).

Fig. 2. Raman spectra of nanostructures obtained from (a) sub-bituminous coal (G1H), (b) lignite (L1H), (c) bituminous coal (B1H).

phase nanostructure including nanospheres, carbon dots, few-layer graphene sheets and multi-layer graphene [19]. The diameter of the spheres ranges from 116 nm to 182 nm. Elemental composition of B1H, computed by EDS revealed the presence of carbon (78.29 %) and oxygen (20.73 %). The SEM micrographs of nano-carbon layers in sub-bituminous coal (G1H) are presented in Fig. 3b. Formation of nano-spheroids and layers with a thickness about 43 nm to 47 nm are noticed. The surface morphology contains the mixed structure of graphene and nanospheres with irregular dimensions. Elemental composition of G1H, computed by EDS reveals carbon (86.78 %) and oxygen (13.22 %) as the major constituents.

The SEM micrograph of L1H (Fig. 3c) shows the formation of graphite layers with a thickness ranging between 540 nm and 879 nm. This indicates the stacking of graphene layers due to the formation of the bulk structure [18–20]. This result is consistent with the findings of Raman and X-ray analysis. Elemental composition of L1H, computed by EDS reveals the presence of carbon (88.09 %) and oxygen (11.91 %) without any mineral impurity.

The SEM analysis confirms the formation of layered structure in the coal. The bituminous and sub-bituminous coals have few-layer graphene and dots embedded in the structure while the lignite is prone to stack, like bulk graphite. Bituminous and sub-bituminous coal are the ideal precursors for the synthesis of graphene quantum dots and graphene layers.

3.5. Transmission electron microscopic analysis

The TEM images of the carbon nanodots formed in the bituminous coal (B1H) are presented in Fig. 4. Spherical carbon nanodots of the size of 14 nm to 4.8 nm are observed in the micrographs. The SAED pattern (Fig. 4c) shows the formation of highly crystalline carbon dots or nanocrystalline diamond.

The TEM images of the nanocarbon obtained from the sub-bituminous coal are presented in

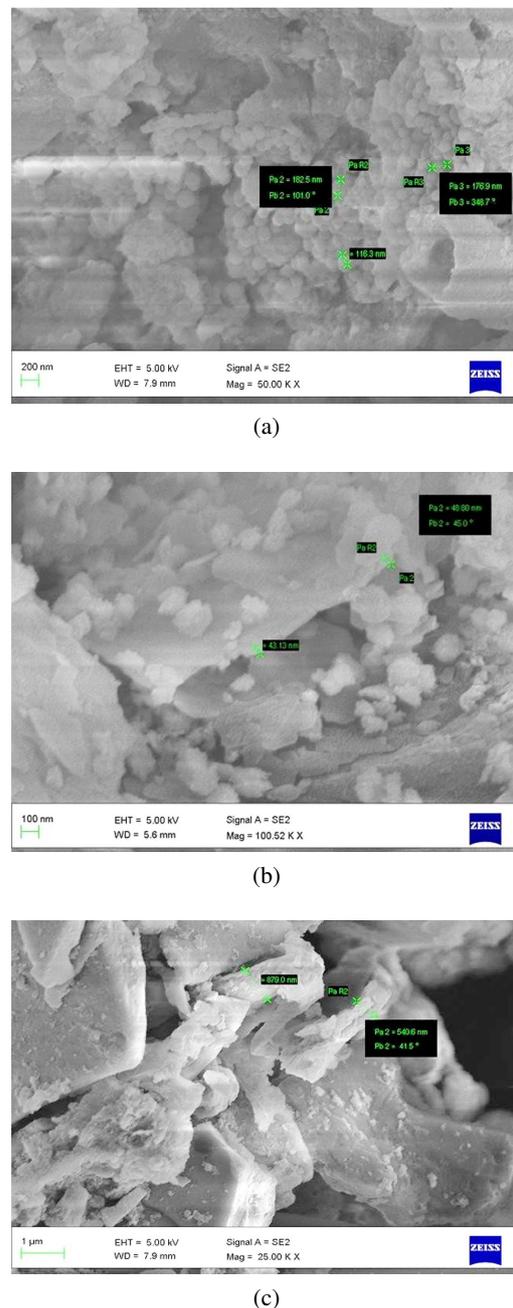


Fig. 3. SEM micrographs of nanostructures obtained from (a) bituminous coal (B1H), (b) sub-bituminous coal (G1H), (c) lignite (L1H).

Fig. 5a to Fig. 5c. Formation of graphene structure with hexagonal, spherical and corn-shaped carbon nanotubes is noticed. Carbon nanotubes in the form of Y-junction and bamboo junction are also observed in the micrograph. At some parts, graphene layers and carbon dots are embedded

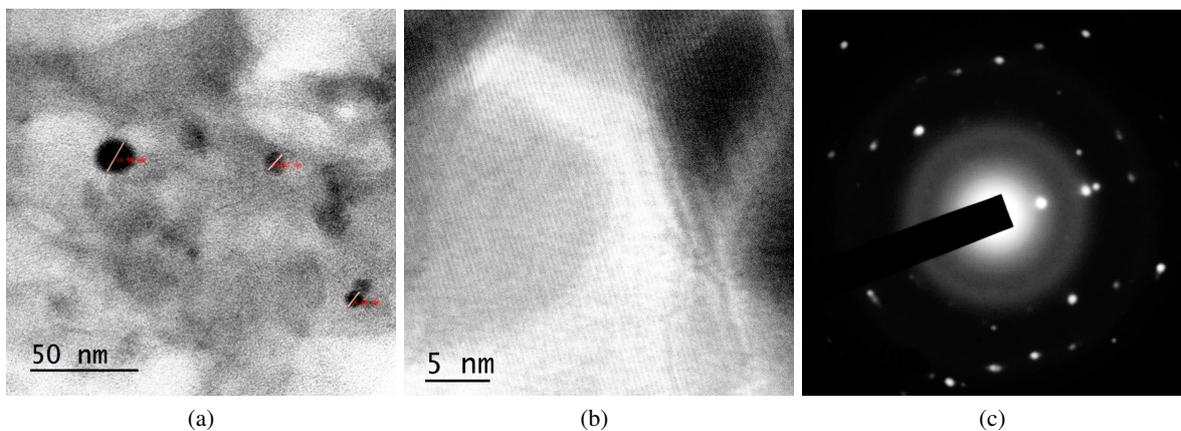


Fig. 4. TEM micrographs of nanostructure obtained from bituminous coal (B1H): (a) at lower magnification, (b) at higher magnification, (c) SAED pattern of nanostructure obtained from bituminous coal (B1H).

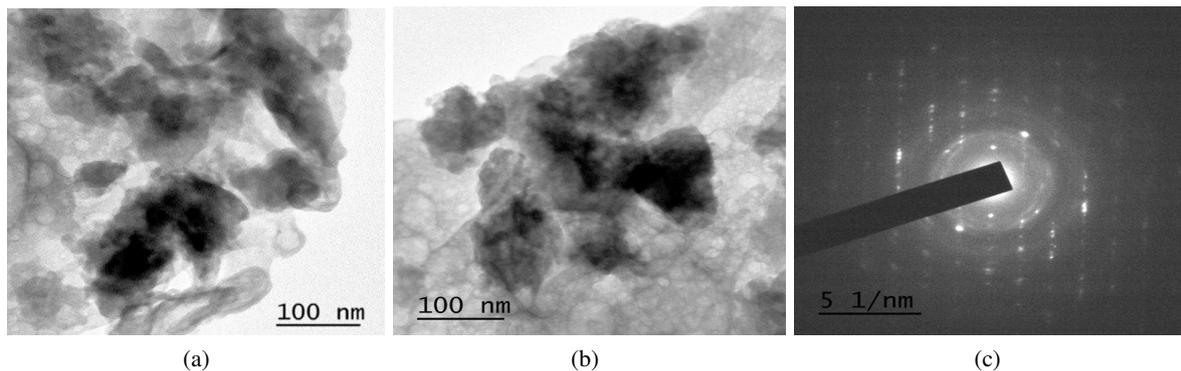


Fig. 5. (a) and (b) TEM micrographs of nanostructure obtained from sub-bituminous coal (G1H), (c) SAED pattern of nanostructure obtained from sub-bituminous coal (G1H).

in carbon multilayers due to agglomeration. The SAED pattern shows that there is better crystalline ordering in the sample. The TEM analysis confirms the formation of mixed phase structure of carbon nanomaterial in the leached product of sub-bituminous coal [2, 4].

Fig. 6 shows the TEM images of the carbon nano-materials formed in the lignite sample. Agglomerated carbon spheres and dots have been formed in the sample. These carbon dots have been formed by stacking of multilayers of carbon as is evident from the SAED pattern and Raman analysis [14, 15]. The TEM analysis confirms the presence of nanostructures in the coal whose size, shape and stacking depends on the rank of coal.

4. Conclusions

In summary, three types of coal are chosen as precursors and are investigated for the effective production of mixed phase graphene-like nanostructures by simple oxidation followed by sonication. They have a unique structure and are ideal precursors for the synthesis of graphene quantum dots, nano-diamonds, graphene layers, carbon dots and mixed-phase graphene structure. The properties of the carbon structure, its shape and size is highly dependent on the rank of the coal used. It could be concluded that sub-bituminous, bituminous and lignite coal can serve as efficient precursors for the production of carbon nanostructures at low cost by exploiting a simple acidic oxidation method. The fabricated nanostructures are mixed phase

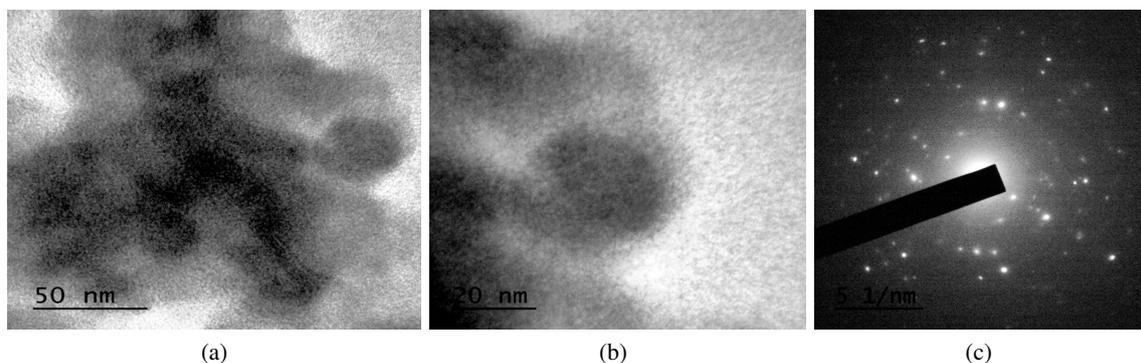


Fig. 6. TEM micrographs of nanostructure obtained from lignite (L1H) (a) at lower magnification, (b) at higher magnification, c) SAED pattern of nanostructure obtained from lignite (L1H).

in nature. These materials are potential precursors for the formation of carbon dots and graphene quantum dots. Their size dependent properties are worth investigating for advanced applications.

Acknowledgements

The authors acknowledge the grant by the Centre for Research, Christ University, to carry out this work in the form of Major Research Project (MRP DSC 1515).

References

- [1] RAO C.N.R., SOOD A.K., SUBRAHMANYAM K.S., GOVINDARAJ A.L., *Angew. Chem. Int. Edit.*, 48 (2009), 7752.
- [2] MANOJ B., *Russ. J. Phys. Chem. A*, 89 (2015), 2438.
- [3] KANIYOOR A., RAMAPRABHU S., *AIP Adv.*, 2 (2012), 13.
- [4] RAMYA A.V., MOHAN A.N., MANOJ B., *Mater. Sci.-Poland*, 34 (2016), 330.
- [5] MANOJ B., *J. Environ. Res. Develop.*, 9 (1) (2014), 209.
- [6] XIAO J., LIU P., YANG G.W., *Nanoscale*, 7 (2015), 6114.
- [7] BALACHANDRAN M., *Am. J. Appl. Chem.*, 7 (2014), 367.
- [8] MANOJ B., *Int. J. Min. Met. Mater.*, 21 (2014), 940.
- [9] YE R., XIANG C., LIN J., PENG Z., HUANG K., YAN Z., COOK N.P., SAMUEL E.L.G., HWANG C.C., RUAN G., *Nat. Commun.*, 4 (2013), 2.
- [10] DONG Y., LIN J., CHEN Y., FU F., CHI Y., CHEN G., *Nanoscale*, 6 (2014), 7410.
- [11] MANOJ B., *Res. J. Biotechnol.*, 8 (3) (2013), 49.
- [12] MANOJ B., RAJ A.M., CHIRAYIL G.T., *Sci. Rep-UK*, 7 (2017), 18012.
- [13] FERRARI A.C., ROBERTSON J., *Physical Review B*, 61 (20) (2000), 14095.
- [14] RAMYA A.V., ANU N.M., MANOJ B., *Asian J. Chem.*, 28 (7) (2016), 1501.
- [15] ANU N.M., MANOJ B., *Res. J. Chem. Environ.*, 21 (2) (2017), 1.
- [16] MANOJ B., *Int. J. Coal. Sci. Tech.*, 3 (2016), 123.
- [17] MANOJ B., *Asian J. Chem.*, 3 (15) (2014), 4553.
- [18] ILYIN A., GUSEINOV N., NIKITIN A., TSYGANOV I., *Physica E*, 42 (2010), 2078.
- [19] KUNJOMANA A.G., MANOJ B., *Russ. J. Appl. Chem.*, 87 (11) (2014), 1726.
- [20] ELCEY C.D., MANOJ B., *Asian J. Chem.*, 28 (2016), 1557.

Received 2016-10-28

Accepted 2018-02-16