

Facile green synthesis of carbon nanoparticles using medicinally potent *Pongamia pinnata* shoots

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SHORT COMMUNICATION **BSTRACT**

The emergence of carbon nanoparticles (CNPs) has received greater potential in biological labeling, bioimaging and other different optoelectronic device applications. Preparation of CNPs using *Pongamia pinnata* shoots in the presence of castrol oil is reported in the present study. The structural and optical properties of CNPs were studied using X-Ray diffraction (XRD), Raman spectroscopy, Field Emission Scanning Electron Microscope (FE-SEM) and Energy Dispersive X-Ray (EDAX) analysis.

KEYWORDS

carbon; nanoparticles; pyrolysis; SEM; XRD

1. INTRODUCTION

Carbon-based nanomaterials (CNPs), which include carbon nanotubes, fullerenes, and nanofibers, have promising applications in nanotechnology, biosensing, and drug delivery (Pierson, 1993). Recently CNPs, a new class of carbon-based nanomaterials with interesting photoluminescence properties, has been reported (Sun et al., 2006; Chang et al., 2010). Carbon has been fascinating to scientists for centuries and still remains to intrigue the scientific community in the form of nanometer sized allotropes such as bucky balls and nanotubes and more just, in the form of the ideal atomic laver, graphene (Pierson, 1993). Numerous chemical variants of these have also been studied. Both single-walled carbon nanotubes (SWNTs) and graphene possess unique properties with various applications in electronics and quantum computing (Bottini et al., 2006) and above all possess the ability to unravel countless fundamental questions related to ballistic thermal and electronic transport. SWNTs

require high purity and accurate characterization in terms of chiralities as well as length and diameter distribution for them to be used in most of the specific applications. Nanoribbons are considered significant because of the emerging local magnetism with very specific edge states (Huang et al., 2013). There are also attempts to use these nanoribbons in electronics by imagining them as active channel materials in field effect transistors. Hence, it is required to have a precise method without any over oxidation to convert specific SWNTs to graphene nanoribbons and thereby create graphenic materials of desired properties. This concept was also aided by the ability to separate SWNTs according to their metallicity and diameter, which eventually helps in getting graphene ribbons of specific width and edge structure. In this context, recently, Shinde et al. (2011) devised an electrochemical route to convert multiwalled nanotubes into multilayered graphene nanoribbons (Heller et al., 2004). In brief, nanoribbons of a few layers of graphene have been prepared from carbon nanotubes (CNT) by a two-step

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Recieved: 08-09-2015 Revised: 01-03-2016 Accepted: 15-03-2016 Available online: 01-04-2016 electrochemical approach consisting of oxidation of CNTs at controlled potential, followed by reduction to form graphene nanoribbons having smooth edges and fewer defects, as showed by multiple characterization techniques, including Raman spectroscopy, atomic microscopy and transmission microscopy. However, neither the role of electric field nor the mechanism of opening and the order of events between CNT breach (oxidative cleavage of the (c bond) and graphene nanoribbons formation has been probed. Answers to questions such as, is unzipping fundamentally different for metallic and semiconducting CNTs, where does the curvature break, and what is the reason for choosing a mixture of semiconducting and metallic CNTs, have not been explored. While both single and multiwalled CNTs have been shown to generate graphene nanoribbons with controlled widths and fewer defects. An in situ spectroscopic investigation of various stages of the above sequential processes can possibly reveal the mechanism of unzipping of nanotubes and selective breaking (Elias et al., 2010), if any. This will also be important to understand the mechanism of unzipping of SWNTs to graphene nanoribbons by other methods such as laser cutting and chemical unzipping (Robin et al., 2014).

Carbon nanomaterials have received recent attention as biomolecular carriers, capable of transporting covalently bonded drugs or molecular probes across cell membranes (Kam et al., 2004). The poor cellular penetration of many small molecules and proteins can be overcome by conjugation to a nanomaterial carrier, whose size, shape, and external chemistry can be engineered for optimal cellular uptake. Numerous structures of carbon nanomaterials have attracted a great deal of attention from the research community due to their excellent properties and potential technological applications after the finding of fullerene (Kroto et al., 1985; Baughman et al., 2002; Yan et al., 2006; Fang and Chen, 2012; Ban et al., 2012).

In the present study, CNPs were prepared from a bio-precursor which is economically cheap and naturally abundant. The conversion method involved were simple thermal pyrolysis without any passivating or stabilizing agents. The synthesized CNPs were characterized using Raman spectroscopy, XRD, SEM with EDAX and UV-Vis spectroscopy to study their structural and optical properties.

O. MATERIALS AND METHODS

2.1. Materials

Pongamia pinnata shoots (Figure 1) were collected in and around Sathyabama University campus, Chennai, India. Castrol oil was purchased from local market. Toluene and acetone were purchased from Qualigens chemicals, India. All chemicals were used as received. All solutions and suspensions were prepared using deionized water.



Figure 1. Pongamia pinnata dried shoots

2.2. Methods

2.2.1. Drying of shoots

Around 10 g of *Pongamia pinnnata* shoots were cut into pieces and cleaned with distilled water. Further, the shoots were kept in an oven at 80 °C for 24 h. The dried shoots were used for further studies.

2.2.2. Preparation and synthesis of carbon nanoparticles using of Castrol oil

The dried shoots were soaked in 15 mL of castor oil in a beaker for 1h. Then, the shoots were taken out to remove excess oil. The shoots were then burnt using a candle with a steel plate placed over the shoots to collect the particles coming out of the flame. The process is continued until the black fumes get completely stacked at the vicinity of the steel plate. The steel plate was then allowed to cool for about 20 min and the black powder stacked over it was collected which is now termed as CNPs.

2.2.3. Purification of CNPs

The black mass so obtained were ground to a powder, washed with toluene, acetone, and water to remove soluble organic byproducts. The resultant black powder was centrifuged and subsequently dried.

2.3. Characterization of CNPs

2.3.1 Raman Spectroscopy

Raman spectroscopy was performed to determine the impurities as well as derived carbon content in the sample. The synthesized CNPs was analyzed on Raman spectrometer Bruker, RFS 27 equipped with a laser light operating at 100 mW.

2.3.2 X-Ray Diffraction

X-Ray Diffraction (XRD) analysis was performed to study the crystallinity of CNPs. The analysis was performed using Rigaku smart lab instrument operated at a voltage of 40 kV and a current of 30 mA with Cu $K_{\alpha l}$ radiations. Powdered CNPs were used for the analysis.

2.3.3 Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray Spectroscopy (EDAX)

FE-SEM analysis was performed to understand the surface morphology of CNPs. CNPs were dried in hot air oven at 105 °C and the fine powder was surface coated over a copper grid, gold sputtered and the images were obtained using SUPRA 55-CARL ZEISS, Germany microscope. EDAX analysis was performed to know the elemental composition of synthesized CNPs.

3. RESULTS AND DISCUSSION

During synthesis of CNPs, the following results were obtained in the characterization techniques. Raman spectrum of carbon nanoparticles (Figure 2) show vibrations of approximately equal intensity at 1591 cm⁻¹ (G mode) and at 1304 cm⁻¹ (D mode), expected for the sp2 and sp3 hybridized carbon, respectively (Li et al., 2011).

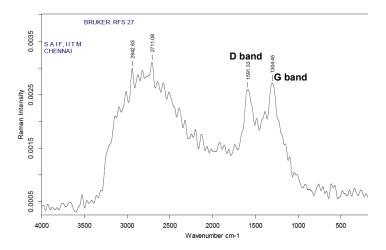


Figure 2. Raman spectra showing the characteristic D and G bands of carbon nanoparticles

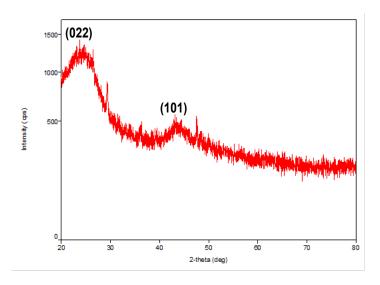


Figure 3. X-Ray Diffraction pattern of carbon nanoparticles

Figure 3 shows the XRD pattern of CNPs. The XRD pattern have exhibited an intense peak at $2\theta = 22.90^{\circ}$ and a weak peak at $2\theta = 41.60^{\circ}$ that corresponds to the (022) and (101) diffraction patterns of graphitic carbon respectively (Li et al., 2012; De and Karak, 2013; Kumar et al., 2013). In order to investigate the surface morphology, average size and elemental composition of synthesized carbon nanoparticles, FE-SEM and EDAX were performed. Figure 4 shows the typical FE-SEM images of carbon nanoparticles with average size of 85-98 nm, in which most of carbon nanoparticles were spherical shaped and well dispersed in aqueous solution with uniform size. Figure 5 shows the EDAX pattern of carbon nanoparticles. From the EDAX

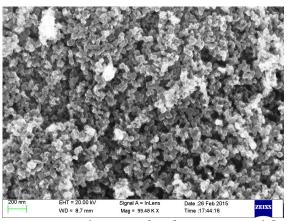


Figure 4. FE-SEM images of carbon nanoparticles

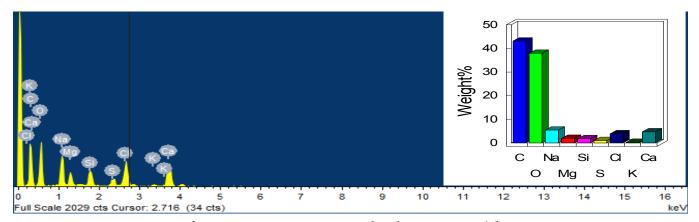


Figure 5. EDAX spectrum of carbon nanoparticles

spectrum, it was found out that carbon was present in higher amounts and other elements like oxygen and sodium were present in lower amounts along with the presence of trace elements like magnesium, chlorine and calcium, etc.

4. CONCLUSIONS

Carbon nanoparticles were prepared from a bioprecursor which is economically cheap and naturally abundant. The conversion method involved was simple thermal pyrolysis without any passivating or stabilizing agents. The results suggest that this methodology could provide an easy and lower cost technique for producing carbon nanoparticles and *Pongamia pinnata* shoots can be used as an alternative raw material for production of carbon nanoparticles.

REFERENCES

Ban, F.Y., Majid, S.R., Huang, N.M. and Lim, H.N. (2012) Graphene Oxide and its electrochemical performance. International Journal of Electrochemical Science, 7, 4345–4351.

Baughman, R.H., Zakhidov, A.A. and De Heer, W.A. (2002) Carbon nanotubes the route toward applications. Science 297, 787–792.

Bottini, M., Bruckner, S., Nika, K., Bottini, N., Bellucci, S., Magrini, A., Bergamaschi, A. and Mustelin, T. (2006) Multi-walled carbon nanotubes induce T lymphocyte apoptosis. Toxicology Letters, 160, 121–126.

Chang, H., Tang, L., Wang, Y., Jiang, J. and Li, J. (2010) Graphene fluorescence resonance energy transfer aptasensor for the thrombin detection. Analytical Chemistry, 82, 2341–2346.

De, B. and Karak, N. (2013) A green and facile approach for the synthesis of water soluble fluorescent carbon dots from banana juice. RSC Advances, 3, 8286–8290.

Elias, A.L., Botello-Mendez, A.R., Meneses-Rodriguez, D., Gonzalez, V.J., Ramirez-Gonzalez, D., Ci, L., Munoz-Sandoval, E., Ajayan, P. M., Terrones, H. and Terrones, M. (2010) Longitudinal cutting of pure and doped carbon nanotubes to form graphitic nanoribbons using metal clusters as nanoscalpels. Nano Letters, 10, 366–372.

Fang, Q.L. and Chen, B.L. (2012) Adsorption of perchlorate onto raw and oxidized carbon nanotubes in aqueous solution. Carbon, 50, 2209–2219.

Heller, D.A., Mayrhofer, R.M., Baik, S., Grinkova, Y.V., Usrey, M.L. and Strano, M.S. (2004) Concomitant length and diameter separation of single-walled carbon nanotubes. Journal of American Chemical Society, 126, 14567–14573.

Huang, L.F., Zhang, G.R., Zheng, X.H., Gong, P.L., Cao, T.F. and Zeng, Z. (2013) Understanding and tuning the quantum-confinement effect magnetismin zigzag graphene nanoribbon. Journal of Physics: Condensed Matter, 25, 055304.

- Kam, S.N.W., Jessop, T.C., Wender, P.A. and Dai, H. (2004) Nanotube molecular transporters: Internalization of carbon nanotube-protein conjugates into mammalian cells. Journal of American Chemical Society, 126, 6850-6851.
- Kroto, H.W., Heath, J.R., Brien, S.C.O. and Curl, R.F. (1985) Smalley C60 Buckminster fullerene. Nature, 318, 162–163.
- Kumar, V., Toffoli, G. and Rizzolio, F. (2013) Fluorescent carbon nanoparticles in medicine for cancer therapy. ACS Medicinal Chemistry Letters, 4, 1012–1013.
- Li, H., Kang, Z., Liu, Y. and Lee, S.T. (2012) Carbon nanodots: synthesis, properties and applications. Journal of Materials Chemistry, 22, 24230–24253.
- Li, H., Ming, H., Liu, Y., Yu, H., He, X., Huang, H., Pan, K., Kang, Z. and Lee, S.T. (2011) Fluorescent carbon nanoparticles: electrochemical synthesis and their pH sensitive photoluminescence properties. New Journal of Chemistry, 35, 2666–2670.
- Pierson H.O. (1993) Handbook of carbon, graphite, diamond, and fullerenes: Properties, processing, and applications. Noyes Publications; Park Ridge, New Jersey.

- Robin, J., Shinde, Lili, L., Feng, D., Zhiping, X., Cherianath, V., Pillai, V.K. and Pradeep, T. (2014) Sequential electrochemical unzipping of SWNTs to graphene ribbons revealed by in-situ Raman spectroscopy and imaging. ACS Nano, 8, 234-242.
- Shinde, D.B., Debgupta, J., Kushwaha, A., Aslam, M. and Pillai, V.K. (2011) Electrochemical unzipping of multi-walled carbon nanotubes for facile synthesis of high-quality graphene nanoribbons. Journal of American Chemical Society, 133, 4168–4171.
- Sun, Y.P., Zhou, B., Lin, Y., Wang, W., Fernando, K.A., Pathak, P., Meziani, M.J., Harruff, B,A., Wang, X., Wang, H., Luo, P.G., Yang, H., Kose, M.E., Chen, B., Veca, L.M. and Xie, S.Y. (2006) Quantum-sized carbon dots for bright and colorful photoluminescence. Journal of American Chemical Society, 21, 7756-7757.
- Yan, A., Lau, B.W., Weissman, B.S., Külaots, I., Yang, N.Y.C., Kane, A.B. and Hurt, R.H. (2006) Biocompatible, hydrophilic, supramolecular carbon nanoparticles for cell delivery. Advanced Materials, 18, 2373-2378.