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Synthesis of carbon nano beads from 2-propanol by spray pyrolysis and its use in microwave absorption

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Abstract: Present work is an attempt to synthesize metal (Ni and Ni-Al alloy) nano catalyst by Solvo-thermolytic process and use for synthesizing carbon nano materials by spray pyrolysis. The precursor used was 2-propanol. The optimal temperature was found to be 900ºC for pyrolysis in presence of Ni-Al alloy. The carbon nano material thus synthesized was confirmed to be multi walled hollow carbon nano bead by TEM and SEM. Moreover, its graphitic nature was confirmed by XRD. Further characterization by Raman spectra showed both G & D bands. The carbon synthesized using Ni-Al catalyst was found to be a good candidate for microwave absorption. Microwave absorption capacity was studied in the frequency range of 12- 18 GHz.

Key words: **Carbon nano beads, solvo-thermolytic process, spray pyrolysis, microwave absorption.**

I. INTRODUCTION

Carbon nanomaterials (CNM) like carbon nanotubes (CNT), carbon nano beads (CNB), carbon nanofibers (CNF), etc. are of great importance due to their various inherent properties like mechanical, electrical, thermal, optical, micro-wave absorption, drug delivery properties among many other [Sharon and Sharon 2006, Sharon *et.al*. 2005, Deanne *et.al.* 2008]. Alcohols are excellent precursors for both single-wall and multi-wall CNTs formation [Maruyama *et.al.*, 2002; Li *et.al*., 2004; Zheng *et.al*., 2004, Igarashi *et.al*., 2004, Miyauchi *et.al*. 2004, Nasibulin *et.al.*, 2006]. Alcohol molecules decomposes to produce OH radicals which further take part in the etching reactions resulting in the purification of CNTs formed [Maruyama *et.al.*, 2002; Murakami *et.al*., 2003]. Alcohols viz. ethanol, octanol [Nasibulin *et.al.*, 2006] have been used alone or in presence of promoters like thiophene to produce CNTs. CNBs have been prepared from different sources but not using alcohols. In this article the effort to successfully synthesize CNB from 2-propanol and study its use in microwave absorption using Vector Network Analyzer (VNA) apparatus in 12-18 GHz frequency ranges is presented.

II. EXPERIMENTAL

Preparation of Nano Catalyst **–** The catalyst required in these experiments was produced by modified Solvo-Thermolytic method [Pramanik 1996, Ko and Hwang 2003, Kundu *et.al.*, 2003]. Two types of catalysts were prepared (i) Ni and (ii) Ni-Al alloy. Nickel catalyst was prepared from Nickel nitrate while Ni-Al alloy was prepared from a mixture of nickel nitrate and 10% aluminum chloride. The nano size Ni-Al catalyst was confirmed by SEM (Fig. 1).

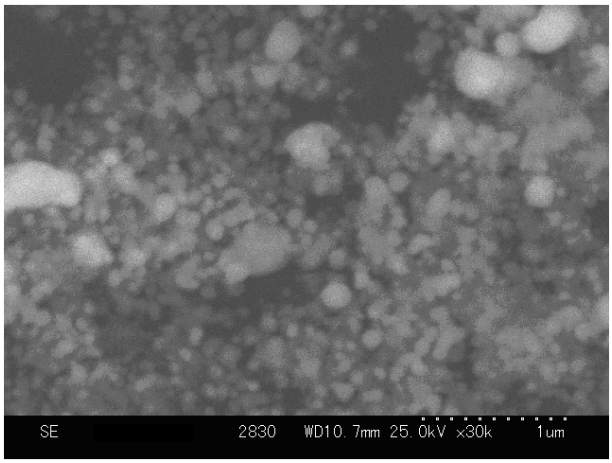


Fig. 1 -SEM of Ni-Al nanoparticles

Preparation of nano carbon by Spray Pyrolysis method- Spray-pyrolysis is an extension of CVD technique. The advantage of this method is that, it can be used either for continuous or for batch process by feeding the precursor and the catalyst in the reactor continuously or batch wise. The other advantage is that, the process can be scaled-up easily [Biro *et.al.*, 2003, Vivekchand *et.al.*, 2004, Tapaszto *et.al.*, 2005].

In the present work, the method slightly deviates from this classical method in a way that the catalyst was used in the form of a thin layer in a quartz boat instead of a solution of precursor of carbon material and precursor of the catalyst.

The precursor, 2-propanol was reacted at 700º - 900ºC. With respect to the catalyst two series of experiments were carried out, one using nickel nano catalyst and the other using nickel-aluminum alloy.

The carbon material obtained was purified by dilute hydrochloric acid (2N) and sonicated. It was characterized by different techniques and used to study the microwave absorption capacity using a VNA at frequency range 12-18 GHz.

Characterization method - The purified carbonaceous material was analyzed by Raman Spectroscopy, XRD, SEM and HRTEM.

III. Results and Discussions

Impact of Ni catalyst on production of CNM- Best parameters found for synthesis of carbonaceous material was 900ºC, 2 L/min flow rate of carrier gas and 0.3 ml/min spray release rate of alcohol with an annealing time of 45 minutes. Under these conditions approximately 30% CNM was obtained, which contained a mixture of different carbonaceous materials including nano beads. The as obtained carbon contained small amount of diamond like carbon (DLC).

Impact of Ni-Al catalyst on prouction of CNM- It was found that the yield of the carbonaceous materials obtained was maximum when parameters used were identical to those used in case of nickel catalyst. The major difference was that the yield of carbonaceous materials was approximately 8% without formation of DLC. Also, the particles formed on analysis were found to have more uniformity than when nickel was used. The analysis supports the claim of formation of carbon nano beads.

Raman spectroscopic analysis- of purified carbon nano beads shows D band as well as G band thus confirming its graphitic nature (Fig 2). Raman spectroscopy is used to differentiate between graphite, multi walled and single walled carbon nanotubes and layers. The Raman spectrum (Fig. 2) of the same sample shows two typical peaks of MWCNT at 1562 cm^{-1} and at 1318 cm^{-1}; corresponds to the typical Raman peaks of graphitic carbon and defects in graphitic carbon respectively. The peak at 1562 cm^{-1} is attributed to the Raman active E_{2g} in plane vibrational mode and is related to the vibration of sp^2 bonded carbon atoms in a two-dimensional hexagonal lattice. The peak at 1318 cm^{-1} is associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite. The intensity of D–band peak is weaker than that of G–band peak, which originates from the in-plane shows less defects i.e. more graphitic carbon and less disorder of the product. [Dresselhaus *et. al.*, 2005].

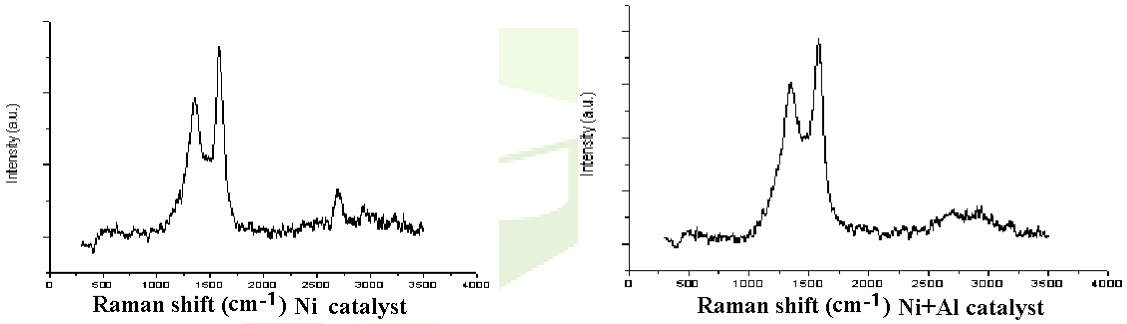


Fig.2 - Raman spectrum of CNM prepared from spray pyrolysis of 2-propanol at 900ºC using Ni catalyst and Ni-Al alloy as a catalyst.

The intensity ratio I_G/I_D =1.18, (Ni catalyst)

The intensity ratio I_G/I_D =1.14, (Ni-Al catalyst)

XRD analysis –

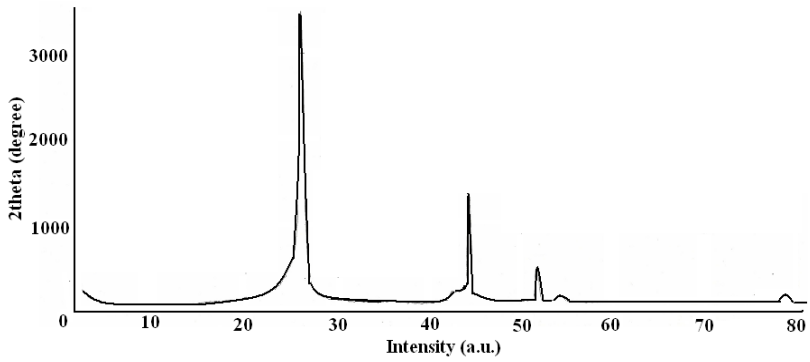
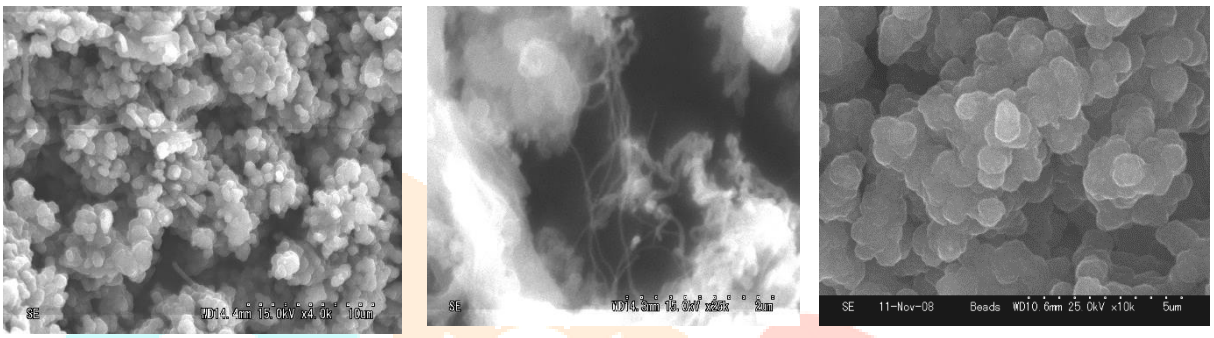


Fig. 3: XRD graph of CNM obtained using Ni catalysts.

According to Garcia-Gutierrez (2007) - XRD pattern of typical CNM shows diffraction peak at 26° {002} designated to graphitic carbon. The peak at 44° is associated with carbon {111} and peak at 54° is attributed to Ni {100}.
The peak at 78° depicts the presence of the Silica, which could be due to the boat in which the catalyst was placed.XRD of CNM obtained by using Ni/Al alloy was also of the same type as shown in figure 3 and hence it is not shown here.

SEM analysis - SEM micrograph of samples prepared at lower temperature of 700° to 800°C (using NI-Al) (Fig. 4a & b) shows formation of few nano fibers and tubular structures along with nano beads. The formations of these structures were observed to decrease at higher temperature. This probably was due to higher kinetic energy associated with C_2, the precursor of CNTs (Yasuda *et.al.*, 2002), thus preventing the growth of the structures. Whereas, at 900°C along with very slow flow rate of precursor restricted the availability of C_2 particles, decreased the chances of growth of tubular structures and only carbon nano beads were formed (Fig 4c). The use of aluminum in the alloy also seems to have a role to play in the shunted growth of the tubular structure resulting in the formation of multiwalled hollow beads and catalyst encapsulated multiwalled beads. This is justified by carrying out experiments under identical conditions but using nickel nano catalyst. The products obtained by this method on analysis by SEM and TEM shows formation of tubular structures. Moreover, at higher temperature and slower flow rate of precursor, formation of amorphous carbon was reduced; such results have also been reported by Nasibulin *et.al.* (2006). The size of nano beads ranged between 30 nm and 90 nm.

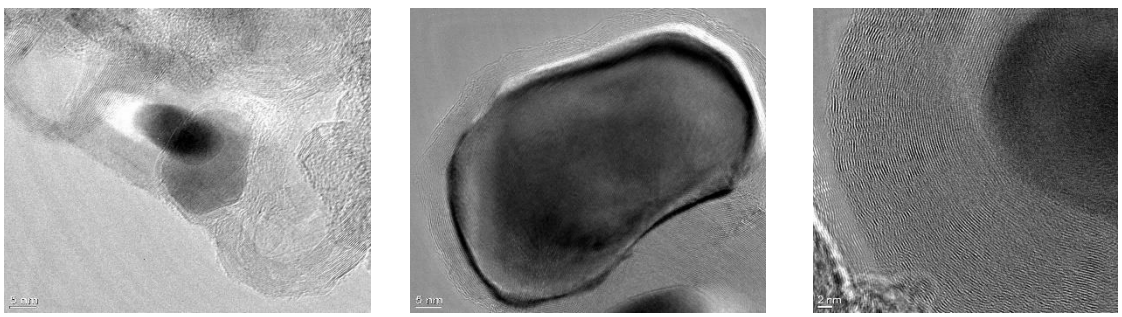


(a) **(b)** **(c)**

Figure -4: SEM analysis of carbon obtained by spray pyrolysis of 2-propanol using Ni-Al catalyst at (a) 700°C & (b) 800°C showing fibers and tubular structures and at (c) 900°C showing formation of beads

HRTEM analysis results - The HRTEM of samples (using Ni-Al) show formation of multilayered nano beads of sizes ranging from 50 to 90 nm. Formation of bead by multilayered graphene sheet, enclosing the nano catalyst, can also be clearly seen in the figure 5a, 5b & 5c.
So far different groups have used alcohol viz. ethanol, octanol and have synthesized different forms of CNTs. Many groups have prepared nano beads, nano balls [Sharon *et.al.*, 1997, Zhong *et.al.*, 2000, Pradhan and Sharon 2002, Liu *et.al.*, 2002, Qian *et.al.*, 2004] from precursors like camphor, commercial kerosene etc.; however, in this work synthesis of carbon nano beads from an alcohol is being reported.
A composite of the carbon materials synthesized using Ni and Ni-Al alloy catalyst were prepared using epoxy resin. The microwave absorption by CNB prepared using Ni-Al alloy was found to be up to 99%, -20dB loss at 12-18 GHz range while the CNM prepared using Ni catalyst was found to be up to 90% under similar conditions.

of five years. The time series monthly data is collected on stock prices for sample firmsand relative macroeconomic variables for the period of 5 years. The data collection period is ranging from January 2010 to Dec 2014. Monthly prices of KSE -100 Index is taken from yahoo finance.



a b c

Figure - 5: (a) HRTEM of carbon nano beads showing a Ni-Al catalyst surrounded by multi walled graphitic carbon forming hollow bead like structure (b & c) Ni-Al nano particle encapsulated by multi wall graphene sheet.

IV. CONCLUSIONS

2-propanol is a precursor for synthesis of carbon nano beads using nano Ni-Al as catalyst. The beads thus formed are hollow structures composed of multi graphene layers. The material is a good candidate for microwave absorption.

V. REFERENCES

1 A. Kundu, C. Upadhyay and H. C. Verma, 'Magnetic properties of a partially inverted zinc ferrite synthesized by a new coprecipitation technique using urea' Physics letters A, May 2003, vol311, issues 4-5, 410-415.

2 Albert G. Nasibulin, Anna Moisala, Hua Jiang and Esko I. Kauppinen, Carbon nanotube synthesis from alcohols by a novel aerosol method, Journal of Nanoparticle Research (2006) 8: 465–475.

3 Ayumu, Yasuda, Noboru, Kawase & Wataru, Mizutani, 'Carbon-Nanotube Formation Mechanism Based on in Situ TEM'. J. of Physical Chemistry B, 2002, 106, (51).

4 Deanne L.V. Greenwood, Kemperly Dynon, Martha Kalkanidis, Sue Xiang, Magdalena Plebanski, Jean-Pierre Y. Scheerlinck, Vaccination against foot-and-mouth disease virus using peptides conjugated to nano-beads. Vaccine, 26 (22), 2706-2713 (2008).

5 Debabrata Pradhan and Maheshwar Sharon, Carbon nanotubes, nanofilaments and nanobeads by thermal chemical vapor deposition process, Material Science and Engineering B, 96,1,2002, 24-28.

6 H. Igarashi, H. Murakami, Y Murakami, S Maruyama and N. Nakashima, "Purification of Zeolite-Supported High-Quality Single-Walled Carbon Nanotubes Catalytically Synthesized from Ethanol," Chem. Phys. Lett., (2004), vol. 392, pp. 529-532.

7 Hai-sheng Qian, Feng-mei Han, Bing Zhang, Yan-chuan Guo, Jun Yue and Bi-xian Peng, Non-catalytic CVD preparation of carbon spheres with a specific size, Carbon Volume 42, Issue 4, 2004, 761-766.

8 Ko Taegyung & Hwang, Deok-Ki 'Preparation of nanocrystalline lead zirconate powder by homogeneous precipitation using hydrogen peroxide and urea' Materials Letters, May 2003, vol. 57, issues 16-17, 2472-2479.

9 L. P. Biro, Z. E. Horvath, A. A. Koos, Z. Osvath, Z. Vertesy, Al. Darabont, K. Kertész, C. Neamtu, Zs. Sárközi, L. Tapaszto, Direct synthesis of multi-walled and single-walled carbon nanotubes by spray-pyrolysis, 2003, Journal of Optoelectronics and Advanced Materials Vol. 5, No. 3, , p. 661 – 666S.

10 L. Tapaszto a, K. Kertesz a, Z. Vertesya, Z.E. Horvatha, A.A. Koosa, Z. Osvatha, Zs. Sarkozib, Al. Darabontb and L.P. Biro. Diameter and morphology dependence on experimental conditions of carbon nanotube arrays grown by spray pyrolysis, 2005, Carbon, Volume 43, Issue 5, 970-977.

11 L.X. Zheng, M.J O'Connell, S.K Doorn, X.Z Liao, Y. H Zhao, E.A Akhadov, M.A Hoffbauer, B.J. Roop, Q.X Jia, R.C Dye, D.E Peterson, S.M Huang, J Liu & Y.T Zhu, 2004. Ultralong single-wall carbon nanotubes, Nature Materials 3, 673–676 (2004).

12 M. Dresselhaus, G. Dresselhaus, R. Saito and A. Jorio, Raman spectroscopy of carbon nanotubes, Physics Reports 409 (2005) 47-99.

13 M. Garcia-Gutierrez, A. Nogales, J. Hernandez, D. Rueda and T. Ezquerra, X-ray scattering applied to the analysis of carbon nanotubes, Poly. and Nanocom., Opt. Pura. Apl. 40: 195-205(2007).

14 Maheshwar Sharon, Kingsuk Mukhopadhyay, Kiyoshi Yase, Sumio Iijima, Yoshinori Ando and Xinluo Zhao, European Materials Research Society 1997 Meeting, Symposium A: Fullernes and Carbon based Materials Spongy carbon nanobeads –A new material, Carbon, 1998, Volume 36, Issues 5-6, Pages 507-511.

15 Maheshwar Sharon, Madhuri Sharon, "Carbon nano forms and applications", McGraw-Hill Professional Publishing (2010).

16 Maheshwar Sharon, Debabrata Pradhan, Renju Zacharia, Vijaya Puri,, Application of Carbon Nanomaterial as a Microwave Absorber, J. Nanoscience and Nanotechnology, 5 (12), 2117-2120 (2005).

17 P. Pramanik, 'Chemical synthesis of nanosized oxides' Bulletin of Materials Science, Dec. 1996, vol. 19, Number 6, 957-961.

18 R. C. Vivekchand, L. M. Cele, F. L. Deepak, A. R. Raju and A. Govindaraj Carbon nanotubes by nebulized spray pyrolysis, Chemical Physics Letters Volume 386, Issues 4-6, 11 March 2004, 313-318.

19 S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi and M. Kohno, "Low-Temperature Synthesis of High-Purity Single-Walled Carbon Nanotubes from Alcohol," Chem. Phys. Lett. 360 (3-4), 229-234 (2002).

20 Xin-Ying Liu, Bi-Chun Huang and Neil J. Coville, The Fe(CO)5 catalyzed pyrolysis of pentane: carbon nanotube and carbon nanoball formation, Carbon, Volume 40, Issue 15, 2002, 2791-2799.

21 Y. Li, I. A. Kinloch & A. H. Windle, Direct spinning of carbon nanotube fibers from chemical vapor deposition synthesis, Science 304, 276–278 (2004).

22 Y. Miyauchi, S. Chiashi, Y. Murakami, Hayashida Y. and Maruyama S., "Fluorescence spectroscopy of single-walled carbon nanotubes synthesized from alcohol," Chem. Phys. Lett., (2004), vol. 387, no. 1-3, pp. 198-203.

23 Y. Murakami, Y. Miyauchi, S. Chiashi and S. Maruyama, "Direct synthesis of high-quality single-walled carbon nanotubes on silicon and quartz substrates," Chem. Phys. Lett., 377, 49-54 (2003).

24 Ziyi Zhong, Huayi Chen, Songbei Tang, Jun Ding, Jianyi Lin and Kuang Lee Tan, Catalytic growth of carbon nanoballs with and without cobalt encapsulation, Chemical Physics Letters, Volume 330, Issues 1-2, 2000, 41-47.