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Spray Pyrolysis for Controllable Synthesis of One Dimensional Nanostructured Carbon Materials from Plastic Pyrolytic Oil

B. Parasuram[1], S. Sundram[2], S. Karthikeyan[3*]

[1]The Salem Polytechnic College, Salem, TN, India.
[2]Vidyaa Vikas Engineering College, Tiruchengodu, TN, India.
[3]Department of Chemistry, Chikkanna Govt. Arts College, Tiruppur, TN, India.*

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Abstract

MWCNTs were synthesized by spray pyrolysis method at 950 °C on quartz substrate from plastic pyrolysis oil derived from waste polystyrene plastic using Argon gas was used as a carrier gas. The chemical compound composition of the plastic pyrolysis oil has been determined by Gas Chromatography-Mass Spectroscopy. The GC-MS analysis was conducted on the polystyrene pyrolytic oil to confirm alkanes and alkenes compound. As-grown MWCNTs were characterized by SEM, HR-TEM and Raman spectroscopy. Raman spectroscopy reveals that as grown multiwall carbon nanotubes are well graphitized.

Keywords: *Carbon nanotubes; Ferrocene; Plastic pyrolytic oil; Polystyrene.*

1. INTRODUCTION

The disposal of waste plastic has become a major environmental problem all over the world. Huge part of the municipal plastic wastes is from packing sector, which are basically commodity plastics. The amount of plastic solid waste produced continuous to increase despite some continuous efforts to reduce, reuse, recycle and recover. Conventional routes to recycle plastics such as mechanical recycling, land filling, incineration and chemical recycling (Miskolczi *et al.* 2006). Various alternative routes have been proposed in order to process the plastic wastes. Nevertheless, not all these alternatives are widely, sometimes due to economic viability (Howard, 2002; Al-Salem *et al.* 2009). By pyrolysis there are able to convert into liquid hydrocarbons with high yields and moderate quality.

Carbon nanotubes play a large part in a dimension into the knowledge of carbon science. Almost every day, new concept and experimental framework to the goal of CNT is identified (Zobir *et al.* 2013; Azmina *et al.* 2012; Yusop *et al.* 2012). Because of outstanding electrical, thermal and mechanical properties CNTs have potentials for applications in nanoelectronics, sensors, field emission and as reinforcing agents in composite materials (Khan *et al.* 2007; Melissa Paradise and Tarun Goswami, 2007). Well-known methods of synthesizing CNTs include arc-discharge, laser vaporization and chemical vapour deposition (CVD). Among them, CVD is currently the most widely used, because it requires relatively low cost equipment and it's capable of producing relatively large amount of CNTs (Karthikeyan *et al.* 2008). It was also found that the variety of carbon nanomaterials was formed using metal catalysts and therefore, Fe was chosen to be the metal catalyst (Kiang *et al.* 1996). Several papers had been published and described a simple routine for synthesizing low-cost CNT arrays in large scale from petroleum-based precursors such as benzene, xylene and hexane. This carbon precursor would not be sustainable due to an unstable supply of oil resources. As the CNT researchers it was advisable to choose a hydrocarbon precursor (starting materials) from unconventional and waste one, such as botanical hydrocarbon based CNTs and waste chicken fat (Kumar and Ando, 2003; Afre *et al.* 2005; Ghosh *et al.* 2007; Suriani *et al.* 2009; Paul and Samdarshi, 2011; Karthikeyan and Mahalingam, 2010; 2010; Mageswari *et al.* 2012; Angulakshmi *et al.* 2012; 2013; 2013; Suriani *et al.* 2013). The production of carbon nanotubes (CNTs) using alternative sources for tire Pyrolysis oil derived from waste plastic material. One of the proposed options has been using plastic polymers as the carbonaceous feed. If a feasible process is found which can transform readily available carbon rich plastic waste into highly value added products such as CNTs.

In this study, we report a novel and eco friendly for synthesis of carbon nanotubes from waste plastic on a quartz substrate at 950 °C by spray pyrolysis method.

2. EXPERIMENTAL METHOD

2.1 Polystyrene pyrolysis process

Polystyrene was crushed in to powder were washed, dried and stored. Required quantity of

S. Karthikeyan** **Tel. No.: +91 9442264501
E-mail : environkarthi@gmail.com

precursor with bentonite as catalyst was feed in steel boat which is placed in the center of the reactor. The temperature was maintained in the reactor at 380-420 °C under N gas atmosphere. The residence time of the feed stock in the reactor was 2 hrs. The products of pyrolysis in the form of vapors were sending through a water cooled condenser and the condensed liquid was collected as a fuel. The yield of the products in the a pyrolysis process were plastic pyrolytic oil : 53 to 75 wt%, Pyro gas : 15 to 46 wt% and Char : 2 to 9 wt%. The resultant plastic pyrolytic oil was characterized by GC-MS which is shown in the fig 1.

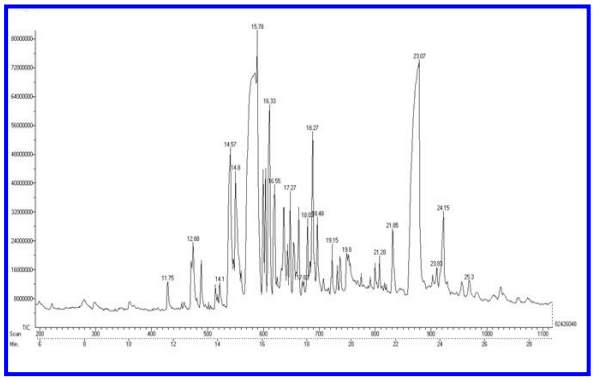

Fig. 1: GC-MS chromatograms of polystyrene pyrolytic oil

2.2 Synthesis of Carbon Nanotubes from polystyrene pyrolytic oil

The synthesis of CNTs was carried out using the spray pyrolysis method. In this spray pyrolysis method pyrolysis of the carbon precursor with a catalyst take place followed by deposition of CNTs occurs on suitable substrate. Plastic pyrolytic oil from polystyrene was used as carbon source and ferrocene [Fe $(C_5H_5)_2$] (Sigma Aldrich, high purity 98%) was used as a source of Fe which acts as a catalyst for the growth of CNTs. A quartz substrate of size (1x1 cm^2) was used as a substrate material. The spray pyrolysis setup consisted of a nozzle (inner diameter ~0.5 mm), attached to a precursor solution supply used for spraying the solution into a quartz tube (500 mm long with an inner diameter of 30 mm). The outer part of the quartz tube was attached with a water bubbler. Before used, substrate was cleaned properly in acetone by ultra-sonication followed by de-ionized water and finely dried using argon blower. The substrate was kept in a quartz boat which was then placed at the center of the quartz tube. In a typical experiment, the quartz tube was first flushed with argon (Ar) gas in order to eliminate air from the quartz tube and heated to a reaction temperature. The precursor solution (plastic pyrolytic oil and ferrocene mixtures) was sprayed into the quartz tube, using Ar gas. The concentration of ferrocene in polystyrene pyrolytic oil was ~25 mg/mL. The solution was sonicated for 5 min to prepare the homogeneous mixture. The flow rate of Ar was 200 sccm/min. The experiments were conducted at 950 ºC and 1 atmospheric pressure, with reaction time of 45 min was maintained for each deposition. After deposition, the furnace was switched off and allowed to cool down to room temperature under Ar gas flow. A uniform black deposition on the quartz substrate at the reaction zone was observed. Finely, the substrate containing entangled CNTs was removed from the quartz tube for characterization.

The as-grown CNTs materials were characterized using scanning electron microscope (SEM was performed by Hitachi-3000 H). For Transmission electron microscope (TEM was performed by JEOL-JEM-2010F) studies, the samples were prepared by sonication of products in isopropanol and few drops of resultant suspension was put on to holey carbon grid and dried. Raman spectroscopy of samples was performed by JASCO NRS-1500 w, green laser with excited on wave length 532 nm.

3. RESULT & DISCUSSION

Since the polystyrene pyrolytic oil consist of numerous and derives components it was difficult to quantity them. Almost all of the researchers had used GC-MS analytical techniques to identity and quality possible compounds in the pyrolytic oils derived from different types of plastic materials.

The GC-MS analysis was to get an idea about the nature and type of compounds of such liquids. The NIST search software was used to analysis the peak provided by the chromatogram, from which more than the half was not properly identified. Table 1 showed the tentative compounds assigned and they are it can be seen from GC-MS result that (fig. 1), polystyrene pyrolytic oil were very complex mixture containing many aromatic and small amount of aliphatic compounds. The GC-MS analysis was conducted on the polystyrene pyrolytic oil to confirm alkanes and alkenes compound.

Table 1. Tentative GC-MS characterization of polystyrene pyrolytic oil

Retention time	Tentative assignment
11.75	Diphenylmethane
12.88	4-Cyclohepta-2,4,6-trienylphenylamine
14.1	Benzene, 1,1' (1-butene-1,4-diyl) bis [z]
14.57	Benzene, 1,1' (1,3-propanedyl) bis
14.8	Benzene, 1,1' (3-methyl-1-propene-1,3-diyl)bis
15.78	Benzene, 1,1' (1,3-butenylidene) bis
16.33	Benzene, [2-methylene-1-phenylcyclopropyl]-
16.55	Thiocarbamic acid,N,N-dimethyl, s-1,3-diphenyl-2- butenyl ester
17.27	1,3-Pentadiene, 1,1-diphenyl [z]
17.82	2,4-Diphenyl-4-methyl-2[E]-pentene
18.03	2,3-Diazabicyclic [2,2,21] hept-2-ene,1,4-diphenyl
18.27	1,3-Pentadiene,1,1-diphenyl [z]
18.48	Cyclopentane, 1-phenyl-3-phenylmethylene
19.15	11-Octadecenoic acid, methyl ester
21.85	Thiocarbamic acid, N,N-dimethyl, S-1,3-diphenyl-2-butenyl ester
23.07	N,Normethadol
24.15	Thiocarbamic acid, N,N-dimethyl, S-1,3-diphenyl-2-butenyl ester
25.3	Spiro[2,3]hexane-5-carboxlic acid, 1,1-diphenyl-methyl ester

Fig. 2(a) showed the scanning electron microscope image of multi-walled carbon nanotubes using polystyrene pyrolytic oil. The as-grown carbon nanotubes were smooth surface cylinders structured with diameters in the range of ≈ 50-80 nm. Small bright catalyst particles were present in the MWNTs. The typical HR-TEM image of the as-grown CNTs was shown in fig. 3. The HR-TEM investigation the image clearly showed compartment-like graphitic structures inside the nanotube (which, as the name indicates, resemble the structure of the bamboo plant) with the presence of MWNTs fig. 3a (Ding *et al.* 2006; Liu *et al.* 2012; Banks and Compton, 2006). The side-wall of CNT was found to consist of ≈75 graphitic layers fig. 4b. The insert in fig. 3a selected area electron diffraction (SAED) pattern was taken from CNTs showed the presence of sharp graphitic (002) and (004) reflections.

Fig 4. displays Raman spectra of as-grown multiwalled carbon nanoubes. The spectra show three peaks at around 1344, 1573 and 2684 cm^{-1}. Which are attributed to D, G and G' bands respectively. The G bands are related to stretching vibration in the basel plane of graphite crystal, which have been normalized to the same intensity. D bands are associated with disorder or detective planner graphite structure. G' band is a second order two phonon process. The intensity ratio I_D/I_G could be used to diagnose wall-defects and disorder in graphitic structure. The lower I_D/I_G value indicates a higher degree of graphitization (Dresselhausa *et al.* 2002; Costa *et al.* 2008).

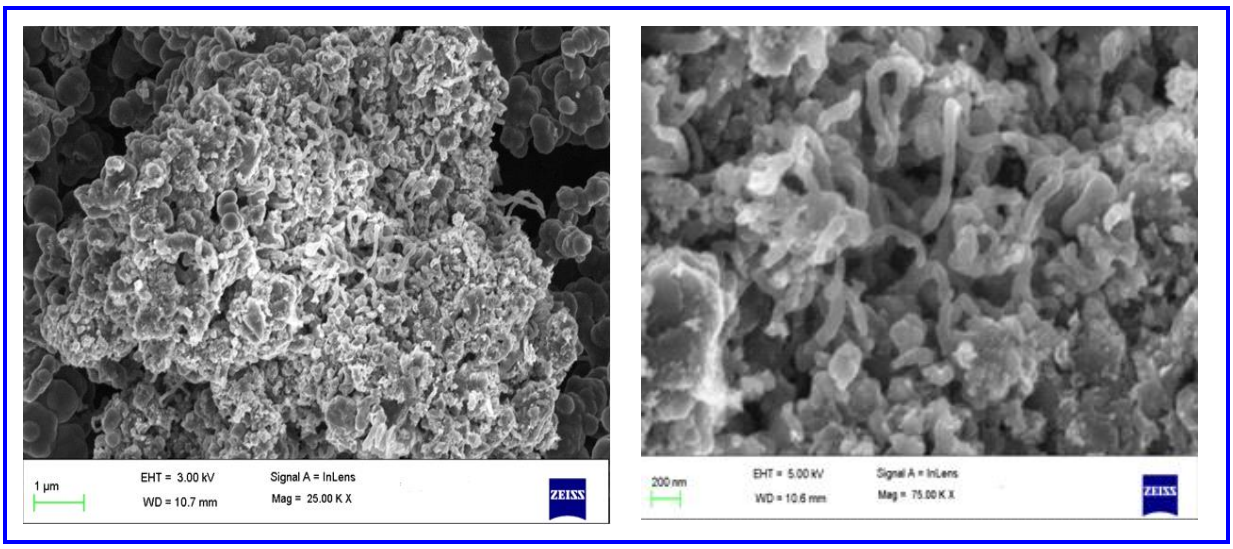

Fig. 2: FE-SEM images of MWNTs grown at 950 ºC (a) as-grown CNTs on quartz substrate. (b) Zoom-in side view of the side structure of MWNTs.

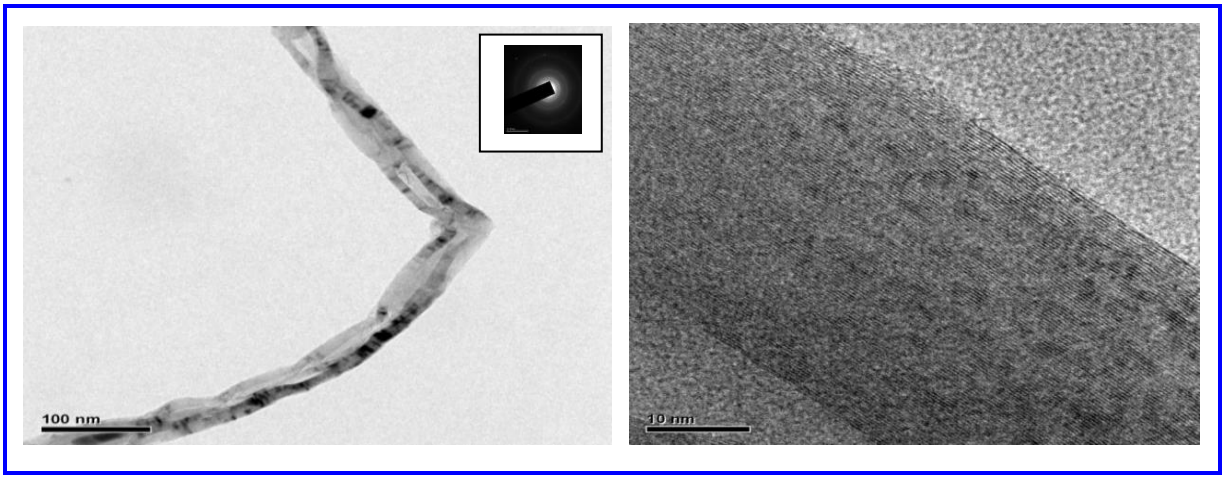

Fig. 3: TEM images of (a) as-grown MWNTs (SAED inset of fig 3 (a)) (b) Magnified view of MWNTs

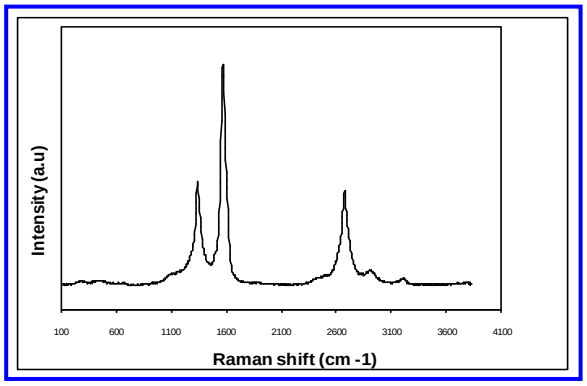

Fig. 4: Raman spectrum of MWNTs grown at 950 ºC

4. CONCLUSION

The MWNTs have been successfully prepared with low cost by spray pyrolysis of polystyrene pyrolytic oil on Quartz substrate at 950 ºC under an Ar atmosphere. The GC-MS analysis was conducted on the polystyrene pyrolytic oil to confirm alkanes and alkenes compound. Graphitization of these CNTs is fairly good and the presence of catalyst particles in as-grown CNTs is almost negligible.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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