



Pyrolysis of waste polypropylene for the synthesis of carbon nanotubes

Neeraj Mishra^{a,*}, Gobind Das^b, Alberto Ansaldo^c, Alessandro Genovese^b, Mario Malerba^b, Mauro Povia^b, Davide Ricci^c, Enzo Di Fabrizio^b, Ermanno Di Zitti^d, Madhuri Sharon^e, Maheshwar Sharon^e

^a Nanotechnology Research center (NTRC), Birla College of Arts Science and Commerce, Kalyan (w) 421301, Thane, Maharashtra, India

^b Nanobiotech Facilities, Italian Institute of Technology, Via Morego 30, I-16163 Genoa, Italy

^c Soft Material Design Lab., Dept. of Robotics, Brain, and Cognitive Science, Italian Institute of Technology, Via Morego 30, I-16163 Genoa, Italy

^d Dept. of Biophysical and Electronic Engineering, University di Genova, Via Opera Pia 11a, I-16145 Genoa, Italy

^e N. S. N. Research Centre for Nanotechnology & Bionanotechnology, Ambernath (W), Maharashtra, India

ARTICLE INFO

Article history:

Received 17 June 2011

Accepted 24 November 2011

Available online 13 December 2011

Keywords:

Polypropylene

Pyrolysis

MWCNTs

XRD

Raman scattering

SEM

TEM

HRTEM

ABSTRACT

Waste polypropylene (PP) is used as precursor for synthesizing multi-walled carbon nanotubes (MWCNTs) by single stage chemical vapor deposition (CVD) method using nickel as catalyst. The pyrolytic degradation of PP to MWCNT was achieved by exposing the catalyst and precursor to temperature 600, 700 and 800 °C under argon and hydrogen atmosphere for an hour. The resultant carbon was purified and characterized by XRD, Raman scattering, SEM, TEM and HRTEM. All the analysis confirmed the graphitic nature and multi-walled morphology of the CNT. Moreover the MWCNT was found to exhibit high transmittance to visible light up to 85% at 550 nm, comparable to that of typical ITO films (90%), suggesting that MWCNTs can be used for optoelectronic devices.

The present work could be employed for synthesizing CNTs, having wide range of applications, and for environment protection as well since waste plastic is being used.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Plastic is a nuisance and destruction for mangrove ecosystem due to its non-dissociation property in nature [1]. Thin plastic bags have no recyclable value and are abandoned/disposed by public directly or by packing refuse in it. Being cheap, hawkers, vendors, and shopkeepers use them for packing items. Governments from all over the world have taken a serious note of this plastic menace and even banned plastic below 50 μm (along with plastic carry bags). It is necessary to have mechanism in place for regulating its use, recycling and disposal instead of banning or stop making of plastics to remove the plastics from the environment [2,3]. Recycling and combustion process make new product which is less valuable compared to product form by pyrolysis method.

Converting waste plastics into valuable products such as carbon nanotubes (CNTs) could be an important and profitable option for industry and for environmental protection as well. CNTs, due to its high tensile strength, mechanical, electrical, and chemical properties, offer a great potential for different applications spanning from

textile [4], electronics [5], microwave absorption [6], actuator [7] to biomedical [8].

In particular, various methods have been developed for the synthesis of CNTs such as arc discharge [9], pyrolysis [10], laser ablation [11], plasma assisted deposition [12] and thermal chemical vapor deposition [13]. Among them, chemical vapor deposition (CVD) is currently the most widely used, because it requires relatively low-cost equipment and is capable of producing comparatively large amounts of CNTs in a short time. Catalytic decomposition of hydrocarbons is a promising means to produce CNTs on a large scale [14]. Synthesis of CNTs through thermal decomposition of polymer (or plastic derivatives such as polyethylene (PE), polypropylene (PP)) and using catalysts has also been reported [15–19]. Kong and Zhang [17] and Zhang et al. [19] has used PE and MA-PP as precursor for synthesis of CNTs in which they have mixed PE and PP and ferrocene/Ni as catalyst in the stainless steel autoclave heated at 700 °C for 100 min. Jiang et al. [18] has used combustion method for synthesis of CNTs using Ni compound/organic-modified montmorillonite (OMMT) and polypropylene as a source. Multi-walled carbon nanotubes (MWCNTs) were efficiently synthesized by catalytic combustion of PP using Nickel compounds as catalysts in the presence of OMMT at 630–830 °C by Tang et al. [20]. Mass production of MWCNTs by means of pyrolysis of virgin or recycled

* Corresponding author. Tel.: +91 9322912462; fax: +91 251 2680800.

E-mail address: mishraneerajprakash@gmail.com (N. Mishra).

polyolefins was described by Arena et al. [21]. In an earlier effort by Zhou et al. [22], two step processes combustion and pyrolysis were used for synthesis of carbon nanomaterials using catalyst. In our case, all the catalytic reaction occurs in single stage CVD system in hydrogen and Ar gas ambient. Consequently, the residual gases such as aliphatic hydrocarbons were predominantly generated without any pollutant.

In the present work, we have made an attempt to exploit waste plastic as potential precursor for synthesis of CNTs using CVD. The synthesis of MWCNTs from waste PP plastics using Ni as a catalyst in CVD chamber at pyrolysis temperature 600–800 °C is reported. The samples were analyzed by means of Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and optical absorption spectroscopy. In addition, gas chromatography–mass spectrometry (GC–MS) was also performed to understand the type of the residual gas coming out during the whole process. Furthermore, we also investigated the variation in Raman spectra peak intensity by varying the laser wavelength in order to reveal the purity of sample.

2. Experimental

2.1. Sample preparation

Waste polypropylene, collected from Brihanmumbai Municipal Corporation (BMC) garbage disposal center, was used in the present work. The samples were washed, air-dried and shredded into small pieces. 10 g of shredded PP and 1 mg of nickel (Ni) catalyst were kept into quartz boat separately. Both were placed inside a long stainless tube of a furnace (Fig. 1). Ni catalyst was prepared from nickel nitrate by urea decomposition method [23]. Thermal treatment using electrical-heated furnace was performed under controlled H₂ (10 sccm) and Ar (90 sccm) gas atmosphere at fixed temperature with 1 h dwell time in the temperature range between 600 and 800 °C in order to catalyze the pyrolysis reaction. The ramp temperature of 30 °C/min was used during this whole reaction process until the required temperature (600, 700 and 800 °C, in our case) was achieved. The furnace temperature was allowed to cool down naturally once the reaction time was over in the atmosphere of 100 sccm Ar gas.

2.2. Process mechanism

Precursor molecule such as PP decomposes during interaction with the catalyst particle surface. This leads to the diffusion of carbon onto the surface of catalyst or through the catalyst particle [24,25]. When the catalyst gets supersaturated with carbon particle, growth/nucleation of CNTs begins with the precipitation of carbon on surface, exposed to reactant gases. It was reported that

when the concentration of carbon source such as polypropylene is too high, there is an over-abundance of decomposition and not enough precipitation resulting in amorphous carbon formation. Therefore, H₂ gas is essential for growth because it maintain the activity of the Catalyst. According to Baker et al. [25], temperature gradient (TG) must be created with vapor–liquid–solid (VLS) model while studying the growth mechanism of carbon nanotubes. Decomposition of PP takes place at around 400 °C and dissolution of carbon takes either over the surface of catalyst which is an exothermic reaction. After some time due to carbon accumulation on to the surface of catalyst, precipitation of C atoms takes place forming nucleating sites for proper growth of CNT which is purely an endothermic reaction. TG arises between the hot and cold regions during growth of CNTs, first is hot region where carbon atoms dissolves onto catalyst and the cold region, where carbon atom gets precipitated after diffusion of carbon on to the catalyst. These two regions of TG are significant for growth of CNTs. Initially TG provides heat flow through the particles that can support the transport of dissolved carbon atom from hot to cold region. Finally, the deposition of carbon atom over the catalyst leads to saturation and formation of precipitate. In this process cold region needs a lower carbon concentration compared to hot region. Due to hot region, continuous dissolution of carbon atom takes place over the surface of catalyst and that leads to large surface area for decomposition of more carbon atom since continuous deposition of carbon atom on to catalyst particles leads to catalyst poisoning. Therefore hot region helps to prevent catalyst poisoning and formation of amorphous carbon while cold region preferentially leads to the formation of CNTs, thus preventing the growth of graphene sheets.

2.3. Characterization techniques

Raman measurements were carried out using Jobin-Yvon Labram spectrometer. The laser excitation wavelength was 632.8, 532 and 488 nm with a spectral resolution of <1.5 cm⁻¹. All measurements were performed using a 50× objective and with power around 0.5 mW on the sample. The accumulation time was fixed to 50 s. Raman spectra were firstly baseline corrected with 3rd order polynomial and, thereafter, have been normalized to the max of the peak intensity.

The X-rays diffraction (XRD) pattern was recorded using Rigaku smatlab 9 kW (Japan) D/max-γAX-ray diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 1.54178 \text{ \AA}$).

Purified MWCNTs (15 mg) was dispersed in 40 ml of aqueous sodium dodecyl sulfate (SDS) surfactant (1 wt%) for 2 h of high-shear mixing. The mixture of CNT and SDS was then sonicated for 15 min. After sonication, samples were centrifuged at speed of 4000 rpm for 4 h. The solvent was then carefully decanted, leaving micelle-suspended nanotubes solutions at a typical mass concentration of 20–25 mg/l as our MWCNTs sample [26]. Decanted

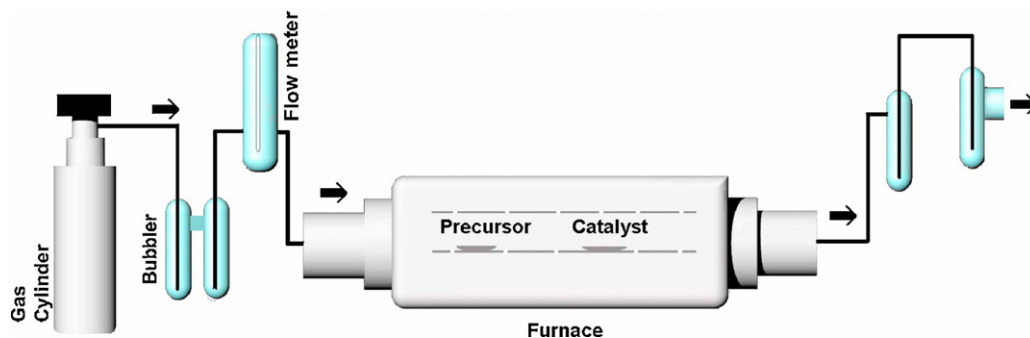


Fig. 1. Schematic diagram of unit used for synthesizing CNT by CVD method. In this diagram, a) gas cylinder, b) bubbler, c) flow meter, d) stainless steel, e) furnace, f) boat containing precursor, and g) boat containing catalyst.

Download English Version:

<https://daneshyari.com/en/article/1197425>

Download Persian Version:

<https://daneshyari.com/article/1197425>

[Daneshyari.com](https://daneshyari.com)