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Synthesis of branched, nano channeled, ultrafine and nano carbon tubes from PET wastes using the arc discharge method

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ABSTRACT

Upcycling polymer wastes into useful, and valuable carbon based materials, is a challenging process. We report a novel catalyst-free and solvent-free technique for the formation of nano channeled ultrafine carbon tubes (NCUFCTs) and multiwalled carbon nanotubes (MWCNTs) from polyethylene terephthalate (PET) wastes, using rotating cathode arc discharge technique. The soot obtain from the anode contains ultrafine and nano-sized solid carbon spheres (SCS) with a mean diameter of 221 nm and 100 nm, respectively, formed at the lower temperature region of the anode where the temperature is approximately 1700 °C. The carbon spheres are converted into long "Y" type branched and non-branched NCUFCTs and MWCNTs at higher temperature regions where the temperature is approximately 2600 °C, with mean diameters of 364 nm and 95 nm, respectively. Soot deposited on the cathode is composed of MWCNTs with a mean diameter of 20 nm and other nanoparticles. The tubular structures present in the anode are longer, bent and often coiled with lesser graphitization compared to the nanotubes in the soot on the cathode.

1. Introduction

Increased usage of synthetic polymers in recent years has resulted in the generation of a substantial amount of polymer based wastes (Hopewell et al., 2009; Zhang and Wen, 2013). These synthetic polymer based wastes are an environmental hazard (Barnes et al., 2009). Polyethylene terephthalate (PET) is one of such synthetic, non-degradable polymer, commonly used to make soft drink and water bottles, which contributes a significant volume of solid waste similar to that attributed to plastic bags. Recycling polymer wastes to a high quality serviceable product is not cost-effective (Cleetus et al., 2013), but they can be converted into useful technologically demanding nanomaterials such as carbon nanotubes (CNTs) (Altalhi et al., 2013). CNTs are being used in several technological applications such as support for catalysts in fuel cells (Li et al., 2003), fabrication of electronic devices (Bradley et al., 2003), membranes (Che et al., 1998), composites (Cooper et al., 2002; Haggenmueller et al., 2000), and sensors (Mirica et al., 2012).

Carbon nanotubes are tubular form of graphene sheets, classified as single walled carbon nanotubes (SWCNTs) (Iijima and Ichihashi, 1993) and multi walled carbon nanotubes (MWCNTs) (Iijima, 1991) based on the number of walls present in the nanotubes. MWCNTs are generally synthesized by arc discharge method (Iijima, 1991; Paladugu et al., 2005; Zhao et al., 1997) and chemical vapor deposition (CVD) (Colomer et al., 2000; Guzmán de Villoria et al., 2009) in large quantities. The arc discharge method is relatively cost effective and produces MWCNTs with fewer defects and in a larger scale (Ebbesen and Ajayan, 1992; Joseph Berkmans et al., 2013) compared to the chemical vapor deposition technique. Graphite is used as a precursor in conventional stationary cathode arc discharge method (Ando, 2010) to synthesize MWCNTs. Using this technique, button like soot containing MWCNTs and nanoparticles at the core of the soot surrounded by a hard graphitic shell (Ando et al., 2002) will be formed on the cathode while the anode is consumed. Flake like soot containing MWCNTs with no hard shells can be continuously produced in a larger scale in inert (Joseph Berkmans et al., 2013; Yumura et al., 1999) and open air atmospheres (Joshi et al., 2008) by modifying the stationary cathode into a rotating cathode. Earlier attempts were made to convert various types of plastic wastes into carbon nanotubes in the presence of catalysts using pyrolysing techniques (Kong and Zhang, 2007; Kukovitskii et al., 1997; Dosodia et al., 2009; Liu et al., 2011) as well as into hard carbon microspheres (Pol, 2010; Zhang et al., 2010). Here, we report a novel solvent-free and catalyst-free synthesis technique for the formation of ultrafine

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and nano solid carbon spheres (SCS) along with branched and non-branched nano channeled ultra fine carbon tubes (NCUFCT) and MWCNTs, from non-degradable PET wastes. The processing time in this technique is low and is typically less than a minute. This technique is simple, cost-effective and will provide an eco-friendly solution for the disposal of polymer wastes.

2. Experimental

Used mineral water bottles were collected and chopped into small pieces of size $10 \times 10\ mm^2$. 10 g of uniformly chopped pieces of PET waste were placed in a stainless steel container of diameter 150 mm and height 250 mm and pyrolysed at 815 °C for 20 min under a nitrogen atmosphere. The nitrogen gas was flushed through the container with a pressure of 0.1 bar throughout the heating and cooling cycles. Brittle black polymer char obtained from the container after pyrolysis was crushed into fine powders using a mortar and pestle.

Schematic diagram of arc discharge method for producing ultra-fine and nanostructures of carbon from PET waste is illustrated in Fig. 1. A hollow graphite rod (99% purity) of length 150 mm, outer diameter 12 mm and inner diameter 8 mm with a hole depth 130 mm, and density 1.8 g/cc was used as an anode for the rotating cathode arc discharge setup which was used to produce CNTs described elsewhere (Joseph Berkmans et al., 2013; Joshi et al., 2008). The experiment was carried out in nitrogen atmosphere at a pressure of 500 Torr for 1 min. Approximately 5 g of the crushed PET char was tightly packed manually in the hole of the anode and continuously arced for a minute. Black soot formed inside the hole of the anode and was scraped out, and weighed approximately 1.2 g. After arcing the anode was cut into pieces of equal length of 25 mm from the arcing tip. The first two pieces (up to a total length of 50 mm) were labeled as Region I and Region II respectively, and the rest labeled as region III as shown in Fig. 1. Soot inside the cut pieces were scraped and analyzed. Another hard black flake like soot deposited on the rotating cathode disc was scraped out continuously during deposition and collected on a plate inside the chamber. The weight of the scraped cathode soot was approximately 0.75 g. The quantity of the soot is reproducible with the same set of experimental parameters.

The morphology of the nanotubes was characterized by FEI Inspect F field emission scanning electron microscope (FE-SEM) with an accelerating voltage 30 kV. A small quantity of the soot obtained from the anode and the cathode was dispersed in ethanol using an ultrasonicator with a frequency of 25 kHz for a minute. A drop of the dispersed sample was placed on a lacey carbon coated copper grid and analyzed using a Philips CM12 transmission electron microscope (TEM). WITec alpha 300 R Raman spectrometer with a laser wavelength of 532 nm was used to perform the Raman spectroscopy analysis on the soot. X-ray diffraction (XRD) analysis was performed on the PET char and the soot using PANalytical X-ray diffractometer with Cu Kα radiation of wavelength 1.54 Å. Temperature of the outer surface of the anode at different regions (shown in Fig. 1) was measured using a Raytek, Marathon Series MR1s pyrometer.

3. Results and discussion

Flakes of pyrolysed PET char, dark brown and black in color are shown in Fig. 2a. The flakes are very brittle and easily crushable into powders (Fig. 2b) using mortar and pestle. No interesting morphologies such as spheres or tubes are identified in the pyrolysed char by electron microscope analysis. Initially, the tip of the graphite anode stuffed with the polymer char evaporates and establishes an arc between the electrodes. Subsequently, the charred polymer inside the anode hole is co-evaporated along with the graphite anode (Fig. 2c) at the arcing temperature and deposited as hard soot containing black and grey colored regions on the rotating cathode disc (Fig. 2d). The PET char was converted into soot containing ultra fine sized SCSs and tubular structures inside the anode as shown in Fig. 2c and it can be easily removed from the anode. While arcing, the temperature measured using a pyrometer

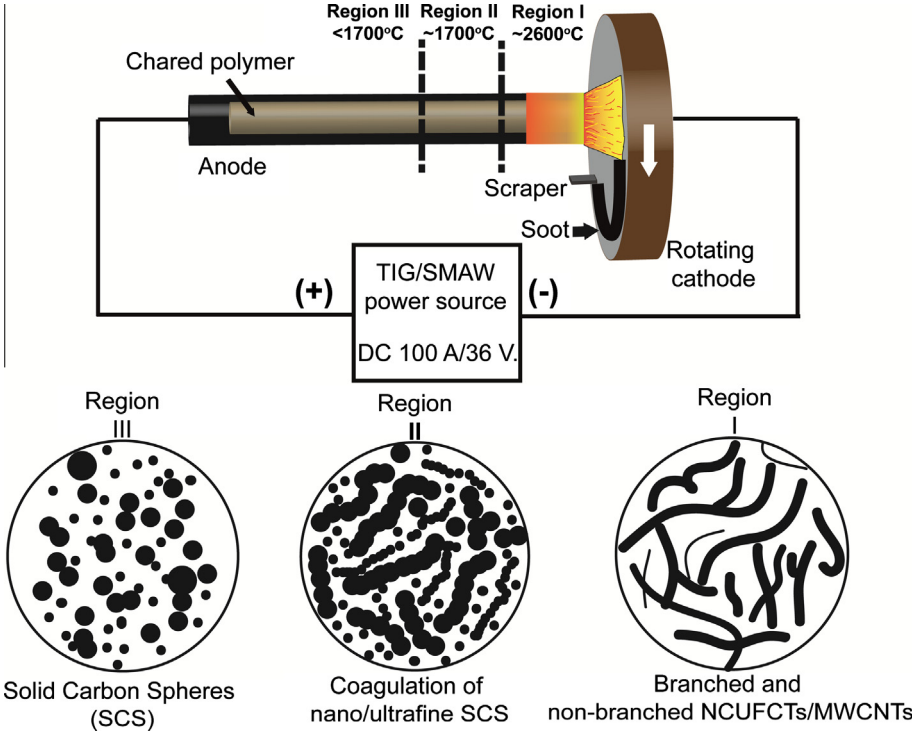

Fig. 1. Illustration of the formation of NCUFCTs, MWCNTs and SCS from PET waste using the arc discharge technique.

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