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Flame synthesis of carbon nano onions using liquefied petroleum gas without catalyst

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ABSTRACT

Densely agglomerated, high specific surface area carbon nano onions with diameter of 30–40 nm have been synthesized. Liquefied petroleum gas and air mixtures produced carbon nano onions in diffusion flames without catalyst. The optimized oxidant to fuel ratio which produces carbon nano onions has been found to be 0.1 slpm/slpm. The experiment yielded 70% pure carbon nano onions with a rate of 5 g/h. X-ray diffraction, high-resolution electron microscopy and Raman spectrum reveal the densely packed sp^2 hybridized carbon with (002) semi-crystalline hexagonal graphite reflection. The carbon nano onions are thermally stable up to 600 °C.

1. Introduction

Carbon nano onions (CNO) are 10–45 nm spherical shaped high surface area [1,2] graphitic carbon. These particles are called "nano onions" because of the arrangement of deformed graphitic concentric layers in circular pattern, which resembles like that of onion. The presence of non-covalent interactions like Van der Waals forces, π–π stacking [3–5] in nanoparticles or nanostructured materials results in agglomeration. This causes the onions to form a necklace like pattern when their size is <1 μm. Carbon nano onions can be classified into different types based on the size, morphology and shapes. First, spherical particles made of solid, hollow or core- shelled. Second depending upon their texture they are classified as concentric, stellate or random layered. Third, depending on the dimensions they are categorized as well graphitized onion (2–20 nm), less graphitized onion (50 nm –1 μm) and carbon-beads (>1 μm) [6]. Carbon nano onions are being explored for its novel gas storage [2,7,10], microwave frequency range [8], chemical and physical [9], biological [7,10], lubrication [2,10,11] and electrochemical properties due to their unique structure [12]. Due to their specific size and catalytic property they can be regarded as nano reactors [12]. Carbon nano onions have been synthesized using various processes like CVD, laser ablation, plasma arc discharge, shock compression and pyrolysis [1]. Carbon nano onions have also been synthesized using counter diffusion flames in the presence of nascent substrate catalyst with 5% ethylene (C_2H_4), 15–45% methane (CH_4) and oxygen (O_2) 50% [9,13]. Carbon nano onion production has been enhanced acoustically in flame synthesis [13]. Carbon spheres as termed by Jin et al. [14] have been obtained by using direct pyrolysis of different hydrocarbons like toluene, styrene, benzene, ethane and cyclohexane in the absence of catalyst in the range of 900–1200 °C. They observed that by increasing the temperature from 800 to 1200 °C the yield of carbon spheres increased from 95 mg to 250 mg/h [14]. Also they observed that catalyst is required for CNT synthesis but not for carbon nano spheres. Liu and Li [14,15] termed their nano onions as carbon nanocapsules and have produced them in an oxy acetylene flames with oxidant to fuel (O/F) ratio of 0.25 slpm/slpm in the absence of catalyst. The yields of as-prepared carbon nanocapsules have been observed to be around 12 g/h. Choucair and Stride [16] synthesized carbon nano onions by igniting the naphthalene vapors continuously to its flash point (79–87 °C) in air under an open flame. They observed that the CNO yield has been around 0.4 g/h. Onion like carbon nanoparticles have been produced without catalyst in a combustion chamber of a gas turbine engine using 9:1 propane/butane mixture at an O/F ratio of 0.833 slpm/slpm [17]. Choi et al. synthesized catalyst free onion like shell shaped carbon nano particles with continuous bents of graphene layers in an acetylene flame at a rate of 1 g/h under laser irradiation [18]. They released acetylene at a rate of 0.1 l/min mixed with nitrogen (0.35 l/min), hydrogen (1 l/min) and oxygen (0.5 l/min). They continuously irradiated the bulk quantities to an external radiation using infrared CO_2 laser.

In the present work we have used flame reactor to synthesize carbon nano onions in liquefied petroleum gas (LPG)/air flames without any catalyst/acoustic/laser irradiation. LPG (Propane/Butane mixture 1.4:1), flow rate (0.4 slpm), and air flow rate (0.2 slpm), where the

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oxidant to fuel ratio is 0.1 slpm/slpm, have been used. The experimental study yielded 70% pure CNOs with a production of 5 g/h. During flame synthesis, carbon nano onions are formed in the soot. The paper also discusses the growth mechanism and factors affecting the growth of carbon nano onions in flame.

2. Experimental

Experiments have been carried out in the O/F ratio range of 0.05 to 0.1 slpm/slpm in a flame reactor. Carbon nano onions have been obtained at an O/F ratio of 0.1 (slpm/slpm) with flame temperatures in the range of 800–950 °C. Design details of the flame reactor is published elsewhere [19,20]. The experiment is carried out by releasing measured quantities of liquefied petroleum gas (0.4–0.85 slpm) along with a constant flow of air (0.2 slpm) into the flame reactor chamber through a burner. LPG enters the central pipe (ID = 4 mm) and air enters the middle pipe (ID = 8 mm) of the burner. Calibrated Rota-meters have been used for measuring the flow rates. After ignition of hydrocarbon and air mixture by an electric spark plug the partial combustion reaction takes place and produces soot containing carbon nano onions. The flame reaction is carried out at 900 °C and 1 atm pressure. Flame temperature is measured by K-type thermocouple. The experiment has been carried out for about 30 min. The soot and carbon nano onions have been collected on a glass fiber filter (Axiva, GF/AF) with the aid of vacuum pump. The amount of "as prepared soot" has been weighed after cooling and is found to be ~3.56 g. The soot is subjected to heat treatment in the presence of air at 600 °C for half an hour to remove amorphous carbon. The remaining amount after heat treatment is 2.50 g. The CNO purity (%) is calculated by Eq. (A.1).

$$\%\ \text{CNO purity} = \frac{\text{The amount of CNO remained after heat treatment}}{\text{Total amount of soot subjected to heat treatment}} \times 100 \quad \text{(A.1)}$$

The soot has been analyzed for crystallinity, morphology, quality, surface area and thermal stability using XRD, SEM, HREM, Raman, BET surface area analyzer and TGA respectively. The X-ray diffraction study has been carried out using PW1830 Phillips X-ray diffractometer using Cu–K_α, radiation with a (λ) wavelength of 1.5406 Å operated at 40 kV, 30 mA. The data has been collected in the 2θ angle range of 10–80° with a step size of 2° min^{-1}. The sample has been further analyzed using SEM for surface morphology using Phillips XL 30 Series field emission scanning electron microscope operating at an accession voltage of 25 kV under vacuum (10^{-5} mbar). The sample has been analyzed by sticking the sample powder on a double sticking conducting carbon tape affixed on an aluminum stub. High-resolution transmission electron microscope (FEI-TECNAI G20, Netherlands) operated at 200 kV has been used for TEM and HREM analysis. A very small amount of the sample has been sonicated in 5 ml of ethanol for 5 min at 75% power with sonicating frequency of 33 kHz. Later a drop of the sonicated solution was added on to the copper grid and analyzed. Raman spectroscopy of carbon nano onions sample has been carried out using HORIBA Jobin Yvon, T64000 Raman spectrometer equipped with 514.5 nm Argon laser. The scan has been carried out in the range of 950–2000 cm^{-1} with the laser power of 3 mW to analyze the G and D-bands of the obtained carbon nano onions. The surface area of carbon nano onion sample has been obtained using SMART SORB 93 BET surface area analyzer at a regeneration temperature of 200 °C for 2 h with N_2 purging. Thermal analysis of the samples has been investigated using thermal analyzer (EXSTAR-6000 TG/DTA AST-2) at a rate of 10 °C/min in the presence of air. The required amount of the sample has been taken in a platinum pan along with the company provided standard alumina in another pan as reference. The sample has been assessed for its quality by the function of its weight loss occurring due to the increasing rate of temperature.

3. Results and discussions

The XRD (Fig. 1) shows a single semi-crystalline peak, but has a vivid amorphous broadening. A strong peak (002) reflection at 2θ angle 25.9° matches with a hexagonal system (ICDD-JCPDS No. 75–1621) attributed to graphite [21,22]. The broadening of the peak can be an indication of a widespread disordering of the structure due to the smaller size [22] of the carbon nano onions as observed in the electron micrographs. The XRD also shows a very low unresolved intensity peak between 40 and 50° 2θ angle, this may be attributed to the disordered structure of the graphene rings within the nano onions. The XRD result is in agreement with the work published by Han et al. [22], Mordkovic et al. [23] and Zhu and Liang [24]. The SEM image (Fig. 2) shows the presence of large cottony mass of clustered amorphous soot along with few carbon micro/nanofibers obtained with varying fuel flow rates between 0.4 and 0.85 slpm. Fig. 2a shows the presence of clustered and compact flake like layer of cottony soot produced at a fuel flow rate of 0.4 slpm (i.e. O/F : 0.105 slpm/slpm). The soot produced at a flow rate 0.5 slpm (i.e. O/F : 0.08 slpm/slpm) of fuel reveals the cottony structure of soot at higher magnification as visualized in Fig. 2b. As the fuel flow rate is increased from 0.6 (i.e. O/F: 0.07 slpm/slpm) to 0.85 slpm (i.e. O/F: 0.05 slpm/slpm), the presence of carbon microfibers (Fig. 2c–d) and a mixture of micro- and nanofibers (Fig. 2e) have been observed. The sample has been analyzed further by TEM and HREM to resolve the topology and the structure of the soot. Fig. 3a shows the TEM image of the agglomerated carbon nano onions produced at a fuel flow rate of 0.4 slpm with size varying between 30 and 40 nm. The same has been focused for a higher magnification using an HREM. Fig. 3b shows HREM image of the carbon nano onions produced at 0.4 slpm. The presence of circular deformed patterns of graphite rings within the soot structure can be clearly seen, attributing it to its non-crystalline nature and planar deformations occurring during the synthesis process. The inset in Fig. 3c shows the SAD pattern indicating the semi-crystalline nature, dominated by the amorphous phase. Fig. 3d and e shows TEM and HREM images of the sample produced at 0.5 slpm of liquefied petroleum gas. The HREM image clearly shows the presence of denatured and compact graphene layers closely packed to form a quasi-spherical structure. The Raman spectrum wavelength ranges from 800 to 2000 cm^{-1}. Raman spectrum (Fig. 4) strongly shows a broadened peak with high similarity to disordered graphite plane around 1348 cm^{-1} contributing to D band [1,24]. A high frequency narrow band at 1599 cm^{-1} represents the E_{2g} mode contributing to the first order [24] graphitized zone in G band. Also the in-plane stretching and vibration of the sp^2 C–C bond is the signature characteristic of the G-band [21]. The I_D/I_G ratio of the carbon nano onions is ~0.95, which reveals that the onions are partially

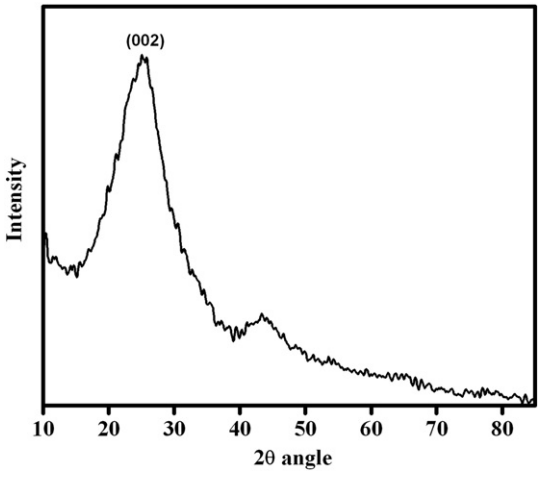

Fig. 1. XRD of flame synthesized carbon nano onions.