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In situ lithium intercalation of carbon nanorods using flame synthesis

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ABSTRACT

Intercalation of nanocarbons with alkali earth metals like, K, Mg, Li is known to enhance overall gravimetric hydrogen storage to 10–15 wt.%, which has great potential for application in energy systems. In this paper we report the lithium intercalation of carbon nanorods by an *in situ* method using meth-oxy-acetylene flames in the presence of lithium acetate as a precursor, under atmospheric conditions. The morphological analysis of carbon nanomaterials using SEM and TEM suggested that they have diameter around 50–200 nm. XRD studies indicated the presence of Lithium carbide (LiC) peak systems and crystal configurations, which are typical chemical signatures of lithium interaction with carbon and oxygen at high temperatures. Raman spectroscopy analysis revealed that the Lithium ions attack the inner edges of the planar structure resulting in the formation of the surface buds which increases the width of the D band and the downward shift in G band.

1. Introduction

The research field of rechargeable lithium batteries has boomed due to the increased demand from the portable market [1] of electronic devices such as cellular phones, portable cameras, notebook computer [2] and hydrogen storage [3–5]. In the recent years there have been number of reported attempts for intercalating lithium [6–10] in carbon nanomaterials. Nanotubes are special because they have small dimensions, a smooth surface topology, and perfect surface specificity, since only the basal graphite planes are exposed in their structure. Based on the applications, carbon nanomaterials find themselves to be a promising intercalating recipient for Li-intercalation. In this paper we report the direct Li-intercalation of carbon nanorods using flame synthesis in the presence of Lithium acetate as a precursor, since flame synthesis is an attractive method to produce carbon nanorods in bulk quantities for commercial uses [11–13]. It can be a very effective process since the fuel serves as both the heating and the reactant source and the synthesis process is highly scalable.

2. Experimental

Carbon nanorods (CNR's) were synthesized by flame synthesis method. In our previous work [14] we produced CNR's using methane (0.6 slpm), (slpm = standard litre per minute), oxygen (0.1 slpm) and acetylene (0.5 slpm) in the absence of catalyst, which were produced in good amounts. The same experiment is repeated using lithium acetate as a precursor, which gets directly intercalated in the soot produced by meth-oxy-acetylene diffusion flame. The flame reactor (Fig. 1) consists of a burner through which the measured flows of fuel and oxidant enter the reactor chamber. The burner consists of three concentric SS 316 tubes of thickness 1 mm each. The outer diameter of central tube is 4 mm and the spacing between the successive tubes is 2 mm. Partial combustion reaction takes place in the flame where the soot containing nanorods are produced. The soot and carbon nanorods formed in the flame are collected on a glass fiber filter (Axiva, GF/AF) by the aid of vacuum pump. The filter paper is placed in a filter holder, which is made up of SS 304. It is held at 300 mm above the burner face so that the temperature of filter would not exceed 300 °C so as to prevent the damage of filter and paper. The hot effluent gases are cooled by a water cooler. Reactor operates under atmospheric pressure.

The flame is encased in a top open 300 mm diameter steel chimney to shield the flame over its entire length and to prevent air entrainment from the surroundings. A toughened glass viewport allows visible monitoring of the combustion process. Check valves are installed right before the burner to avoid backflow of gases. Flame arrestors are provided in oxidant/hydrocarbon lines to avoid explosions. Tubing used for all gases is designed to withstand explosions. Two stage gas regulators are used for reducing the gas pressure to the reaction conditions [14]. In this method,

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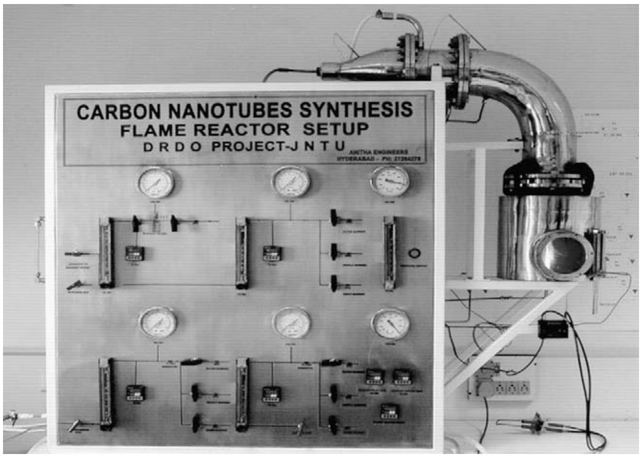

Fig. 1. Flame synthesis unit for production of nanocarbons and nanorods.

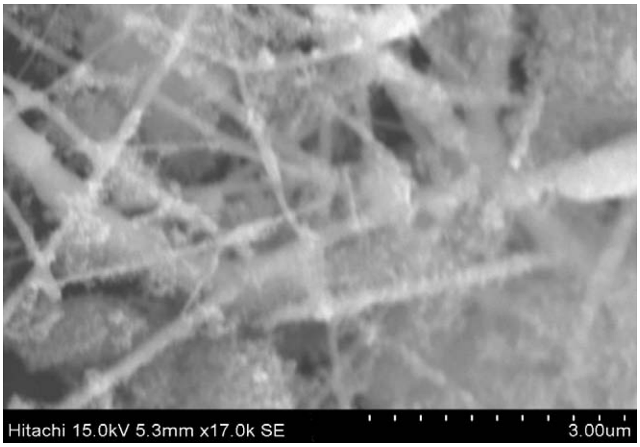

Fig. 2. SEM image of flame synthesized Li-intercalated nanorod.

lithium acetate (0.3 g) is dissolved in the reagent vessel containing methanol (100 ml), where it gets vaporized at 120 °C using a heat tracer. This is done to make sure that, the Li-methanol solution is in vapor phase all throughout the tubing. The lithium acetate vapors then travel to the inner burner through the heat traced piping. The vapors are directly released into the burning flame resulting in the bright red coloring of the flame where the lithium oxide after reduction gets intercalated with the nascently developing nanorods & nanofibers with a maximum temperature of 665 °C. The oxidation of the lithium acetate takes place directly in the flame at higher temperatures ($\geqslant$320 °C) [15] resulting in the formation of a nanometal oxide (Li_2O) [16] rather than carbonate because of high temperatures. Further heating results in the deoxidation of Li_2O to lithium metal which later forms lithium carbide systems like LiC [17,18] and more dominantly Li_2C_2 [19] at higher temperatures (640 °C) within the flame after associating itself with the nucleating carbon particles. The intercalated soot is captured on the glass fiber filter paper (Whatman GF/A) with the aid of the vacuum pump. The collected as-prepared samples were then air oxidized at 600 °C for 90 min to remove impurities in the form of amorphous carbon. The morphology of the sample is then characterized by SEM and TEM, whereas the crystal structure and the presence of lithium carbide crystal peaks/unit cells were characterized by XRD. Raman analysis is performed to assess the nature and quality of graphitization of the lithium intercalated CNM's.

3. Results and discussion

3.1. Scanning electron microscope (SEM)

The SEM analysis is performed on Li-introduced methoxy-acetylene-flame purified sample using Phillips XL 30 Series Microscope as given in Fig. 2. The scan shows a image of nanorods. The nanorods mostly appear straight with its diameter varying between 50 and 200 nm and extending several micrometers in length.

3.2. Transmission electron microscope (TEM)

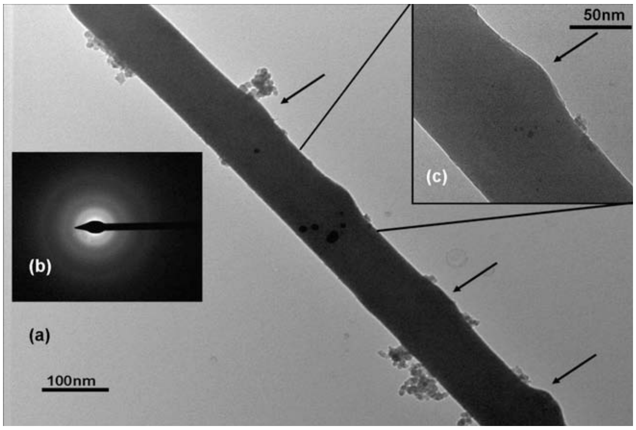

Fig. 3. (a) TEM image of lithium intercalated CNRs with four buds like projections (black arrows). (b) The inset image shows SAED pattern depicting amorphous and particulate nature of the sample. (c) Inset image showing a higher magnification of the bud, which is presumably a point of lithium attack.

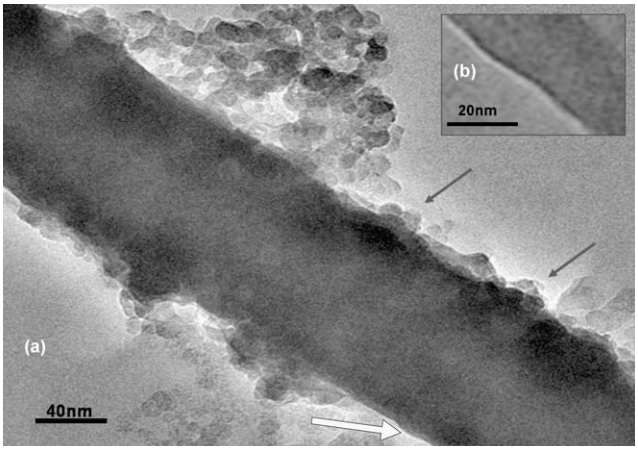

Fig. 4. (a) TEM image of lithium intercalated CNRs with multiple buds like projections (black arrows). (b) Inset image showing a higher magnification and a higher resolution of the bud present at the lower portion of the CNR, which is presumably a point of lithium attack (block arrow) on the edge.

Figs. 3 and 4 show the TEM (Hitachi H7500) and HRTEM (crystal structure) micrograph of lithium introduced flame synthesized sample possibly a Lithium carbide nanorod. From the TEM analysis, Fig. 3a shows lithium intercalated CNRs with four buds like projections (black arrows) expected to be the site of lithium attack for the intercalation. Fig. 3b inset image shows SAED (Selected Area Electron Diffraction) pattern showing amorphous and particulate nature of the sample, whereas the Fig. 3c inset image shows a higher magnification of the bud, from the image the nanorods diameter is found to be around 90 nm with length approximately stretching greater than 900 nm, which we presume to be nascent