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Synthesis of Carbon Nano-structures by Low-Temperature Hydrothermal Technique

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ABSTRACT

Carbon nanostructures (CNSt) have been prepared by a Hydrothermal deposition technique based on the polymer Polyethylene glycol (PEG-20.000Mw-$(C_2H_4O)_{n+1}H_2O$*, bp:56-63°C) dissolved in D.I. water and Ethanol alcohol of a new carbon sources materials mixed with* $PdCl_2$ *as a catalyst mixed with Sodium hydroxide (8gm NaOH) using Parr reactor at temperature (190°C). A detailed study of how the synthesis parameter such as growth temperature affects the morphology of the carbon nanostructures is presented. The obtained (CNSt) are investigated (in Georgia Institute of Technology-MSE, Georgia, USA) by scanning electron microscope (SEM), transmitting electron microscope (TEM), X-ray diffraction (XRD) and Raman spectroscopy. It is observed that at (190 °C), normal CNTs are formed multi-walled carbon nanotubes (MWCNTs) and carbon nanosheets (CNS) but in little bit amount. Coiled carbon nanotubes (CCNTs) were obtained as main products high pure MWCNTs with lengths of (2–5* μm*) and diameters of (60±20 nm) could be synthesized at as low temperature as (190 °C).*

Keywords: Synthesis of Carbon Nano-structures, Hydrothermal Technique.

INTRODUCTION

Nanostructured materials have attracted intense research interest over the past few years, as they provide the critical building blocks for the booming nanoscience and nanotechnology industries. Ever since the discovery of fullerene in 1985 [1] and carbon nanotubes (CNTs) in 1991 [2], carbon nanoscale materials have been reported to be very attractive candidates. Various forms of carbon nanomaterials have been reported such as fullerenes [1], carbon nanotubes (single-walled and multi-walled) [2,3], carbon nanofibres [4], carbon nanohorns [5], carbon nanocapsules [6], carbon nano-onions [7], carbon nanospheres [8], helical carbon nanotubes (HCNTs) [9], ferromagnetic-filled carbon nanotubes[10] and carbon nanosheets[11]. Due to their unusual properties, a wide variety of scientific and technological research has been focused on the use of nanocarbons, in terms of their potential applications as well as their large scale synthesis. For the production of nanocarbons, there exist several techniques such as arc discharge [2,3], laser vaporization [1], hydrocarbon pyrolysis [12], high-pressure catalytic decomposition of carbon monoxide (HiPCO) [13], pyrolysis [14,15], flame synthesis [13], chemical vapor deposition(CVD) [16], plasma-enhanced CVD (PECVD) [17], electrophoretic deposition (EPD)[17] and Hydrothermal technique[18],etc. Each and every synthesis method is related with obtaining adequate active atomic carbon species or clusters from the carbon source materials and assembles them into nanocarbons in the presence of or without catalyst. The commonly used gaseous hydrocarbons as carbon source materials are acetylene, methane, n-butane or butane, propane, and ethylene. Moreover, liquid hydrocarbons are also used extensively for the synthesis of carbon nanostructures. The advantage of liquid hydrocarbons as carbon source materials is that they are cheaper and controlled insertion of liquid additive can be introduced into the reactor where they form active carbon species for carbon nanostructure’s growth. Different carbon nanostructures have been obtained from different carbon source materials. Many parameters, such as pressure, reaction temperature, gas composition and flow rate, duration of treatment, catalyst natures and sizes, have been reported to affect the nature of the carbon species in the resulting material [11,18–24]. However, the effect of the above parameters for the growth mechanism of carbon nanomaterials is still unclear. The commonly used liquid hydrocarbons as carbon source materials are benzene (C_6H_6, bp:79–80.5 ºC), toluene (C_7H_8, bp: 110–111 ºC), n-hexane (C_6H_{14}, bp: 66–70 ºC), cyclohexane (C_6H_{12}, bp: 80–82 ºC), methanol (CH_3OH, bp: 64–65 ºC), ethanol (C_2H_5OH, bp: 78 ºC), xylene (C_8H_{10}, bp: 135–145 ºC), and styrene (C_8H_8, bp: 145 ºC), etc. The liquid carbon source materials with low boiling points can be pyrolyzed relatively at low temperature to obtain the active carbon species for the growth of CNTs[19,20]. This has inspired to look for a new carbon source material such as polymer Polyethylene glycol(PEG-20.000Mw/$(C_2H_4O)_{n+1}H_2O$,bp: 56-63°C) dissolved in water and alcohol, which is having lower boiling point compared to most of the above mentioned carbon source materials. There is a lower risk of contaminating delicate electronics during processing and handling because of different characteristics. Carbon nano-tubes have antistatic properties in PEEK, PPS, PC and other polymers at a low level of addition and a precise control of electrical conductivity and therefore volume and surface resistance due to superior dispersion. To gain maximum benefits from CNT reinforcement in polymer composites, it is critical to exfoliate the entangled structure into an individually dispersed one[1,19]. The utilization of nanocarbons in science and technology merely depends on the efficient production of vast CNSt by a simple and low cost method. This has also invoked us to search for a simple synthesis method for the production of good quality various carbon nanostructures on a large scale. Here, report the various CNSt prepared by pyrolyzing Polyethylene glycol (which is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen (or any halogen). It involves the simultaneous change of chemical composition and physical phase, and is irreversible) with the help of $PdCl_2$ as a catalyst mixed with Sodium hydroxide (8gm NaOH) using Parr reactor at (190 ºC)[24,25]. The obtained various CNSt are attributed to the preparation temperature effect with good reproducibility.

MATERIALS AND METHODS

In a typical synthesis, 90 mL ethyl alcohol, 10 mL distilled water, 8 g NaOH and 3 g polyethylene glycol (PEG-20.000Mw-$(C_2H_4O)_{n+1}H_2O$) supported from (VWR Company), were added to a 250 mL flask. The mixture was stirred with a magnetic stirrer for 30 min. Then prepared palladium chloride solution by dissolving 0.1 g $PdCl_2$ in 10 mL distilled water as a catalyst, which is stirred with a magnetic stirrer for 1 h. After that mix all of them in 125 mL Teflon Jar and stirred again with a magnetic stirrer for 30 min. Finally, transferred to a Parr reactor (Parr Company, Manufactured locally in Georgia Institute of Technology-MSE, Georgia, USA) as in fig.1, with a capacity of 250 mL. The Parr reactor was sealed and then kept at 190 °C for 24 h in a furnace, and then cooled down to room temperature. The products were washed with alcohol and distilled water for several times, and then dried in a vacuum oven at 65 °C for 12 h .

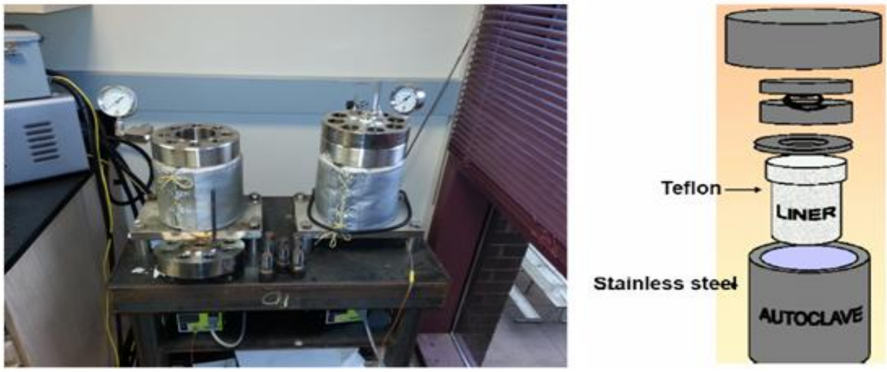

Fig.(1): Schematic of Autoclave Parr (Manufactured locally in Georgia Tech.).

RESULTS AND DISCUSSION

As shown in fig.2 a, it became carbon in its various forms is a precipitate formed gray and black color because of the cofactors of the reaction, which created a suitable environment for the growth of carbon structures by the role of Palladium chloride, which represents a new role for these two factors in determining the color of the emulsion dark brown and very thick by hydrothermal technique, This preliminary result, consistent with the findings of the other researchers[23-25]. Fig.2 b , c represents the forms of the final product (powder) with a dark gray color tends to blackness. Where was the liquidation of the emulsion resulting from the synthesis by the filter under the influence of vacuum to isolate the sludge from the solution and then purifying the product thick by ethanol and distilled water for five times under the influence of ultrasonic device for half an hour and drying of the product inside the oven under vacuum for 12 h at 65 ºC, this consistent with the findings of the other researchers[22,25,26].

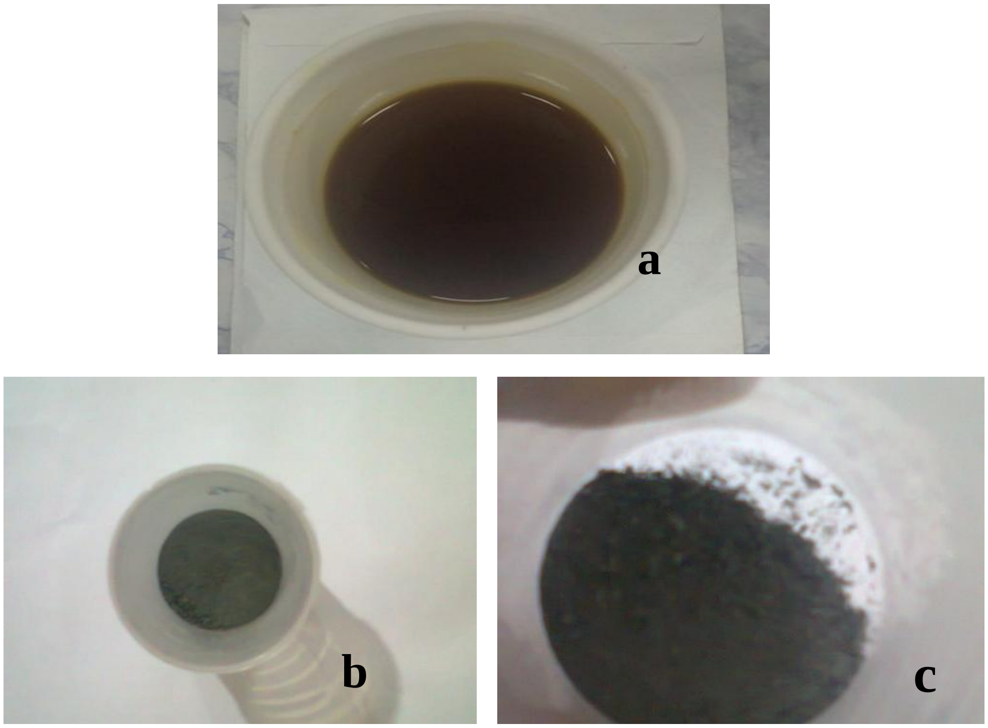

Fig.2. Images of: a .Resulting emulsion of preparation; b & c.final product of powder.

In Fig. 3 a, b , c show the SEM images (Zeiss ULTRA 60 FE-SEM, at the Georgia Tech./MSE.-USA) of the as-synthesized CNSt and MWCNTs at different magnifications. It can be seen that the MWCNTs look like a coil carbo nanotubes (CCNTs) have outer diameters ranging (20-100 nm) and inner diameters ranging (4-8nm). It is worth pointing out that the diameters of the as-prepared MWCNTs by the current low-temperature hydrothermal route are much smaller than those prepared by high-temperature hydrothermal method[12]. The length of the MWCNTs is up to several micrometers.

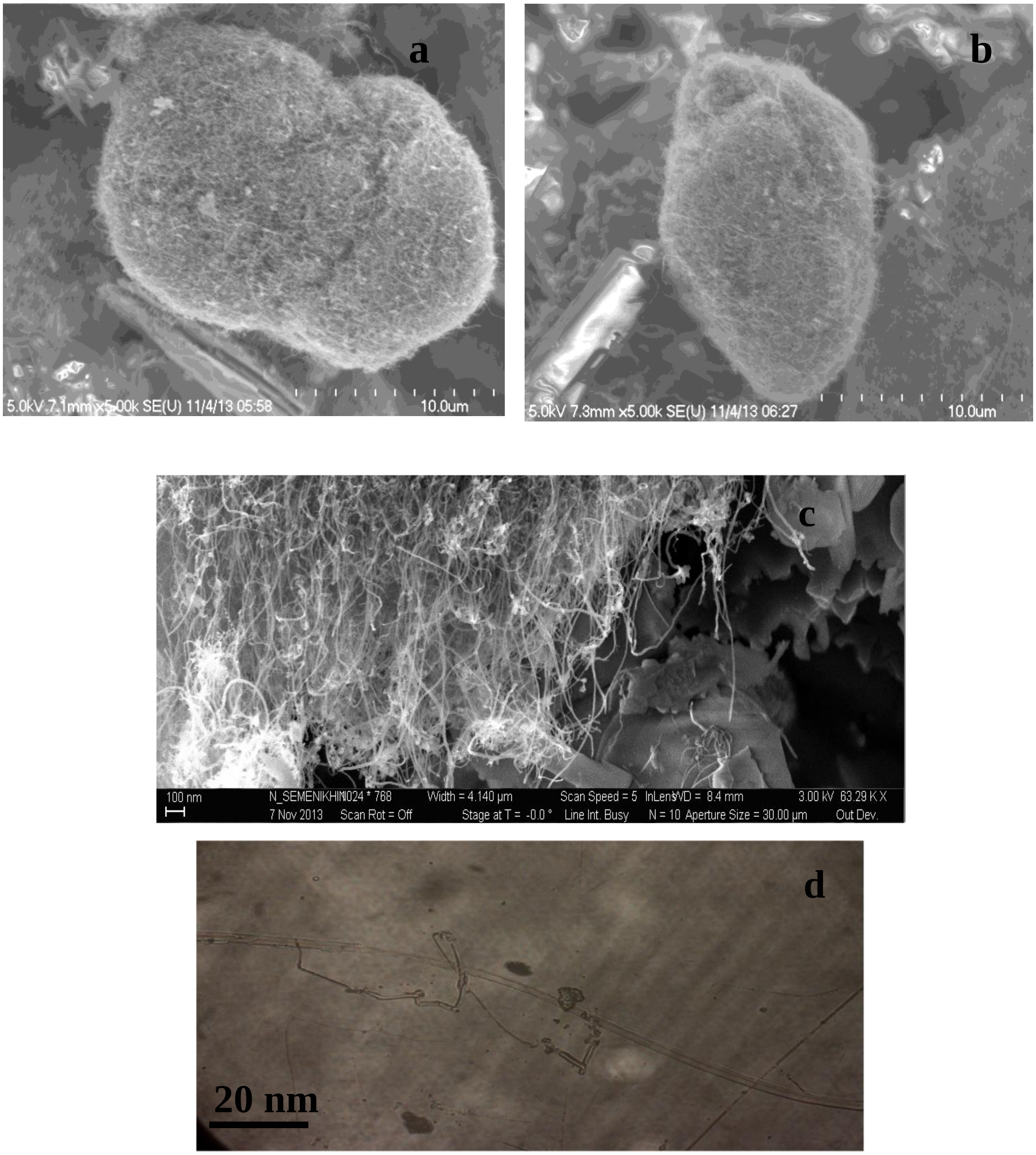

Fig.(3): SEM Images of: a, b & c, Carbon nanostructures (CCNTs & CNSs); d, TEM Image of CNTs.

From the point of view of chemistry, the compound is stable and by Le Chatelier's principle. which if a chemical system at equilibrium experiences a change in concentration, temperature, volume, or pressure, then the equilibrium shifts to counteract the imposed change and a new equilibrium is established, then will disintegrate chemical compound $C_2H_5O^-$ Na+ to $C_2H_5O^-$ and Na^+, when it is mixed with the PEG presence of heat and pressure will produce the chemical compound, this case is called polymerization. It is a process of reacting monomer molecules together in a chemical reaction to form polymer chains or three-dimensional networks. There are many forms of polymerization and different systems exist to categorize them. So, will replaced OH^- with $C_2H_5O^-$ due to the high temperature and pressure and will be formed Etheric bond because the beginning of the interaction. There for, the required time is not enough to produce chain of MWCNTs or CNSt, but important thing is the increase in temperature leads to an increase of particle size and then in the small surface area and thus less efficient product.

The yield of the as-prepared MWCNTs estimated by TEM observation (JEOL 100CX II (TEM) 100kV, at the Georgia Tech./MSE.-USA) shows that this Multi Walled Carbon Nano Tubes (MWCNTs) and Carbon Nano Sheets (CNSs) have fairly good graphitization, corresponding to the(002) plane of graphite carbon [13,14,16,25]. A further investigation on the microstructures of the as-prepared MWCNTs was performed by TEM, fig. 3 d shows a typical TEM image of a bundle of MWCNTs, indicating that the MWCNTs have clear graphite layers with defects aligned to the tube axis. The TEM observations also show that the MWCNT have open- and closed-end structures and so little bi of CNSs. In the absence of PEG, no CNTs and CNSs were observed, indicating that the CNTs and CNSs were formed by the decomposition of PEG. Our experiments also indicated that a NaOH aqueous solution with high concentration was essential for the formation of the MWCNTs and CNSs. There were no CNTs or CNSs detected by the TEM observations when the reactions were conducted in aqueous solutions with low NaOH concentration. We propose that the role of high concentration NaOH during the formation of MWCNTs and CNSs is most likely as a chemical activation agent to activate PEG. At the present hydrothermal conditions, the activated PEG becomes easy to decompose into element carbon and other products. The (C) with active surfaces is probably preferential for the growth of CNTs under the hydrothermal conditions. The X-ray diffraction pattern (XRD) of the product was determined on X-ray diffractometer equipped with graphite monochromatized Cu-Ka radiation as in fig. 4.

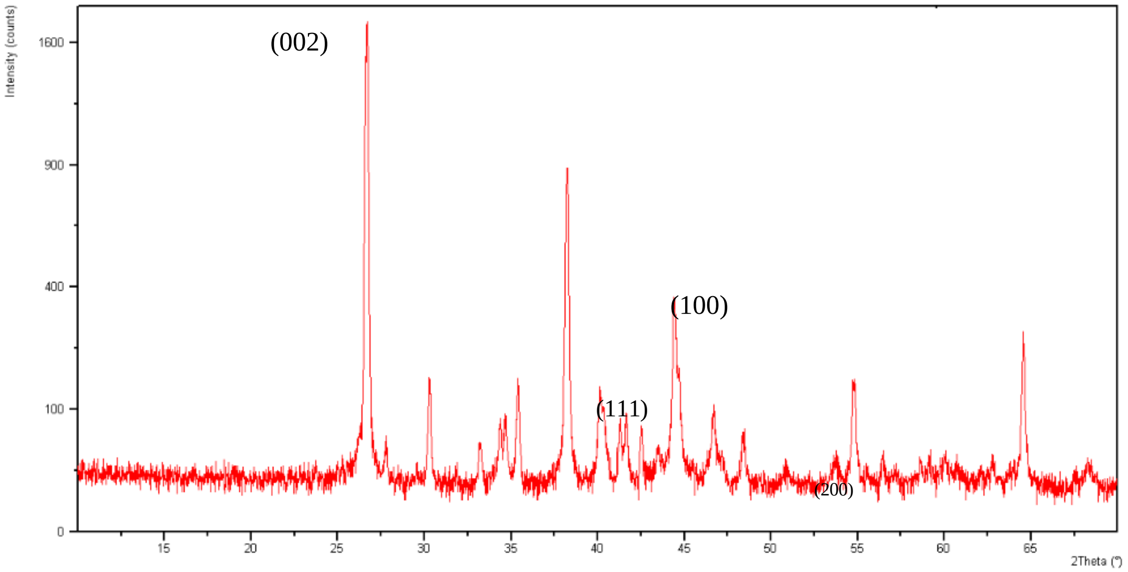

Fig.4. XRD pattern of Carbon Nano-Structures.

The X-ray powder diffraction patterns were performed to follow the reaction process. Fig.4 shows the XRD pattern of the product. The peaks can be indexed to (1 1 1) and (2 0 0) reflections of cubic close-packed Pd and the other peak can be indexed to (0 0 2) reflection of graphene layers. The peak at 26.5° can be indexed as the (0 0 2) reflection of graphene layers. The above results confirm the reduction reaction of sodium hydroxide to sodium and disintegrate chemical compound $C_2H_5O^-$ Na+ to $C_2H_5O^-$ and Na^+, when it is mixed with the PEG presence of heat and pressure will produce the chemical compound, this case is called polymerization, which occurs according to our design. According to XRD pattern, it exhibits a pair of small but strong arcs for (0 0 2) which indicates that [0 0 1] is the radial direction of carbon nanotubes. The results indicate that carbon nanotubes were grown from the catalytic particles[12,15,18,20,21].

The Raman spectrum (Thermo Nicolet -Georgia Tech.-MSE-USA) of the resulting product indicates two peaks at 1559 and 1347 cm^{-1} as in fig. 5, corresponding to the vibration of sp^2-bonded carbon atoms in a 2D hexagonal lattice and the vibrations of carbon atoms with dangling bonds in the plane terminations of turbostratic and poorly ordered carbon, respectively. This peak indicates that the carbon nanotubes exhibit a rather defective structure. The crystalline graphite (such as highly oriented pyrolytic graphite) has a characteristic Raman peak at $1559cm^{-1}$ (called the G band), whereas disorder in carbon materials gives rise to “defect-induced” band at $1347cm^{-1}$ (called the D band). The relatively high intensity of the G peak and the intensity ratio of the D and G peaks imply that the carbon products contain less disordered carbon structures[19,21,22,26].

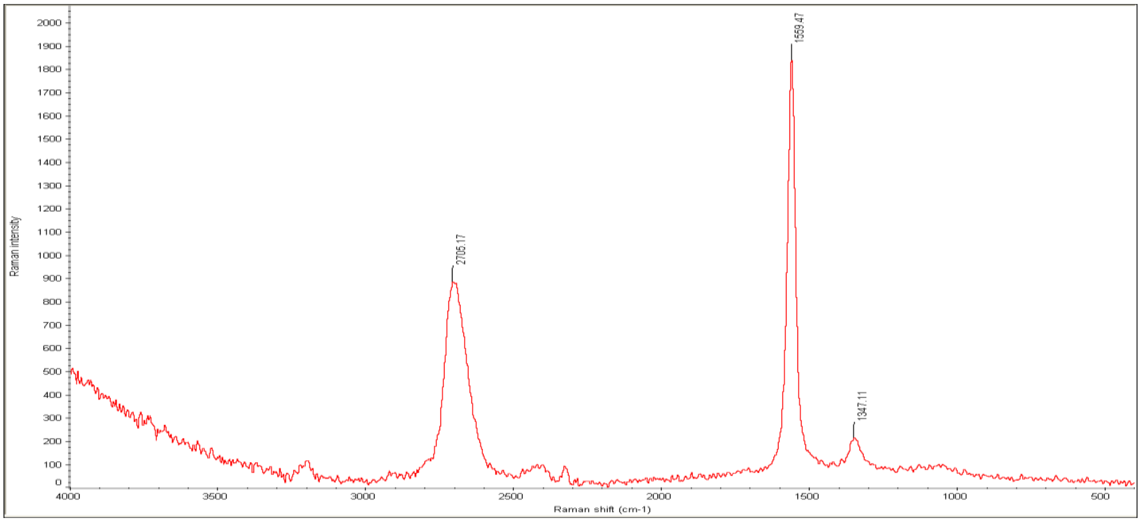

Fig.5. Raman spectrum of the products containing the MWCNTs & CNSs.

This is quite consistent with what can be guessed from the TEM images, despite their low resolution. Regarding the growth process, it is believed that the hydrothermal treatment of the solution mixture is an important step prior to the hydrothermal reactions at (190 °C), which could generate a considerable amount of multi-walled carbon nanotubes and CNSs for the subsequent hydrothermal growth. Without this treatment, the observed uniform nanotube morphology simply cannot be attained. For example, much larger and shorter carbon nanotubes and nanoparticles had been generated from the untreated precursor solution after only 3 h reactions at (190 °C). Furthermore, the usage of a high basic condition and an alcoholic environment are the two crucial keys in ensuring the formation of MWCNTs under the hydrothermal condition. However, until now the role of NaOH for the formation of MWCNTs and CNSs is not clear[18,20,22,25].

This low temperature synthetic route, based on simple reactions with participation of catalyst and catalyst supports and requiring no expensive and precise equipment, will ensure higher purity in the products and greatly reduce the production cost, and thus offer great opportunity for scale-up preparation of one dimensional nanostructure materials.

APPLICATIONS

The method of hydrothermal guarantees the production of multi-walled carbon nanotubes (MWCNTs) and Carbon Nano-Sheets (CNSs) for different applications, especially for reinforcement materials.

CONCLUSIONS

In summary, low-temperature hydrothermal route has been successfully developed to synthesize MWCNTs and CNSs at (190 $^{\circ}$C) with catalyst $PdCl_2$ by using PEG as the carbon source. To our knowledge, the synthesis temperature is the lowest ever reported. The diameters of the as-prepared MWCNTs are much smaller than those prepared by high-temperature hydrothermal method. Which could generate a considerable amount of multi-walled carbon nanotubes and Carbon Nano-Sheets for the subsequent hydrothermal growth. Finally, high pure MWCNTs with lengths of 2–5 μm and diameters of 60±20 nm could be synthesized at as low temperature as 190 °C. As a matter of fact, the method of hydrothermal guarantees the production of multi-walled carbon nanotubes (MWCNTs) and Carbon Nano-Sheets (CNSs) for different applications, especially reinforcement materials.The catalytic of $PdCl_2$ particles may play an important role in the nucleation of nanotubes and nano sheets. So, it has been shown that hydrothermal treatment of the solution mixture before hydrothermal condition culminated in the formation of multi-walled carbon nanotubes (MWCNTs) and Carbon Nano-Sheets (CNSs).

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