Scientia Iranica F (2013) 20(6), 2382–2385

SCIENTIA IRANICA

Sharif University of Technology
Scientia Iranica
Transaction F: Nanotechnology
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Research Note

Synthesis of novel carbon nanostructures through the solvothermal route

P. Zarabadi-Poor[a], A. Badiei[*,a] and A.A. Yousefi[b]

a. *School of Chemistry, College of Science, University of Tehran, Tehran, Iran.*
b. *Department of Plastic Materials Processing and Engineering, Iran Polymer and Petrochemical Institute, Tehran, Iran.*

Received 6 April 2013; received in revised form 3 June 2013; accepted 21 September 2013

KEYWORDS
Carbon nanotubes;
Solvothermal;
Ferrocene;
Chlorinated solvents.

Abstract. Novel morphologies of carbon nanotubes obtained through the solvothermal reaction of various chlorinated solvents in the presence of various catalysts are described. The reaction mixture, including C_2Cl_4 as solvent and ferrocene as catalyst, exhibited most interesting novel arrangements of carbon nanotubes. Therefore, more characterizations, such as Raman spectroscopy and thermogravimetry analysis, were performed on the mentioned sample for further investigation into the novel pine-tree-like morphology of carbon nanostructures.

1. Introduction

The remarkable discovery of Iijima [1], in 1991, which presented carbon nanotubes to scientists, caused an exponential growth of attention to CNTs for undertaking detailed research. CNTs became fascinating due to their unique and extraordinary physical, electronic and thermal properties [2]. The current synthesis methods of CNTs are classified into the following methods: arc discharge [1], laser ablation [3], chemical vapor deposition [4-6], solvothermal [7] etc. To the best of our knowledge, one active research area is the development of synthesis methods for the production of CNTs, considering three main objectives; synthesis of CNTs with desired properties, reduction of production costs and large scale production. The solvothermal method seems to be a promising approach to the low temperature synthesis of carbon nanotubes, which is under development. An important date in the timeline of solvothermal synthesis of carbon nanotubes is 1998, when Qian and his co-workers reported the application of a Wurtz-like reaction for the synthesis of diamond powder via the solvothermal reduction of carbon tetrachloride by metallic sodium in the presence of Ni-Co alloy [8]. Wang et al. presented a novel benzene thermal route, following previous efforts, on the solvothermal synthesis of CNTs [9]. The reaction mixture consisted of C_2Cl_4, benzene, and different catalysts. Their proposed mechanism is similar to the one reported by Jiang et al. [7]. It is seen that using Fe-Au catalysts leads to the production of carbon nanotubes, while using Ag ends in the formation of carbon nanorods. In 2008, Shen et al. [10] proposed a new deposition method for the synthesis of CNTs, based on decomposition of CCl_4, in the presence of ferrocene and through a free radical production pathway.

According to our knowledge, further studies on synthesis parameters, such as different catalysts and solvents in various amounts, are still required. In this paper, we intend to report the effect of adding co-catalysts, such as $FeCl_3.6H_2O$, $CoCl_2.6H_2O$ and $NiCl_2.6H_2O$, to the reaction mixture to investigate the effect of bimetallic catalysts on the reaction product.

*. *Corresponding author. Tel.: +98 21 61112614; Fax: +98 21 66495291*
E-mail addresses: pzarabadip@khayam.ut.ac.ir (P. Zarabadi-Poor), abadiei@khayam.ut.ac.ir (A. Badiei), a.yousefi@ippi.ac.ir (A.A. Yousefi)

The effect of changing the CCl_4 with other chlorinated solvents such as dichloromethane, tetrachloroethylene and chloroform was also investigated.

2. Experimental

2.1. Materials

Carbon tetrachloride (CCl_4), tetrachloroethylene (C_2Cl_4), chloroform ($CHCl_3$), ferrocene ($FeCp_2$), iron(III) chloride hexahydrate, cobalt(II) chloride hexahydrate, nickel(II) chloride hexahydrate and ethanol were purchased from Merck and used as received.

2.2. Synthesis

The synthesis procedure was similar to [10] with slight modification. Ferrocene was dissolved in 25 ml of the desired solvent. Then, 0.2 g of the desired catalyst was added to the reaction mixture. For bimetallic reaction mixtures, appropriate amounts of $FeCl_3.6H_2O$, $CoCl_2.6H_2O$ or $NiCl_2.6H_2O$ were mixed with $FeCp_2$ before adding to the reaction mixture in 1:1 molar ratio and a total weight of 0.2 g. In the case of examination of the effect of different solvents, an appropriate amount of ferrocene was dissolved in the mentioned solvents. Then, the reaction mixture was transferred into a stainless steel autoclave and kept at 180°C for 24 h. Afterward, the black precipitate was filtered off and washed several times with ethanol and distilled water. The list of synthesized samples, along with their corresponding synthesis condition, is given in Table 1.

2.3. Characterizations

Scanning Electron Microscopy (SEM) was carried out on a LEO 1455VP instrument. Raman spectra were recorded using a Brucker SENTERRA Raman microscope equipped with a 785 nm laser and CCD detector. Thermogravimetric analysis (TGA) was performed on a Q50 instrument of Thermal Analysis (TA) from ambient temperature to 800°C with the ramp rate of 10°C/min. The N_2 adsorption-desorption isotherms were measured on a BELSORP mini-II at -196°C. All samples were degassed at 100°C before measurement.

Table 1. List of synthesized samples at reaction temperature of 180°C and reaction time of 24 h.

Sample	Catalyst	Solvent
S1	$FeCl_3/FeCp_2$	CCl_4
S2	$CoCl_2/FeCp_2$	CCl_4
S3	$NiCl_2/FeCp_2$	CCl_4
S4	$FeCp_2$	C_2Cl_4
S5	$FeCp_2$	$CHCl_3$
S6	$FeCp_2$	CH_2Cl_2

3. Results and discussions

The SEM images of as-synthesized S1, S2, and S3 samples are given in Figure 1. It is observed that addition of metal salts to the reaction mixture not only does not improve the production of carbon nanotubes, but also dramatically diminishes the presence of tubular structures. The main formed structures are spherical and in a bulky shape.

Since the spherical particles are formed and no tubular structure is observed, it is proposed that the cleavage of ferrocene and subsequent formation of spherical particles occurred, but further decomposition of the solvent and cyclopentadien rings did not occur to provide carbon feedstock for the growth of carbon nanotubes.

The SEM images of as-synthesized S4, S5, and S6 samples are given in Figure 2. Replacing the CCl_4 with C_2Cl_4 exhibits the most interesting structures.

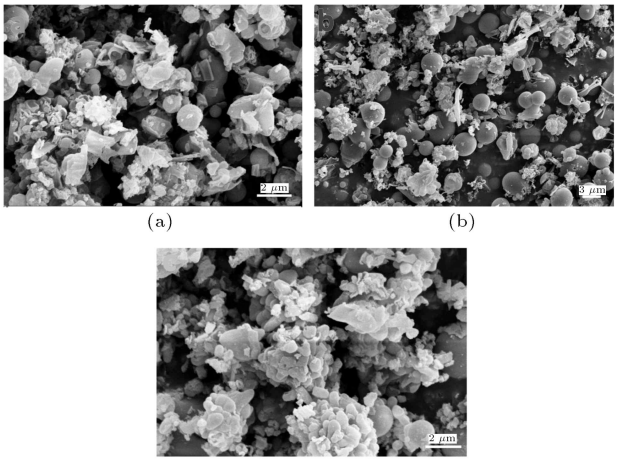

Figure 1. SEM images of a) S1, b) S2, and c) S3 samples.

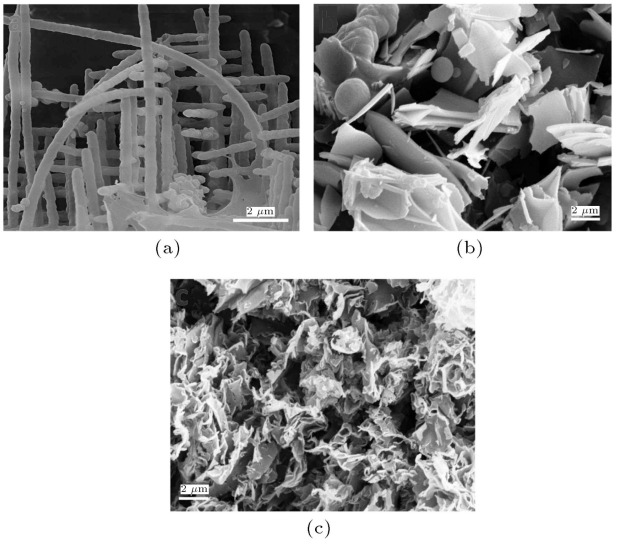

Figure 2. SEM images of a) S4, b) S5, and c) S6 samples.

It is obviuos in Figure 2(a) that tubular stuctures formed in the product different from previusly reported structures for the CCl_4/ferrocene system. Herein, a novel arrangment of carbon nanotubes is observed in the form of pine-tree-like or ramified structures with an average outer diameter of ~ 350 nm and closed ends.

It is also observed that there are long CNTs, as it is the main stem having shorter CNT growth prependicular to the main stem that is making the ramified structure. Figure 2(b) and (c) show that chloroform/ferrocene and dichloromethane/ferrocene systems did not produce tubular structures. The former system's main product consisted of sheet-like structures, however, the latter produced thinner sheets that formed flower-like structures.

It should be mentioned that among the tested systems, only the C_2Cl_4/ferrocene system provided tubular stuctures and, therefore, is favored in our future research. Then, furthor characterization were performed on the synthesized sample. Figure 3 provides the Raman spectrum of the mentioned sample. Two main characteristic peaks of carbonecous structures are obvious in the spectrum. The D-band that corresponds to disordered structures is observed at 1340 cm^{-1}, and the G-band indicates that the graphitized sp^2 carbon-carbon bonds are observed at around 1600 cm^{-1}.

Figure 4 shows the TGA curve of the C_2Cl_4 sample that is used to evaluate the yield of carbon nanotube production. Three weight loss regions can be attributed to this curve. The first small weight loss occurred from ambient temperature to 150°C, which is attributed to the removal of physically adsorbed volatiles. Then, the main weight loss is observed, which can be attributed to the removal of carboneceous materials. It shows that 60% of the sample was removed. Finally, it can be observed that almost 40% of sample weight remained after heating to 800°C. This ash content can be referred to the remaining materials in the sample, such as remaining catalysts etc.

The N_2 adsorption-desorption isotherms of the

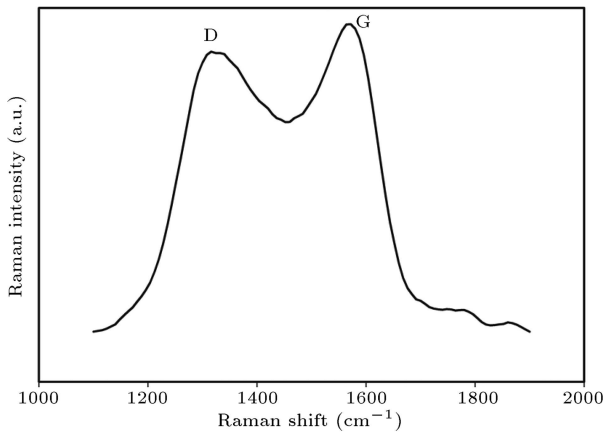

Figure 3. Raman spectrum of S4 sample.

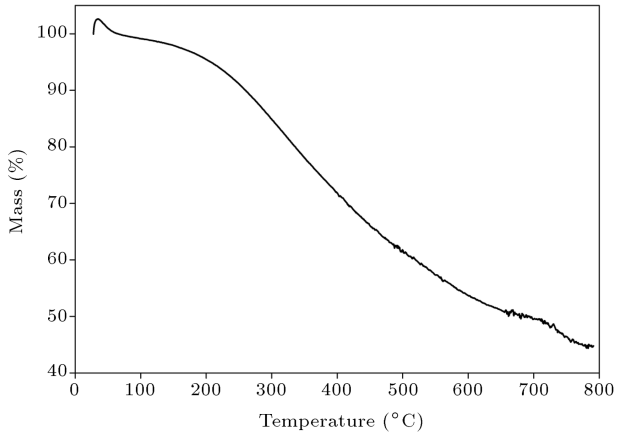

Figure 4. TGA curve of S4 sample.

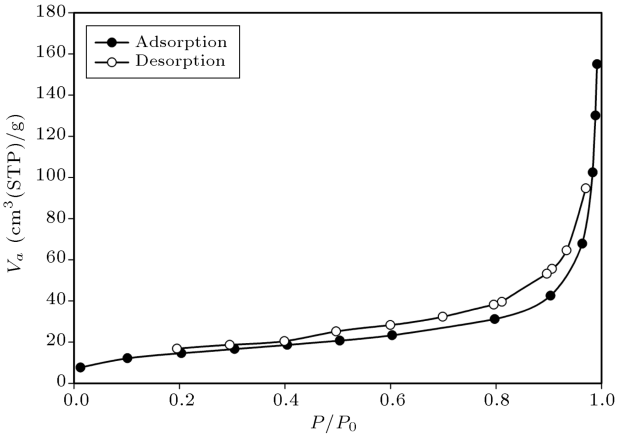

Figure 5. N_2 adsorption-desorption isotherms of S4 sample.

C_2Cl_4 sample is given in Figure 5. It is similar to the type III IUPAC standard isotherm, which corresponds to the presence of porousity in the material with special adsorbate-adsorbant interaction. The observed open hysteresis loop indicates that desorption of adsorbed nitrogen molceules cannot have taken place at the measurement temperature.

The calculated specific surface area is 52 m^2/g, which is dramatically lower in comparison with previously reported values by Shen et al. [10] for the CCl_4/ferrocene system (413 m^2/g). Considering the TGA observation on high ash content, besides the siginificant lowering of specific surface area, it can be proposed that metallic species formed during the solvothermal process and remained in the sample.

4. Conclusion

Different solvothermal systems, consisting of various metal ions or chlorinated solvents, have been examined for the synthesis of carbon nanotubes. Adding $FeCl_3$, $NiCl_2$ and $CoCl_2$ introduced a negative effect on the synthesis of carbon nanotubes and, then, no tubular

structure formed. The C_2Cl_4/ferrocene system produced carbon nanotubes with novel interesting arrangements consisting of pine-like or ramified structures. Using $CHCl_3$ and CH_2Cl_2 instead of CCl_4 also resulted in non-tubular structures and is not favored for carbon nanotube production. So, further characterizations were undertaken on the synthesized sample in the C_2Cl_4/ferrocene system by Raman, N_2 adsorption-desorption measurements and TGA for more detailed investigation to provide basic information for future studies. These investigations revealed that tubular structures were successfully synthesized and that probably catalysts or carbonaceous nano and microparticles exist in the product. Therefore, it can be proposed that the suggested reaction mechanism changed by altering the catalyst or reaction solvent. Probably, the presence of C_2Cl_4 and oxygen in the reaction mixture caused the formation of iron species, which remained in the product, and were initially observed as high ash content. At this point of time, further investigation of the C_2Cl_4/ferrocene system is being undertaken by our research group to obtain more explanations regarding the effect of different parameters on the properties of synthesized materials.

Acknowledgment

The authors would like to thank the research council of the University of Tehran for its financial support.

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Biographies

Pezhman Zarabadi-Poor was born in 1983, in Qazvin, Iran. He obtained his diploma from National Organization for Development of Exceptional Talents (NODET) in 1995, his BS degree in Applied Chemistry from Bu-Ali Sina University, Hamedan, Iran, and his MS and PhD degrees in Inorganic Chemistry from the University of Tehran, Iran. His research interests include synthesis, characterization and application of novel nanomaterials such as mesoporous silica materials and carbon nanotubes.

Alireza Badiei was born in Iran, in 1965. He received BS and MS degrees in Chemistry and Inorganic Chemistry from Tarbiat Moallem University, Tehran, Iran, in 1988 and 1991, respectively, and his PhD degree in the synthesis and modification of nanoporous materials from Laval University, Quebec, Canada, in 2000. He is currently Associate Professor in the Chemistry Department of Tehran University, Iran. His research interests include nanoporous materials synthesis, modification and its applications.

Ali Akbar Yousefi was born in Iran, in 1965. He obtained his BS degree in Pure Chemistry from Chamran University, Ahwaz, Iran, in 1987, his MS degree in Organic Polymer Chemistry from Kharazmi University, Tehran, Iran, in 1991, and his PhD degree in Chemical Engineering on the rheology of polymer modified asphalts from Laval University, Quebec, Canada, in 1999. He is currently Faculty Member and Professor at the Iran Polymer and Petrochemical Institute.