Synthesis, Characterization and Electrical Conductivity of Metal/Metal ion Incorporated Fullerene Nanowhiskers

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ABSTRACT

Fe incorporated C_{60} nanowhiskers were prepared by using liquid-liquid interfacial precipitation route. $FeCl_3.6H_2O$ is used as source for the Fe incorporation in the nanowhiskers. The prepared nanowhiskers are characterized using SEM, TEM, Raman spectroscopy and XRD. The obtained nanowhiskers are ~100-150 nm size and *fcc* crystalline nature. The Raman spectroscopy reveals the polymerization of C_{60} molecule in the nanowhiskers. Uniform incorporation of Fe in the nanowhiskers has been identified using TEM-mapping analysis.

Keywords: C_{60} nanowhiskers, metal ion incorporation, electrical conductivity, fullerene, interfacial precipitation

1 INTRODUCTION

The material synthesis and characterization has gained much attention in the recent days due to the unusual properties of materials in the nanometer scale. The carbon based nanomaterials are under extensive investigation for electrochemical and hydrogen storage application [1, 2, 3]. The carbon nanotubes are generally used for various applications including electrode support in the fuel cells [4]. Similarly, fullerene (C_{60}) nanowhiskers have also received much attention in the recent days due to their atypical tubular morphology and application in various fields like anode material for fuel cell, sensors, solar cells etc. Various attempts have been made for the preparation C_{60} nanowhiskers in the recent literature including template synthesis and solvent evaporation [5-7]. However, a quite simple method has been reported by Miyazawa *et al* for the preparation of fullerene nanowhiskers using fullerene saturated toluene and isopropyl alcohol [8-10]. Furthermore, a detailed investigation has been made for the effect of various parameters like temperature, solvent ratio and effect of light on the nanowhiskers formation. Also, the structural characterization of C_{60} and C_{70} nanowhiskers and the effect of heat treatment of the nanowhiskers have been studied [11].

The recent thrust in the fullerene research is focused on the synthesis of fullerene nanowhiskers/nanotubes, as anode material for fuel cell application. The major drawback associated with the fullerene nanowhiskers is the low electrical conductivity. However, the rare-earth metal doped C_{60} fullerides have been reported for superconductivity. Though, there is no clear understating on the origin of the superconductivity [12, 13]. Fe incorporated onion like fullerene has also been reported in literature [14, 15]. It is presumed that the polymerization of fullerene molecules as nanowhiskers or nanotubes will result enhancement in the conductivity of the fullerene molecule. As excepted the C_{60} nanowhiskers show good electrical conductivity when compared to pristine C_{60} powder. Evidently, our earlier studies on conductivity of fullerene nanowhiskers show, a whisker of C_{60} with a diameter of 8 μm has a resistivity of about 10^5 Ω cm. Whereas, the pristine C_{60} crystals have the resistivity value in the range of 10^8 to 10^{14} Ω cm [16, 17]. Further, the conductivity of the C_{60} nanowhiskers could be increased by high temperature treatment in N_2 atmosphere. Again, it is speculated that the incorporation of transition metal ion like Fe, Co, Ni etc in the C_{60} nanowhiskers could also increase the electrical conductivity of the nanowhiskers to greater extent. In this present work, an attempt has been made to incorporate Fe metal/metal ions into C_{60} nanowhiskers and study their electrical conductivity.

2 EXPERIMENTAL

The metal ion incorporated C_{60} nanowhiskers have been prepared by forming interface between C_{60} saturated benzene and metal ion containing isopropyl alcohol (IPA) at 5 °C. The C_{60} saturated benzene solution was prepared by dissolving excess amount of C_{60} powder (~ 0.1 g, 99.5 % pure, MTR Ltd., USA) into benzene/CTC (25 mL) followed by ultrasonication for 30 min, and the final solution was filtered in order to remove the undissolved C_{60} powder. For the typical preparation, C_{60} saturated benzene solution was taken into a 10 ml of thoroughly cleaned glass bottle and cooled to 5 °C in an ice water bath. Calculated amount of metal precursor ($FeCl_3.6H_2O$) is dissolved into IPA solution at 5 °C and slowly added to the C_{60} solution. During the addition, the temperature was maintained at 5 °C using ice water bath. The above mixture was kept for 5 min at the same temperature without disturbance, and then ultrasonicated for 1 min. The resulting mixture was stored at 5 °C in an incubator with transparent plastic window

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(SANYO MIR-153, SANYO Electric Co Ltd., Japan) for 24 h to grow C_{60} nanowhiskers. The structure and morphology of the obtained C_{60} nanowhiskers after 24 h incubation were characterized using Raman spectrometry (JASCO, NRS-3100, using 532 nm laser), optical microscopy, transmission electron microcopy (TEM, JEOL JEM-2100F, 200kV), scanning electron microscopy (FE-SEM, Hitachi-4800, 20 kV) and X-ray diffraction measurements (XRD, RIGAKU, RITT 2000) with CuK_α radiation.

3 RESULTS AND DISCUSSIONS

Recently we have observed porous C_{60} nanowhiskers at the C_{60} saturated benzene and IPA interface [18]. In which various metal ions were incorporated by in situ precipitation. The Raman spectrum of the prepared Fe incorporated C_{60} nanowhiskers is compared with pristine C_{60} powder in Fig. 1. Many additional lines were observed for the Fe incorporated nanowhiskers when compared to pristine C_{60} powder. However, there are no significant lines corresponding to the incorporated Fe. Similar observation has been reported for the Co-C_{60} compound by Sakai *et al.* [19] and the additional lines are ascribed to the Raman forbidden modes and split components of Raman active modes. The inset of Fig 1 shows the shift in the $A_{(g)}2$ line to lower frequency region (1458 cm^{-1}), which is an indication for the polymerization of C_{60} molecule in the nanowhiskers [20, 21]. This indicates that when the concentration of metal in IPA is optimum, the polymerization will not be effected. The satellite peak at 272 cm^{-1} indicates the good crystalline nature of the nanowhiskers.

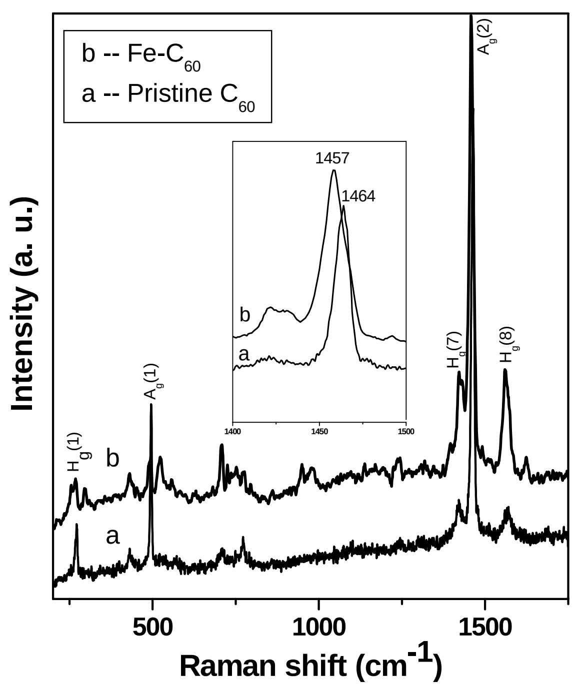

Figure 1. Raman Spectra of (a) pristine C_{60} powder (b) Fe incorporated C_{60} nanowhiskers.

Fig 2 shows the TEM image of the Fe incorporated C_{60} nanowhiskers. Formation of C_{60} nanowhiskers has been observed at the low magnification. Whereas, at higher magnification some black patches could be seen all over the nanowhiskers. The average size of the nanowhiskers is around ~ 100-150 nm in diameter and few hundred micrometers in length. The uniform tube diameter has been observed throughout the length of the nanowhiskers. However the formation of tubular nanowhiskers has been observed very rarely in the metal ion incorporated sample. While in pure C_{60} nanowhiskers formation, tubular and non-tubular nanowhiskers have been observed with equal prospect. This observation could be attributed due to the high viscous nature of the metal containing solution. Generally, it is assumed that the formation of tubular nanowhiskers occurs due to the flow out of the solution which has entrapped inside during the C_{60} nanowhiskers formation. The dissolution of metal salts in the IPA increases the viscosity of the solution, which makes less flow rate and thereby facilitates the formation of non-tubular nanowhiskers.

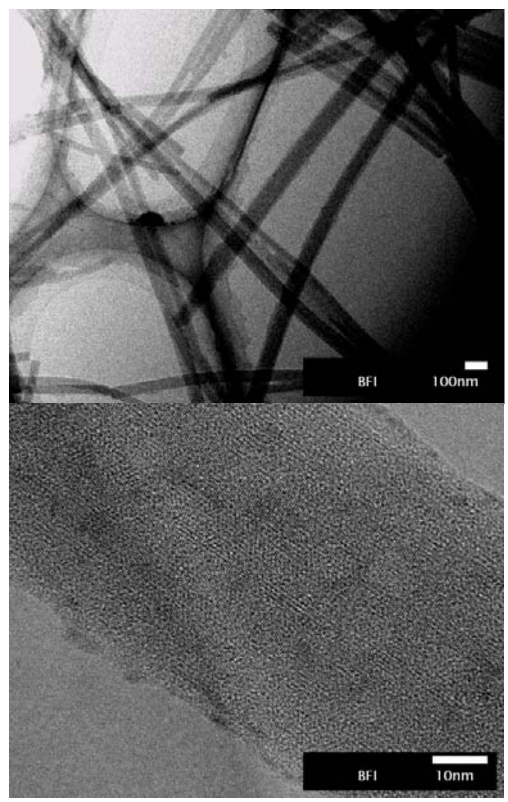

Figure 2. TEM image of Fe incorporated C_{60} nanowhiskers (a) at lower magnification (b) at higher magnification

The crystalline nature of the prepared C_{60} nanowhiskers is evaluated by using XRD. The observed peaks at 2θ value of 10.75°, 17. 7° and 20.68° are attributed to (111), (220) and (311) plane reflections respectively. There is no significant change in the lattice plane spacing due to the incorporation of Fe ions. Also, there are no additional lines due to the incorporated metal ions. It indicates that the incorporated metal ion concentration is very low and the fine dispersion of metal ion over the nanowhiskers. The obtained XRD pattern could be compared to metal free nanowhiskers, which has *fcc* crystal system [22, 23]. Thus, the reflection corresponding to (200) plane was not observed for the metal incorporated nanowhiskers [24]. The calculated lattice plane spacing from the TEM image shows 4.35 Å corresponding to (311) plane, which is slightly higher than value observed for the Fe free C_{60} nanowhiskers.

Fig 3 demonstrates that the SEM image of metal incorporated C_{60} nanowhiskers. It could be very clear that the prepared nanowhiskers size is uniform though out the sample and absence of other impurities. Unlike the metal free C_{60} nanowhiskers, the Fe incorporated nanowhiskers could be seen very clearly without Pt sputtering. This observation gives some indirect indication on more conducting nature of the nanowhiskers. There are no pores have been observed on the surface of the nanowhiskers even at high magnifications.

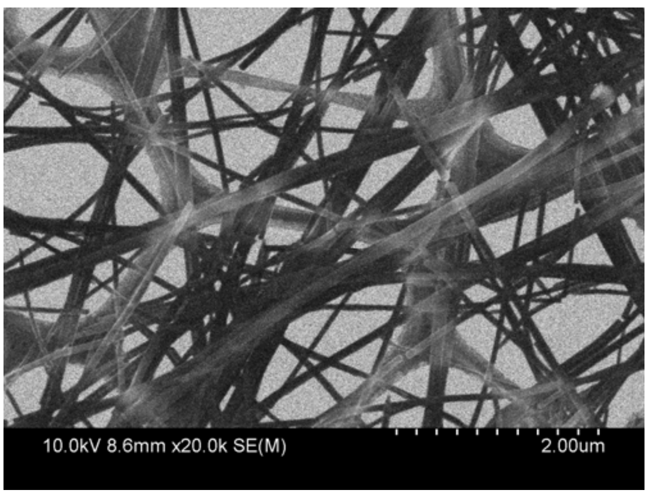

Figure 3. SEM image of Fe incorporated C_{60} nanowhiskers.

The metal ion concentration in IPA plays a vital role in the nanowhiskers formation. When 0.1 M $FeCl_3$ solution is used for the interfacial reaction, the formation of nanowhiskers have not been observed. In this case, simple precipitation of C_{60} molecules occurs with irregular shape and size. When the metal ion concentration is reduced to 0.05 M, formation of nanowhiskers observed with some precipitates and also the yield of the nanowhiskers is very low. The amount of the Fe incorporated in the prepared nanowhiskers is calculated form TEM-EDX analysis. For more conformation a TEM-mapping analysis was carried out by choosing a particular part in the nanowhiskers. Fig. 4 (a&b) shows the TEM-mapping images of Fe doped C_{60} nanowhiskers. Fig 4(a) shows the nanowhiskers part which is taken for the mapping analysis. The red color spots in Fig 4(b) show the Fe ions, which incorporated in the prepared C_{60} nanowhiskers. It could be very clearly seen that the red color spots with high intensity are corresponding to the black patches in the nanowhiskers. This confirms that the black patches on the nanowhiskers indicate the presence of metal ions. The mapping image corresponding to the carbon atoms are shown as inset in Fig 4 (a).

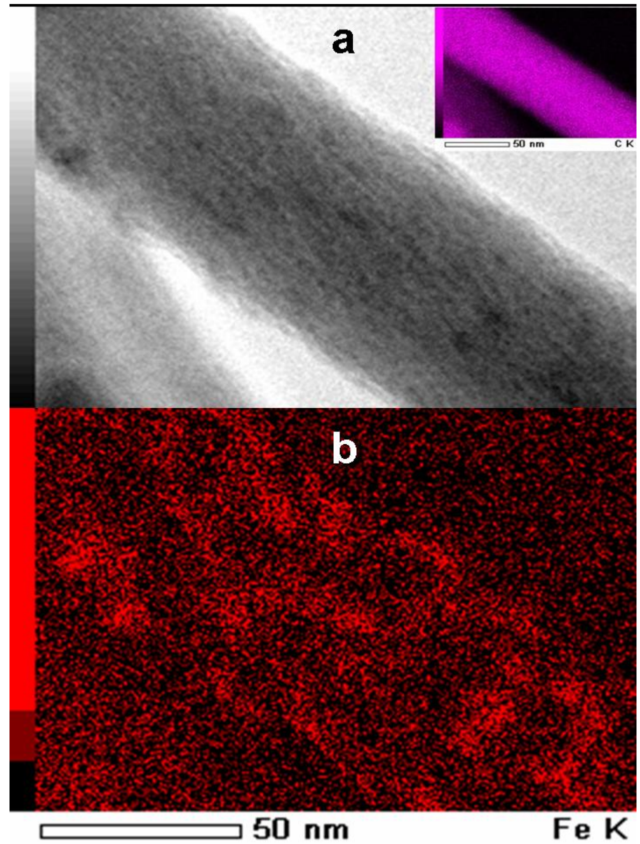

Figure 4. TEM-mapping image of (a) Fe incorporated nanowhiskers (b) Fe ions in the nanowhiskers

The electrical conductivity measurement of the prepared Fe incorporated and pure C_{60} nanowhiskers are under progress. The experimental details and observed results are to be discussed in detail.

4 CONCLUSIONS

Fe incorporated C_{60} nanowhiskers have been successfully prepared by liquid-liquid interfacial precipitation method. The optimum concentration for the formation of Fe incorporated C_{60} nanowhiskers is calculated as $1x10^{-3}$ M, when $FeCl_3$ is used as Fe source. The TEM and SEM image shows the prepared nanowhiskers are uniform in size (100-150 nm in diameter) and TEM-mapping analysis reveals the fine dispersion of metal over the entire nanowhiskers. Polymerization of C_{60} molecule in the nanowhiskers have identified by the observed shift of the $A_{(g)}2$ line in the Raman spectroscopy. XRD pattern of the C_{60} nanowhiskers shows presence of the *fcc* crystalline structure. The electrical conductivity of the prepared nanowhiskers is under progress.

REFERENCES

[1] G. Che, B. B. Lakshmi, C. R. Martin and E. R. Fisher, *Langmuir*, 15,750, 1999.
[2] R. M. Baum, *Chem. Eng. News*, 75, 39, 1997.
[3] Y. Ye, C. C. Ahn, C. Witham, B. Fultz, J. Liu, A. G. Rinzler, D. Colbert, K. A. Smith and R. E. Smalley, *Appl. Phys. Lett*, 74, 2307, 1999.
[4] G. Che, B. B. Lakshmi, E. R. Fischer and C. R. Martin, *Nature*, 393, 346, 1998.
[5] Y. Jin, R. J. Curry, J. Sloan, R. A. Hatton, L. C. Chong, N. Blanchard, V. Stolojan, H.W. Kroto and S. R. P. Silva, *J. Mater. Chem.*, 16, 3715, 2006.
[6] L. Wang, B. Liu, S. Yu, M. Yao, D. Liu, Y. Hou, T. Cui, G. Zou, B. Sundqvist, H. You, D. Zhang and D. Ma, *Chem. Mater.*, 18, 4190, 2006.
[7] H. Liu, Y. Li, L. Jiang, H. Luo, S. Xiao, H. Fang, H. Li, D. Zhu, D. Yu, J. Xu, and B. Xiang, *J. Am Chem Soc.*, 124, 13370, 2002.
[8] K. Miyazawa, J. Kuwasaki, A. Obayashi and M. Kuwabara, *J. Mater. Res.*, 17, 83, 2002.
[9] M. Tachibana, K. Kobayashi, T. Uchida, K. Kojima, M. Tanimura and K. Miyazawa, *Chem Phys Lett.*, 74, 279, 2003.
[10] J. Minato and K. Miyazawa, *Carbon*, 43, 2837, 2005.
[11] K. Miyazawa, J. Minato, M. Fujino and T. Suga, *Diamond Relat. Mater.* 15, 1143, 2006.
[12] E. Ozdas, A. R. Kortan, N. Kopylov, A. P. Ramirez, T. Siegrist, K. M. Rabe, H. E. Bair, S. Schuppler and P. H. Citrin, *Nature* 375, 123, 1995.
[13] X. H. Chen and G. Roth, *Phys. Rev*. B 52, 15534, 1995.
[14] W. Xiaomin, X. Bingshe, J. Husheng, L. Xuguang and I. Hideki, *J. Phys. Chem. Soli*, 67, 871, 2006.
[15] X. Wang, B. Xu, X. Liu, J. Guo and H. Ichinose, *Diamond Relat. Mater.* 15, 147, 2006.
[16] K. Miyazawa, J. Minato, H. Zhou, T. Taguchi, I. Honma and T. Suga, *J.Eur.Ceram.Soc.* 26, 429, 2006.
[17] K. Miyazawa, Y. Kuwasaki, K. Hamamoto, S. Nagata, A. Obayashi and M. Kuwabara, *Surf. Interface Anal.* 35, 177, 2003.
[18] M. Sathish, K. Miyazawa and T. Sasaki (communicated)
[19] S. Sakai, K. Yakushiji, S. Mitani, K. Takanashi, H. Naramoto, P. V. Avramov, K. Narumi, V. Lavrentiev and Y. Maeda, *Appl. Phys. Lett*, 89, 113118, 2006.
[20] Y. Iwasa, T. Arima, R. M. Fleming, T. Siegrist, O. Zhou, R. C. Haddon, L. J. Rothberg, K. B. Luons, H. L. Carter Jr, A. F. Hebard, R. Tycko, G. Dabbagh, J. J. Krajewski, G. A. Thomas and T. Yagi, *Science* 264, 1570, 1994.
[21] M. C. Martin, D. Koller, A. Rosenberg, C. Kendziora and L. Mihaly, *Phys Rev.* B, 51, 3210, 1995.
[22] K. Miyazawa, Y. Kuwasaki, A. Obayashi and M. Kuwabara, *J. Mater. Res.* 17, 83, 2002.
[23] V. Gupta, P. Scharff and N. Miura, *Mater. Lett.* 60, 3156, 2006.
[24] J. E. Fischer, P. A. Heiney, D. E. Luzzi and D. E. Cox, “Fullerenes” American Chemical Society, Washington, D.C. 55–69, 1992.