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Preparation and characterization of C_{60} needle-like crystals using liquid-liquid interface precipitation: effect of solvent on the crystal size

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Nanowhiskers and hexagonal nanocrystals of C_{60} have been successfully prepared using liquid - liquid interfacial precipitation method. C_{60} saturated benzene and carbon tetrachloride solution has been used for the interfacial precipitation reaction. Alcohols like methanol, ethanol, isopropyl alcohol, *n*-butanol, 2-butanol and *n*-pentanol have been used for the precipitation. The prepared C_{60} nanocrystalline solids from these disparate interface show different crystalline nature and assortment of morphologies. The optical microscopic image of the prepared hexagonal nanocrystals reveals clear change in the particle size for different alcohols. The effect of solvent on the crystal size has been studied by varying the amount of alcohol in the mixture. The Raman spectra of the prepared C_{60} nanowhiskers or hexagonal nanocrystals show polymerization of C_{60} molecule at the surface. The formation of tubular, non-tubular C_{60} nanowhiskers and C_{60} hexagonal nanocrystals has been confirmed using scanning electron microscopy and transmission electron microscopy.

Key words: nanowhiskers, C_{60} polymerization, needle like crystal, solvent effect

1. INTRODUCTION

Fullerene nanowhiskers have 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. Consequently, various attempts have been made to prepare C_{60} nanowhiskers with uniform size and narrow diameter. Among the available methods, the method developed by Miyazawa et al for the preparation of fullerene nanowhiskers using fullerene saturated toluene and isopropyl alcohol is quite simple and convenient [1, 2, 3]. In general, this method is called as liquid-liquid interfacial precipitation. Other than the liquid-liquid interfacial precipitation method, various other methods including template synthesis and solvent evaporation have been reported in the literature for the preparation of fullerene nanowhiskers [4, 5, 6]. Recently, Miyazawa's research group has shown that the effect of various parameters like temperature, ratio between the solvent, and irradiation of blue light and UV light on the nanowhiskers formation has been studied. Moreover, the structural characterization of C_{60} and C_{70} nanowhiskers and the effect of heat treatment of the nanowhiskers have been studied [7]. In our present study, an attempt has been made to study the effect of nature of the solvents on the structure and the morphology of C_{60} nanowhiskers.

2. EXPERMENTAL

The C_{60} nanowhiskers have been prepared by forming interface between C_{60} saturated benzene or carbon tetrachloride (CTC) solution and alcohols [isopropyl alcohol (IPA), ethanol (EtOH), methanol (MeOH)] at 5 °C. The C_{60} saturated benzene/CTC 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 or CTC solution was taken into a 10 ml of thoroughly cleaned glass bottle and cooled to 5 °C in an ice water bath. Alcohol (IPA, EtOH, MeOH) was also cooled to 5 °C and slowly added to the C_{60} solution, the temperature was maintained at 5 °C using ice water bath during the addition. The above mixture was kept at 5 °C for 5 min without disturbance, and then subjected to ultrasonication for 1 min. The resulting mixture was stored at 5 °C in an incubator with transparent plastic window (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), optical microscopy, transmission electron microcopy (TEM, JEOL JEM-2100F, 200kV) and scanning electron microscopy (FE-SEM, Hitachi-4800, 15 kV).

3. RESULTS AND DISCUSSION

3.1 Benzene and IPA system

Fig 1 shows the microscopic image of C_{60} nanowhiskers prepared at 1 to 4.5 ratio (v/v) of IPA and benzene. The obtained nanowhiskers are in the range of 100-200 nm in diameter and a few microns in length. Fig 2 shows the SEM image of Pt sputtered C_{60} nanowhiskers. It can be very clearly seen from this image that the diameter of nanowhiskers is uniform throughout in its length. TEM image of nanowhiskers dried at room temperature is shown in Fig 3. The formation of non-tubular nanowhiskers could be seen and the calculated diameter of the nanowhiskers is around 100 nm. Furthermore, significant number of tubular crystalline nanowhiskers has also been observed along with the non tubular C_{60} nanowhiskers. The average diameter of the tubular nanowhiskers is in the range of 100-200 nm, slightly higher than that of non-tubular nanowhiskers. The ratio between the IPA to benzene has been periodically varied from 3 to 12 with 1 ml interval of IPA. The formation of nanowhiskers has been observed until the ratio of 1:9, above this ratio there is no whiskers formation even after 10 days. The yield of nanowhiskers was decreased with increasing the IPA to benzene ratio.

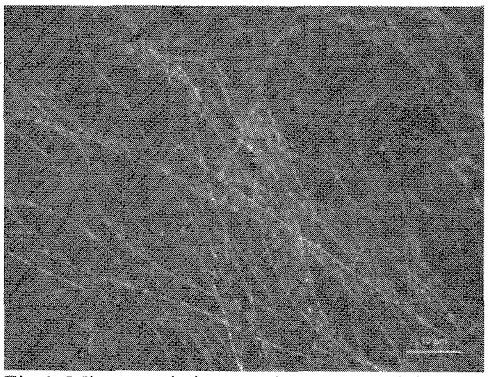

Fig.1, Microscopic image of C_{60} nanowhiskers

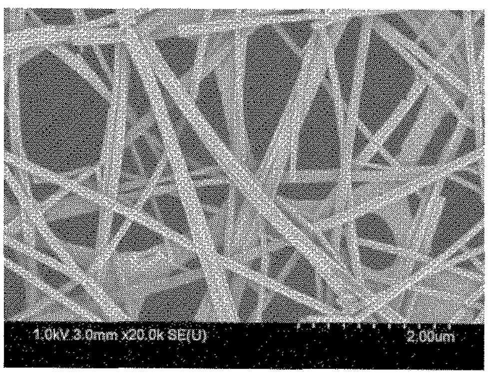

Fig.2, SEM image of platinum coated C_{60} nanowhiskers grown by the liquid–liquid interfacial precipitation method.

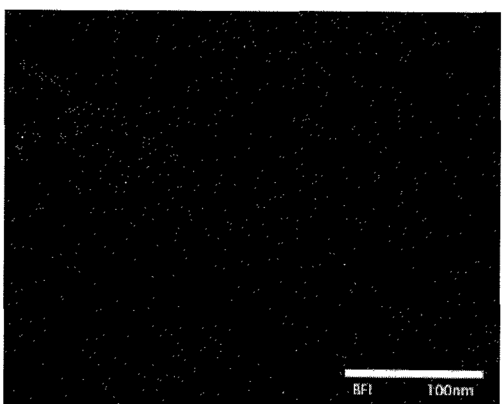

Fig.3, TEM image of C_{60} nanowhiskers

3.2 Benzene and higher chain length alcohol system

In the case of benzene and higher chain length alcohols like *n*-butanol, 2-butanol and *n*-pentanol systems there was no appreciable amount of precipitation with the present experimental condition i.e. 1 to 4.5 ratio of alcohol and C_{60} saturated benzene at 5 °C.

3.3 CTC and alcohol (IPA, EtOH, MeOH) system

In the case of C_{60} saturated CTC and alcohol system, hexagonal crystalline C_{60} nanoparticles has been observed. The size of the hexagonal particles varies with the nature of the alcohol used. The optical microscopic images of the hexagonal particles prepared with C_{60} saturated CTC and IPA, EtOH and MeOH are shown in Fig 4, 5 & 6 respectively. It can be very clearly seen that the size of C_{60} hexagonal nanoparticles decreases with increasing the chain length of the alcohol. Certainly, the size of the nanocrystals is in the following order; IPA > EtOH > MeOH. It is presumed that the length of the carbon chain in the alcohols plays a significant role in determining the particle size of the C_{60} nanocrystals. However, the reason for the hexagonal C_{60} nanocrystal formation and the variation in the crystal size is not apparent.

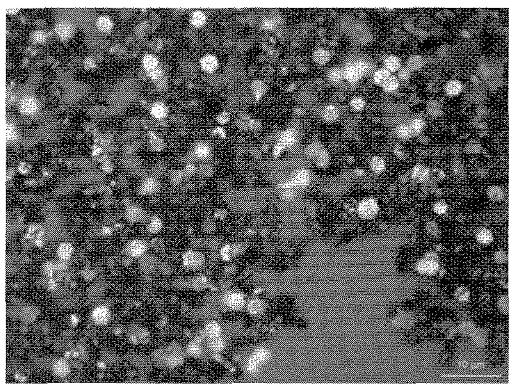

Fig.4, Microscopic image of C_{60} nanocrystals formed at CTC and IPA interface

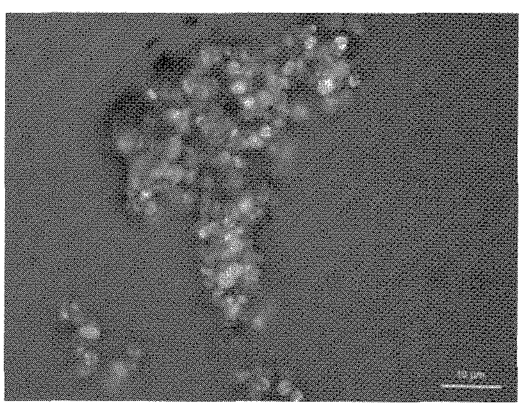

Fig.5, Microscopic image of C_{60} nanocrystals formed at CTC and EtOH interface

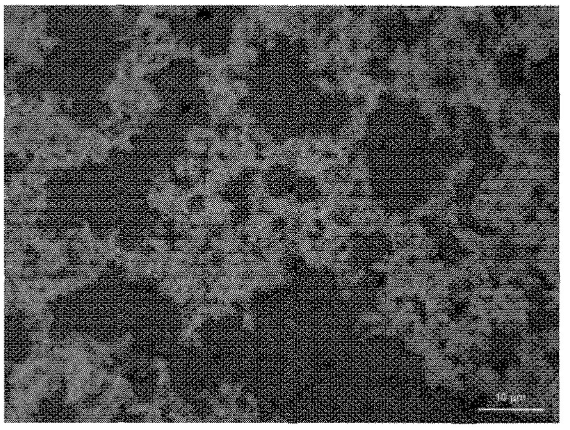

Fig.6, Microscopic image of C_{60} nanocrystals formed at CTC and MeOH interface

3.4 CTC and other alcohol systems

A preliminary study has also been carried out for the C_{60} saturated CTC and the other alcohol system (*n*-butanol, 2-butanol, *n*-pentanol). However, there is no significant amount of precipitation of C_{60} nanowhiskers/nanocrystals at the studied experimental conditions. It is surmised that the low solubility of C_{60} molecule in the CTC may influence the formation of nanocrystals. The alcohol other than IPA does not have sufficient solubility in CTC to precipitate the C_{60} nanocrystals. Nevertheless, the detailed investigation on the formation of C_{60} nanowhiskers/nanocrystals at different temperature and concentration ratio is under progress.

3.5 Raman spectroscopic studies

The Raman spectra of C_{60} nanowhiskers and the hexagonal nanoparticles are shown in Fig. 7. Basically, among the Raman active lines of C_{60}, the most significant one is the line at 1469 cm^{-1}, which is typically used as an analytical probe for the structural and electronic properties of C_{60} and ascribed to the pentagonal pinch mode.

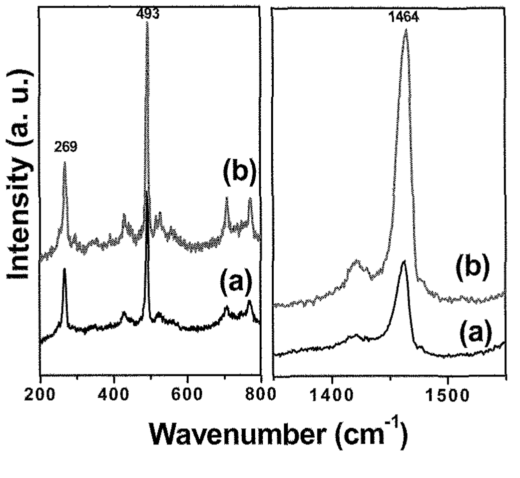

Fig.7, Raman spectra of (a) hexagonal C_{60} nanocrystals (b) C_{60} nanowhiskers

The observed peak at 1464 cm^{-1} for the nanowhiskers and the hexagonal crystals is almost similar to that of pristine C_{60} molecule [8]. Even though, no significant difference between the Raman spectrum of C_{60} nanowhiskers and the hexagonal crystalline C_{60} nanoparticles is noticed, the observed spectral features of the nanowhiskers/hexagonal crystals are slightly fluctuate from the pristine C_{60} powder. There is no shift in the peak position at 1464 cm^{-1}, but one could clearly see the peak broadening in the lower frequency region. It indicates that the polymerization of C_{60} molecules at the surface of the nanowhiskers or nanoparticle is occurred.

4. CONCLUSIONS

The tubular and non tubular C_{60} nanowhiskers have been prepared using benzene and IPA interface whereas only hexagonal crystalline C_{60} nanocrystalline particles have been observed at CTC and alcohol interface. The polymerization of C_{60} in the nanowhiskers and the hexagonal crystals has been confirmed from the observed shift in the Raman lines. The size of the hexagonal C_{60} nanocrystals changes with the nature of the alcohol. Similarly, the ratio between the solvents has a strong influence on the structure and the morphology of the nanowhiskers. C_{60} precipitates or nanowhiskers were not observed when higher chain length alcohols like *n*-butanol, 2-butanol and *n*-pentanol were used.

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