Synthesis of Fullerene Nanowhiskers and Their Electrical and Superconducting Properties

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Fullerene nanowhiskers (FNWs) are thin crystalline fibers composed of fullerene molecules such as C_{60}, C_{70}, endohedral fullerenes or other fullerene molecules with functional groups. FNWs are n-type semiconductors with various application examples such as field-effect transistors, solar cells, chemical sensors, photocatalysts and so forth. Alkali metal-doped C_{60} (fullerene) nanowhiskers (C_{60}NWs) become superconductors. The K-doped C_{60}NWs have the highest superconducting volume fraction as ever have been realized in the alkali metal-doped C_{60} crystals and a very high critical current density J_c up to a magnetic field of 50 kOe. On the other hand, the growth control of fullerene nanowhiskers is a very important theme for their practical application. This paper reviews the research development of FNWs, focusing on their electrical and superconducting properties as well as their growth mechanism.

Keywords: Fullerene Nanowhisker, Fullerene Nanotube, Liquid-liquid Interfacial Precipitation Method.

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1. INTRODUCTION

Fullerene molecules have cage-typed closed structures that are fully composed of carbon atoms. The best known fullerene molecule is C_{60} that was discovered by Kroto et al. in 1985 [1]. The secondly well-known molecule is C_{70} that was also identified in ref. [1]. C_{60} molecule has a soccer ball shape with 12 pentagons and 60 apexes where carbon atoms are located, and has 30 six-membered ring/six-member ring joints with double bonds of carbon and 60 five-membered ring / six-membered ring joints with single bond of carbon. C_{60} molecules can be polymerized by [2+2] cycloadditions through formation of four-membered rings, so-called [2+2] cycloaddition mechanism with the rehybridization from sp^2 to sp^3 [2].

Various properties of C_{60} have been studied by forming thin films on suitable substrates or preparing bulk samples by sintering at high temperatures. Owing to the above chemical bonding structure of C_{60}, C_{60} molecules are known to be polymerized by UV or visible light illuminations [3, 4], high pressure sintering [5, 6, 7, 8] and electron beam irradiation [9, 10]. It has been shown that the hardness of high-pressure sintered C_{60} reaches 200 GPa - 300 GPa [11, 12].

On the other hand, very fine needle-like crystals (whiskers) composed of C_{60}, "C_{60} (fullerene) nanowhiskers (C_{60}NWs)", were disovered in a colloidal solution of PZT added with C_{60} [13,14,15].

The fullerene nanowhiskers (FNWs) are the thin needle-like crystals composed of fullerene molecules and have diameters less than 1000 nm [16, 17]. Fullerene nanosheets (FNSTs) are thin two-dimensional substances composed of fullerene molecules. The thickness of fullerene nanosheets is defined to be less than 1000 nm. The fullerene molecules forming fullerene nanowhiskers and nanosheets can include various fullerene molecules and their derivatives such as C_{60}, C_{70}, $Sc_3N@C_{80}$ [18], $C_{60}[C(COOC_2H_5)_2]$ [19, 20, 21], $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ [22],

and so forth. The aspect ratio, the ratio of length/ diameter, of FNWs is defined to be greater than three [16]. The FNWs with tubular structures are specially called fullerene nanotubes (FNTs) [23, 24, 25, 26, 27]. FNWs can take multicomponent structures as well as the monocomponent structures like C_{60}NWs, C_{60} (fullerene) nanotubes (C_{60}NTs), C_{70} (fullerene) nanowhiskers (C_{70}NWs), C_{70} (fullerene) nanotubes (C_{70}NTs) [23, 25, 28], FNWs composed of $C_{60}[C(COOC_2H_5)_2]$ molecules ($C_{60}[C(COOC_2H_5)_2]$ NWs), and so forth. As for the multicomponent FNWs, C_{60}-C_{70} two-component NWs [29], C_{60}-C_{70} two-component NTs [23], C_{60}-$C_{60}[C(COOC_2H_5)_2]$ two-component NWs [19], C_{60}-$(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ two-component NWs [22] and so forth have been synthesized.

The FNWs, FNTs and FNSTs can be synthesized by a simple method named "liquid-liquid interfacial precipitation method (LLIP method) " [30] and has been widely applied for their synthesis [31, 32, 33, 34, 35, 36, 37, 38]. In this review, the synthetic method of FNWs and FNTs and their application studies so far performed will be described.

The terminology "fullerene nanowhisker" represents all the needle-like crystals composed of fullerene molecules with diameters less than 1000 nm. The words such as "nanorod" and "nanowire" are identified with "nanowhisker" in order to avoid confusion [16].

2. SYNTHESIS OF FULLERENE NANOWHISKERS BY LLIP METHOD

The LLIP method has been most widely used to synthesize FNWs, FNTs and FNSTs [30]. This method uses good solvents of fullerene and the poor solvents of fullerene that intermingle with the good solvents of fullerene. The LLIP process typically proceeds as follows for the case using toluene (good solvent) and isopropyl alcohol (IPA) (poor solvent). An aliquot of C_{60}-saturated toluene solution is put into a glass bottle, next, an appropriate amount of IPA is gently added to

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the solution to form a liquid-liquid interface. The temperature of the solution is usually set to be around at room temperature, typically lower than 25 °C. The nucleation of C_{60}NWs occurs at the liquid-liquid interface where the solution becomes a supersaturated state of C_{60} by the mixing of toluene and IPA. The supersaturated state of the C_{60} solution is maintained through the interdiffusion of toluene and IPA, and this supersaturated state assists the growth of C_{60}NWs. The above procedure is named "static LLIP method" [30, 39]. While the glass bottle is kept still in an incubator, the C_{60}NWs grow like a cotton ball by self-assembly.

The static LLIP method has been variously modified in combination with ultrasonic mixing or manual mixing or injection [24, 39, 40]. The ultrasonication enhances the rapid mixing of good solvents and poor solvents, leading to the formation of fine fullerene nuclei that grow into FNWs, FNTs or FNSTs.

In the static LLIP method, a liquid-liquid interface is formed just by layering a poor solvent of fullerene onto a good-solvent solution of fullerene or layering a good solvent solution of fullerene onto a poor solvent of fullerene. The static LLIP method can be combined with manual mixing, supersonic mixing, mixing by injection of liquid or ultrasonic mixing of liquid droplets [41]. These methods are collectively named "dynamic LLIP method".

Cha et al. invented the diaphragm LLIP method (DLLIP method) that injects a poor solvent of fullerene into a good solvent solution of fullerene through a suitable porous membrane [40, 42, 43]. This modified method, for example, slowly injects IPA into a C_{60}-saturated toluene solution through an anodic aluminum oxide (AAO) membrane with nanosized through-holes, and obtains vertically grown microtubes of C_{60}. All the processes that mix two solvents can be classified into the LLIP processes.

Using a system similar to the DLLIP method, the influence of chain length of alcohols (methanol, ethanol, and isopropyl alcohol) on the length of C_{60} whiskers was investigated [44]. Amer et al. reports that the length of C_{60} whiskers decreases with increasing the length of alcohol. Although the synthetic temperature is not shown in their paper, it is suggested that the length of alcohol influences the desolvation energy of solvated C_{60} molecules that governs the rate limiting process of surface reaction [45].

The Young's modulus of C_{60}NWs was examined, using a transmission electron microscope (TEM) equipped with the function of AFM (atomic force microscope) [46]. The Young's modulus of C_{60}NWs was found to increase with decreasing their diameter [46, 47, 48, 49]. This phenomenon can be explained by the fact that the C_{60}NWs have a core-shell structure with a porous inside and a dense outer surface [48, 50]. Kizuka et al. describes that solvent molecules contained in C_{70}NWs produces a higher density of lattice defects in their interior regions and reduce the Young's modulus of C_{70}NWs [51]. Further, the Young's modulus of C_{70}NTs was found to increase with decreasing their diameter [25]. The above facts conclude that the FNWs with smaller diameters have the better crystallinity and greater Young's modulus in general.

It was suggested that FNWs grow from seed crystals in the LLIP process [52, 53, 54]. The nucleus size of C_{60}NWs was found to be influenced by the supersaturation of C_{60} in solution that is determined by the mixing ratio of good solvents and poor solvents [39]. C_{60}NTs were shown to grow to both directions along their growth axis from the seed crystals [53, 54]. However, the seed crystals should disappear by the core dissolution mechanism to form the through-hole structure [55].

The regrowth of C_{60}NTs was observed in ultrasonically pulverized C_{60}NTs [53]. The ultrasonically fractured C_{60}NTs have steep edge-shaped walls to whose apexes C_{60} molecules accumulate and crystallize [53]. This preferential accumulation of C_{60} to the places with small curvature radii such as the hexagonal apexes is an important growth mechanism of FNTs [53, 54].

The growth of C_{60}NWs is influenced by time, temperature, light, solvent species, the ratio between the good solvents and the poor solvents for C_{60} and impurity water [39, 56, 57, 58, 59]. The growth mechanism has been minutely studied in the system of C_{60}-saturate toluene solutions and IPA. The growth activation energy was calculated by changing the growth temperature, and an activation energy of 52.8 kJ/mol was obtained. This activation energy, 52.8 kJ/mol, is greater approximately by a factor of 4 than 13.1 kJ/mol for the diffusion of C_{60} in a mixed solvent of toluene and acetonitrile (4:1, v/v) [56, 60]. This high activation energy means that the growth of C_{60}NWs is rate-limited by the desolvation process of C_{60} molecules bonded with solvent molecules on the crystal surface.

In the dynamic LLIP process, a good solvent solution of fullerene (A) and a poor solvent (B) are coercively mixed with each other. However, a liquid-liquid interface where a supersaturated state of fullerene is inevitably generated at all the microscopic interfaces between A and B during the forced mixing. Hence, the nucleation of fullerene crystals occurs dynamically at the microscopic liquid-liquid interfaces, leading to the rapid nucleation of fine fullerene crystals. Granular, linear or sheet morphologies of fullerene crystals from the nucleated crystals depend on the growth kinetics that may be governed by the degree of supersaturation, the solvent species and temperature.

The size control of FNWs is a very important subject for the practical application. Wakahara et al. measured the diameter of C_{60}NWs that varies depending on the size of glass bottles. Linear relationships between the liquid-liquid interface area and the diameter of C_{60}NWs were obtained under the condition that the total volume of solution was fixed [61]. Further we examined the size of C_{60}NWs, varying the solution volume in the system of C_{60}-saturated toluene and IPA [62]. Length and diameter of individual C_{60}NWs were measured, using the C_{60}NWs prepared by a dynamic LLIP method. In this experiment, C_{60} NWs were prepared by manual mixing of 30 times after forming a liquid-liquid interface by layering IPA on the equal amount of C_{60}-saturated toluene solution.

It was found that the mean number density of C_{60}NW in solution was approximately proportional to the inverse of the square root of solution volume V.

3. ELECTRICAL PROPERTIES OF C_{60}NWS

C_{60}NWs are n-type semiconductors that have been applied for field effect transistors [63], solar cells [64, 65], photocatalysts [66], chemical sensors [27], photosensors [67], and so forth. On the other hand, Wakahara et al. recently synthesized ambipolar FETs using the C_{60} - cobalt porphyrin hybrid nanosheets by a LLIP method [81]. The carrier mobility of C_{60}NWs was measured to be 2×10^{-2} cm^2/Vs in vacuum by forming a FET [63]. However, the as-synthesized solution grown C_{60} needle-like crystals exhibited a very high mobility up to about 11 cm^{2}V^{-1}s^{-1} [68]. Since such a vary wide range of carrier mobility of C_{60}NWs or needle-like crystals of C_{60} should depend on the contained impurity solvent molecules, impurity oxygen, crystal structure and lattice defects, the electrical properties of C_{60}NWs should be further investigated, using the C_{60}NWs with better crystallinity and chemical purity.

The electrical resistivity of C_{60} whiskers with diameters greater than 1 μm (~10 μm - a few hundred μm) was measured by two-terminal method at room temperature [69]. The electrical resistivity of the C_{60} whiskers rapidly decreased with decreasing diameter. Later, Larsson et al. measured the electrical resistivity using four-point probe method [70]. A C_{60}NW with a diameter of 650 nm showed a low resistivity of 3 Ωcm [70]. The decrease in the resistivity with decreasing the diameter suggests the better crystallinity and higher overlapping of π electrons in the C_{60}NWs with the smaller diameters and shorter C_{60} intermolecular distances [69]. Xu et al. showed that C_{60}NWs are conductive where the surface is not covered by oxygen [71].

To understand the electrical properties of semiconductor, it is necessary to measure the temperature dependence of electrical conductivity of the semiconductor. Ji et al. measured the temperature dependence of electrical conductivity of a C_{60}NW with a face-centered cubic structure and a C_{60}NW with a hcp structure [72], and found that the fcc C_{60}NW has a higher electrical conductivity than the hcp C_{60}NW. Although the effect of solvent molecules contained in the hcp C_{60}NW is not clear, this result shows the crystal structure influences the electrical properties of C_{60}NWs. The closer packing of C_{60} molecules is expected to induce the higher overlapping of π electrons that leads to the higher electrical conductivity of C_{60}NWs [69, 72].

The superconductivity of C_{60} doped with potassium (K) was discovered by Hebard et al. in 1991 [73]. The superconducting transition temperature T_c was 18 K in the K-doped C_{60} films and bulk samples. Tanigaki et al. reported the highest T_c of 33 K in $Cs_2Rb_1C_{60}$ powder [74].

Three phases are known for the K-doped C_{60} [75], i.e., (a) fcc (K_3C_{60}), (b) bct (K_4C_{60}), and (c) bcc (K_6C_{60}). Only the fcc phase exhibits the superconductivity. Hence, the fcc C_{60}NWs should be superconducting by doping alkali metals as previously predicted [15]. In 2011, we successfully fabricated superconductive C_{60}NWs by doping potassium (K) for the first time [76, 77].

T_c of the K-doped C_{60}NWs with a nominal composition of $K_{3.3}C_{60}$ was 17 K which is lower than that of reported value of 18 K [73]. However, the supercon-

ducting shielding volume fraction was as high as 80 %, although the doping was performed at 200 °C only for

On the other hand, the shielding volume fraction of K-doped C_{60} crystal powder was less than 1 % using the same process of doping. This finding of high shielding volume fraction in the K-doped C_{60}NWs will open the way for the use of superconducting carbon cables that are light, flexible and recyclable. In the initial stage of K-doped C_{60} superconductivity research, the superconducting shielding volume fraction of C_{60} crystals was at most about 35 % even after the heat treatment of more than 20 days at higher heating temperatures up to 250 °C [78] .

The effort to increase the T_c value of alkali-doped C_{60}NWs has been continued. The T_c values of C_{60}NWs have been elevated up to 26 K by doping Rb [79], and the volume fraction of Rb-doped C_{60}NWs was higher by a factor of about five than that of Rb-doped C_{60} powder. Since Rb is more abundant than common metals such as copper, lead or zinc [80], and carbon is also a very abundant elements, the lightweight Rb-doped C_{60}NWs are expected to be applied for superconducting motor cars, superconducting cables for power delivery, superconducting wind generator and so forth in the future.

4. SUMMARY

Up to now, various types of FNWs, fullerene nanotubes and fullerene nanosheets have been synthesized by the LLIP method, and various application studies of those fullerene nanomaterials have been performed in solar cells, chemical sensors, photo sensors, photocatalysts, ambipolar field effect transistors and so on. The experimental result in the dynamic LLIP synthesis of C_{60}NWs using a C_{60}-saturated toluene solution and IPA suggests that the nucleation of C_{60}NWs is governed by the volume of liquid-liquid interface produced by the interdiffusion between the good solvents of fullerene and the poor solvents of fullerene.

The alkali-metal doped C_{60}NWs are the first carbon fibers that became superconductors and have excellent properties such as lightweight and flexibility. Especially, the C_{60}NWs doped with K or Rb are promising superconductors with T_cs higher than any other practically used metal superconductors, and are composed of non-toxic, abundant and recyclable elements. In the future, the fullerene nanomaterials will find a wide application in electronic, electrical, optical fields and so forth.

REFERENCES

1. H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, *Nature* **318**, 162 (1985).
2. S. Okada, S. Saito, A. Oshiyama, *Phys. Rev. Lett.* **83**, 1986 (1999).
3. A.M. Rao, P. Zhou, K.-A. Wang, G.T. Hager, J.M. Holden, Y. Wang, W.-T. Lee, X.-X. Bi, P.C. Eklund, D.S. Cornett, M.A. Duncan, I.J. Amster, *Science* **259**, 955 (1993).
4. R. Katoб and K. Miyazawa, *J. Nanotech.* **2012**, 101243 (2012).
5. Y. Iwasa, T. Arima, R.M. Fleming, T. Siegrist, O. Zhou, R.C. Haddon, L.J. Rothberg, K.B. Lyons, H.L. Carter, Jr., A.F. Hebard, R. Tycko, G. Dabbagh, J.J. Krajewski, G.A. Thomas, T. Yagi, *Science* **264**, 1570 (1994).
6. K. Miyazawa, H. Satsuki, M. Kuwabara, M. Akaishi, *J. Mater. Res.* **16**, 1960 (2001).
7. J. Minato, K. Miyazawa, T. Suga, H. Kanda, M. Akaishi, K. Yamaura, E. Muromachi, H. Kakisawa, *J. Mater. Res.* **20**, 742 (2005).
8. K. Miyazawa, M. Akaishi, Y. Kuwasaki, T. Suga, *J. Mater. Res.* **18**, 166 (2003).
9. M. Nakaya, T. Nakayama, M. Aono, *Thin Solid Films* **464-465**, 327 (2004).
10. K. Miyazawa, J. Minato, M. Fujino, T. Suga, *Diam. Relat. Mat.* **15**, 1143 (2006).
11. M. Popov , V. Mordkovich , S. Perfilov, A. Kirichenko, B. Kulnitskiy, I. Perezhogin, V. Blank, *Carbon* **76**, 250 (2014).
12. V. Blank, M. Popov, G. Pivovarov, N. Lvova, K. Gogolinsky, V. Reshetov, *Diam. Relat. Mat.* **7**, 427 (1998).
13. K.Miyazawa, A. Obayashi, M. Kuwabara, *J. Am. Ceram. Soc.* **84**, 3037(2001).
14. K. Rauwerdink, J. Liu, J. Kintigh, G. P. Miller, *Micros. Res. Tech.* **70**, 513 (2007).
15. K. Miyazawa, M. Kuwabara, *US Patent*, US 6890505B2.
16. K. Miyazawa, *J. Nanosci. Nanotechnol.* **9**, 41 (2009).
17. K. Miyazawa (Ed.), *Fullerene Nanowhiskers* (Singapore: Pan Stanford Publishing Pte. Ltd., 2011).
18. T. Wakahara, Y. Nemoto, M. Xu, K. Miyazawa, D. Fujita, *Carbon* **48**, 3359 (2010).
19. K. Miyazawa, J. Minato, T. Mashino, S. Nakamura, M. Fujino, and T. Suga, *NUKLEONIKA* **51** Supplement 1, S41 (2006).
20. K. Miyazawa, T. Mashino, T. Suga, *Trans. Mater. Res. Soc. Jpn.* **29**, 537 (2004).
21. K. Miyazawa, T. Mashino, T. Suga, *J. Mater. Res.* **18**, 2730 (2003).
22. K. Miyazawa, T. Suga, *J. Mater. Res.* **19**, 2410 (2004).
23. K. Miyazawa, J. Minato, T. Yoshii, M. Fujino, T. Suga, *J. Mater. Res.* **20**, 688 (2005).
24. K. Miyazawa, C. Ringor, *Mater. Lett.* **62**, 410 (2008).
25. T. Kizuka, K. Miyazawa, T. Tokumine, *J. Nanotech.* **2012**, 969357 (2012).
26. H. Liu, Y. Li, L. Jiang, H. Luo, S. Xiao, H. Fang, H. Li, D. Zhu, D. Yu, J. Xu, B. Xiang, *J. Am. Chem. Soc.* **124**, 13370 (2002).
27. X. Zhang, Y. Qu, G. Piao, J. Zhao, K. Jiao, *Mater. Sci. Eng. B* **175**, 159 (2010).
28. T. Kizuka, K. Miyazawa, T. Tokumine, *J. Nanosci. Nanotechnol.* **12**, 2825 (2012).
29. K. Miyazawa, M. Fujino, J. Minato, T. Yoshii, T. Kizuka, T. Suga, *Proc. SPIE 5648, Smart Materials III*, 224 (2004).
30. K. Miyazawa, Y. Kuwasaki, A. Obayashi, M. Kuwabara, *J. Mater. Res.* **17**, 83 (2002).
31. K. Osonoe, R. Kano, K. Miyazawa, M. Tachibana, *J. Cryst. Growth* **401**, 458 (2014).
32. T. Wakahara, M. Sathish, K. Miyazawa, C. Hu, Y. Tateyama, Y. Nemoto, T. Sasaki, O. Ito, *J. Am. Chem. Soc.* **131**, 9940 (2009).
33. L.K. Shrestha, M. Sathish, J.P. Hill, K. Miyazawa, T. Tsuruoka, N. M. Sanchez-Ballester, I. Honma, Q. Ji, K. Ariga, *J. Mater. Chem. C* **1**, 1174 (2013).
34. L.K. Shrestha, J.P. Hill, T. Tsuruoka, K. Miyazawa, K. Ariga, *Langmuir* **29**, 7195 (2013).
35. L. Kumar Shrestha, Q. Ji, T. Mori, K. Miyazawa, Y. Yamauchi, J. P. Hill, K. Ariga, *Chem. Asian J.* **8**, 1662 (2013).
36. L.K. Shrestha, Y. Yamauchi, J.P. Hill, K. Miyazawa, K. Ariga, *J. Am. Chem. Soc.* **135**, 586 (2013).
37. L.K. Shrestha, J.P. Hill, K. Miyazawa, K. Ariga, *J. Nanosci. Nanotechnol.* **12**, 6380 (2012).
38. M. Sathish, K. Miyazawa, *J. Am. Chem. Soc.* **129**, 13816 (2007).
39. K. Miyazawa, K. Hotta, *J. Cryst. Growth* **312**, 2764 (2010).
40. S.I. Cha, K. Miyazawa, J.-D. Kim, *Chem. Mater.* **20**, 1667 (2008).
41. K. Miyazawa, J. Minato, T. Mashino, T. Yoshii, T. Kizuka, R. Kato, M. Tachibana, T. Suga,*Proceedings of the 2nd JSME/ASME International Conference on Materials and Processing 2005 – The 13th JSME Materials and Processing Conference- M&P2005*, pp.(SMS23)-1 - (SMS23)-4, June 19-22, 2005, Seattle, USA.
42. K. Miyazawa, R. Kuriyama, S. Shimomura, T. Wakahara, M. Tachibana, *J. Cryst. Growth* **388**, 5 (2014).
43. S.I. Cha, K. Miyazawa, J. Kim, *United States Patent* US8,685,160 B2.
44. M. S. Amer, T. K. Todd, J. D. Busbee, *Mater. Chem. Phys.* **130**, 90 (2011).
45. K. Hotta, K. Miyazawa, *NANO* **3**, 355 (2008).
46. K. Asaka, R.Kato, R. Yoshizaki, K. Miyazawa, T. Kizuka, *Diam. Relat. Mat.* **16**, 1936 (2007).
47. T. Kizuka, K. Saito, K. Miyazawa, *Diam. Relat. Mat.* **17**, 972 (2008).
48. K. Saito, K. Miyazawa, T. Kizuka, *Jpn. J. Appl. Phys.* **48**, 010217 (2009).
49. K. Asaka, R. Kato, K. Miyazawa, T. Kizuka, *Appl. Phys. Lett.* **89**, 071912 (2006).
50. R. Kato, K. Miyazawa, *Diam. Relat. Mat.*, 20 (2011) 299-303.
51. T. Kizuka, K. Miyazawa, T. Tokumine, *J. Nanotech.* **2012**, 583817 (2012).
52. K. Miyazawa, K. Hamamoto, S. Nagata, T. Suga, *J. Mater. Res.* **18**, 1096 (2003).
53. J. Minato, K. Miyazawa, T. Suga, *Sci. Technol. Adv. Mater.* **6**, 272 (2005).
54. H.-X. Ji, J.-S. Hu, Q.-X. Tang, W.-G. Song, C.-R. Wang, W.-P. Hu, L.-J. Wan, S.-T. Lee, *J. Phys. Chem. C* **111**, 10498 (2007).
55. C.L. Ringor, K. Miyazawa, *J. Nanosci. Nanotechnol.* **9** 6560 (2009).
56. K. Hotta, K. Miyazawa, *NANO* **3**, 355 (2008).
57. M. Tachibana, K. Kobayashi, T. Uchida, K. Kojima, M. Tanimura, K. Miyazawa, *Chem. Phys. Lett.* **374**, 279 (2003).
58. K. Kobayashi, M. Tachibana, K. Kojima, *J. Cryst. Growth* **274**, 617(2005).
59. K. Miyazawa, K. Hotta, *J. Nanopart. Res.* **13**, 5739 (2011).
60. M. Wei, H. Luo, N. Li, S. Zhang, L. Gan, *Microchem. J.* **72**, 115 (2002).
61. T. Wakahara, K. Miyazawa, Y. Nemoto, O. Ito, *Carbon* **49**, 4644 (2011).
62. K. Miyazawa, C. Hirata, T. Wakahara, *J. Cryst. Growth* **405**, 68 (2014).
63. K. Ogawa, T. Kato, A. Ikegami, H. Tsuji, N. Aoki, Y. Ochiai, *Appl. Phys. Lett.* **88**, 112109 (2006).
64. P.R. Somani, S.P. Somani, M. Umeno, *Appl. Phys. Lett.* **91**, 173503 (2007).
65. R.G. Shrestha, L.K. Shrestha, A.H. Khan, G.S. Kumar, S. Acharya, K. Ariga, *Appl. Mater. Interfaces* **6**, 15597 (2014).
66. B.H. Cho, K.B. Lee, K. Miyazawa, W.B. Ko, Asian *J. Chem.* **25**, 8027 (2013).
67. J. Yang, H. Lim, H.C. Choi, H. S. Shin, *Chem. Commun.* **46**, 2575 (2010).

68. H. Li, B. C-K. Tee, J.J. Cha, Y. Cui, J.W. Chung, S.Y. Lee, Z. Bao, *J. Am. Chem. Soc.* **134**, 2760 (2012).
69. K. Miyazawa, Y. Kuwasaki, K. Hamamoto, S. Nagata, A. Obayashi, M. Kuwabara, *Surf. Interface Anal.* **35**, 117 (2003).
70. M.P. Larsson, J. Kjelstrup-Hansen, S. Lucyszyn, *ECS Transactions* **2**, 27 (2007).
71. M. S. Xu, Y. Pathak, D. Fujita, C. Ringor, K. Miyazawa, *Nanotechnology* **19**, 075712 (2008).
72. H.-X. Ji, J.-S. Hu, L.-J. Wan, Q.-X. Tang, W.-P. Hu, *J. Mater. Chem.* **18**, 328 (2008).
73. A.F. Hebard, M.J. Rosseinsky, R.C. Haddon, D.W. Murphy, S.H. Glarum, T.T.M. Palstra, A.P. Ramirez, A.R. Kortan, *Nature* **350**, 600 (1991).
74. K. Tanigaki, T.W. Ebbesen, S. Saito, J. Mizuki, J.S. Tsai, Y. Kubo, S. Kuroshima, *Nature* **352**, 222 (1991).
75. R.C. Haddon, *Acc. Chem. Res.* **25**, 127 (1992).
76. H. Takeya, K. Miyazawa, R. Kato, T. Wakahara, T. Ozaki, H. Okazaki, T. Yamaguchi, Y. Takano, *Molecules* **17**, 4851 (2012).
77. H. Takeya, R. Kato, T. Wakahara, K. Miyazawa, T. Yamaguchi, T. Ozaki, H. Okazaki, Y. Takano, *Mater. Res. Bull.* **48**, 343 (2013).
78. D.W. Murphy, M.J. Rosseinsky, R.C. Haddon, A.P. Ramirez, A.F. Hebard, R. Tycko, R.M. Fleming, G. Dabbagh, *Physica C* **185**-**189**, 403 (1991).
79. H. Takeya, K. Miyazawa, Y. Takano, *Mater. Integration* **25**, 38 (2012) [in Japanese].
80. W.C. Butterman, R.G. Reese, Jr., *Mineral Commodity Profiles* - Rubidium, U.S. Geological Survey, http://pubs.usgs.gov/of/2003/of03-045/of03-045.pdf.
81. T. Wakahara, P. D'Angelo, K. Miyazawa, Y. Nemoto, O. Ito, *J. Am. Chem. Soc.* **134**, 7204 (2012).