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Preparation and characterization of fullerene dimer [C_{120}] by trichloroperbenzoic acid oxidation method

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Abstract: In this study, we present the preparation and characterization of oxidized fullerene and fullerene dimer [C_{120}]. From the XRD data, other weak peaks with pristine fullerene [C_{60}] peaks were observed in the X-ray diffraction patterns for fullerene dimer [C_{120}]. SEM micrographs for the fullerene dimer [C_{120}] indicated that practically all the surface state was shown the drastic morphology changes and its outer surface is clearly visible and resulted in clogging and frost-like formation. From the MALDI-TOF mass spectra, the differences in the spectra recorded on two kinds of fullerene are due to the oxidation including chemical bonding and bridging between the C_{60} molecules. We also obtained additional information from FT-IR spectra on functional component on the chemically modified surface of oxidized fullerene and fullerene dimer [C_{120}].

Key words: fullerene dimer [C_{120}], XRD, SEM, MALDI-TOF, FT-IR

1. Introduction

The attention of materials scientists has been attracted by the synthesis of new materials based on the family of fullerene molecules. Covalent functionalization of fullerene dimer continues to attract the interest of synthetic and materials chemistry fields with all the intense research activities in the area, the major problem still remains the poor yield of the synthetic transformations. In order for fullerene dimmer science to become truly useful core technology in the 21st century, the synthetic transformations must be quantitative based on the starting fullerene used for the reaction, and must be achieved in a simple and efficient procedure without production of noxious waste. Unfortunately, the current state of the technique is far from satisfactory. The modification of molecular systems that can spontaneously self-assemble and generate three-dimensionally extended structure such as cluster is of interest in new material nanotechnologies. Fullerene dimmers and their larger assemble form a newer class of molecular system with potential applications in molecular electronic devices and superconducting materials and hydrogen storage. Dimers of fullerene are synthesized either by covalently linking C_{60} through bifunctional cyclo-addition reactions or by attracting C_{60} units directly.[1] The large-scale synthesis of fullerene derivatives are know to form clusters in mixed solvents that are optically transparent and thermodynamically stable.[2,3] Studies related to fullerene derivatives can provides information bridging

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the solution and solid-state properties of molecular systems and interesting photochemical and photoectrochemical properties of fullerene-based cluster systems.[4,5] The proper design of molecules that contain controlled numbers of fullerene units can provide basic information on the cluster systems. Fujiwara *et al.* have previously reported a highly selective synthesis of fullerene dimmer C_{100} by the solid-state reaction of C_{60} using Bingel reaction technique. The simplest fullerene dimmer, C_{120}, is regarded ad the essential submit of fullerene polymers and the study of its chemical reactivity is of great interest, particularly with respect to the problem of how one of the C_{60} cages would affect the reactivity of the other. Recently, Wang *et al.* developed a new method to derivative C_{60} in the solid state by the use of high-speed vibration milling method.[6] The key feature of the method is vibrating milling technique, which can activated the reaction system by bringing the reagents into very close contact at the preparation scale and by providing extra mechanical energy, much more effectively than ball-milling technique.

In this paper, we studied a simple preparation method for a new C_{60} derivative with the elemental composition C_{120}, together with the results of SEM, XRD, FT-IR and MALDI-TOF mass spectroscopic measurements. The structure proposed is that of a C_{60} dimer bridged.

2. Experimental

2.1. Materials

Crystalline C_{60} powder of 99.9 % purity from TCI (Tokyo Kasei Kogyo Co. Ltd., Japan) was used as a starting material. Reagents were purchased reagent-grade for Duksan chemical Co and Daejung cheimical Co. and used without further purification unless otherwise stated. All solvents were purified using standard procedures. Evaporation and concentration in vacuum were done at water aspirator pressure and compounds were dried at 1.33 Pa.

2.2. Chemical oxidation by TCPBA method

3-chloroperbenzoic acid (TCPBA, ca. 0.96 g) was suspended in 60 mL benzene, and fullerene [C_{60}] (ca. 40 mg) was added, mixture was refluxed at air atmosphere for 6 h. And the solvent dried at boiling point (353.13 K) of benzene. The solid precipitates were transformed to white color. After completion, white precipitates were washed with ethyl alcohol and then dried at 363 K.

2.3. Characterization

For the measurements of structural variations, X-ray diffraction patterns were taken using an X-ray generator (Shimatz XD-D1, Japan) with Cu Kα radiation. Scanning electron microscopy (SEM, JSM-5200 JOEL, Japan) was used to observe the surface state and structure of oxidized fullerene [C_{60}] and fullerene dimer [C_{120}] after oxidation compare to pristine fullerene [C_{60}]. As one of the analysis of mass transformation for those samples, matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy (Voyager, DE-STR, U.S.A) was used to characterize of structural transformation by oxidation and behavior of fullerene derivatives [C_{120}]. The two kinds of fullerene derivatives were examined by a cyano-4-hydroxyl sinamic acid as matrix using the spectroscopy. The reflectance mode FT-IR (Nicholet 380, USA) spectra were collected from two kinds of fullerene samples with smart miracle ATR method.

3. Results and discussion

Fig. 1 had shown the X-ray diffraction patterns of (a) oxidized fullerene [C_{60}] and (b) fullerene dimer [C_{120}]. It was observed that diffraction peak positions are accurately measured with XRD, which makes it the best representation for original fullerene [C_{60}]. XRD is very important experimental technique that has long been used to address all issues related to the crystal structure of solids, including lattice constants and geometry, identification of unknown materials orientation of single crystals, preferred orientation of polycrystals, defects, stress, etc. According to the structure parameters measured former studies,[7,8] the distance between the C-C covalent bond in C_{60} cages

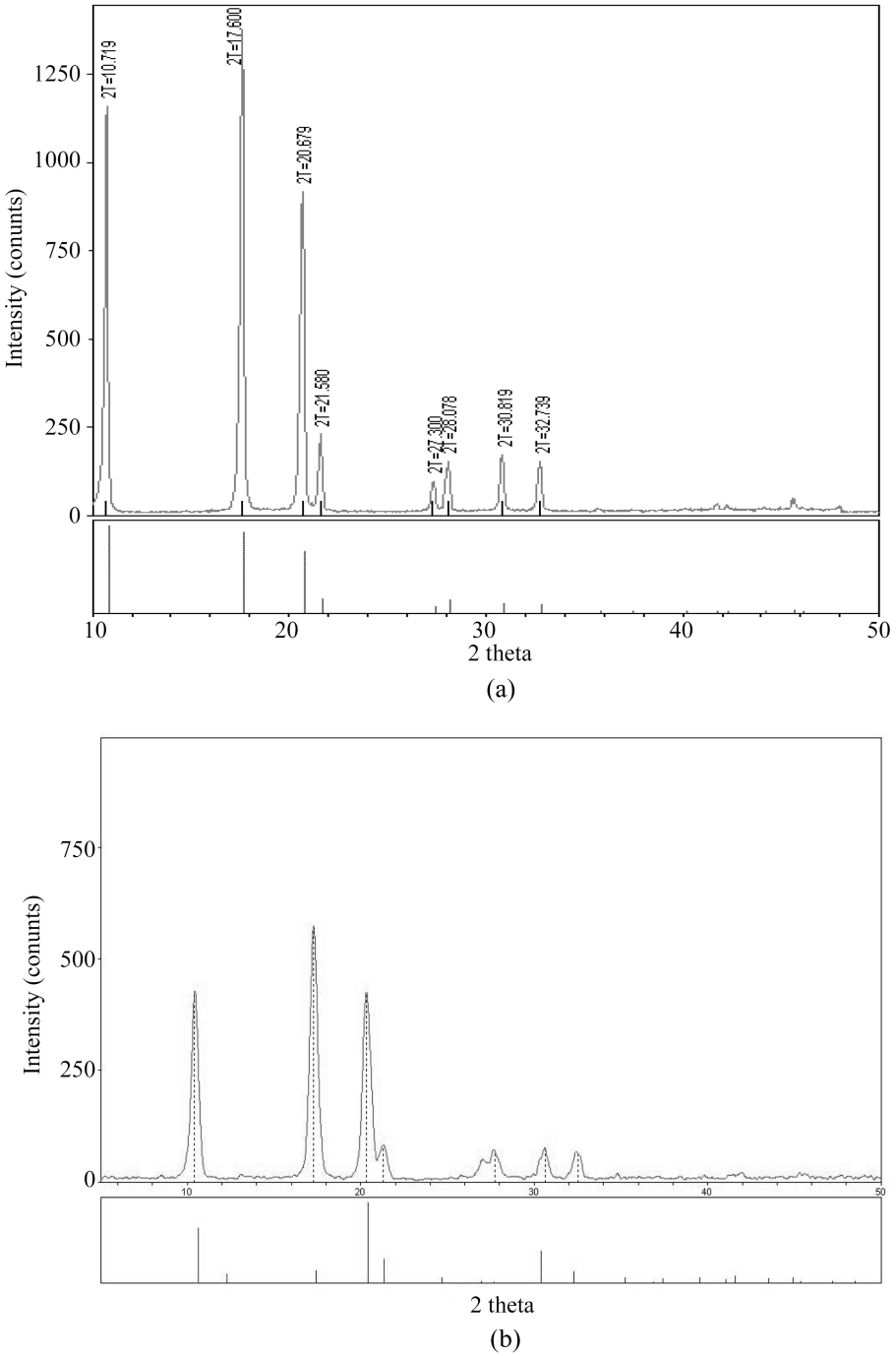


Fig. 1. XRD patterns of fullerene derivatives; (a) oxidized fullerene and (b) fullerene dimer [C_{120}].

is 10.02 Å packed into the fcc cell. According to the *Fig.* 1, high intensity and very sharp peaks of fullerene [C_{60}] were observed in the XRD patterns for the two kinds of samples. From the peak position of fullerene dimer [C_{120}], however, it could not found that diffraction peak patterns for the oxidized

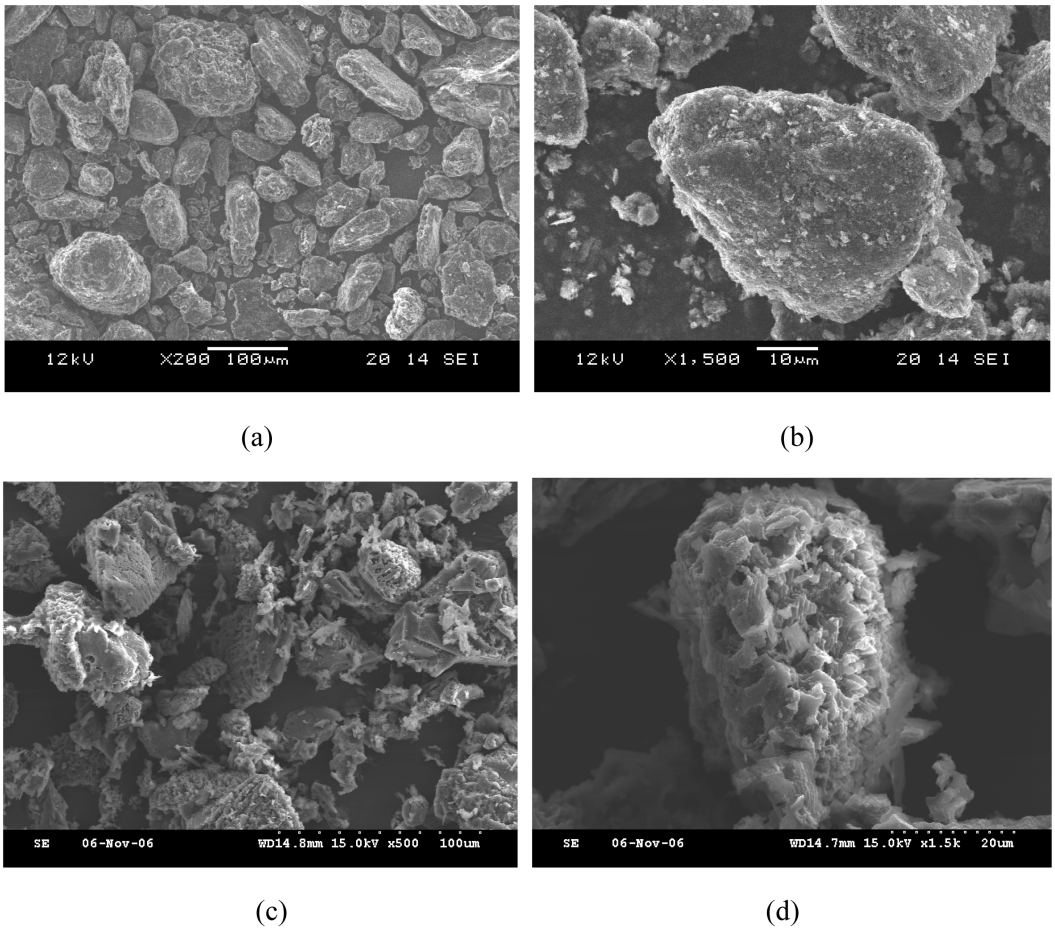
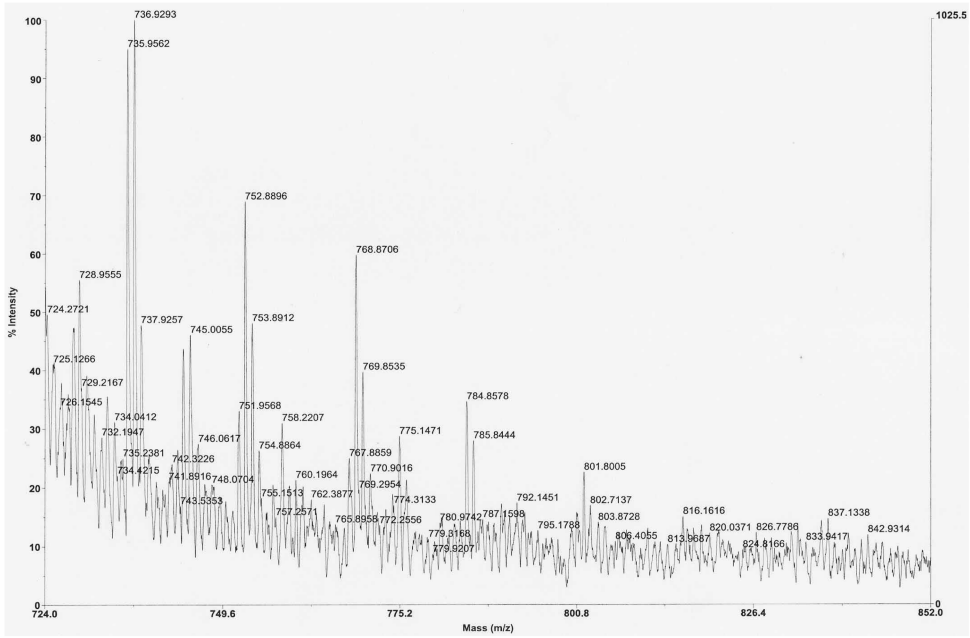


Fig. 2. SEM micrographs of pristine fullerene and fullerene derivatives; (a) pristine fullerene (×200), (b) pristine fullerene (×1500), (c) oxidized fullerene and (d) fullerene dimer [C_{120}].

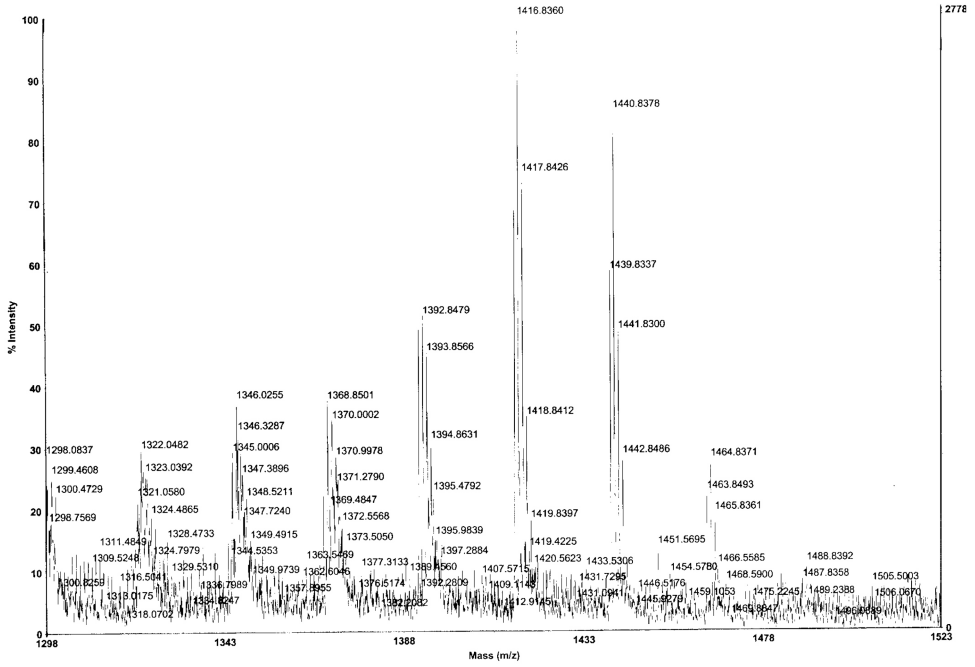
fullerene are different from that of fullerene dimer [C_{120}] except decreasing intensity. It is reasonable that the formation of linkage of cage to cage, it may be partially and structurally a little changed to fullerene monomer of C_{60} by oxidation reaction.

SEM is one of the most widely used techniques used in characterization of surface state and structures of materials. Not only does the SEM produce topographical information as optical microscopes do, it also provides the chemical composition information near the surface. *Fig.* 2 shows SEM micrographs of pristine fullerene [C_{60}], oxidized fullerene, and fullerene dimer [C_{120}]. This figure presents results from the characterization of surface texture on the fullerene [C_{60}] sample and their derivatives. SEM pictures (*Fig.* 2(a) and (b)) of pristine fullerene [C_{60}] sample provide information about the surface state of smooth pebble-like C_{60}. After oxidation treatment, it was shown that the surface properties are modified in some cases, this effect being developed to surface state from smooth pebble-like to coarse bread-like in oxidized fullerene [C_{60}] (*Fig.* 2(c)). In case of fullerene dimer [C_{120}], this observation indicated that practically all the surface state was shown the drastic morphology changes and its outer surface is clearly visible and resulted in clogging and frost-like formation.

The matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra of the synthesized product were shown *Fig.* 3. Since further



(a)



(b)

Fig. 3. Mass spectra of fullerene derivatives; (a) oxidized fullerene and (b) fullerene dimer [C_{120}].

information on the structure of these materials was needed for a combination of XRD analysis and MALDI-TOF-Mass spectroscopic measurements. These measurements gave additional evidence for

the difference of the two kinds of materials. Details of the obtained results are, however, rather surprising, as in the MALDI-TOF mass spectra are observed for the fullerene dimer [C_{120}], as compared to the material transformed with oxidation. The traditional mass spectrum of pure C_{60} was shown at former study.[9,10] *Fig.* 3(a) is presented mass spectrum of transformed C_{60} by oxidation. It shows peaks for pristine C_{60} at 720 m/z and oxidized C_{60} by oxidation. In *Fig.* 3(a), the O signals of oxidized fullerene are 736.92, 752.68, 768.87, 784.85, 801.80 and 816.16 m/z. From these results, it was indicated that these dominating peaks of the spectrum correspond to increasing O elements in pristine fullerene [C_{60}] by structural transformation. MALDI-TOF mass spectrum of fullerene dimer [C_{120}] was shown *Fig.* 3(b). The appearance of the peak due to the formation of dimer was observed at 1440.83 m/z. The differences in the spectra recorded on two kinds of fullerene [C_{60}] illustrate the influence of the chemical components on the oxidation and formation of fullerene dimer. This influence has its origin in the different chemical reactivity against the substrate fullerene [C_{60}]. Taking into account that the differences in the spectra recorded on two kinds of fullerene [C_{60}] are due to the oxidation including chemical bonding and interposing of a metallic silver in the C_{60} molecules. We interpreted these results as a conversion of C_{120} back to C_{60}. It is consider that the structure synthesized is that of a high yielded-fullerene dimmer.

The FT-IR spectra gave additional information on functional component on the surface of fullerene derivatives. The FT-IR spectra of fullerene derivatives by smart miracle ATR method are shown in *Fig.* 4. Observation of the absorption bands shows that the changes between the oxidized C_{60} and fullerene dimer [C_{120}] are mainly due to the formation functional groups. As shown in *Fig.* 4, the (C-O) mode of the methoxy groups depends on the chemical structure of the adsorption sites. Absorption of C-O followed by IR spectra has been used to characterize treated and non-treated metal catalysts.[11,12] The frequency of (C-O) of adsorbed carbon monoxide is often treated as an indicator characterizing the local coordination. This is also suitable for examining the state of metal ions situated differently on the solid surface. The most characteristics changes are observed at 1379.6 cm^{-1} of the presence of C-O- containing structures. The oxidation treatment is consequently associated with the linkage of bridged C_{60}. In the former study[13] for oxidation of C_{60}, authors attributed the strong band near 1722 cm^{-1} to five-membered-ring lactones and other broad bands in the 1750-1850 cm^{-1} region to cyclic anhydrides. It also noted that there one or two bands near 1619 cm^{-1} in the spectra of compounds with five-membered ring. The band observed at 2362.6 cm^{-1} is usually ascribed to the presence of aliphatic compounds. The main goal of oxidation is to obtain a more hydrophilic surface

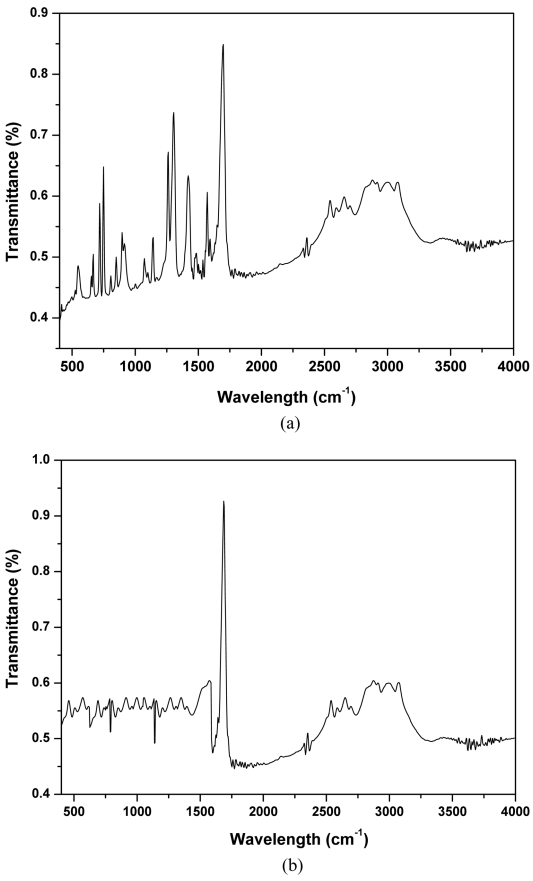


Fig. 4. FT-IR spectra of fullerene derivatives; (a) oxidized fullerene and (b) fullerene dimer [C_{120}].

with a relatively large number of oxygen containing oxygen groups on the C_{60} surfaces for the linkage of bridged C_{60}. A broad band in the 3100-3500 cm^{-1} region, typically attributed to O-H stretches from hydroxyl, phenolic and carboxylic groups are absent. Thus FT-IR spectra confirm the formation of carbonyl groups during the oxidation process. The FT-IR spectrum by smart miracle ATR method of C_{120} shows a splitting of the original C_{60} vibrations into sub features indicating a decrease of symmetry (*Fig.* 4(b)). In the spectrum, the main peaks at 1590 cm^{-1} and 1490 cm^{-1} corresponding to quinine and benzene ring deformation with the spectrum are reshifted to 1570 cm^{-1} and 1480 cm^{-1} coupled with the spectrum of original. The band characteristic of conducting protonated form is observed at 1240 cm^{-1} and 780 cm^{-1} peak is assigned to a characteristic mode of quinine ring.

4. Conclusion

The structural variations, surface state and mass transformation of C_{60} are investigated through preparation of oxidized fullerene [C_{60}] and fullerene dimer [C_{120}] compare to pristine fullerene [C_{60}]. The XRD, SEM, MALDI-TOF mass spectrometry and FT-IR were conducted for these new species. From the XRD data, other weak peaks with pristine fullerene [C_{60}] peaks were observed in the X-ray diffraction patterns for fullerene dimer [C_{120}]. SEM micrographs for the fullerene dimer [C_{120}] indicated that practically all the surface state was shown the drastic morphology changes and its outer surface is clearly visible and resulted in clogging and frost-like formation. From the MALDI-TOF mass spectra, the differences in the spectra recorded on two kinds of fullerene are due to the oxidation including chemical bonding and bridging between the C_{60} molecules. We also obtained additional information from FT-IR spectra on functional component on the surface of oxidized fullerene and fullerene dimer [C_{120}].

References

1. M. Fujitsuka, C.P. Luo, O. Ito, Y. Murata, K. Komatzu, *J. Phys. Chem. A*, **103**, 7155 (1999).
2. M. Sandahl, T. Anderson, K. Nilson, O. Wannerstrom, G. Westman, *Synth. Met.*, **55**, 3252 (1993).
3. S. Math, H. Pal, D.K. Palit, A.V. Sapre, J.P. Mittel, *J. Phys. Chem. B*, **102**, 10158 (1998).
4. P.V. Kamat, S. Barazzouk, K.G. Thomas, S. Hotchandani, *J. Phy. Chem. B.*, **104**, 4014 (2000).
5. V. Bijo, S. Barazzouk, K.G. Thomas, M.V. Gorge, P.V. Kamat, *Langmuir*, **17**, 1930 (2001).
6. K. Fujiwara, K. Komatsu, G.W. Wang, T. Tanaka, K. Hirata, K. Yamamoto, M. Saunders, *J. Am. Chem. Soc.*, **123**, 10715 (2001).
7. G. Cao, *Nanostructures and nanomaterials*, Imperial college press, p.230 (2004).
8. R. Setton, P. Bernier, S. Lefrant, *Carbon molecules and materials, Taylor & Francis*, p.201 (1998).
9. B. Burger, H. Kuzmany, T.M. Nguyen, H. Sitter, M. Walter, K. Martin, K. Kullen, *Carbon*, **36**, 661 (1998).
10. Z. Gu, L. Zhang, J.L. Margrave, V.A. Daveydov, A.V. Rakhmanina, V. Agafonov, V.N. Khabashesku, *Carbon*, **43**, 2989 (2005).
11. W.C. Oh, M.H. Yum, *Bull. Korean Chem. Soc.*, **25**, 8, 1189 (2004).
12. W.C. Oh, C.S. Park, J.S. Bae, Y.S. Ko, *Carbon Science*, **7**, 1, 34 (2006)
13. A.M. Vassallo, L.S.K. Pang, P.A. Cole-Clarke, M.A. Wililson, *J. Am. Chem. Soc.*, **113**, 7820 (1991).