The preparation and characterization of a silver-containing fullerenes [C$_{60}$]

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In this study, we present the preparation and characterization of some Ag-containing fullerenes [C$_{60}$]. From the XRD data, weak peaks of silver with pristine fullerene [C$_{60}$] peaks were observed in the X-ray diffraction patterns for the fullerene [C$_{60}$] treated with silver sequentially after oxidation. SEM and TEM micrographs for the Ag-containing fullerenes [C$_{60}$] indicated that practically all the Ag atoms introduced are located onto the carbon edges or inside pores and consequently, it is dispersed into very small crystallites with the growth of Ag metals. From the Maldi-TOF-Mass spectra, the differences in the spectra recorded on three kinds of fullerene [C$_{60}$] are due to the oxidation including chemical bonding and interposing of metallic silver in the C$_{60}$ molecules. The FT-IR spectra gave additional information on functional components on the surface of silver-containing fullerene [C$_{60}$]. The EDX spectrum of silver-containing fullerene [C$_{60}$] showed the presence of C and O with strong Ag peaks.

Key words: Fullerene [C$_{60}$], XRD, SEM, TEM, Maldi-TOF-Mass spectra.

Introduction

The discovery of the C$_{60}$ molecule stimulated scientists to search for other related forms of carbon and reinterpret older data in terms of the new concept of carbon cage structures. Since their first discovery in 1985 [1], fullerenes have received much attention in terms of their physical and chemical properties as novel carbon materials [2]. Fullerene is a generic term for closed cage carbon molecules with 60, 70, 80 and more carbon atoms, and it is known as the third carbon allotrope following diamond and graphite. Among these molecules, C$_{60}$ is the most common fullerene, and it is known as buckminsterfullerene or Buckyball because it is approximately spherical and resembles a soccer ball with 12 pentagons and 20 hexagons. In a related study, it was quite clear that one should try to intercalate the new modification of carbon indeed intercalated fullerene showed metallic and superconducting behavior [3], as did the intercalated graphite. Macroscopic amounts of endohedral fullerenes have became available which represent a second class of compounds, in which the charge on the fullerene molecule can be changed by counterions encapsulated inside the carbon cage. The heterofullerene, C$_{59}$N, could be produced in macroscopic quantities [4] using an organic synthesis route. The three classes of fullerene compounds in which the charge on the carbon cage can be changed are depicted in Fig. 1. Endohedral metallofullerenes
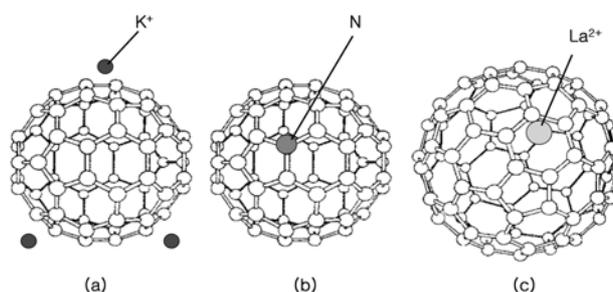

Fig. 1. Sketch of the three ways to change the charge on the carbon cage of fullerene: (a) intercalated compounds (e.g. K$_x$C$_{60}$); (b) heterofullerenes (e.g. C$_{59}$N); and (c) endohedral fullerenes (e.g. La@C$_{82}$).

have attracted much attention because of their unique structures and novel properties [5]. These types of material are expected to show promising applications in diverse areas, such as an electronic device material and in biological science.

Here we present the preparation and characterization of some Ag-containing fullerenes [C$_{60}$]. They were synthesized by an improved oxidation method. The structural variations, surface state and mass transformation of C$_{60}$ are investigated through preparation of oxidized fullerene [C$_{60}$] and fullerene [C$_{60}$] treated with silver sequentially after oxidation compared to pristine fullerene [C$_{60}$]. X-ray diffraction (XRD), scanning electron microscopy (SEM), Maldi-TOF-Mass spectrometry, energy dispersive X-ray (EDX) spectroscopy and Fourier transformation infrared spectroscopy (FT-IR) were conducted for these new species.

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Experimental

Materials

Crystalline C_{60} powder of 99.9 wt.% purity from TCI (Tokyo Kasei Kogyo Co. Ltd., Japan) was used as a starting material. Reagents were purchased as reagent-grade from 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 a water aspirator pressure and compounds were dried at 1.33 Pa.
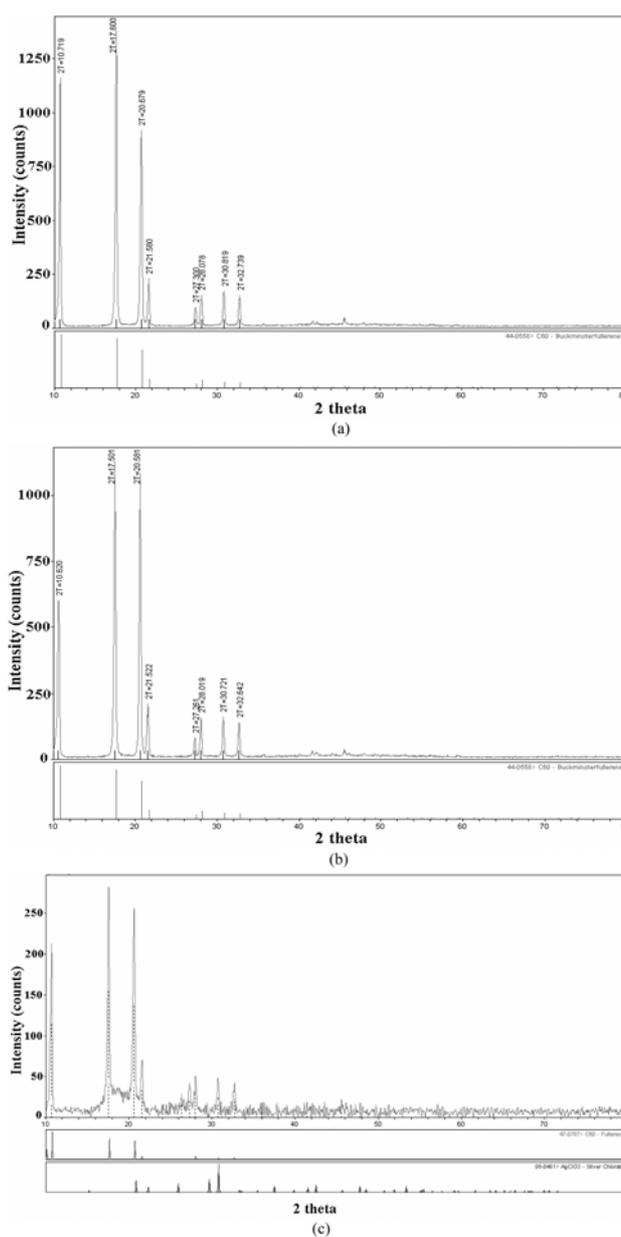
Chemical oxidation and silver treatments

3-chloroperbenzoic acid (ca. 0.96 g) was suspended in 60 ml benzene, and fullerene [C_{60}] (ca. 40 mg) was added, the mixture was refluxed in an air atmosphere for 6 h. Then the solvent was dried at the boiling point (353.13 K) of benzene. The solid precipitates were transformed to a dark brown color. After completion, dark brown precipitates were washed with ethyl alcohol and then dried at 363 K. We prepared to 0.1 M $AgNO_3$, for the silver treatment. Doubly distilled water to dissolve the chemicals free from impurities was used. For the treatment, 20 mg of oxidized fullerene [C_{60}] were dipped in to 20 ml of each silver ion dissolved aqueous solutions and stirred for 6 h at room temperature. Finally, these samples were dried at 368 K for 72 hours in an air atmosphere.

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 [C_{60}] treated with silver sequentially after oxidation compared to the pristine fullerene [C_{60}]. For the elemental analysis of the pristine fullerene [C_{60}], oxidized fullerene [C_{60}] and Ag-containing fullerene [C_{60}], energy dispersive X-ray analysis (EDX) was also used. As one of the analysis of mass transformation for those samples, Maldi-TOF Mass spectroscopy (Voyager, DE-STR, U.S.A) was used to characterize of structural transformation by oxidation and behavior of the treated metallic silver on fullerene [C_{60}]. The two types of fullerene derivatives were examined with a cyano-4-hydroxyl sinamic acid as matrix using the spectroscopy. The reflectance mode FT-IR (Nicholet 380, USA) spectra were collected from two types of fullerene samples with a smart miracle attenuated transmission of reflectance (ATR) method.

Results and Discussion

XRD is very important experimental technique that has long been used to address all issues related to the


Fig. 2. XRD patterns of (a) raw fullerene [C_{60}], (b) oxidized fullerene [C_{60}] and (c) fullerene [C_{60}] treated with silver sequentially after oxidation.

crystal structure of solids, including lattice constants and geometry, identification of unknown material orientations of single crystals, preferred orientation of polycrystals, defects, stress, etc. According to the structural parameters measured in former studies [6, 7], the distance between the C-C covalent bond in C_{60} cages is 10.02 Å packed into an fcc cell. Figure 2 shows the X-ray diffraction patterns of (a) the pristine fullerene [C_{60}], (b) the oxidized fullerene [C_{60}] and (c) the silver-containing fullerene [C_{60}]. It was observed that diffraction peak positions are accurately measured by XRD, which makes it the best representation for the original fullerene [C_{60}]. High intensity and very sharp peaks from fullerene [C_{60}] were observed in the XRD

patterns for the three types of samples. From the peak position of the oxidized fullerene [C$_{60}$], however, the diffraction peak patterns for the pristine fullerene were not different from that of the oxidized fullerene except a decrease intensity. It is reasonable that the formation of the O element to grapheme may partially slightly change the pristine structure of C$_{60}$ by the oxidation reaction. The silver treatment after oxidation yields a silver-containing C$_{60}$ product with XRD patterns distinguishable from that of the pristine fullerene [C$_{60}$]. In the XRD patterns of the silver containing C$_{60}$, new peaks from the original C$_{60}$ peaks appear at $2\theta = 27.5^{o}$, 29.5^{o}, 41.3^{o}, 47.5^{o} and 53.5^{o} as well as overlapping peaks ($2\theta = 20.6^{o}$ and 20.8^{o}). Almost all weak peaks of

silver with pristine fullerene [C$_{60}$] peaks were observed in the X-ray diffraction patterns for the silver-containing fullerene [C$_{60}$] after oxidation, as shown in Fig. 2(c).

SEM is one of the most widely used techniques used in the characterization of nanomaterials and nanostructures. Not only does the SEM produce topographical information as optical microscopes do, it also provides the chemical composition information near the surface. Figure 3, 4 and 5 show SEM micrographs of C$_{60}$ the sample series before and after oxidation, and after the silver treatment. These figures present results from the characterization of surface texture on the fullerene [C$_{60}$] samples before and after oxidation and the silver distributions on the surfaces after the silver treatment.
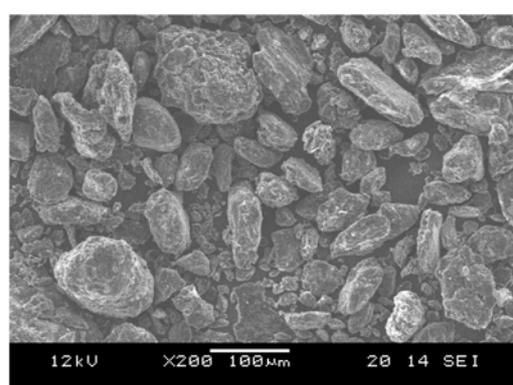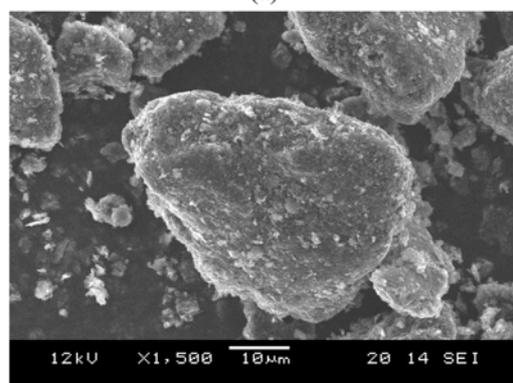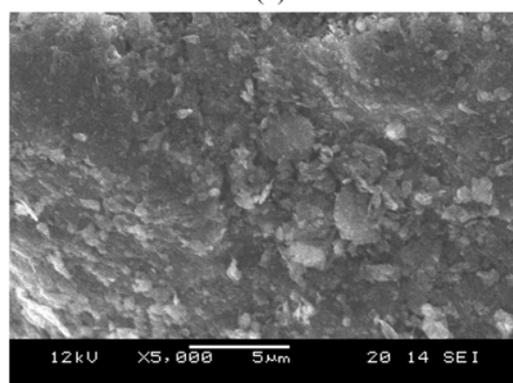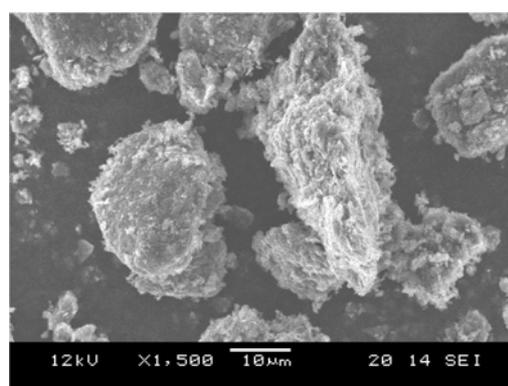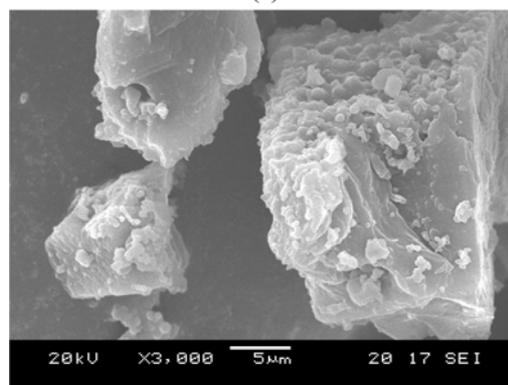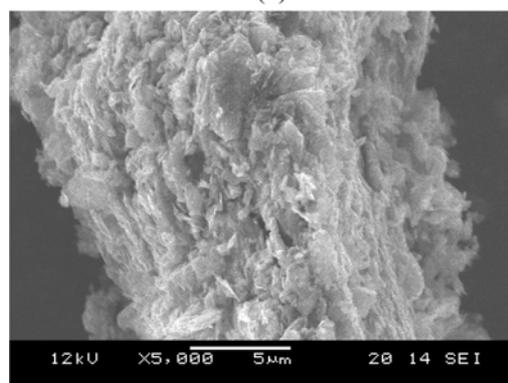

Fig. 3. SEM micrographs of pristine fullerene [C$_{60}$]: (a) and (b) overall, and (c) close-up view.

Fig. 4. SEM micrographs of oxidized fullerene [C$_{60}$]: (a) and (b) overall, and (c) close-up view.
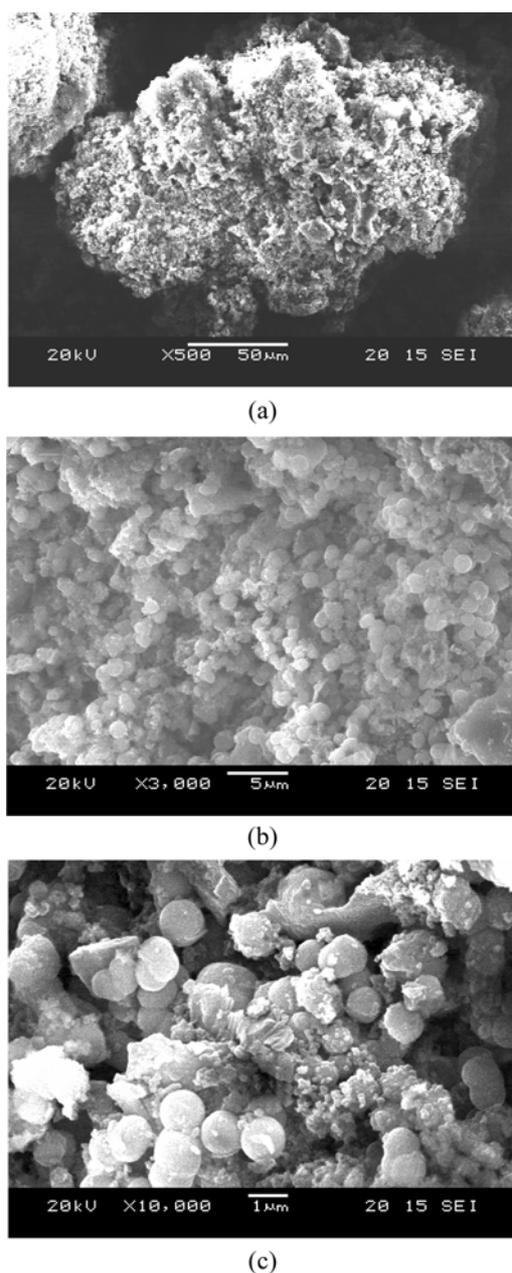
Fig. 5. SEM micrographs of silver treated fullerene [C_{60}] after oxidation: (a) overall, (b) and (c) close-up view.

SEM micrographs (Fig. 3) of the pristine fullerene [C_{60}] sample provide information about the surface state of the smooth pebble-like C_{60}. After the oxidation treatment, it was shown that the surface properties are modified in some cases, this effect being developed to a surface state from smooth pebble-like to a coarse bread-like in the oxidized fullerene [C_{60}] (Fig. 4). In the case of the silver-containing fullerene [C_{60}], this observation indicated that practically all the Ag introduced is located onto the carbon edges (Fig. 5(c)) and consequently, it is dispersed into very small crystallites with the growth of Ag metal. Treatment by Ag lead to drastic morphological changes: large grown Ag particles on the fullerene [C_{60}] outer surface are clearly visible
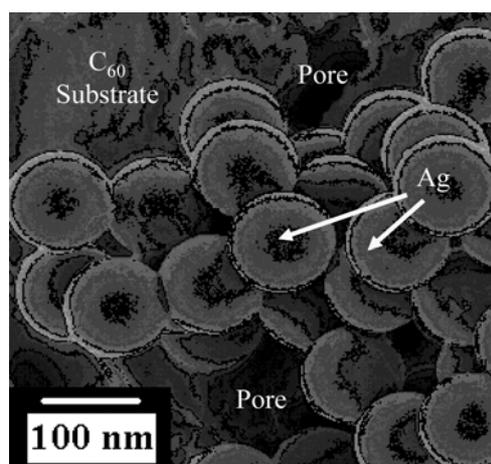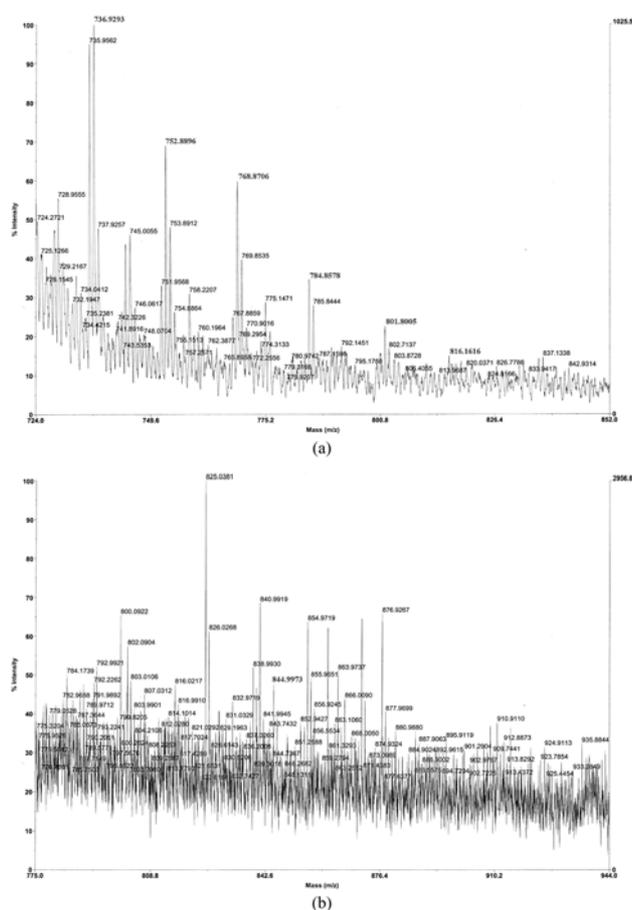

Fig. 6. TEM image of silver treated fullerene [C_{60}] after oxidation.

and resulted in clogging and frost-like formation, as shown in Fig. 5. Finally, the metallic Ag grown is located between the in- and outside surfaces of the fullerene [C_{60}] in the form of metallic crystals and aggregates (Fig. 5(c)). Figure 6 shows a TEM image of the silver treated fullerene [C_{60}] after oxidation. Accord- ing to this result, it could be estimated that the silver atom on the fullerene surfaces are located with agglomerated particles inside pores. For the observation of the substrate fullerene sample treated silver, substantial parts of the small pores are present on the fullerene surface.

Since further information on the structure of these materials was needed this was achieved by a combination of XRD analysis and Maldi-TOF-Mass spectroscopical measurements. These measurements gave additional evidence on the difference of the three types of material. Details of the results obtained are as in the Maldi-TOF Mass spectra are observed for the silver-containing fullerene [C_{60}], as compared to the material transformed by oxidation. The traditional mass spectrum of pure C_{60} was shown in a former study [8, 9]. Figure 7 presents the mass spectrum of C_{60} transformed by oxidation. It shows peaks for pristine C_{60} at 720 m/z and oxidized C_{60} by oxidation. In Fig. 7, the O signals of the oxidized fullerene are 736.92, 752.68, 768.87, 784.85, 801.80 and 816.16 m/z. These results indicate that these dominating peaks of the spectrum correspond to an increase of O element in the pristine fullerene [C_{60}] by a structural transformation. The Maldi-TOF-Mass spectrum of the silver-containing C_{60} is shown Fig. 7(b). An appearance of a peak due to the silver treatment is observed at 844.9 m/z. The differences in the spectra recorded on the two types of fullerene [C_{60}] illustrate the influence of the chemical components on the oxidation and silver treatment process. 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 types of fullerene [C_{60}] are due to the oxidation including chemical bonding and interposing of a metallic
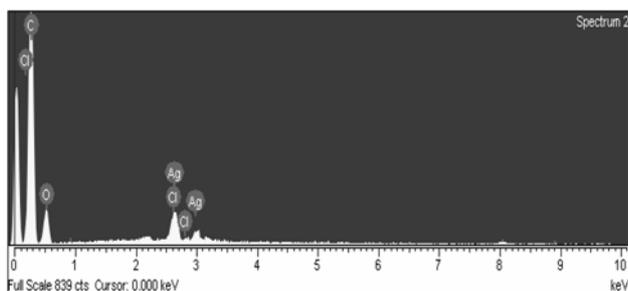
Fig. 7. Mass spectra detected before and after the silver treatment; (a) transformed C$_{60}$ by oxidation and (b) silver-containing C$_{60}$.

Fig. 8. FT-IR spectra before and after the silver treatment; (a) pristine C$_{60}$ and (b) silver-containing C$_{60}$.

silver atom in the C$_{60}$ molecules, it is considered that Ag has a strong tendency to oxidize and form the stable compounds C$_{60}$O$^-$Ag$^+$, which as a surface layer presents the direct interaction between C$_{60}$ and the treated metallic silver. Pristine fullerenes [C$_{60}$], however, may not react with metallic silver without the oxidation process [10].

The FT-IR spectra gave additional information on the functional component on the surface of silver-containing fullerene [C$_{60}$]. The FT-IR spectrum of a silver-containing C$_{60}$ is shown in Fig. 8. Observation of the absorption bands shows that the changes between the oxidized C$_{60}$ and silver-containing C$_{60}$ samples are mainly due to the formation of functional groups. As shown in Fig. 8, the υ (C-O) mode of the methoxy groups depends on the chemical structure of the adsorption sites. Absorption of C-O followed by the IR spectra has been used to characterize treated and non-treated metal catalysts [11, 12]. The frequency of υ (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 characteristic changes are observed at 1379.6 cm^{-1} in the presence of C-O- containing structures. The oxida-

tion treatment is consequently associated with the homogeneous distribution of silver with the increased surface acidity of C$_{60}$. The peak at 1722 cm^{-1} may be related to oxygen bonding to carbon in the C$_{60}$. It was observed that the stretching mode of –C = O group usually exhibits a strong bond near 1722 cm^{-1}. In a former study [13] for oxidation of C$_{60}$, the 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 was also noted that there were 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. A broad band in the 3100-3500 cm^{-1} region, is typically attributed to O-H stretching from hydroxyl, phenolic and carboxylic groups are present. Thus FT-IR spectra confirm the formation of carbonyl groups during the oxidation process. The main goal of oxidation is to obtain a more hydrophilic surface with a relatively large number of oxygen-containing oxygen groups on the C$_{60}$ surfaces.

For the elemental microanalysis of the silver-containing fullerene [C$_{60}$] sample, the sample was analyzed by