PREPARATION AND CHARACTERIZATION OF Zn-CONTAINING FULLERENE

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1. Introduction

The metallofullerenes remain exciting molecules combining the carbon cluster of simple fullerenes with the enhanced functionality of the treated metal species. The high solution electron affinities of the fullerenes along with the ionization potentials of the transition metals would result in an electron from the transition metal residing on the carbon cage. In this study, we will discuss our experimental results with the preparation of metallofullerene and their hydrogen generation. These kinds of materials are expected to show promising applications in diverse areas, such as electronic device material, substrate materials for hydrogen generation and biological science. Here we present the preparation and characterization of some Zn-containing fullerene. They were synthesized by improved oxidation method. The structural variations, surface state and mass transformation of fullerene [C_{60}] are investigated through preparation of oxidized fullerene [$C_{60}O$] and fullerene [C_{60}] treated with zinc sequentially after oxidation compare to pristine fullerene [C_{60}]. The XRD, SEM, MALDI-TOF mass spectrometry and EDX were conducted for these new species.

2. Experimental

m-chloroperbenzoic acid (MCPBA, 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. The solid precipitates were transformed to 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 $ZnCl_2$, for the zinc treatment. For the treatment, 20 mg of oxidized fullerene [$C_{60}O$] were dipped in to 20 mL of a zinc ion dissolved aqueous solutions and stirred for 6 h at room temperature. Finally, these samples were dried at 368 K for 72 hours in air atmosphere. For the measurements of structural variations, X-ray diffraction patterns were taken using an X-ray generator (Shimatz XD-D1, Japan). Scanning electron microscopy (SEM, JSM-5200 JOEL, Japan) was used to observe the surface state and structure. For the elemental analysis, energy dispersive X-ray analysis (EDX) was also used. MALDI-TOF mass spectroscopy (Voyager, DE-STR, U.S.A) was used to characterize of structural transformation by oxidation and behavior of treated metallic zinc on fullerene.

3. Results and Discussion

From the XRD results, it is seen that Zn-containing fullerene exhibit a pristine fullerene peaks and some metallic peaks with weak intensity at around 11.5, 23, 25 and 60.5°. From the peak position of oxidized fullerene [$C_{60}O$], however, it could not found that diffraction peak patterns for the pristine fullerene are different from that of oxidized fullerene except decreasing intensity. It is be concluded that the zinc treatment after oxidation yields Zn-containing fullerene product with the XRD patterns distinguishable from that of pristine fullerene [C_{60}].

SEM is one of the most widely used techniques for obtaining topographical information as optical microscopes and the chemical composition information near the surface. These results present from the characterization of surface texture on the fullerene [C_{60}] samples before and after oxidation and zinc distributions on the surfaces after zinc treatment. SEM pictures 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 of the pristine to coarse bread-like in oxidized fullerene [$C_{60}O$]. In case of Zn-containing fullerene, this observation indicated that metallic zinc introduced is located onto the carbon cages onside fullerene pore and consequently, it is dispersed into very small crystallites with growth of zinc metals.

For obtain the further information, the structure of these prepared materials was needed for MALDI-TOF mass spectroscopical measurements. Details of the obtained results are, however, rather surprising, as in the MALDI-TOF mass spectra are observed for the Zn-containing fullerene, as compared to the material transformed with oxidation. The traditional mass spectrum of pure fullerene [C_{60}] was shown at former studies [1.2]. It shows major peaks for pristine fullerene [C_{60}] at 720 m/z and oxidized fullerene [$C_{60}O$] by oxidation at 736.92 m/z. Within the limits of resolution this is consistent with the elemental composition $C_{60}O$. From the MALDI-TOF mass spectrum of Zn-containing fullerene, the observation of the peak due to zinc trace was appeared at 801.3 m/z. It is also consistent with the elemental composition $C_{60}O{\cdot}Zn$.

For the elemental microanalysis of Zn-containing fullerene, the sample was analyzed by EDX. This EDX spectrum of Zn-containing fullerene was shown in Fig. 5. This spectrum was shown the presence of C and O with strong Zn peaks. The spectrum was represented richer in C, O and major zinc metal than any other elements. The results of EDX elemental microanalysis of zinc-containing fullerene were listed in Table 1.

4. Conclusion

The structural and morphological variations, and mass transformation of fullerene derivatives are investigated through preparation of oxidized fullerene [$C_{60}O$] and Zn-containing fullerene compare to pristine fullerene [C_{60}]. The XRD, SEM, MALDI-TOF mass spectrometry and EDX were conducted for these species for obtaining new information.

Reference

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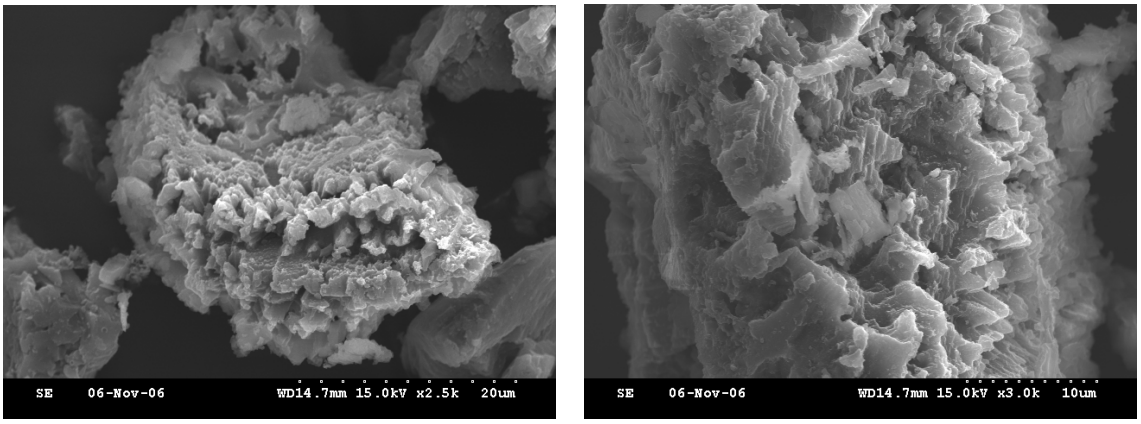

(a) (b)

Fig. 1. SEM micrographs of pristine fullerene and fullerene derivatives; (a) and (b) : Zn-containing fullerene.

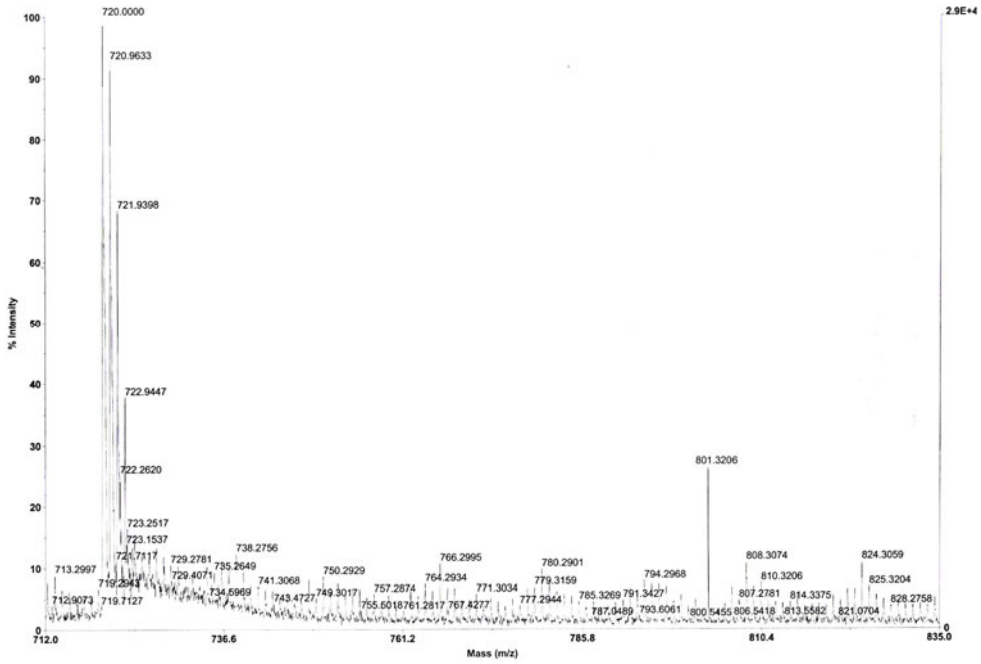

Fig.2. MALDI-TOF mass spectra of fullerene derivatives for the Zn-containing fullerene.

Table 1.EDX Elemental Microanalysis of Prepared Zn-Containing Fullerene

Sample (%)	C	O	Zn	Others
Oxidized Fullerene	55.6	42.5	0.12	1.81
Zn-Containing Fullerene	56.5	38.4	4.52	0.57