Synthesis of the First Dihydroxyl Adduct of Gd@C_{82}

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A new metallofullerene derivative, dihydroxy endohedral Gd metallofullerene, Gd@$C_{82}(OH)_2$ has been synthesized by a reaction of Gd@C_{82} with H_2O_2, which is confirmed by matrix-assisted laser-desorption ionization time-of-flight (MALDI-TOF) mass spectrometry and X-ray photoelectron spectroscopy (XPS).

Endohedral metallofullerenes, fullerenes with metal atom(s) encapsulated, are novel materials, which have attracted great interest from their discovery not only in physics and chemistry but also in biology and material science.[1] For example, they might be used as a nanostructrual material for electronic devices[2] because of the band gaps in endohedral metallofullerenes.[1] They also could be applied in biomedicine as bioradical scavengers,[3] radiotracers,[4] and magnetic resonance imaging (MRI) contrast agent.[3,5–7] Recently, much attention has been paid to its exohedral adducts because it exhibits better performance in MRI contrast agent than commercial metallofullerene does, which encourages further synthesis of water-soluble metallofullerenols.

Much effort has been devoted to introduce hydroxyl group to metallofullerenes because it improves the solubility. By a reaction of Pr@C_{82} with nitric acid solution, Yang[3] et al. have synthesized Pr@$C_{82}O_m(OH)_n$ ($m \approx 10$, $n \approx 10$); while Kato[8] et al. prepared Gd@$C_{82}(OH)_n$ ($n = 30$–40) by a reaction of the aqueous sodium hydroxide, instead of nitric acid, with tetrabutylammonium hydroxide as phase-transfer catalyst. Under an argon atmosphere, Dorn[9] et al. have synthesized $Sc_3N@C_{80}(OH)_{\approx 10}(O)_{\approx 10}$ by refluxing a toluene solution of $Sc_3N@C_{80}$ with sodium metal and exposing to water and air after that. By using the above methods, metallofullerenol with multihydroxide (the number of hydroxyl group is about equal or more than 10) have been prepared. However, the relatively harsh reaction condition and low yield of the product in the above reactions prohibit further application of metallofullerenol.

In this paper, a high yield of dihydroxyl adduct of Gd@C_{82} has been synthesized by a simple reaction and characterized by matrix assist laser-desorption ionization time-of-flight (MALDI-TOF) mass spectrometry and X-ray photoelectron spectroscopy (XPS).

Gd@C_{82} metallofullerene was synthesized by a method of improved direct current arc discharge and purified by high performance liquid chromatogram according to the literature.[10] Analytical grade 1,2-dichlorobenzene and 30% hydrogen peroxide were purchased from Tianjin Chem. Co., China, and used without further purification.

The typical reaction procedure was described as follow: 1,2-dichlorobenzene solution of Gd@C_{82} was mixed with aqueous 30% hydrogen peroxide solution, degassed with nitrogen gas, and sealed in the reaction flask. The final solution has been stirred for 7 h by 100-W ultrasonator. After the reaction, the solution at the bottom layer was picked up and analyzed.

The matrix-assisted laser-desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was measured by a Bruker BIEFLUX III mass spectrometer. The XPS experiments were performed on an ESCALab220i-XL spectrometer.

For the MALDI-TOF mass spectrometry analysis, the solution of metallofullerenol was dropped onto a stainless steel target and then evaporated. A nitrogen gas laser was used to desorb and ionize the sample. The laser beam was attenuated to low energy of several μJ. For the XPS experiment, a uniform film of the product was prepared on a platinum substrate. The concentrated solution was dropped onto the platinum foil. Evaporation of the solvent left a uniform film of the endohedral metallofullerenol on the Pt in an area of about 1 cm^2. XPS measurements were taken using twin-anode Al $K\alpha$ radiation ($h\nu = 1486.6$ eV), the charging shifts for the samples are calibrated using C1s at 284.6 eV. During the XPS experiments, the pressure is about 2×10^{-7} Pa.

Figure 1 shows the MALDI-TOF mass spectrum of the reaction products. Three major groups of high-resolution peaks at $m/z = 1139$–1146, 1155–1162, and 1173–1180 have been observed. The peaks of each group broaden up to 10 amu, which is similar to the MALDI-TOF mass spectra of samarium endohedral fullerenes reported by Lian[10] et al., could be due to the large distribution of seven isotopes of Gd (152, 0.20%; 154, 2.18%; 155, 14.8%; 156, 20.47%; 157, 15.65%; 158, 24.84%; 160, 21.86%).[11] Compared with the LD-TOF mass spectra of other similar water-soluble metallofullerenols reported in the litera-

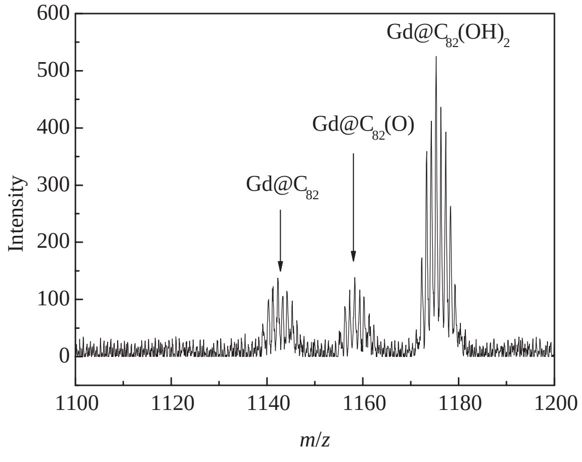

Figure 1. The MALDI-TOF mass spectrum of the reaction product.

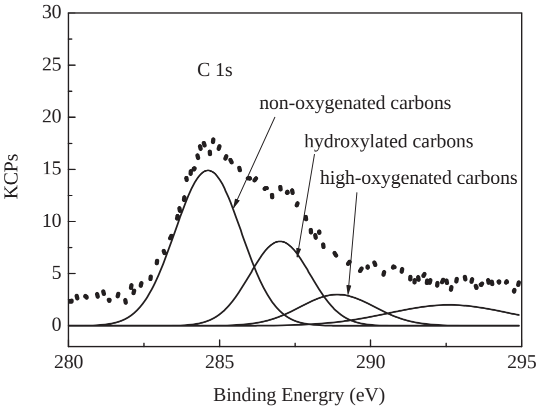

Figure 2. The carbon XPS of the reaction product (the dot line is the original data and the solid lines are the fitting results).

ture,[2,8] the high-resolution mass spectrum observed enables us to definitely assign the peaks at $m/z = 1139$–1146, 1155–1162, and 1173–1180 to $Gd@C_{82}$, $Gd@C_{82}(O)$, and $Gd@C_{82}(OH)_2$, respectively. On the basis of the high-resolution mass spectra, the relative yield could be roughly estimated by comparison of the height of the strongest ion peak for each compound; $Gd@C_{82}(OH)_2$:$Gd@C_{82}(O) \approx 3.8{:}1$. Nearly 80% of the product is $Gd@C_{82}(OH)_2$, suggesting that the majority of metallofullerene reacts with H_2O_2 and forms exohedral derivatives, which would reduce the difficulty in the further purification process.

Figure 2 shows the XPS spectrum of product after the reaction. There is no peak of the electronic state of gadolinium because of the limitation of the instrument sensitivity and no effect of the substituent on the electron state of the encaged metal atom. Therefore, analysis of the carbon peak in the XPS spectrum would provide important evidence into the structural nature of carbon atoms constituting the adducts.[8] The symmetric curve of the core level region of carbon (C1s) in Figure 2 indicates that the hydroxyl or oxo group has been bound to the carbon cage. Four distinct peaks were required to fit the asymmetric curve. The peaks centered at 284.6, 286.8, 288.9, and 292.6 eV, could be assigned to sp^2 carbon atoms of the cage, hydroxylated (–C–OH), highly oxygenated carbon atoms (ether linkages or peroxides) and a π–π transition within the remaining conjugated protons on the cage, respectively, which are similar to the results reported in the literature.[3,8,9] A simple calculation of the relative XPS peak intensities reveals that the yield of $Gd@C_{82}(OH)_2$:$Gd@C_{82}(O)$ is about 2.7:1, which is consistent with the results obtained in mass spectra.

Although the calculation of the relative XPS peak intensities generally could provide the information about the binding of hydroxyl or oxo groups to the metallofullerene,[3,9] the noisy XPS spectrum in Figure 2 prevents our effort; the MALDI-TOF mass spectrum data, instead of the XPS data, are used to determine the composition of the final product.

On the basis of the above result, a synthesis pathway has been proposed as shown in Scheme 1 under the experimental condition, hydrogen peroxide first decomposed and formed active oxygen atom [O*]; [O*] may combine with the π electron in the metallofullerene producing an active center [$Gd@C_{82}O^*$], the second active center then may be hydrated producing the adduct $Gd@C_{82}(OH)_2$, or rearrangement being $Gd@C_{82}(O)$. Compared with the results in the literature,[3,7–9] the formation of $Gd@C_{82}(OH)_2$ in the reaction would be due to the mild reaction activity of H_2O_2 under the neutral condition,[12] which reduce the possibility of further reaction to form $Gd@C_{82}$ with more hydroxyl groups. The high yield of $Gd@C_{82}(OH)_2$ might be attributed to the more stable structure compared with that of $Gd@C_{82}(O)$.

Scheme 1. The proposed scheme for the formation of $Gd@C_{82}$ adduct.

In summary, a new compound, $Gd@C_{82}(OH)_2$, has been synthesized and characterized by using MALDI-TOF mass spectrum and XPS. An interesting aspect of this synthesis is to obtain metallofullerene with two hydroxyl groups. The relatively high yield of $Gd@C_{82}(OH)_2$ in the reaction and the relatively simple preparation method might enable us to explore their properties further.

References

1 H. Shinohara, *Rep. Prog. Phys.*, **63**, 843 (2000).
2 T. Nagano, E. Kuwahara, T. Takayanagi, Y. Kubozono, and A. Fujiwara, *Chem. Phys. Lett.*, **409**, 187 (2005).
3 D. Sun, H. Huang, and S. Yang, *Chem. Mater.*, **11**, 1003 (1999).
4 L. Y. Chiang, F. J. Lu, and J. T. Lin, in “Fullerenes,” ed. by K. M. Kadish and R. S. Ruoff, The Electrochemical Society, Pennington, NJ (1995), Vol. 2, p 699.
5 S. Aime, M. Fasno, and E. Terreno, *Chem. Soc. Rev.*, **27**, 19 (1998).
6 L. J. Wilson, D. W. Cagle, T. P. Thrash, S. J. Kennel, S. Mirzadeh, J. M. Alford, and G. J. Ehrhardt, *Coord. Chem. Rev.*, **192**, 199 (1999).
7 M. Mikawa, H. Kato, M. Okumura, M. Narazaki, Y. Kanazawa, N. Miwa, and H. Shinohara, *Bioconjugate Chem.*, **12**, 510 (2001).
8 H. Kato, K. Suenaga, M. Mikawa, M. Okumura, N. Miwa, A. Yashiro, H. Fujimura, A. Mizuno, Y. Nishida, K. Kobayashi, and H. Shinohara, *Chem. Phys. Lett.*, **324**, 255 (2000).
9 E. B. Iezzi, F. Cromer, P. Stevenson, and H. C. Dorn, *Synth. Met.*, **128**, 289 (2002).
10 Y. Lian, Z. Shi, X. Zhou, X. He, and Z. Gu, *Chem. Mater.*, **13**, 39 (2001).
11 D. R. Lide, in “Handbook of Chemistry and Physics,” CRC Press, Boca Raton, FL (2001), p 17.
12 J. N. Friend and D. F. Twiss, in “A Textbook of Inorganic Chemistry,” Charles Geriffin & Company, Limited, London (1924), Vol. VII, Part I, p 346.

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