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$^{14}N@C_{60}$ formation in a nitrogen rf-plasma

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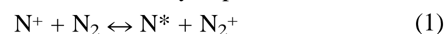
Atomic nitrogen was encapsulated inside a vaporized C_{60} molecule in rf-plasma, which was confirmed by ESR.

Among various endohedral fullerenes, group-V atoms encapsulated C_{60} ($N@C_{60}$ and $P@C_{60}$) attract particular interest due to the atomic nature of the entrapped atoms and their half-filled *p* orbitals ($^4S_{3/2}$ ground state).[1] Potential applications, such as to quantum computation, have been proposed.[2] Further studies, however, are hampered by the difficulties in preparing the materials. Up to now, ion bombardment (ions extracted from either a Kaufmann ion source or high-voltage discharge) has been the only method for preparing this type of endohedral fullerene.[1,3] A mg-scale product containing $N@C_{60}$ in a concentration of 10^{-4}–10^{-6} can be obtained in hours.[3] In this communication, we report an alternative method using a radio-frequency (rf) plasma to generate $N@C_{60}$. Using this method, material containing $N@C_{60}$ in the same concentration range can be much more easily produced even in this preliminary work.

The experimental set-up and procedure for generating $N@C_{60}$ are essentially the same as that we used previously for preparing fullerene polymers,[4] except that we used pure nitrogen (99.99995%) instead of Ar in this work. We had adjusted operational parameters to improve production efficiency. C_{60} (250 mg, MER Corp., USA; purity better than 99.8%) was put in a molybdenum boat and evaporated through resistive heating in nitrogen plasma at a pressure of 25 Pa. The rf-plasma reactor was operated at 13.56 MHz and 50 W. The operation was usually finished within 10 minutes to avoid extended polymerization of the deposit. After cooling down to room temperature, the deposit (up to ~200 mg) containing pristine C_{60}, polymerized C_{60} and $N@C_{60}$ was collected, dissolved in CS_2 and separated from the insoluble material by passing through a short column filled with silica gel. Since there was little material soluble in CS_2 when C_{60} was evaporated slowly (< 10 mg min^{-1}), quick sublimation of C_{60} was critical for the formation of $N@C_{60}$. 10–20% material was soluble in our quick evaporation experiments, which was comparable to the ion bombardment method.[1,3] The filtered fraction was condensed in nitrogen flow for ESR measurement. The ESR tubes filled with liquid samples were sealed under high vacuum.

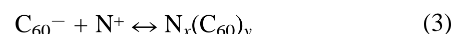
Fig. 1a shows the ESR spectrum of the product. Two sets of splittings each consisting of three equally spaced lines but different sharpness are clearly visible. The hyperfine constants (hfc, ~0.567 mT) and *g* values for both sets of splittings are essentially the same as that reported,[1,3,5] which are attributed to the isotropic hyperfine interaction of the ^{14}N unpaired electron spins with the nucleus spins. We noticed that there were insoluble brown aggregates formed during measurements. The material before aggregation was probably suspended while not really dissolved in CS_2. After careful removal of the aggregates by re-filtering and diluting, the set of splitting with a larger peak-to-peak width (~17.2 μT) disappeared while the three sharp lines with a peak-to-peak width of ~2.0 μT remained, as shown in Fig. 1b. This suggests that the splitting with the smaller peak-to-peak width stems from dissolved pristine $N@C_{60}$ while the splitting with the larger peak-to-peak width originates from the aggregates. The aggregates were no more soluble in CS_2, indicating polymerization of $N@C_{60}$. Since the concentration of $N@C_{60}$ was very low in plasma, the polymerization probably took place between $N@C_{60}$ and C_{60}. This is supported by the substantial line broadening of the dimer $N@C_{60}$–C_{60} compared to $N@C_{60}$.[6] Further study is needed to isolate and characterize the polymerized $N@C_{60}$. Nevertheless, ESR results confirmed that atomic nitrogen was encapsulated inside C_{60} cages in our plasma chamber. The typical dopant concentration was in the order of 10^{-5}–10^{-4}, which was calculated by comparing with standard spin materials.

In the nitrogen rf-plasma, there are various kinds of ionic and neutral species, such as N_2^+, N^+ and excited N^* atoms (*via* N_2^+ and N^+). Upon evaporation, some C_{60} molecules are immediately ionized and excited by the plasma. Since C_{60} is an electron-affinitive molecule, C_{60} will be negatively charged in the plasma and is expected to have mutual dissociative recombination reactions with the N^+ ions. The main species and reactions in the plasma can be briefly expressed as follows.



$$N^+ + N_2 \leftrightarrow N^* + N_2^+ \quad (1)$$

$$N_2^+ + e \leftrightarrow 2N^* \quad (2)$$



$$C_{60}^- + N^+ \leftrightarrow N_x(C_{60})_y \quad (3)$$

Reaction (3) represents formation of both N–C_{60} hybrid compounds and C_{60} polymers. Here *x* and *y* are integers larger than 1.

By adjusting the input power and nitrogen gas pressure, the energy of ionic nitrogen species can be controlled in the range of 10–100 eV, which covers the energy suitable for ion implantation (~40 eV).[3] These reactions toward ion implantation can take place:

$$C_{60}^- + N^+ \leftrightarrow N@C_{60} \quad (4)$$

In addition, similar to reaction (3), further reaction of $N@C_{60}$ is possible.

$$N@C_{60} + C_{60}^- + N^+ \leftrightarrow N@C_{60}–N_x(C_{60})_y \quad (5)$$

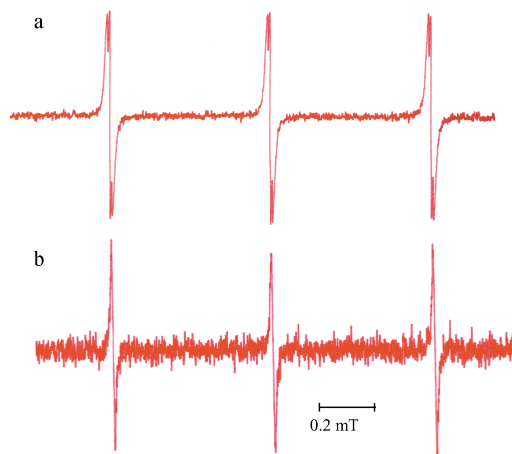


Fig. 1 ESR spectra of a mixture of $N@C_{60}$ and polymers containing $N@C_{60}$ (a), and $N@C_{60}$ after removal of the polymers (b). Both spectra are observed at room temperature with a modulation width of 0.003 mT. The solvent is CS_2.

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It can be seen that the formation of N@C_{60} in rf-plasma is still basically a process of ion implantation while the non-equilibrium plasma may largely facilitate this process. The process of ion implantation is not yet well understood. We propose a general scheme for the ion implantation process, as shown in Fig. 2, which is actually mimicking the reverse process of nitrogen escape from the carbon cage.[7] The nitrogen ion interacts with the C_{60} molecule and forms C–N bonds with the carbon atoms on the cage. The nitrogen ion converts to a nitrogen radical when obtaining an electron from charged C_{60}. The bonded nitrogen radical then swings into the carbon cage. The nitrogen atom is formed inside the cage upon breaking down the C–N bonds and the carbon cage closes after recovering the C–C bond. In fact, the formation of N@C_{60} is largely dependent on plasma power. The ESR signal was hardly detectable when the plasma was operated at over 100 W, and for the sample collected from the electrode plate where the plasma was the most intensive. We suggest that the process of integration and disintegration of N@C_{60} is a dynamic process since both the reactants and products are activated in plasma.

The main point of this work is that we recognized that N@C_{60} and polymerized N@C_{60} could be formed in rf-plasma without separation and acceleration of nitrogen ions in advance. Since rf-plasma can be generated easily in a much larger space than ion beams, this method may pave a way for an efficient synthesis of endohedral fullerenes on a large scale. It is evident that endohedral nitrogen fullerenes at the same concentration level could be formed in our plasma chamber in a much shorter time (about 1/50). Further optimization of the plasma chamber and operation conditions may lead to large-scale production of nitrogen and even other endohedral fullerenes.

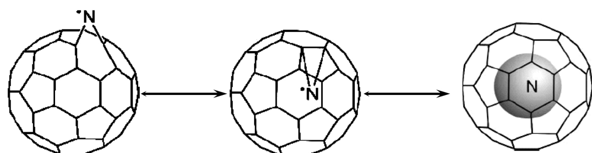

Fig. 2 Possible formation path to N@C_{60}. Note that the reaction is a dynamic process with a trend for N@C_{60} formation.

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