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Pressure induced metastable polymerization in doped C₆₀ materials

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Abstract:

High pressure Raman studies have been carried out on C₆₀/AgNO₃ and C₆₀/Ni(OEP) up to 30 GPa. In both these doped C₆₀ materials, pressure-induced metastable ordered polymers can be observed after pressure release. The results show that both the quenched materials contain chainlike polymers and dimers. We also find that the degree of polymerization is higher in these doped C₆₀ materials than in bulk C₆₀ materials after similar high pressure treatment and that C₆₀/AgNO₃ contains a higher fraction of chainlike polymers than C₆₀/Ni(OEP) after decompression from same pressure. The results can be understood by considering the different initial lattice structures of these materials and the confinement effects of the dopants.

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1. Introduction

The doping of fullerenes C_{60} with various species, such as alkali metals, p-elements such as oxygen, nitrogen, and sulfur, organometallic donors, etc., have attracted great interest because of the resulting unique structures and extraordinary physical properties [1-6]. For example, 3D-polymerized C_{60} was synthesized in C_{60} doped with CS_2 at pressure of 6-7 GPa. The resulting phase can plough diamond and is identical to ultrahard fullerite [7]. Recently, novel superhard carbon materials with hardness comparable to that of diamond and with unique ordered amorphous carbon cluster (OACC) structures have been obtained by compressing C_{60}/m -xylene and reported by our group [8]. Moreover, a reversible polymerization of bulk C_{60} doped by ferrocene (Fc, $Fe(C_5H_5)_2$) was obtained under high pressure [9]. In this case, the Fc molecules formed a layered structure in the crystal and acted as spacers that allow polymerization of C_{60} only within a 2D layer. However, this long-range ordered polymer can not be preserved upon decompression, which makes it difficult to study the polymeric structure in detail. Thus whether pressure induced metastable polymers can be obtained from doped C_{60} materials is another important and interesting subject. Solving this problem is valuable for studying the structures and properties of these new fullerene-based polymers and for understanding the physical mechanism of polymerization.

In a recent study we obtained metastable 1D or 2D polymers from C_{60}/Fc , $C_{60}/AgNO_3$ and $C_{60}/Ni(OEP)$ by a high pressure and high temperature (HPHT) method [10]. It was found that the polymerization degree is always lower than that of pure C_{60} treated at the same conditions. That was attributed to the spatial and geometrical confinement effects of the dopants. The polymeric phases formed in the three doped materials were also different due to the unique initial lattice structures and the different degrees of spatial confinement provided by the dopants. However, in the HPHT method it is difficult to detect and study the phase transition of the samples in situ. Whether the metastable long-range ordered polymers can be retained from doped C_{60} materials and whether the phase transition process can be followed are thus both challenging subjects. Motivated by the progress with C_{60} and doped C_{60} materials, we have here focused on the effect of spatial confinement on the behavior of C_{60} in several typical co-crystals with C_{60} under pressure at room temperature in order to obtain various polymeric phases and create new C_{60} fullerenes with novel properties. Based on these considerations, $Ni(OEP)$ and $AgNO_3$ were again chosen as dopants for this study. The materials have quite different structures, i.e. the $Ni(OEP)$ molecule has large planar surfaces, and $AgNO_3$ forms a porous lattice structure. When cocrystallized with these materials, C_{60} molecules can be confined in a geometrically different environment, resulting in the formation of different frameworks, which thus provide us with good models for studying the effect of spatial confinement on the polymerization of doped C_{60} materials. This study can also improve our understanding on the polymerization mechanism of confined doped C_{60} and inspires us to create more new polymeric structures with extraordinary properties.

In this work, $C_{60}/Ni(OEP)$ and $C_{60}/AgNO_3$ were compressed up to 30 GPa. A Raman study revealed that both materials can form different degrees of long-range ordered polymers under pressure and that these polymers can be preserved upon decompression. The quenched samples contain both chainlike polymers and dimers, but in different amounts. Comparing with bulk C_{60} treated at same condition, we find that the total polymerization degree is higher in doped C_{60} materials than it is in bulk C_{60} materials. The higher degree of polymerization in

doped C₆₀ materials can be attributed to the initial lattice structures of these doped C₆₀ materials and to the confinement effects of the dopants.

2. Experiment

C₆₀/AgNO₃ and C₆₀/Ni(OEP) crystals were both synthesized by the mixed solution method. The detailed procedures have been described in a recent study [10].

The morphologies of the obtained as-grown samples were characterized with scanning electron microscopy (SEM, JEOL JSM-6700F) and the composition of the samples were characterized using a Bruker Vertex80V FTIR spectrometer and using a Raman spectrometer (Renishaw inVia) with a 514 nm Ar⁺ laser line as excitation.

For high-pressure studies, samples were loaded into a 140 μm diameter hole in a T301 stainless steel gasket, with a 4:1 methanolethanol mixture as pressure transmitting medium. In situ high-pressure Raman measurements have been carried out at room temperature using a Raman spectrometer (Renishaw InVia) with a 785 or 830 nm laser line as excitation. The highest pressure reached in this study is about 30 GPa.

3. Results and discussion

3.1. Sample characterization

Figs. 1 and 2 show the SEM images of C₆₀/AgNO₃ and C₆₀/Ni(OEP), respectively. From these figures, we can see that C₆₀/AgNO₃ has uniform cubic morphology with cube sides of 7.5 μm (Fig. 1a), while C₆₀/Ni(OEP) crystals exhibit an irregular block shape (Fig. 2a). Raman and IR spectra are also shown in Fig. 1(b,c) and 2(b,c) to confirm the compositions of C₆₀/AgNO₃ and C₆₀/Ni(OEP), respectively. For comparison, the spectra of pristine C₆₀ and the dopants are presented in the top of these figures. We find that except the Raman spectrum of C₆₀/AgNO₃ (shown in Fig. 1b) which mainly contains the vibration modes of C₆₀, all the other spectra contain characteristic peaks of both C₆₀ and the intercalant molecules. These results indicate that the dopants are efficiently intercalated into the lattice of C₆₀, which is in accord with previous reports [9].

The packing arrangements of C₆₀/AgNO₃ and C₆₀/Ni(OEP) are shown in Fig. 3. The results are calculated by Materials Studio from Refs. [11,12]. It is found that zeolite-like silver nitrate network is observed in the structure of C₆₀/Ag(NO₃) and the hollow section is occupied by fullerenes (shown in Fig. 3a). From Fig. 3b, we can see that the planar surfaces of Ni(OEP) molecules are so large that can cocrystallize with C₆₀ to form solids with remarkably close contact. It has been reported that Ni(OEP) can co-crystallized with C₆₀ by remarkably strong interaction between the curved pi surface of a fullerene and the planar pi surface of a porphyrin, without the need for matching convex with concave surfaces [13,14].

3.2. Results for high pressure treated samples

Raman spectroscopy was employed to study phase transitions and polymerization of C₆₀/AgNO₃ and C₆₀/Ni(OEP) under high pressure.

3.2.1. C₆₀/AgNO₃

From Fig. 4a, we can see that as the pressure increases, some Raman peaks become broader and weaker. At 3-4 GPa, a new peak can be observed around 1000-1100 cm^{-1} and this peak is preserved up to the highest pressure, which indicates the occurrence of some transition in the material. We further analyze the pressure dependence of these modes in Fig. 4b. Since the $A_g(2)$ mode is a characteristic mode for intermolecular bonding in C_{60} , we would like to first discuss the behavior of this mode under high pressure. By carefully studying the pressure dependence of the mode, two abnormal changes can be found in the range of pressure studied. The first one is found at around 1-2 GPa, and another occurs at about 4.5 GPa. From the pressure dependences of other peaks shown in Fig. 4b, we can find that similar changes take place at the same pressures, indicating that some transitions must take place in the sample. In earlier studies, it was found that the face centered cubic (fcc) C_{60} lattice will transform into a simple cubic (sc) structure at a pressure of around 0.3 GPa at room temperature due to the orientational ordering of C_{60} molecules [15,16]. Because the interaction between the C_{60} molecules is weakened by the presence of the $AgNO_3$ we expect the orientational phase transition to occur at a higher pressure, and we suggest that the slope change near 2 GPa in $C_{60}/AgNO_3$ is induced by this transition. At pressure of about 4.5 GPa, an obvious softening is observed in the pressure dependence of $A_g(2)$. Similar significant softening effects can also be found in other modes at the same pressure. Also, a new peak around 1000-1100 cm^{-1} is observed from 3 to 4 GPa. These phenomena indicate that the sample undergoes another transition. In our previous study on C_{60}/Fc , we found an obvious split of the $A_g(2)$ mode at about 5 GPa and with increasing pressure the two peaks shift to higher frequency with a constant frequency difference of 12-13 cm^{-1} , indicating that a chain-like polymer had formed under high pressure [9]. Thus, we propose that a similar polymeric phase may also be formed in $C_{60}/AgNO_3$ from this similar pressure.

To make sure whether $C_{60}/AgNO_3$ indeed polymerize under the high pressure of about 4.5 GPa, we further studied a sample recovered from the highest pressure in detail. It is also necessary to point out that the Raman studies of the recovered samples were carried out using infrared lasers which will not induce photodimerization of C_{60} . Fig. 5 shows the Raman spectrum of a sample decompression from 30 GPa and the spectrum of pristine $C_{60}/AgNO_3$ is also shown for comparison. We find that the typical intramolecular modes of C_{60} molecules are still present, indicating that C_{60} cages in the sample can persist at least to this pressure. However, an obvious red shift of the $A_g(2)$ mode from its initial at 1468 cm^{-1} to approximately 1460 cm^{-1} is observed. From previous literature, it is well known that the peak at 1460 cm^{-1} is the contribution from dimerized or one dimensional, chain-like polymerized C_{60} [17,18]. This result further indicates that $C_{60}/AgNO_3$ may undergo polymerization under high pressure and that the polymerized phase can be preserved after decompression, forming metastable confined C_{60} polymers. This is the first time that we obtain long range ordered metastable doped C_{60} polymers under cold compression. It should be noted, however, that all such pressure-induced polymers can be converted back to the monomer by thermal annealing at about 200 $^{\circ}\text{C}$ [18-20]. To approve this point, we annealed the quenched sample at 200 $^{\circ}\text{C}$ under vacuum for several hours and found the $A_g(2)$ mode returned to 1466 cm^{-1} , which indicated that the pressure-induced polymers can be converted back to the monomer after annealing. (see Fig. S1 in Supporting Information, the quenched $C_{60}/Ni(OEP)$ which will be mentioned below was also treated at same conditions and the result was also shown in Fig. S1). By analyzing further, we find that the $A_g(2)$ peak splits into two peaks with positions at 1459 cm^{-1} and 1465 cm^{-1} (shown in the right inset of Fig. 5), indicating that the quenched sample is probably a mixture of dimers and chainlike polymers. The area of the peak at 1459 cm^{-1} is much larger than the peak at 1465 cm^{-1} , which indicates that the quenched sample contains a large fraction of chainlike polymers with only a few dimers. Although a slight red

shift of the $A_g(2)$ mode was also found in some bulk or C_{60} nano-materials quenched from high pressure, such an obvious shift is not common. The Raman spectrum of bulk C_{60} decompressed from a similar pressure is shown in the left inset of Fig. 5 for comparison. This inset also shows that the $A_g(2)$ peak has split into two peaks, but this time the peak are found to have their positions at 1464 cm^{-1} and 1469 cm^{-1} . The contribution of the peak at 1464 cm^{-1} is larger than that from peak of 1469 cm^{-1} , indicating that this sample is a mixture of free molecules and a high fraction of dimers. The results illustrate that the degree of polymerization in quenched $C_{60}/AgNO_3$ is higher than that in bulk C_{60} after a similar high pressure treatment.

3.2.2. $C_{60}/Ni(OEP)$

Fig. 6a and b shows that most Raman peaks from $C_{60}/Ni(OEP)$ become broader and weaker with increasing pressure, in the same way as in $C_{60}/AgNO_3$. Again we find that some new peaks appear and that some peaks exhibit obvious splits from 6 GPa. In particular we note that from 5 GPa, the $A_g(2)$ mode displays an asymmetry, with a shoulder appearing at 1506 cm^{-1} . The pressure dependence of some characteristic modes is also shown in Fig. 6c. We can find two slope changes in the range of pressures studied, one near 2 GPa and another is at 5-7 GPa, suggesting that similar phase transitions occurred at these two pressures as in $C_{60}/AgNO_3$.

To further investigate the polymerization of $C_{60}/Ni(OEP)$ under pressure, the Raman spectrum of a sample decompression from 30.1 GPa is shown in Fig. 7. The spectra of pristine $C_{60}/Ni(OEP)$ and of C_{60} bulk material decompressed from a similar pressure are also shown in this figure for comparison. Again we find that the whole structure of the C_{60} molecules is still preserved after high pressure treatment. However, an obvious red shift of the $A_g(2)$ mode is observed. From the inset of Fig. 7, it is remarkable to find that the $A_g(2)$ peak again splits into two peaks with positions at 1457 cm^{-1} and 1463 cm^{-1} , further indicating that the quenched sample contains both chainlike polymers and dimers. For this material the contribution of the peak at 1463 cm^{-1} is larger than the peak of 1457 cm^{-1} , which states that the quenched sample contains a high fraction dimers with a few chainlike polymers. The result shows that $C_{60}/Ni(OEP)$ undergo polymerization under high pressure and that the polymerization is metastable. The red shift of the $A_g(2)$ mode in $C_{60}/Ni(OEP)$ is also larger than that in bulk C_{60} , which illustrated a higher degree of polymerization. Comparing all these three materials, we find that the polymerization degree decreases in the order $C_{60}/AgNO_3$, $C_{60}/Ni(OEP)$ and pure C_{60} , when materials are treated under same pressure conditions at room temperature.

The different degrees of polymerization of C_{60} and of confined C_{60} materials treated under the same conditions can be understood by the different initial lattice structures of these materials and the confinement effects of the dopants (Fig. 3a-b). Because pure C_{60} is free from steric effects, the polymerization is random, a large number of randomly oriented dimers can be obtained first and these can grow in any direction to form straight chains, zig-zag “snake” chains and possibly large amorphous structures; because of the low temperature there is no strong driving force to form ordered structures. After decompression from medium pressures (~ 30 GPa), the whole structure of C_{60} molecules can still be observed but the $A_g(2)$ mode was slightly broadened and red shifted (from 1469 cm^{-1} to 1464 cm^{-1}) as mentioned above. However, after decompression from higher pressures (>35 GPa), all the characteristic Raman peaks for C_{60} s disappeared, which was attributed to the formation of an amorphous phase containing sp^3 bonds [21].

In the case of $C_{60}/AgNO_3$ and $C_{60}/Ni(OEP)$, neighboring C_{60} molecules are separated by the dopants, forming spatial confinement (see Fig. 3). The dopant molecules may prevent the intermolecular bonding of neighboring C_{60} molecules in certain direction. For example, in $C_{60}/AgNO_3$, it is highly likely that the polymeric bonds may only be formed in the channels running in the c direction. In $C_{60}/Ni(OEP)$ the intercage polymer bonds can only be formed in the b direction because the $Ni(OEP)$ molecules prevent bonding between C_{60} molecules in the a and c directions. Therefore, in these confined C_{60} materials, the dimers that first form can only grow into linear chains and we thus get a very high proportion of such well ordered structures. After decompression from high pressure, due to the preservation of dopants the partial polymers can be kept and thus the final products should contain a very high fraction of chainlike polymers. Because of the higher degree of spatial confinement in $C_{60}/AgNO_3$ than that in $C_{60}/Ni(OEP)$, the arrangement of C_{60} molecules is more regular in the channels, which provides good conditions for the formation of long-range ordered polymer. This is the reason why we can obtain a higher proportion of chainlike polymers in $C_{60}/AgNO_3$ than in $C_{60}/Ni(OEP)$.

In our previous study, C_{60}/Fc was shown to form 1D chain-like polymers at 5 GPa near room temperature but the polymerization was reversible on pressure release. The weak charge interaction between the C_{60} and Fc molecules is strengthened with increasing pressure, which may affect the redistribution of the electron cloud between the C_{60} and Fc molecules and thus induce polymerization of the C_{60} molecules. However, the stability of the polymer is controlled by the steric repulsion of counterions which can be overridden at high pressure but with decreasing pressure eventually returns to the initial state [9]. However, in the case of $C_{60}/AgNO_3$ and $C_{60}/Ni(OEP)$, the solids are formed with strong Ag^+-C_{60} π -interactions and π - π interaction between the curved surface of a fullerene and the planar surface of a porphyrin, respectively. This strong interaction can not easily be tuned by pressure and the covalent bonds formed can not break during compression and decompression, which makes the present results very different from those for compressed C_{60}/Fc . Therefore we believe that both the structure of the materials and the different interactions between fullerenes and dopants affect the polymerization of the fulleride under pressure. This work inspires us to obtain more metastable polymers from various doped fullerene materials and to create custom-made polymeric structures with different dimensions with the help of the spatial confinement effect.

4. Conclusions

High pressure Raman studies have been carried out on $C_{60}/AgNO_3$, C_{60} and $C_{60}/Ni(OEP)$ up to 30 GPa at room temperature. Our results show that both materials can form polymers under pressure and that these polymers are metastable after decompression. The quenched samples contain both chainlike polymers and dimers. Compared with bulk C_{60} treated at same conditions, we find that the polymerization degree is higher in doped C_{60} materials than in bulk C_{60} , because only dimers and free C_{60} molecules can be obtained upon decompression in pure C_{60} . We also observe that $C_{60}/AgNO_3$ contains more chainlike polymers than $C_{60}/Ni(OEP)$ after decompression from same pressure. The results can be understood by the different initial lattice structures of these doped C_{60} materials and the confinement effects of the dopants.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.carbon.2017.01.067>.

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Figure Captions:

Fig. 1. SEM images of $C_{60}/AgNO_3$ crystals (a); Raman (b) and IR (c) spectra of C_{60} , $AgNO_3$ and $C_{60}/AgNO_3$, respectively.

Fig. 2. SEM images of $C_{60}/Ni(OEP)$ crystals (a); Raman (b) and IR (c) spectra of C_{60} , $Ni(OEP)$ and $C_{60}/Ni(OEP)$, respectively.

Fig. 3. The packing arrangements of (a) $C_{60}/AgNO_3$ and (b) $C_{60}/Ni(OEP)$. The atomic structure of both materials are shown on the bottom and right, respectively in each figure. (A colour version of this figure can be viewed online.)

Fig. 4. In situ Raman (a) spectra of $C_{60}/AgNO_3$ under pressure. (b) The pressure dependence of several Raman modes. (A colour version of this figure can be viewed online.)

Fig. 5. Raman spectra for pristine $C_{60}/AgNO_3$ and for $C_{60}/AgNO_3$ decompressed from 30 GPa. The $A_g(2)$ mode for the decompressed sample is shown on a larger scale in the right-hand inset. The $A_g(2)$ mode of pure C_{60} , decompressed from 30 GPa, is also shown in the left-hand inset for comparison. (A colour version of this figure can be viewed online.)

Fig. 6. In situ Raman (a,b) spectra of $C_{60}/Ni(OEP)$ under pressure. (c) The pressure dependence of two Raman modes. (A colour version of this figure can be viewed online.)

Fig. 7. Raman spectra of pristine $C_{60}/Ni(OEP)$ and of $C_{60}/Ni(OEP)$ decompressed from 30 GPa, with the $A_g(2)$ mode shown on an expanded scale in the lower inset. The $A_g(2)$ mode of pure C_{60} decompressed from 30 GPa is shown in the upper inset for comparison. (A colour version of this figure can be viewed online.)

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7