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Difference in formation of carbon cluster cations by laser ablation of graphene and graphene oxide

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The distributions of positive carbon cluster ions produced by laser ablation of graphene (G) and graphene oxide (GO) are found to be quite different. Under a typical experimental condition, narrow distributions of even-numbered clusters from C_{60}^{+} to C_{162}^{+} were observed for G, and broad distributions including even-numbered clusters from C_{100}^{+} to C_{400}^{+} and odd-numbered clusters from C_{189}^{+} to C_{395}^{+} were observed for GO. The threshold of laser energy for G is lower than that of GO. Further results of collision-activated dissociation mass spectrometry indicate that the cluster ions generated from G are structurally similar but are different with those generated from GO or nanodiamonds. It is proposed that the experimentally observed difference can be attributed to the different mechanisms behind the process. A top-down mechanism including both direct transformation of G to fullerene and fragmentation of large-sized fullerenes is suggested for the generation of carbon cluster cations in the process of laser ablation of G. For GO, the experimental results are close to those of nanodiamonds and other materials reported previously and can be explained by the generally accepted bottom-up mechanism. Copyright © 2012 John Wiley & Sons, Ltd.

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Keywords: carbon cluster cation; graphene; laser ablation; CAD; graphene oxide

INTRODUCTION

The interactions of laser radiation with various carbon materials and their relatives have been attracting much interest for more than 30 years.[1–10] Among these carbon materials, carbon clusters are particularly attractive because of their fascinating structures, chemical properties and significant role in deposition and combustion processes.[1–10] The mass spectrometer (MS) has been widely used for the identification of these carbon cluster ions.[4] For example, Campbell *et al*. have studied the carbon clusters produced by ultraviolet (UV)-laser ablation of polyimide by using time-of-flight MS.[2] With a Fourier transform ion cyclotron resonance (FT ICR) MS, Greenwood *et al*. have observed the formation of carbon cluster ions by laser ablation of coals and other materials.[3] Shibagaki *et al*. have studied the possible mechanisms for the synthesis of large carbon clusters by laser ablation of different polymers in vacuum.[6] Sedo *et al*. have suggested that different carbon materials including graphite, diamond and carbon nanotubes are subjected to similar physicochemical changes by UV-laser pulses.[7]

Because of its utility in the fabrication of functional films of fullerenes and carbon nanotubes, graphite has been widely studied by the method of laser ablation.[3] On the basis of these results, different models have been proposed to explain the formation of fullerene and carbon clusters with different sizes in the process.[11–17] These different mechanisms can be categorized into two groups: bottom-up and top-down. In the bottom-up mechanism, the fullerene cages are considered to be formed from carbon atoms or small clusters.[11–14] Alternatively, in the top-down mechanism, it is proposed that the carbon clusters are generated by fragmentation of large clusters and laser-desorbed carbon dust formed initially.[15–17]

Since it has been prepared by Novoselov *et al*., graphene (G) has emerged to become the most exciting two-dimensional material with many unique characteristics.[18–22] Recently, Chuvilin *et al*. have observed a different process of fullerene formation from a sheet of G in real time by the method of aberration-corrected transmission electron microscopy.[21] They explained the formation of fullerene in their experiment as a top-down process and demonstrated that a direct transformation of G to fullerene was possible. In our previous work, the distributions of carbon cluster anions produced by laser ablation of G and graphene oxide (GO) were analyzed.[22] Large even-numbered carbon cluster anions up to C_{500}^{-} were observed in the mass spectra. The results of collisionally activated dissociation (CAD) MS of some selected cluster anions show that several cluster anions lost units of C_2, C_4, C_6 or C_8 in their collision, whereas others did not. However, the structures of these ions and the mechanism for their formation are still unrevealed.

In the present work, the distributions of carbon cluster cations produced by laser ablation of G and GO are analyzed. It has been found that the distribution of the positive cluster ions generated from G is quite different from that of GO. Effects of laser power

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on cluster distribution are also studied. CAD MS was preformed for some selected cations. A top-down mechanism of the fullerene ions generated by the laser ablation of G is suggested, and these results may also provide some useful information for understanding the results of the anions reported previously.[22]

EXPERIMENTAL

Sample preparation

The sample of GO was prepared from natural graphite with an average particle size of 20 μm (Qingdao Huarun Graphite Co., Ltd., Qingdao, China) by the modified Hummers method.[23,24] The sample of G was gained by the reduction of GO by using the method described previously.[23,24] Nanodiamonds (NDs) used here have an average diameter of 100 nm and are bought from Beijing Grish Hi-tech Corporation.

Instrumentation

All MS experiments were performed with a 7.0 T FT ICR MS employing a matrix-assisted laser desorption/ionization (MALDI) source (Varian IonSpec ProMALDI). G, GO and NDs were suspended in water at a concentration of 5 mg/ml and dispersed by sonication for 1 h prior to usage. Then, 1 μL of solution was dropped onto the MALDI target spot and dried in the laboratory temperature before being placed into the source region of the MS.

Mass spectra reported here were all measured in positive-ion mode. Typically, ions produced by six consecutive laser pulses were accumulated in the hexapole first. After the accumulation, the hexapole exit lens was gated so that ions could be transferred into the quadrupole guide. The DC potential of the trapping plate near the quadrupole was set to be 15 V before the introduction of the ions into the cell. During the period of ion transfer to the cell (2–3 ms in the experiment, which is referred as 'accumulation period in the cell' hereinafter), the trapping plate was pulsed down to 0 V to allow the ions to enter into the ICR cell. The ions were then cooled down by a pulsed nitrogen gas (with pressure in the cell raised to about 10^{-6} Torr) before detection or isolation for tandem MS.

The laser used here is a 355-nm Nd:YAG laser (Orion, New Wave). The frequency was set at 10 Hz, and the laser energy was set to be within the range of 20%–90% relative to the maximum energy of 4 mJ/pulse. In the MS/MS study, the precursor ions of interest were selected by the stored waveform inverse Fourier transform method.[25] Sustained off-resonance irradiation (SORI)[26] excitation was performed at amplitudes of 4.0–7.0 V ($V_{p\text{-}p}$) with a frequency offset of −1000 Hz relative to the precursor ion cyclotron frequency. During each 100 ms SORI event, the pressure in the ICR cell was raised to approximately 10^{-6} Torr by a brief pulse of nitrogen gas.

RESULTS AND DISCUSSION

Laser ablation MS of G and GO

The mass spectrum of carbon cluster cations generated by laser ablation of G is shown in Fig. 1(a). In the experiment, the relative laser energy was 50% and the accumulation period in the cell was 3 ms. The mass spectrum was acquired in the m/z range of 250–8000. Only signals of even-numbered carbon cluster cations with narrow distributions were observed. The mass difference between consecutive carbon cluster ions is 24 m/z units. The peak intensities of C_{60}^{+} and C_{70}^{+} relative to their neighbors show their extraordinary stabilities directly. Remarkably, very strong signals of cluster ions from C_{120}^{+} to C_{160}^{+} were observed. The distribution was centered at about C_{144}^{+} but was asymmetric because of the sharp dropoff at C_{162}^{+}. The experiment was repeated more than ten times under the same condition in different days. Although the centers of the distributions and the largest detectable ions altered in some extent (less than 20 units of C_2), the shapes of the distribution did not change very much.

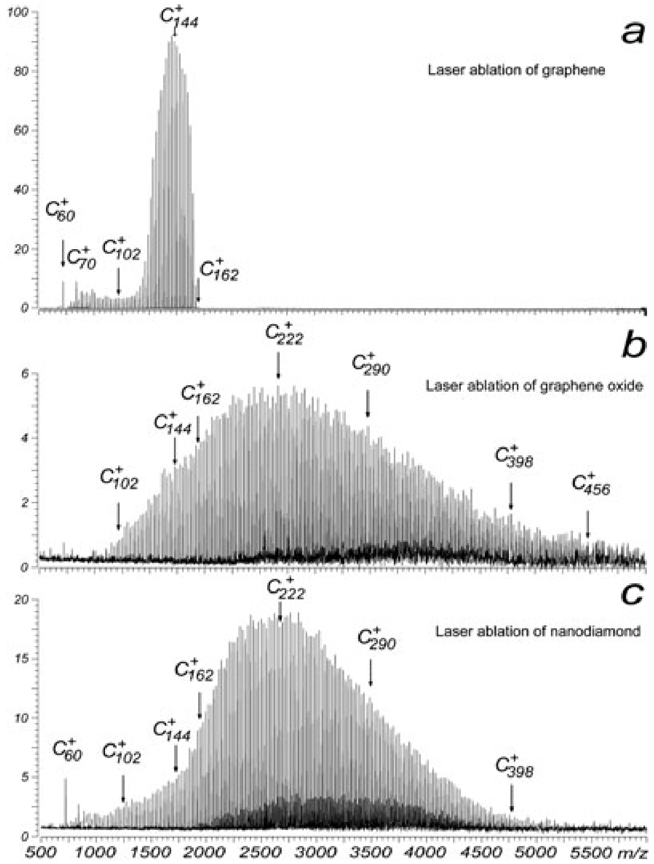

Figure 1. Mass spectra of positive carbon clusters produced by laser ablation of (a) graphene, (b) graphene oxide and (c) nanodiamonds, obtained with a relative laser power of 50% and an accumulation period of 3 ms in cell.

However, the mass spectrum of GO obtained under same experimental conditions is quite different. A wide distribution of cluster cations from C_{94}^{+} to C_{500}^{+} was observed (Fig. 1(b)). The distribution was centered at C_{222}^{+}, and the total intensity of the cations was weaker than that of G. Weak signals of odd-numbered carbon cluster cations from C_{189}^{+} to C_{395}^{+} were also observed. This cluster distribution is very close to results of other carbon materials obtained under similar conditions. For example, the experimental result of NDs under same conditions was shown in Fig. 1(c). Even-numbered clusters from C_{60}^{+} to C_{420}^{+} and odd-numbered clusters from C_{157}^{+} to C_{405}^{+} were observed, and the main distribution was also centered at C_{222}^{+}, which was in good agreement with the result reported by Houska *et al.* previously. [8]

The mass spectra were also acquired in the low m/z range of 200–800 separately with the same laser energy but a short accumulation time in the cell of 2 ms. Fig. 2 shows the results. For the sample of G, two distributions of triply charged ions centered at C_{132}^{3+} and C_{156}^{3+} are clearly identified. Some doubly charged ions such as C_{120}^{2+} are found

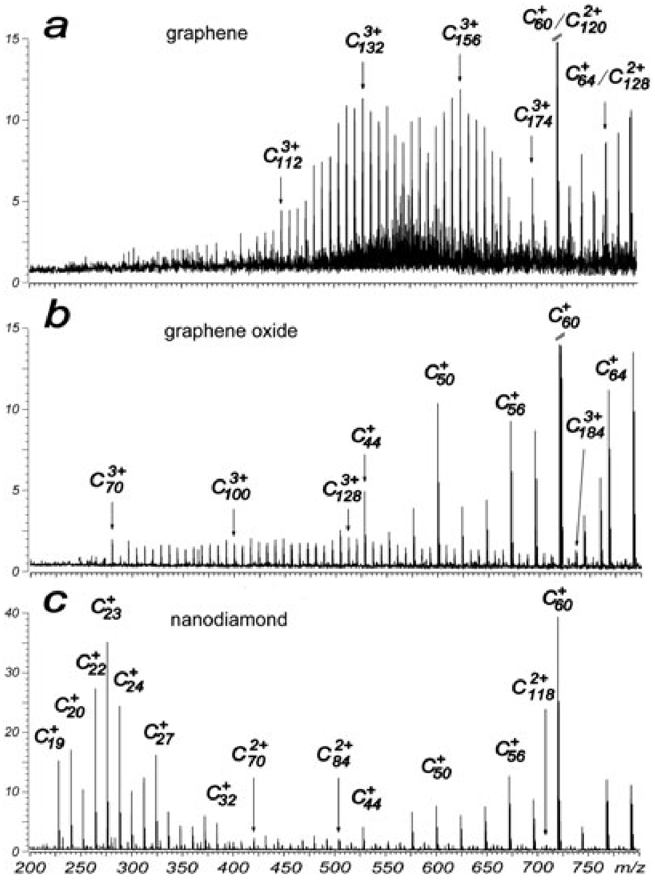

Figure 2. Mass spectra of positive carbon clusters in the low m/z region produced by laser ablation of (a) grapene, (b) graphene oxide and (c) nanodiamonds, obtained with a relative laser power of 50% and an accumulation period of 2 ms in cell.

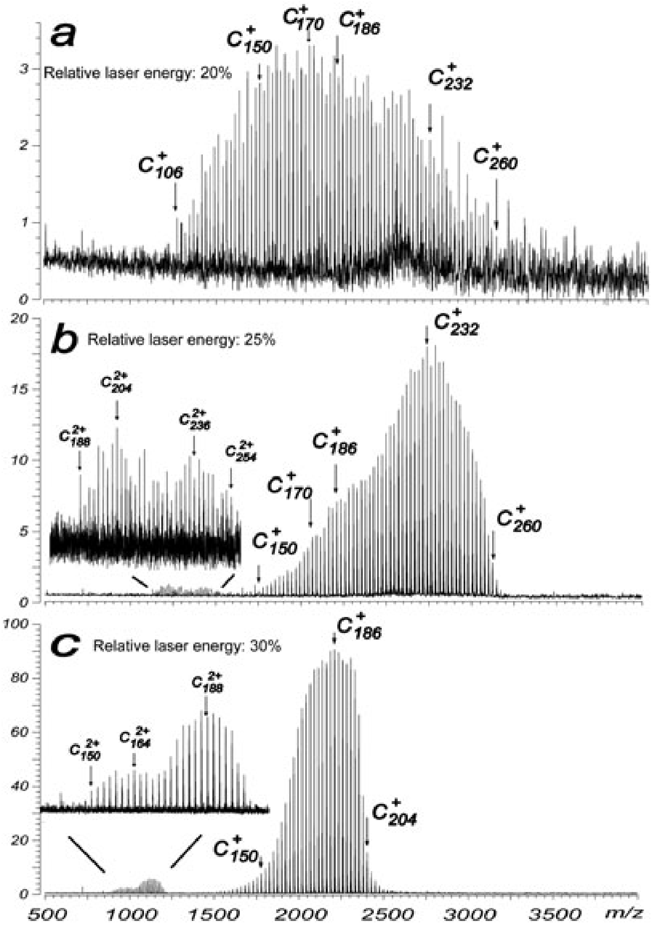

Figure 3. Mass spectra of positive carbon clusters produced by laser ablation of graphene under different laser powers at (a) 20%, (b) 25% and (c) 30%. The insets in (b) and (c) show the multiply charged cluster ions generated in the processes.

in the spectrum, whereas no singly charged ions smaller than C_{60}^{+} can be observed. For GO, there is a wide distribution of the triply charged ions from C_{70}^{3+} to C_{184}^{3+}. Singly charge ions with lower m/z such as C_{44}^{+} can be observed with high abundance, whereas doubly charged ions can be hardly observed. Obviously, these results are very different with results of graphite or other materials reported previously.[10,11] For example, as shown in Fig. 2(c), the spectrum of ND is characterized by the strong signals of singly charged clusters from C_{19}^{+} to C_{32}^{+}. Only weak doubly charged ions from C_{70}^{2+} to C_{118}^{2+}, instead of triply charge ions, can be found.

Effects of laser energy

Effects of laser energy on cluster distribution were also studied here. Figure 3 shows three spectra of positive carbon clusters produced by laser ablation of G obtained with laser energies at 20%, 25% and 30% (the accumulation period is 3 ms). Remarkably, the distribution of the cluster cations is very sensitive to the laser energy applied. At the lowest relative energy of 20% (a further decrease of the laser energy caused all signals lost), signals of even-numbered clusters from C_{106}^{+} to C_{260}^{+} are weak but well distributed in the mass spectrum. The cations are separated by the C_2 unit, and the distribution is centered at ~C_{180}^{+}. When the laser energy increased to 25%, the signal intensities increased about five times. Ion signals from C_{150}^{+} to C_{264}^{+} can be classified to be two distributions: a weak one centered at ~C_{180}^{+} and a strong one centered at ~C_{232}^{+}. Weak signals of doubly charged ions from C_{188}^{2+} to C_{254}^{2+} were observed as two distributions centered at C_{204}^{2+} and C_{236}^{2+}. With a laser intensity of 30%, the distribution centered at ~C_{232}^{+} observed in Fig. 3(b) disappeared, and the signal intensities of the distribution centered at ~C_{186}^{+} increased more than ten times (Fig. 3(c)). The abundance of doubly charged ions increased too, and the ions were distributed in the region from C_{150}^{2+} to C_{202}^{2+}. The spectrum was very close to the result shown in Fig. 1(a) when the relative laser energy was set to 40%. Upon further increase of the energy to 90%, the distribution and intensity of the cluster ions did not change manifestly.

Figure 4 shows the results of GO. With its corresponding threshold laser energy at 30%, C_{60}^{+} and C_{70}^{+} are the most dominant ions in the mass spectrum. A wide distribution of cluster ions from C_{56}^{+} to C_{320}^{+} was detected. With the energy increased to 40%, the signals of small cluster less than C_{100}^{+} decreased very much, and the center of the distribution shifted from C_{150}^{+} to C_{222}^{+}, which was very close to the result observed in Fig. 1(b). Further increasing the energy to 90% did not change the distribution much but increased the signal intensities about two times. In the experiments with laser energies larger than 40%, weak signals of odd-numbered cluster cations were detected. But, no doubly or triply charged ions could be detected in all experiments of GO. Remarkably, no carbonaceous

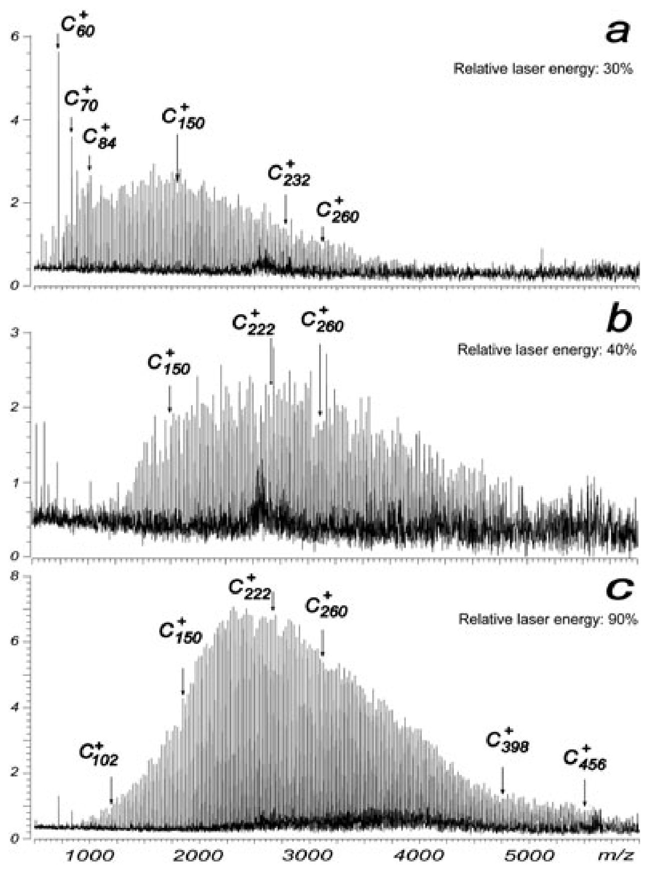

Figure 4. Mass spectra of positive carbon clusters produced by laser ablation of graphene oxide under different laser powers at (a) 30%, (b) 40% and (c) 90%.

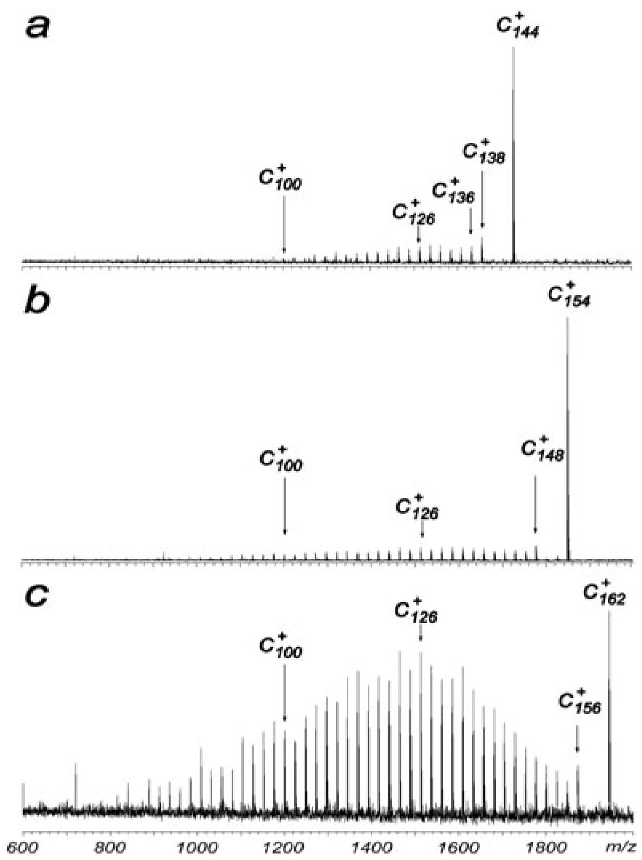

Figure 5. Collisionally activated dissociation mass spectra of selected even-numbered cations of (a) C_{144}^{+}, (b) C_{154}^{+} and (c) C_{162}^{+}. The ions were generated by laser ablation of graphene, followed by isolation and excitation using similar sustained off-resonance irradiation processes with a frequency offset of -1 kHz and a $V_{p\text{-}p}$ of 5.5 V.

oxide cations observed in the spectra for GO in the whole mass range from 50–2000. Small carbonaceous oxide cations with m/z less than 50 might exist but failed to be detected because of the low detecting efficiency of the instrument used here. For comparison, the effect of laser energy on the results of NDs is also studied (Fig. S1). It should be noticed that the threshold of laser energy for NDs increased to be 40%. The cluster distribution was very similar to that shown in Fig. 1(c) and did not change much with the increase of laser energy to 90%.

CAD MS study

In our previous study, the even-numbered carbon cluster anions generated by laser ablation of G from C_{200}^{-} to C_{240}^{-} have been isolated and studied by CAD. Interestingly, among these 21 even-numbered cluster ions, 14 kinds of ions show no fragment ions (lowest detectable m/z is set to be 220), whereas other seven kinds of ions can form different fragment ions by loss of the units of C_2, C_4, C_6 or C_8. The results reflect the structural complexity of the cluster anions. Here CAD experiment has been preformed for carbon cluster cations generated by laser ablation of G (under the same experimental conditions used in Fig. 1(a)) from C_{140}^{+} to C_{166}^{+}. The lowest detectable m/z is set to be 200 in positive-ion mode.

Figure 5 shows some of the CAD results. For the dissociation of C_{144}^{+}, fragments ions from C_{100}^{+} to C_{138}^{+} can be clearly identified. Although very weak signals of C_{140}^{+} and C_{142}^{+} were observed in the mass spectrum, the main dissociation pathway was the loss of the unit of C_6. With the increase of collision energy, the total intensities of the fragment ions increase, but their distributions do not change much, indicating that these fragments are mainly coming from the precursor ions directly, rather than from secondary fragmentation of some fragment ions (Fig. S2). Figure 5(b) and (c) shows the CAD results of C_{154}^{+} and C_{162}^{+}, which are both very similar to that of C_{144}^{+}. One difference for C_{162}^{+} is that the relative intensities of fragment ions to the precursor ion is high, indicating that the ion is much less stable than C_{144}^{+} or C_{154}^{+}. Further CAD results of other ions from C_{140}^{+} to C_{166}^{+} generated by laser ablation of G show the same dissociation behavior, indicating that the structures of all these cluster ions are similar or obey a same mechanism for their formation in the process of laser ablation.

However, this difference between the stabilities of C_{144}^{+} and C_{162}^{+} is unexpected for the cluster ions generated by laser ablation of GO and NDs. In Fig. 1(b) or (c), the distribution is centered at C_{222}^{+}, and no evidence shows that C_{144}^{+} is more stable than C_{162}^{+}. This suggests that the structures of these cluster ions generated by laser ablation of G and GO (or NDs) should be different. Thus, two ions, C_{130}^{+} and C_{160}^{+}, are generated by laser ablation of G, GO and NDs and then separated and studied by CAD at the same conditions (the experimental results of C_{130}^{+} are shown in Fig. S3). Interestingly, both ions generated from G obey the same dissociation rule described previously, whereas no fragments with m/z larger than

500 can be found for both precursor ions generated from GO and NDs under same collision conditions. This difference in CAD MS of G and GO (NDs) cannot be simply explained by the suppose that the plasma generated in the laser ablation of G is hotter, because of two facts: (1) all ions were cooled down in the FT ICR cell by pulsed nitrogen gas before the isolation and (2) the CAD experiments of C_{130}^+ (and C_{160}^+) generated from laser ablation of GO and NDs were also performed under different collisional energies, and no such fragment (or other fragment ion with m/z larger than 500) could be detected in all these experiments. Thus, these results do reflect their structural differences of the trapped ions generated from G and GO (NDs).

DISCUSSION

The results indicate that the components of laser plumes and the mechanisms for the formation of cluster cations in the cases of G and GO are quite different. The distribution of singly charged cluster ions generated from GO is very close to that of ND and also close to the previous results from laser ablation of graphite.[11] To better understand the growth mechanism of the observed carbon clusters from laser ablation of graphite, Shi *et al*. have established an arbitrary combination model to simulate the cluster growth process.[11] In this bottom-up model, the graphite dissociates to very small carbon clusters, which subsequently combine together to form larger clusters by collisions. The simulated distribution based on this model fitted the observed experimental mass spectrum of laser ablation of graphite well for larger clusters ($n > 50$).

For the results of GO and ND obtained here, it is believed that the growth mechanisms of the carbon cluster cations in these two cases are similar and thus can be explained by the bottom-up model. However, the experimental results of G are quite different, thus cannot be explained or simulated by the same model. In Shi's model, it is also found that the association rate constant decreases with the increase of the cluster size because of the decrease of the velocity.[11] But, this change is gradual, causing a long tail in the distribution of cluster ions in the side of lager m/z region.

So, what is the mechanism for the generation of cluster cations from the laser ablation of G? In their wonderful jobs, Chuvilin *et al*. have observed the process of fullerene formation from a G sheet in real time.[21] With the aid of quantum chemical modeling, they explained the process as a top-down mechanism for fullerene formation by four steps: (1) the loss of carbon atoms at the edge of G because of the high-energy e-beam, (2) the formation of pentagons, (3) subsequent curving of the flake to form a bowl-shaped structure and (4) closing the open edges to form a fullerene cage. We think this top-down mechanism can be also applied here to explain our results. The main difference is that the 80-keV electron beam was replaced by the laser pulses at 355 nm in this experiment. Although there is no direct proof such as the experimental transmission electron microscopy images, several results observed in our experiments do support the suggestion: (1) the observed cluster distribution in Fig. 1(a) are much narrower than those observed in Fig. 1(b) or (c), which is consistent with Chuvilin's results, (2) no odd-numbered carbon clusters can be observed in Fig. 1(a) (although the total ion signals are more abundant than those of GO and NDs), which may be a direct result of step 2, (3) the threshold of laser energy is much lower than those of others, which can be explained by the fact that less carbon–carbon bonds are cleaved in a top-down process than in a bottom-up process and (4) the results of CAD MS show that these carbon cluster cations generated from G have similar structures.

Why the formation of the cluster ions stopped at the nearby of C_{162}^+ (Fig. 1(a)) (or C_{204}^+ Fig. 3(c) with a lower laser energy)? Park *et al*. have investigated the energetics of large-sized fullerenes and carbon nanotubes through first-principle pseudopotential calculations for carbon cluster of C_n ($60 \leq n \leq 540$).[27] It has been found that the strain energy because of pentagons and curvature makes a substantial contribution to the energetics of fullerenes. This contribution causes the crossover from fullerenes to nanotubes for the clusters of $n \geq 240$, which is consistent with other previous experimental observations.[28,29] Thus, it is suggested that nanotubes can be hardly formed in the laser ablation of G directly, and the formed large-sized fullerene cations ($n \geq 240$) are unstable because of the strain energy and the curvature effect and thus dissociate to smaller fullerene cations readily. This is consistent with the experiment results in Fig. 3. With lower laser energies of 20% and 25%, larger cluster ions from C_{200}^+ to C_{260}^+ can be obtained readily, but those ions lost quickly by increasing the energy to 30%.

Besides, all steps of (2), (3) and (4) suggested by Chuvilin are thermodynamically favorable. Because there will be a significant energetic penalty in the curving step due to the noncovalent interactions between the underlying G sheet and the flake, the size of the etched G will be limited within the range to enable the thermodynamically driven steps for the formation of fullerene.

Then, why are the results of G and GO so different? Generally speaking, laser ablation results for different carbon materials, polymers and soot samples are different from each other in the distributions, but the physicochemical processes induced by the UV laser are quite similar.[7] However, components of laser plasma differ for different materials, and the reactions happened in the plasma depend on the species involved very much. For example, Maruyama has found that the existence of some trace metal atoms such as Ni could disturb the formation of the cage structures.[30] On the other hand, the unique electronic properties of G (the interaction between electrons and the honeycomb lattice causes the electrons in G to behave as if they have no mass[18,19]) may also distinguish its interaction with laser from those of other materials, and the species included in the laser plasma are also different. The distinctive carbon cluster anions observed under similar conditions support this suggestion too.[22] To better understand the interaction between G and laser, more experimental research and theoretical calculations are needed very much.

However, the carbon cluster anions generated by laser ablation of G under similar conditions are different from the cations in several aspects: (1) the distribution of the anions is broad, (2) odd-numbered carbon cluster anions can be observed, (3) the threshold of laser energy (~25%) is higher and the effect of laser energy is different and (4) CAD MS results of the selected ions from C_{200}^- to C_{240}^- show that their structures are inconsistent. The possible reason is that the proposed top-down mechanism does not exclude possible coexist bottom-up mechanism in the whole process. So, the generated unstable anions can form new stable structures through isomerization or a bottom-up process after their dissociation. And, the CAD results of the selected anions support that there are cluster ions with different structural characteristics near the crossover point predicted by Park *et al*.[27]

On the other hand, the generation of the multiply charged cations in Fig. 2(a) and (b) needs further consideration too. These multiply charged ions are supposed to be the results of multiple photon ionization. And, the difference for the results of G, GO and NDs are more likely due to different reactions induced by different species in their plasmas. Further experiments of dependence of intensity and distribution of the multiply charged ions on laser wavelength and energy (in larger range than the one used in this experiment) will be very helpful. And, tandem MS experiments on these multiply charged ions may also provide some interesting result.

CONCLUSIONS

Remarkably, the distribution of carbon cluster cations produced by laser ablation of G is very different with those of GO and NDs. Only narrow distributions of even-numbered clusters from C_{60}^{+} to C_{162}^{+} can be observed for G, whereas broad distributions of even-numbered clusters from C_{100}^{+} to C_{400}^{+} and weak signals of odd-numbered clusters from C_{189}^{+} to C_{395}^{+} can be observed for GO and NDs under same experimental conditions. Comparing with the result of NDs, triply charged cluster ions from C_{96}^{3+} to C_{168}^{3+}, instead of singly charged small carbon clusters from C_{19}^{+} to C_{32}^{+}, are observed for G in the low m/z region. The thresholds of relative laser energy for G, GO and NDs are 20%, 30% and 40%, respectively. The effects of laser energy on the product ions are also different for G and GO. The CAD mass spectra of the ions from C_{140}^{+} to C_{166}^{+} generated from laser ablation of G show same dissociation ways, indicating their structural consistency. However, the CAD results of the cluster ions generated from G and GO indicate that their structures are different.

These results indicate that the mechanisms for the formation of cluster ions in the laser ablation of G and GO are quite different. A top-down mechanism including both direct transformation of G to fullerene verified by Chuvilin *et al*. previously and fragmentation of large-sized fullerenes is suggested for the process of laser ablation of G. Large-sized fullerenes are energetically less stable because of the contributions from the strain energy and the curvature effect. However, the results of GO are close to those of NDs, thus can be explained by the generally accepted bottom-up mechanism.

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Supporting Information

Supporting information can be found in the online version of this article.

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