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The Inner Nano-Space Control of Carbon Nanotubes Using Collisionless Different-Polarity Ion Plasmas

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Abstract

An original approach based on plasma-ion irradiation method has been performed in order to control the inner nano-space of single-(SWNTs), double-(DWNTs), and multi-walled (MWNTs) carbon nanotubes and resultantly develop novel functional carbon-based nano-materials. When positive bias-voltages are applied to a substrate covered with these carbon nanotubes and immersed in a collisionless different-polarity ion plasma [alkali-fullerene ($\text{Cs}^+ - \text{C}_{60}^-$) plasma], the SWNTs and DWNTs encapsulating fullerene molecules are clearly observed, and the fullerene filling efficiency is found to become enhanced in the order MWNTs, DWNTs, SWNTs. In the case of negative bias application, the Cs encapsulation inside the SWNTs is directly observed for the first time, the configuration of which is demonstrated to comprise three varieties. Finally, when the bias-voltage with polarity change is sequentially applied to the SWNTs, the SWNT encapsulating a junction of Cs atoms on one side and C_{60} molecules on the other is for the first time observed.

1. Introduction

Single-walled carbon nanotubes (SWNTs) [1] are a subject of intensive investigation as a novel type of nano-materials due to their profound condensed physics originated from the 1-dimensional geometry, and potential applications to many fields. Especially, it is very attractive that intrinsic electronic and mechanical properties of carbon nanotubes can be controlled by the introduction of various foreign atoms, molecules, and their derivatives [2]. For example, a recent report has presented the possibility of nano-scale electronic device for the case of intercalation of a (alkali metal/halogen element) junction inside the SWNTs [3]. In order to realize 1-dimensional novel structure mentioned above, we attempt to perform an original approach to the inner-space control of carbon nanotubes using plasma-ion irradiation method in collisionless different-polarity ion plasmas, where various kinds of atoms, molecules or their combinations can be selectively encapsulated within the carbon nanotubes. Here, we present the validity of our plasma method and report the successful formation of the SWNTs encapsulating alkali metals as well as fullerene molecules. On the basis of these works, plasma-ion irradiation effects on double-walled (DWNTs) and multi-walled carbon nanotubes (MWNTs) are also investigated, where the degree of the structural deformation and the fullerene filling efficiency are clarified among SWNTs, DWNTs, and MWNTs. Furthermore, we demonstrate the evident effect of alternative Cs/C₆₀ ions irradiation on SWNTs, which for the first time realizes the junction structure encapsulation inside the SWNT.

2. Experimental details

SWNTs are prepared by an arc discharge. The detail description for both sample preparation and plasma formation can be found in elsewhere [4]. A nanotube-doped substrate is immersed in a magnetized plasma column ($B = 0.2$ T) as schematically shown in Fig. 1. The density and electron temperature of alkali-metal plasmas ($A^+ - e^-$; $A = \text{Cs, K, Na, Li}$) are measured to be $10^9 - 10^{10} \text{ cm}^{-3}$ and about 0.2 eV (\approx positive-ion temperature) by a Langmuir probe, respectively. In order to generate C₆₀ negative ions, fullerene particles are injected into the alkali-metal plasma column. As a result of electron attachment, alkali-fullerene ($A^+ - \text{C}_{60}^-$) plasmas with a very small fraction of the electron density are produced as shown by radial density profiles of the electron, alkali positive ion, and C₆₀ negative ion in Fig. 2, where the C₆₀ oven temperature T_o is raised from 200°C up to 500°C. For the purpose of the plasma-ion irradiation to carbon nanotubes, negative and positive biases ϕ_{ap} with respect to a grounded

hot plate (plasma-source electrode) are applied to the substrate. Thus, positively-charged and negatively-charged particles are substantially accelerated by sheaths in front of the substrate for $\phi_{ap} < 0$ and $\phi_{ap} > 0$, respectively, flowing toward the SWNTs, DWNTs or MWNTs. All plasma-ion irradiation experiments are performed for 1 hour. For the structural and compositional characterization of the carbon nanotubes, field emission transmission electron microscopy (FE-TEM) and energy dispersive X-ray spectrometry (EDS) are used, respectively. Purified and ion irradiated SWNTs are also characterized by Raman scattering spectroscopy (488 nm wavelength).

3. Results and discussion

3.1 Alkali-metal encapsulation inside SWNTs

Cs is selected as dopant because of its large diameter (~ 0.34 nm) and heavier weight as compared to other alkali metals. The latter is advantageous to make the dopants easier to detect by Z-contrast technique in scanning TEM (STEM), while the former is beneficial for doping only through the open end (not via the tube wall) and for the stability of the junction configuration. Thus, Cs tends to enter mainly through the open end when the tubes are relatively free of large defects in their walls.

Figure 3 clearly reveals the difference between the outside adsorption and the inside encapsulation of Cs. Figure 3(a) shows a thin bundle composed of two or three individual nanotubes, which illuminate very brightly due to Cs presence in Fig. 3(b), bridging two thick bundles. The arrows in Figs. 3(c) and (d) designate the junction point between hollow (left-side) and Cs-filled (right-side) regions of the SWNT. These figures imply a very important fact, that Cs ions cannot enter the nanotube, presumably through the side-wall defect, although side-wall diffusion is predicted both experimentally and theoretically in the case of Li, which has a small diameter compared with that of Cs or the hexagonal ring of the tube. If the side-wall defects such as the '5-7 defect', which would be produced by bombardment of numerous Cs ions, act as a window for intercalation, we cannot explain how this local filling takes place. In other words, if Cs is only attached to the exterior of individual nanotubes, it is very hard to consider why Cs does not distribute uniformly over the entire tube as shown in Figs. 3(a) and (b). For these reasons, we finally conclude that the Cs intercalation takes place via opened ends, which are considered to be caused by momentum transfer from the impact Cs ions to SWNTs.

Figure 4 gives high resolved FE-TEM images and an EDS spectrum obtained from the samples treated with $\phi_{ap} = -100$ V in the plasma. The linear and spiral configurations of intercalated Cs are clearly shown in Figs. 4(a) and (b), respectively. The inset in Fig. 4(a) stresses the intercalated Cs by dotting with black circles and the bottom image in Fig. 4(b) is also marked by dotting for a spiral chain of intercalated Cs inside the individual nanotube bridging two nanotube bundles. In Fig. 4(c), on the other hand, we can find two or three individual nanotubes combined each other by Van der Waals attraction. Although the upper tube looks vacant, the lower tube is observed to be partially filled and, presumably, crystallized. The inset especially reveals the regularly located 2 rows of Cs. Strictly speaking, the accurate encapsulation site of Cs has to be determined on the basis of the comprehensive understanding of the detail of interaction energy between the tube wall and intercalant, which is determined by the competition between Van der Waals and coulomb forces. In any case, the result well indicates the existence of Cs in the irradiated SWNTs, as shown in Fig. 4(d). Here, in order to obtain an accurate compositional information from a localized and isolated SWNT bundle, the electron beam size is compressed (~ 5 nm diameter) in the EDS analysis. Concerning the Cs encapsulation, some of our results have recently been published in elsewhere [5,6].

3.2 Fullerene encapsulation inside carbon nanotubes

When the positive-bias is applied instead of the negative bias to the substrate in the alkali-fullerene plasma, on the other hand, more drastic structural changes in the SWNTs are observed in the range of $\phi_{ap} = 5 - 20$ V. Furthermore, we have frequently found isolated SWNTs containing a self-assembled or set of fullerene molecules [7].

Figure 5 shows various FEG-TEM images of C_{60} peapods. The C_{60} molecules having diameter of 0.71 nm are separated from the SWNT walls by a van der Waals distance of ~ 0.35 nm. Therefore, the geometry of spheroidal C_{60} molecules would be the most suitable for encapsulation into general SWNTs. Nanotubes completely filled by close-packed fullerenes are presented in Fig. 5(a). The protruding nanotube tip has an unusual morphology, not hemispherical, which means that nanotube has undergone some structural deformation. A more interesting feature is shown in Fig. 5(b). This SWNT bundle is also composed of two individual tubes, as in Fig. 5(a). Although the lower tube in Fig. 5(b) seems to be empty and maintains a perfect tube structure, the upper tube incorporates a fullerene chain through its open end (black arrow). Figures 5(c) and (d), which present features frequently observed in

this study, give strong evidence that the fullerenes are well intercalated in the case when our plasma irradiation method is used.

In the cases of DWNTs and MWNTs the irradiated fullerenes by 5–20 V are found not to be encapsulated, where the threshold applied-bias voltage of the structural deformation attains to about 50 V in the case of DWNTs ($20 \text{ V} < \phi_{\text{ap}} < 50 \text{ V}$). Not only the structural deformation such as tube opening but also material filled DWNT is also observed after C_{60}^- irradiation with the bias voltage of $\phi_{\text{ap}} = 100 \text{ V}$ as presented in Fig. 6(a), where fullerene-like materials indicated by a black arrow look close-packed within the inner space of DWNT [8]. In addition, the diameters ($< 0.8 \text{ nm}$) of these spherical materials look to be smaller than that of C_{60} ($\sim 0.8 \text{ nm}$). In the case of MWNTs, Ni catalyst on the tube-tip is not observed for $\phi_{\text{ap}} = 100 \text{ V}$ as shown in Fig. 6(b). We can consider from this result that the minimum applied bias voltage necessary to the MWNTs deformation ranges from 50 V to 100 V ($50 \text{ V} < \phi_{\text{ap}} < 100 \text{ V}$) and MWNTs are expected to exhibit higher mechanical strength than that of DWNTs.

3.3 *SWNTs encapsulating Cs/C₆₀ junction structure*

We have performed an experiment of the bias application with instantaneous polarity change between positive/negative values in the $\text{Cs}^+ - \text{C}_{60}^-$ plasma ($\phi_{\text{ap}} = 20 \text{ V}/30 \text{ min.}$ and $\phi_{\text{ap}} = -100 \text{ V}/30 \text{ min.}$), which allows the alternative irradiation of both C_{60}^- ions and Cs^+ ions to the same sample, respectively. As a result of elaborate FE-TEM and EDS analyses, the SWNT actually encapsulates a junction of electron-donor Cs atoms on one side and electron-acceptor C_{60} molecules on the other (not shown here). At present, we do not yet know whether this junction structure filled SWNT really reveals the electronic non-linear property, and it is needed to establish an optimal synthesis condition. However, it is eminently worthy to note that our results show a high feasibility of the creation of this novel-functional nano-material in near future [9].

3.4 *Mechanism of structural modification*

The structural modification of carbon nanotubes by the plasma-ion irradiation is directly related to the material filling. This deformation and consecutive encapsulation mechanism is strongly supported again by a good agreement of the TEM results with the Raman results as given in Fig. 7. It is found that the value of $I_{\text{D}}/I_{\text{G}}$ increases with increasing the absolute value of an applied bias-voltage, which is a key parameter to determine the plasma-ion irradiation

energy. In other words, the amount of disordered nanostructures induced by tube bending or tube cutting increases due to the increased ion irradiation energy because the D-band in Raman spectra is activated from the scattering process by the presence of in-plane defects. Moreover, the value of I_D/I_G at the same substrate bias-voltage is relatively well ordered with their atomic masses. More interesting fact is the value of I_D/I_G of C_{60} irradiation by $\phi_{ap} = 10$ V or 20 V application in the $Li^+ - C_{60}^-$ and $Cs^+ - C_{60}^-$ plasmas (gray region) is much higher than that of the case of positive alkali-metal irradiation.

Considering all these results, therefore, we can confidently conclude that these modified nanotube structures in our experimental system are mainly produced by momentum transfer from the accelerated charged particles to the nanotubes and may contribute to yielding an enhanced encapsulation of intercalants inside the SWNTs [10].

Conclusions

The bias-voltage application to SWNTs, DWNTs, and MWNTs in collisionless plasmas mainly consisting of positive and negative ions is evidenced to be an effective method for controlling the inner nano-space of carbon nanotubes, i.e., the synthesis of carbon nanotubes encapsulating various kinds of foreign atoms. In a series of experiments on this new approach, a remarkable change of the pristine nanotube structure is observed after the plasma-ion irradiation at the first stage. Then the Cs encapsulation is for the first time realized by the negative-bias application leading to positive ion irradiation to SWNTs in the alkali-fullerene plasma, the configuration of which comprises three varieties. In the case of the positive bias application, C_{60} encapsulated SWNTs and DWNTs are found to be effectively synthesized, and the fullerene filling efficiency is found to become enhanced in the order MWNTs, DWNTs, SWNTs. It is also clarified that the structural modification after the ion irradiation is mainly caused by ion-momentum transfer to the carbon nanotubes. Furthermore, the existence of 'Cs/ C_{60} ' junction structure encapsulated SWNTs is directly verified for the first time, which are synthesized successfully by means of the bias application with prompt polarity change in the $Cs^+ - C_{60}^-$ plasma. Finally, it is noteworthy to emphasize our results open a new possibility for the novel structured material synthesis using plasma technology based on plasma physics.

Acknowledgments

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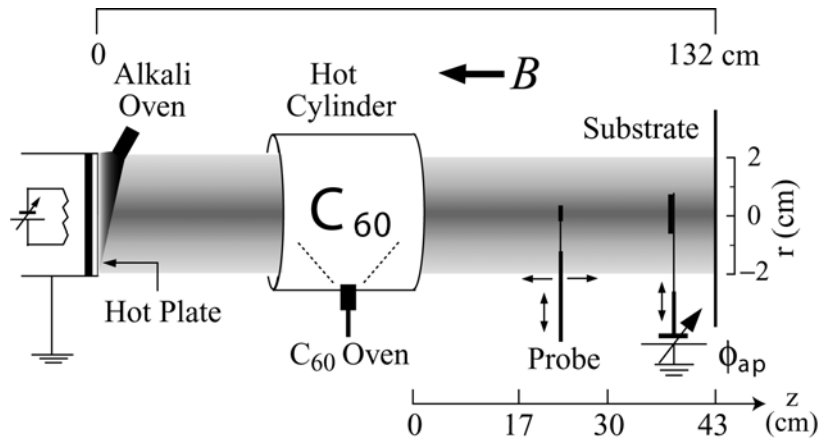


Fig. 1: Schematic of experimental apparatus.

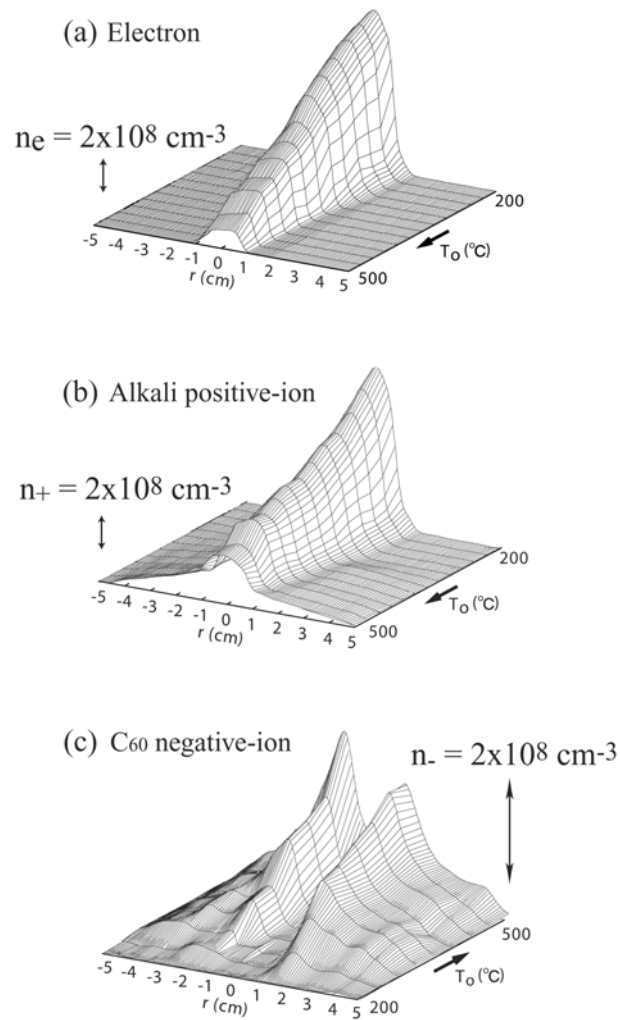


Fig. 2: Variations of radial density profiles of the electron (a), alkali positive ion (b) and C₆₀ negative ion (c) for C₆₀ sublimation oven temperature.

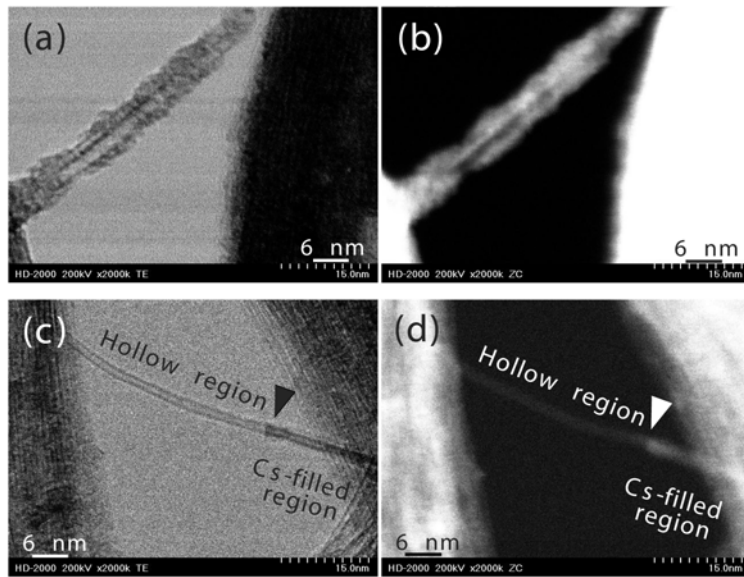


Fig. 3: (a) Bright-field STEM image of Cs adsorbed SWNTs. (b) Z-contrast image corresponding to (a). (c) Bright-field STEM image of Cs filling inside individual nanotube. (d) Z-contrast image corresponding to (c). Arrows in (c) and (d) indicate the junction of hollow and Cs-filled regions.

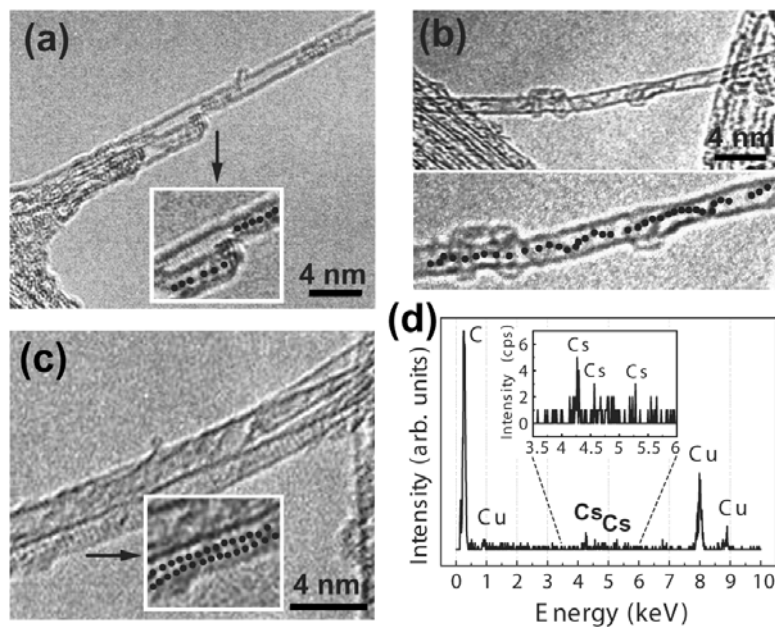


Fig. 4: (a) Linear configuration of Cs inside SWNTs, (b) helical configuration of Cs, (c) partially crystallized feature, and (d) corresponding EDS result.

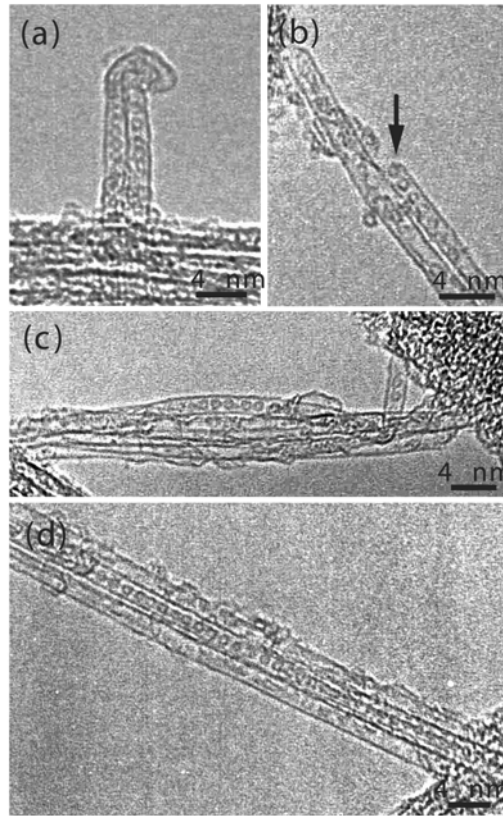


Fig. 5: Highly resolved FEG-TEM images showing various C_{60} encapsulated SWNTs obtained from samples treated with $\phi_{ap} = 20$ V in a $Cs^+ - C_{60}^-$ plasma. (a) Nanotubes completely filled by close-packed fullerenes. (b) Although the lower tube appears to be empty, the upper tube incorporates fullerene chain through its open end (black arrow). (c) and (d) Typical features of peapods frequently observed in this study.

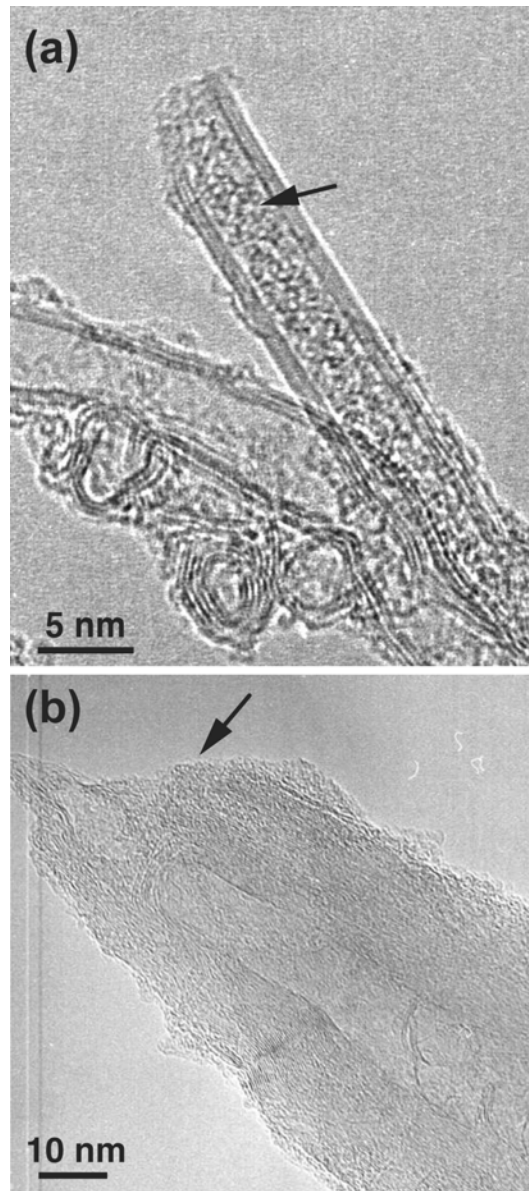


Fig. 6: FE-TEM images after C_{60}^- irradiation with the bias voltage of $\phi_{ap} = 100$ V. (a) Open-ended DWNT is filled with spherical materials, which are indicated by black arrow and expected to be one of the fullerene families. (b) Black arrow designates the Ni-tip removed MWNT by $\phi_{ap} = 100$ V.

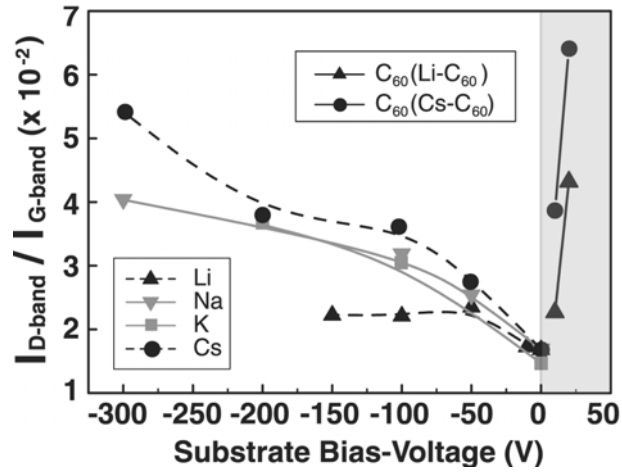


Fig. 7: Variations of I_D/I_G values for substrate bias voltage. In the case of positive alkali-metal ion irradiation, the value of I_D/I_G is relatively well ordered as their atomic masses at the same substrate bias voltage. Moreover, the value of I_D/I_G of negative C_{60} ion irradiation by $\phi_{ap} = 10$ or 20 V application in $Li^+ - C_{60}^-$ and $Cs^+ - C_{60}^-$ plasmas (gray region) is much higher than that of the case of positive alkali-metal irradiation.