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Raman Spectroscopy Investigation of Laser-Irradiated Single-Walled Carbon Nanotube Films

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Raman spectroscopy (RS) is the tool of choice for the analysis of carbon nanomaterials. In graphene and carbon nanotubes (CNT), RS provides rich information such as defect concentration, CNT chirality, graphene layer number, doping, strain, and other physical parameters of interest. This work presents the RS investigation of a semiconducting CNT film after high power laser irradiation. Changes were observed in the D band revealing the change in the defect concentration induced by the laser. More importantly, it was found the relative intensity decrease of G$^-$ and some radial breathing modes which suggests that the effects of laser irradiation induce diameter-selective effects in CNTs. The spectroscopic changes to the selective electronic structure modification for some semiconducting CNTs were attributed as due to those CNTs getting closer to resonance conditions with the fixed laser excitation.

1. Introduction

The Raman effect was discovered 90 years ago, and during this time it has been making a significant contribution to the physical and chemical characterization of materials becoming one of the essential tools in several fields, including the study of biological and carbon-based materials.[1–4] Some of the advantages of Raman spectroscopy (RS) include the non-destructive nature of the method, the little sample preparation required, the possibility to operate in different environments, and the rich information it can rapidly provide.[5,6]

Before the research explosion on graphene started with its rediscovery in 2004, there was a significant progress in the understanding of the Raman spectra in sp^2 carbon systems such as graphite,[7] carbon fibers, fullerenes, and carbon nanotubes (CNTs).[8] This understanding, particularly for CNTs and graphene, was largely established by the groups of Dresselhaus[9,10] and Ferrari.[11,12] Besides the important findings that have been reported before,[9,13] RS can give information about the graphitization and the functionalization of graphene and graphene oxide.[14,15] We aim at investigating the physical and structural changes that occur in carbon nanomaterials that are subject to high-power laser. This question is of particular interest given the rise of laser-processing methods for the creation and patterning of circuits, and especially, the possibility to tune the Schottky barrier of CNT/metal electrodes interfaces by laser irradiation.[16] Here we will build on those works to investigate the effect of high-power laser irradiation on CNTs. These effects are not straightforward to address by any other technique except for RS which further highlights the impact and versatility of this spectroscopic method. Previous works have shown the effects of UV laser irradiation and the impact on field emission[17] and also the photolysis of metallic CNTs using resonant laser illumination.[18] Here, we investigate films of enriched (99%) semiconducting carbon nanotubes and report for the first time the selective effect on a particular set of chiralities as a result of high-power laser irradiation. These new insights are partly possible thanks to the hyperspectral Raman imaging capabilities that allow localizing and investigating a single tightly focused spot.

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2. Results and Discussion

2.1. Laser-Modification of Carbon Nanotubes

We use RS imaging of a square-shaped area of interest around the region where the CNT film was illuminated for 60 s by a tightly focused laser ($\lambda = 514.7$ nm, power 10 mW, objective 100×, N.A. 0.9). The Raman imaging results and spectra extracted from the irradiated and non-irradiated regions are shown in **Figure 1**a and b. The high-power laser irradiation resulted in material removal which is evidenced in our case by the direct observation of the 3D film morphology by atomic force microscopy (AFM) shown in Figure 1c. The thickness decrease is about 30 nm according to the AFM cross-section analysis in Figure 1d. Beyond the material removal, we are interested in identifying the structural changes in CNTs that can be obtained by RS.

2.2. Raman Spectra of sp^2 Carbons

The understanding of CNTs spectroscopic signature requires an introduction to the Raman spectra of sp^2 carbons that are presented in **Figure 2**. The Raman spectrum from pristine

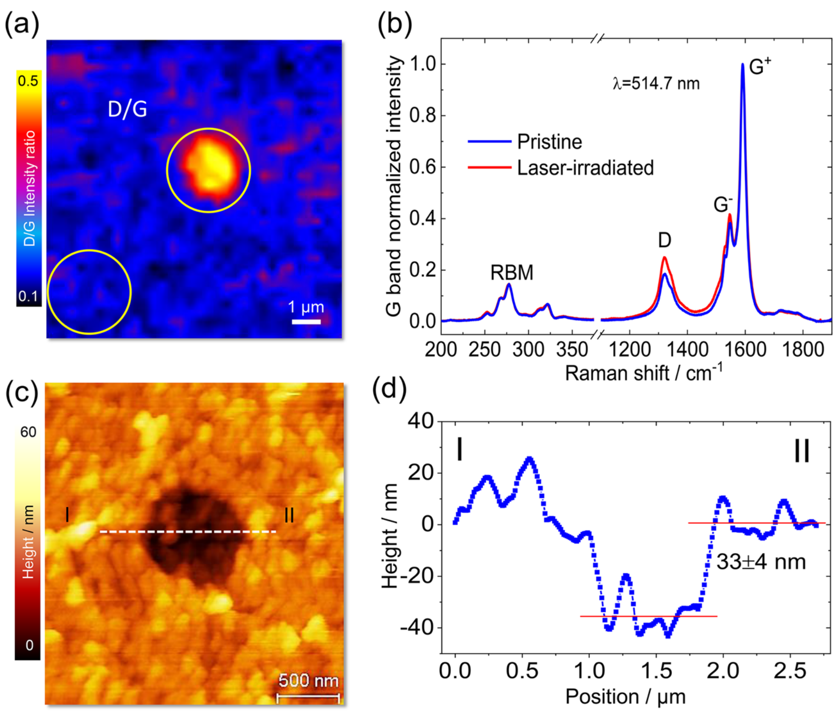

Figure 1. a) Raman hyperspectral imaging of the D/G intensity ratio in a CNT film. The bright region corresponds to the laser-irradiated spot. b) Raman spectra averaged from the regions marked by circles in (a). c) Atomic force microscopy image of laser-irradiated area and d) the cross-section profile along the dashed line in (c).

graphene is characterized by two main bands, the G peak and the 2D (also called G') peak that are located around 1590 and 2700 cm^{-1}, respectively.[10] The G label comes from the universality of this mode that is present in all graphitic material with sp^2 hybridization. When defects are present in graphene, another band becomes visible, the D band, labeled so because of its relation to defects.[10] The D band position is around 1350 cm^{-1}, and similarly to the D band, the second-order 2D band is also dispersive, with its position depending on the energy of the Raman excitation. Two phonons with opposite wave-vectors ensure the momentum conservation making the 2D band always visible in the Raman spectrum. Other second-order modes such as G* and 2G are also detected for these materials, as shown in the Raman spectra in Figure 2b. This is not the case for the D band that requires scattering on a defect for its Raman activation. This effect is strikingly obvious when comparing the graphite and graphene spectra to those of graphene oxide (GO) and reduced graphene oxide (rGO). Both show very high D/G ratio due to a large concentration of attached oxygen-containing groups. It also results in the damping of the second order bands and broadening of all detected modes. Defect healing achieved by laser reduction of GO results in partial removal of the attached functional groups and partially restoring the sp^2 graphene-like lattice. This effect results in the drop of the relative D band intensity which is contradictory[19–21] to several other reports on GO reduction.[22] Notice that this is contrary to the case of CNTs (see Figure 1b and 2b). While in CNTs the high-power laser can induce defects, in GO the laser also restores the graphitic nature of GO decreasing the apparent defect concentration. That is why the changes in D/G ratio are different for the two materials. The decrease in the intensity of the second order bands was not reported or explained in the current work (or anywhere else before) but it is an ongoing investigation that will be reported elsewhere.

The symmetry of the different Raman modes is schematically shown in Figure 2a. The G mode is degenerated giving rise to the in-plane vibrations E_{2g1} and E_{2g2}. The 2D is the symmetric out-of-plane mode A_1. The Raman spectrum of a pristine graphene sample and the spectrum from graphite are shown in Figure 2b with the modes explicitly labeled. These spectra illustrate the sensitivity of Raman to the physical properties and structural arrangement of sp^2 carbon. A notable difference is the 2D/G band intensity ratio, and the 2D band shape that can be used as indication of the presence of single-layer graphene. Such ease of analysis makes Raman an analytical method of high interest for graphene research that has contributed to the progress of 2D materials, for example, to confirm the presence of monolayers in mechanically exfoliated samples.[10] The D/G ratio is negligible in the case of high-quality graphite, but it shows a non-zero value for graphene. The presence of defects in graphene, and even the defect quantification can be easily achieved from the D/G band intensity ratio analysis.[23,24]

The high curvature in graphene that occurs for CNT introduces new modes that are not visible in pristine graphene. The CNT curvature lifts the degeneracy of the G band making the appearance of the G^+ and G^- for vibrations along and perpendicular to the nanotube axis, respectively. The frequency difference can be used to evaluate the CNT diameter.[26] For the current CNTs, the G^- frequencies of 1514, 1528, and 1547 cm^{-1} correspond to the range of CNT diameters from 0.8 to 1 nm. The lineshape of the G^+ and G^- modes confirms the semiconducting character of the CNTs.[27] Furthermore, the CNT curvature induces the appearance of low frequency modes resulting in the out-of-plane vibration of carbon atoms in the CNT, the so-called radial breathing modes (RBM). Each chirality, or the way the graphene sheet is rolled into a CNT, is characterized by its own RBM frequency. Thus, the RBM analysis enables the determination of carbon nanotube chirality and diameter, especially when RS measurements are performed with different laser excitation wavelengths that are resonant with the different optical transitions of the studied CNTs.[28] It is also worth noticing that, although less studied with respect to the RBM modes, the D, G^-, and G^+ bands depend on the CNT chirality.[28–30]

The (G^+) normalized spectra show a clear increase in the defect concentration of the laser-irradiated region reflected by the higher intensity of the D band.[17,18,31] We can also notice that there seems to be a relative increase of the G^- intensity. Such relative change in G^- band intensity could indicate that a

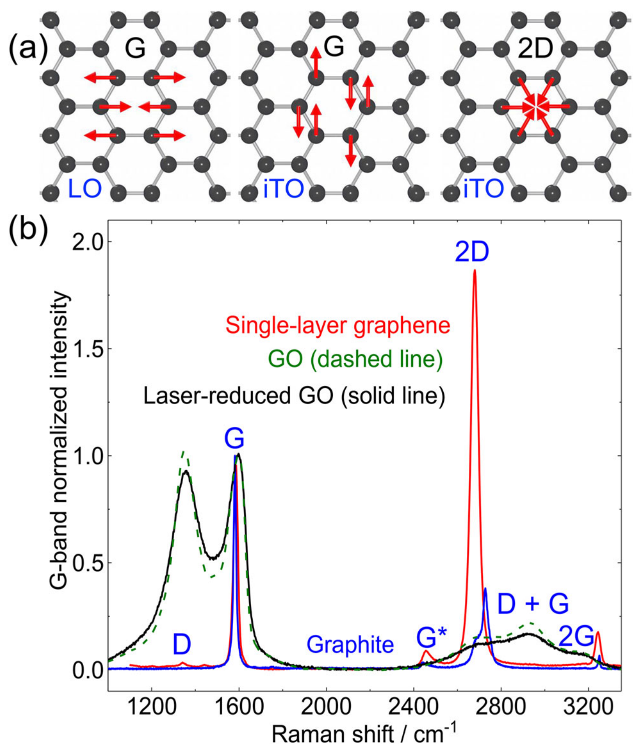

Figure 2. a) Illustration of the vibrational symmetry of G and 2D modes adapted from ref. [25]. b) Raman spectra of pristine single layer graphene, graphite, graphene oxide (GO), and laser-reduced GO.

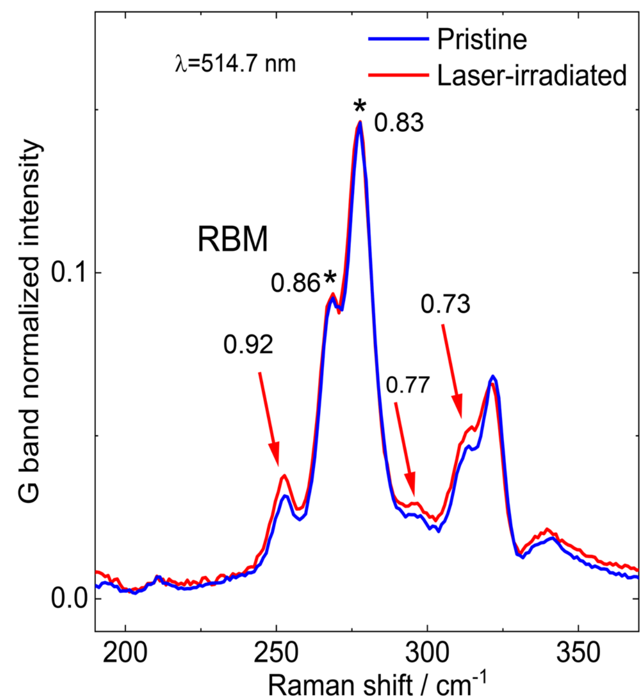

Figure 3. RBM region showing the different modes affected by the laser irradiation as well as the corresponding diameters shown by numbers. The diameter unit is in nm.

particular CNT chirality is being affected more than others. However, the slight background increase around the D and G bands make this observation questionable. Therefore, we opt to focus on the RBM analysis to confirm whether or not a particular CNT chirality was selectively changed by the laser irradiation.

2.3. Analysis of RBM Modes

Such an analysis is in line with our previous work on the RBM changes for a Au nanoparticle/system that demonstrated selective SERS enhancement of some RBM modes in CNT bundles.[32] The RBM region is shown in **Figure 3** with the modes that changed differently marked by arrows. Since the spectra are normalized with respect to the G mode, we expect to have an overlap for the spectra before and after laser irradiation if all chiralities were affected the same. However, the experimental observations show that there is a slight increase in intensity for the RBM modes marked by arrows in Figure 3. While the modes marked by asterisks did not change in intensity with respect to the G^+ band. There are a few parameters that determine the intensity of the RBM peaks. Since the spectra are normalized with respect to the G^+ band, the changes in the RBM intensity imply the change only in the CNTs corresponding to specific diameters. Notice that this result is contrary to observations previously reported that showed the change in CNT diameter as a consequence of laser irradiation.[31] We can easily rule out that possibility in our case since there is no shift in the position of RBM peaks but only the change in intensity ratio.

The intensity of the Raman mode depends on the properties of the Raman tensor, and it drastically increases when the resonance conditions are met. In a mixture of CNTs with different chiralities, we can induce resonant Raman scattering by adjusting the laser excitation to match the electronic optical transition corresponding to a particular chirality.[28] This is what made the application of RS in the determination of CNT chirality possible in conjunction with the so-called Kataura plot.[33] Following previous works,[28,34,35] we were able to determine the diameter of tubes from the RBM positions (see the numbers in Figure 3). The fitted RBM positions at 252, 267, 278, 297, and 313 cm^{-1} confirm that the film consists of a CNT mixture with the diameter range from 0.7 to 1 nm.

A previous work showed that laser annealing of CNT mixtures can selectively destroy metallic CNTs.[36] However, according to the Kataura plot by Jorio et al.,[28] when measuring the CNTs with a green laser, these diameters correspond to semiconducting CNTs. Here we are dealing with 99% semiconducting CNT mixture, also supported by the G^+ and G^- lineshape. Thus, the effect on the CNTs is also selective among semiconducting CNTs with different diameters.

There are two possible explanations for the diameter-selective changes in the RBM region. One possibility is the destruction of the CNTs that appear to be most in resonance and thus absorb the photons better, this would result in the decrease in the relative intensity of the RBM modes marked by asterix (*).

On the other hand, the change in the resonance conditions could occur. In our case, the laser excitation used in Figure 2 and

3 is the same for the analysis of the two CNT film regions (laser-annealed and non-annealed). Therefore, the high-power laser irradiation induces changes in the electronic structure of CNTs. By shifting the optical resonance energies, the CNT could come closer to resonance with the fixed laser excitation resulting in an increase in the relative Raman intensity of the RBM modes marked by arrows in Figure 3. Pinpointing the exact chiralities affected is beyond the aim of this work, also due to the requirement for a large number of points for the RBM at different laser energies.[28,33] Therefore, we can conclude that for a semiconducting-enriched CNT film the laser irradiation can modify the resonance conditions. These results have a potential impact in the technological application of CNTs, and the laser processing of this nanomaterial. In particular, elucidating the effects of laser irradiation on CNTs is critical, for example, considering works like the one from Nurbawono et al.[16] who showed the possibility to modify the Schottky barrier in CNT field-effect transistors (CNT-FET) by laser irradiation. It is also interesting that the selective irradiation could modify metallic CNT instead of semiconducting ones, providing a way to treat CNT-FET devices in which the presence of a single metallic nanotube could render the device useless.[18] This idea goes also in hand with an alternative contribution to the changes we observed. We saw from the AFM results that the laser irradiation results in material removal. The open question is: were those CNTs removed the ones with chiralities most in resonance with the laser excitation? This is also expected since those resonant chiralities are the ones with the largest photon absorption that translates into ablation due to an enhanced photothermal excitation. Identifying the exact chirality and establishing the influence of resonance conditions could be addressed in a follow-up investigation by performing a similar Raman hyperspectral imaging as done in this work but using different excitation wavelengths.

3. Conclusion

We analyzed with RS the effects of localized laser-annealing on a SWCNT film. We observed partial material removal and the selective influence on a particular set of carbon nanotubes. This selective change was deduced from the low-frequency analysis of the RBM modes showing the dissimilar intensity ratio changes between CNT regions with and without laser annealing. Although RS is possibly the most versatile tool in the investigation of carbon nanomaterials, a unified view on the changes that laser annealing makes in the Raman spectra is still in the horizon. We expect that our work illustrates and will further help the spectroscopic and technological advances of this field, especially for the analysis and development of laser-irradiated optoelectronics.

4. Experimental Section

CNT Films: The semiconducting enriched SWCNT (99% electronic purity, Nanointegris Inc.) were dispersed in 1 wt.% of sodium dodecyl sulfate (SDS). CNT films were obtained on silicon substrates by drop-coating. The laser irradiation was performed for 60 s with a green laser with 10 mW power and focused on the sample using a 50× long-working distance objective (N.A. 0.5).

RS: The RS investigations were performed in a LabRam HR800 Raman spectrometer. The green laser excitation (514.7 nm) was focused on the sample with 1 mW power using a 100× objective (N.A. 0.9). The hyperspectral Raman imaging was performed by scanning the sample under the objective using a computer-controlled stage with a 300 nm step.

AFM: The AFM investigations were performed using an Agilent 5420 in the semi-contact mode using commercial Si cantilevers.

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Conflict of Interest

The authors declare no conflict of interest.

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