Nanoscale Imaging and Identification of a Four-Component Carbon Sample

Evgeniya Sheremet,[†] Raul D. Rodriguez,^{*,†,§} Alexander L. Agapov,[‡] Alexei P. Sokolov,^{**,‡,||}
Michael Hietschold,[†] Dietrich R.T. Zahn^{†,§}

[†]Institut für Physik, Technische Universität Chemnitz, D-09107, Germany

[§]Cluster of Excellence “Center for Advancing Electronics Dresden” Carbon Path, cfaed,
Germany

[‡]Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA

^{||}Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

Corresponding Authors:

* Tel: +49-176-634-13369 E-mail: raul.rodriguez@physik.tu-chemnitz.de (Raul Rodriguez)

** Tel: +1-865-974-3852 E-mail: sokolov@utk.edu (Alexei Sokolov)

Abstract

We demonstrate the unprecedented chemical imaging of individual constituents in a four-component sample made of several carbon allotropes: single-wall carbon nanotubes, graphene oxide, C₆₀ fullerene, and an organic residue. This represents a significant advance with respect to previous works that were mainly limited to systems with one or two components having very different chemical composition. Despite the spectral and spatial overlap from different components, plasmon-based nanospectroscopy allows the discrimination of all individual carbon nanomaterials here investigated. Among other physical insights such as doping observed in carbon nanotubes, the detailed chemical imaging of graphene oxide reveals higher defect concentration at the flake edges similarly to the case of graphene. We found that the organic residue have either low adsorption or lack of resonant enhancement on GO, in contrast to graphene, suggesting a decreased van der Waals interaction. This report paves the way for routine nanoscale analysis of complex carbon systems with spatial resolution of 15 nanometers and below.

1. Introduction

Raman spectroscopy is an optical spectroscopy method that provides information on *e.g.* the vibrational frequencies of the material studied. This is particularly true for the case of carbon since it is one the very few techniques that is sensitive to the structure and chemistry of all carbon allotropes known so far. The vibrational frequencies in Raman spectroscopy are defined by the mass of the atoms and their interactions with the neighboring ones. This property allows

1 using the vibrational spectrum in Raman spectroscopy as a unique fingerprint characteristic for a
2 specific carbon allotrope [1]. However, this method has two main limitations: the low scattering
3 cross-section, and the low spatial resolution limited by the Abbe diffraction limit (*ca.* $\lambda/2$, where
4 λ is the wavelength of incident light), typically few hundreds of nanometers. Samples of practical
5 relevance often contain multiple components that need to be reliably differentiated. If the size of
6 each component in the mixture and the distance between these components are smaller than the
7 diffraction limit of light, then conventional Raman spectroscopy simultaneously detects their
8 spectral responses, and therefore the measured signal would represent the weighted average of
9 the components. As long as their spectral signatures are substantially different, each of the
10 sample components can be reliably differentiated. However, the situation gets more complicated
11 if the chemical identification is attempted on a sample whose components have similar chemical
12 nature, such as carbon-based nanostructures: fullerene (C_{60}), carbon nanotubes (CNTs),
13 graphene, and graphene oxide (GO).

14 Tip-enhanced Raman spectroscopy (TERS) [2-5] allows enhancing the Raman signal and
15 improving the spatial resolution simultaneously by employing a drastic local enhancement of the
16 electric field and spatial confinement by a plasmonic tip. The enhanced electric field is confined
17 to the volume directly under the tip apex, with a characteristic size comparable to the tip apex
18 radius (typically tens of nanometers). A few groups achieved spatial resolution below 10 nm by
19 employing so-called gap-mode TERS [6-8], when the material investigated is deposited on a
20 gold or silver substrate, which improves the confinement of the enhanced electric field due to the
21 image dipole and plasmon hybridization [9, 10].

Here we demonstrate the identification of constituents of a multi-component sample, containing several carbon-based materials: fullerene, single-walled carbon nanotubes, graphene oxide, and an organic residue. TERS imaging is especially interesting in this case, since it allows mapping the spatial distribution of each of the sample components on the surface within a region compared to the diffraction-limited laser spot size.

2. Methods

2.1. Sample preparation

The sample contains graphene oxide (GO), CNTs, fullerene (C_{60}), and an organic residue. A piece of gold coated (50 nm) glass slide (Ted Pella) was functionalized with a monolayer of amino-terminated PAMAM dendrimer (4th generation, Sigma Aldrich) in order to create a charged surface for effective adhesion of GO and CNTs. Next 100 μ L of GO suspension (Graphene Supermarket) was placed on top of the functionalized gold slide for two minutes, and then spun away. After that 100 μ L of CNT suspension (70% metallic, Nanointegris) was placed on top of the sample, held there for 2 minutes, and spun away in a spin coater. After that 100 μ L of fresh Piranha solution was placed on the sample for 5 seconds to remove the surfactant and the amino-terminated PAMAM dendrimer (4-th generation, Sigma Aldrich). Finally, the sample was rinsed in small amount of distilled water and dried at room temperature. As the final step, 50 μ L of 10-5M C_{60} (Sigma Aldrich) dissolved in toluene was spin coated on the sample. Organic residue detected by TERS is either the adhesion layer of the PAMAM dendrimer, or surfactant from CNTs suspension.

2.2. TERS imaging

The TERS measurements were performed in the side illumination / collection configuration using the TERS system from AIST-NT. It consists of an OmegaScope-R (AIST-NT Inc., CA, USA) coupled to XPlora Raman spectrometer (Horiba JY). The incident laser wavelength was 638 nm with a laser power of 300 μ W on the sample. The spectral resolution achieved was 8 cm^{-1} . The as-deposited structure was imaged by atomic-force microscopy (AFM) based TERS using an electrochemically etched gold tip [11]. The scanning step size was 9 nm along the vertical axis and 15 nm along the horizontal axis. The spectral analysis was performed using AIST 3.5.47 software (AIST-NT, Inc., USA). The qualitative preservation of the Raman spectra in TERS configuration was repeatedly verified on single component samples for each of the components.

3. Results and discussion

3.1. Nanoscale Imaging and Chemical Identification

The sample containing CNTs, GO, C_{60} and organic residue was imaged in a gap-mode TERS configuration.

Fig. 1. Sketch (not to scale) of the 4-component sample with graphene oxide, carbon nanotubes, C_{60} fullerene, and an organic residue deposited on a gold substrate. The AFM TERS tip was made of solid gold. The laser excitation was the 638 nm of a solid state laser focused in side-illumination by a long working distance 100x objective, N.A. 0.7.

A sketch of the 4-component sample with the side illumination/collection configuration is shown in Fig. 1. AFM topography acquired during the TERS scan is shown in Fig. 2a. The GO flake is clearly visible, while smaller features such as CNTs and C_{60} are not resolved. Their presence could be confirmed from TERS imaging taking into account both the Raman spectra and the shape of the feature. Representative TERS spectra of each component are shown in Fig. 2b-e. The sample components could be mapped using bands marked as D (1350 cm^{-1}), C_5 (1470 cm^{-1}), 2D (2700 cm^{-1}), and $-C-H$ (2900 cm^{-1}). These band intensities were used for constructing the TERS images presented in Fig. 2g-j. Fig. 2f is a composite TERS image overlaying the intensities of D, C_5 , and 2D bands. For comparison, the diffraction limited laser

spot size incident at 65° and focused by an objective with N.A. 0.7 is represented by a white dashed ellipse, demonstrating the superior resolution achieved by TERS. Here we first discuss the spectral features relevant for the identification of the components. A more detailed analysis of GO and CNT spectra and imaging is given in the subsequent sections.

GO is a graphene sheet with attached $-\text{OH}$ and $-\text{COOH}$ groups, maintaining its 2D structure [12]. Therefore, spectrally it corresponds to highly disordered graphene, and shows a so-called G band at around 1610 cm^{-1} arising from $\text{C}=\text{C}$ $\text{E}_{2\text{g}}$ vibrations in the six-membered carbon ring [13]. Such a high frequency position compared to graphene, which has a G band at 1588 cm^{-1} , was attributed in the literature to doping effects, as well as to disorder effects resulting in the presence of small isolated double-bond segments [14]. The attachment of the additional groups leads to defects, and thus to the activation of the broad D band centered at 1350 cm^{-1} [13]. The intensity ratio between the D and G modes is routinely used to estimate the defect concentration in graphene and CNTs, which makes the D band intensity a good indicator of the GO flake location in the TERS image (Fig. 2b, g, green in Fig. 2f). The broken symmetry of GO also allows for efficient enhancement of the in-plane G mode by the out-of-plane electric field at the tip apex, which is not the case for graphene [15]. In contrast to graphene where it is very intense, the 2D (G') mode at 2700 cm^{-1} is inhibited in GO when the electron-phonon coupling is disturbed due to high defect concentration [16].

Fullerene is a buckyball formed from five- and six-membered ring units of sp^2 and sp^3 hybridized carbon (see illustration in Fig. 1), which was also the molecule used in one of the pioneering TERS experiments [17]. Pristine C_{60} can be identified by a characteristic pentagonal pinch mode at 1470 cm^{-1} , arising from $\text{A}_{\text{g}2}$ five-ring vibrations [18, 19]. In our experiments the respective mode is centered at 1450 cm^{-1} (marked as C_5 in Fig. 2c), and its full width at half

1 maximum varies from 40 to 60 cm^{-1} . Taking into account the spectral resolution of 8 cm^{-1} , it can
2 be explained by the presence of several polymerization states of C_{60} [20].

3 This mode was used for generating the TERS image in Fig. 2h. Note that this mode partially
4 overlays with the modes of other components, therefore the position of C_{60} had to be identified
5 manually from the full Raman spectra, and is marked by white circles in Fig. 2h. The G band of
6 fullerene is observed at 1585 cm^{-1} . Single wall CNTs can be considered as roll ups of single layer
7 graphene sheets, leading to the splitting of the G band into G^+ and G^- bands for the C=C
8 vibrations along the CNT axis and along the circumferential direction, respectively [13, 23].

Fig. 2. (a) AFM topography of the 4-component sample, (b-e) representative spectra of the sample components and (g-j) corresponding TERS images for each component. The bands used for generation of the TERS image are marked as D, C₅, 2D, and C-H. (f) is a composite TERS image made from intensities of D (green), C₅ (blue), and 2D (red) bands. White ellipse in (f) illustrated the size of the laser spot. White circles in (h) mark the positions where the C₆₀ signal was detected. The intensity profile of the 2D band shown in (i) is taken along the white arrow.

Due to CNT bundling (see below CNT Analysis), the presence of the 2D band is a more reliable indicator of the CNT than the G⁺/G⁻ splitting. **Benefiting from the damping of 2D band**

1 in GO spectra, we used the 2D band intensity for generating the TERS image of CNT
2 distribution (Fig. 2d,i, red in Fig. 2f). For the case of more complex systems containing also
3 graphene a full spectral modeling may be required. As visible from the CNT profile indicated by
4 the white arrow (2D intensity profile, Fig. 2i), the achieved spatial resolution in this case is
5 limited by the step size of 15 nm.

6 In addition to the sample components discussed so far, an organic residue is detected all over
7 the substrate. The spectra in the fingerprint region (below 2000 cm^{-1}) are varying dramatically,
8 which has been observed for carbonaceous species in SERS and TERS experiments [24, 25]. In
9 the literature blinking was attributed to single molecule detection, as well as to the modification
10 of molecules in highly enhanced electric fields [24]. A band between 2800 and 3000 cm^{-1} is
11 reliably detected on the substrate and is attributed to the C–H bond vibrations of the organic
12 residue (Fig. 2e). This allows the discrimination of the organic residue from the other three
13 sample components. Interestingly, there is no organic residue detected on GO or CNTs. These
14 observations are contrary to the Raman enhancement reported for rhodamine with single layer
15 graphene [21] and reduced graphene oxide [22]. Two possible scenarios can explain this
16 situation: the organic residue molecules have low adsorption on GO as a consequence due to low
17 van der Waals interaction, or simply there is no chemical (resonant) enhancement for these
18 molecules on GO.

19 Quantitative estimation of the amount of material needs to be approached with caution. In
20 conventional Raman spectroscopy the signal intensity is linearly dependent on the amount of
21 material, but even then quantitative statements are only possible with careful Raman intensity
22 calibration procedures. Moreover, in the experimental results presented here one has to take into
23 account the resonant properties of single-wall CNTs, which strongly depend on the CNT

chirality [26-28]. Second challenge lies in the nature of TERS experiments. With the introduction of the tip, the electric field is enhanced in the cavity between the gold tip and the gold substrate [29]. The enhancement will not only depend on the resonant properties of the tip, the refractive index of the material in the cavity (in this case CNTs, GO or C₆₀), but also on the size of the cavity, *i.e.* on the thickness of the material. Fine interactions between the tip and the studied material such as charge transfer may also play a role. This entire set of effects make the quantitative estimation of the amount of a given material by TERS challenging. Therefore, although of critical importance, the question on material quantification by TERS is beyond the scope of the present work and remains an open question in the TERS community.

3.2. Graphene oxide

The resolution achieved in TERS experiments allows the analysis of localized changes in defect concentration and the corresponding peak widths and positions, that otherwise are not available using conventional micro-Raman spectroscopy. The D to G intensity ratio and the corresponding spectra for GO are presented in Fig. 3. GO is characterized by D to G ratio of (1.5 ± 0.1), which corresponds to the end of the first stage in the three stage model of disorder introduction in graphene (graphite to nanocrystalline graphite) [16, 30]. It is also supported by high position of the G peak. In the first stage the defect concentration n_D can be estimated as:

$$n_D^2 [cm^{-2}] = \frac{5.9 \times 10^{14} [cm^{-2} eV^4]}{E_L^4 [eV^4]} \left(\frac{I(G)}{I(D)} \right)$$

where E_L is the energy of the laser excitation. It gives us n_D of $1.4 \times 10^7 cm^{-1}$.

We also observe slightly higher D peak intensity at the edges of GO. It is additionally illustrated by a profile (Fig. 3b), as well as representative spectra along it (Fig. 3c). Note that this

small difference in defect concentration between the edges and the central area of the GO flake was not observed for other GO flakes analyzed, and therefore it should not be generalized. A possible reason for this result is that the activation of the D band depends on the nature of the edge structure similarly to the case of graphene for which zig-zag edges do not activate the D band [31]. Further studies on this question are beyond the aims of this work.

3.3. Carbon nanotubes

CNTs are probably the most studied material using TERS, giving different insights on the CNT properties such as: local distribution of strain [32] and defects [33, 34], change of the CNT chirality along a single CNT or bundle [35-37], and even defect nature [38].

The G band in CNTs is shifted to 1610 cm^{-1} in TERS, while the reference micro-Raman spectra of the same CNT dispersion on Si show the G band position at 1588 cm^{-1} . The shift is attributed to doping [39, 40] due to oxidation during the acid cleaning treatment (piranha). The regions with high defect concentrations can be identified by higher D/G intensity ratio (Fig. 3d). Selected spectra along the CNTs are presented in Fig. 3e. Note that for highly defective regions, the CNTs show spectra similar to those of GO, and thus they can be distinguished due to the geometrical shape of the component obtained from the TERS image only.

The spectra along line 1 show clearly resolved G^+ and G^- features, which can be used to estimate the CNT diameter. Due to in-plane nature of the G vibration, the result of this estimation is expected to be less sensitive to environmental changes than the radial breathing mode (RBM). Since 70% of the CNTs in the mixture are metallic, it is justified to use the estimation of the CNT diameter d_t for metallic CNTs [41]:

$$d_t^2 [nm^2] = \frac{79.5 [cm^{-1} nm^2]}{(\omega_{G^+} - \omega_{G^-}) [cm^{-1}]}$$

Where ω_{G^+} (ω_{G^-}) is the frequency of the G^+ (G^-) band. From the splitting of the two G features we can estimate the CNT diameter as being 1.7 nm. The spectra along line 2 show a wide G band, where G^+ and G^- features are not resolved. It suggests that the region comprises a bundle of the CNTs with different diameters. Finally, the spectra along the line 3 show wide G band as the one discussed above, but closer to the end of the CNT the G band appears to have small width where the G band splitting could be resolved. This result implies that the signal comes from fewer CNTs with the dominant diameter of 2 nm [41]. Such approach would be interesting for the analysis of bundle formation relevant for CNT-based devices.

Fig. 3. (a) and (d) D to G ratio (identical images with different color scales). The markings indicate the positions relevant for the analysis of GO (a) and CNT (d) TERS data. (b) D to G ratio along the line marked in (a), averaged within the rectangle. (c) Averaged spectra along the profile. (e) Selected TERS spectra along lines in (d).

4. Conclusions

The identification of CNT, GO, C₆₀, and an organic residue deposited on a gold substrate using AFM-based TERS was demonstrated under ambient conditions with a lateral resolution below 15 nm. CNTs can be identified by the presence of the 2D band, as well as from the G⁺/G⁻ splitting, while GO shows high D to G ratio without a detectable 2D band. The difference in defect concentration along the CNT bundles and in the GO flake could be analyzed from the D to G intensity ratio. Finally, fullerene was identified by the five-membered carbon ring band at 1470 cm⁻¹, and the organic residue by a reliably detected C–H band between 2800 and 3000 cm⁻¹. This demonstration shows the nanoscale capability of TERS for use in practical applications for non-ideal carbon systems, such as in multi-component samples typically found *e.g.* in biosciences.

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