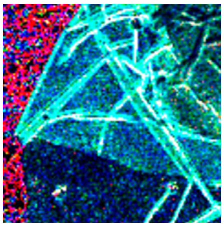
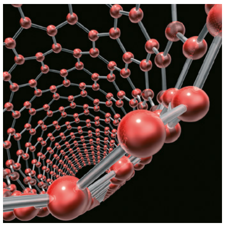
AFM-Raman

Correlated TERS and KPFM of Graphene Oxide Flakes





Application Note

Nanotechnology AFM15

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Abstract : AFM-Raman and its TERS mode are used to show nanoscale surface mapping of structural defects and chemical groups on graphene oxide (GO) flakes with 10 nm spatial resolution. TERS mapping is combined with Kelvin probe force microscopy (KPFM) measurements for simultaneous topographical, electronic and chemical imaging of GO surface. The multi-parameter measurement methodology proposed in this note extends the capability of TERS allowing a direct correlation of local chemical composition and physical properties at the nanoscale not only for 2D materials but for almost any sample surface.

Keywords : Graphene oxide (GO), Tip-Enhanced Raman Spectroscopy (TERS), Kelvin Probe Force Microscopy (KPFM), correlated measurements

Context and issues

Visualizing the distribution of structural defects and functional groups present on the surface of two-dimensional (2D) materials such as graphene oxide challenges the sensitivity and spatial resolution of most advanced analytical techniques. Here we demonstrate mapping of functional groups on a carboxyl-modified graphene oxide (GO–COOH) surface with a spatial resolution of ≈10 nm using tip-enhanced Raman spectroscopy (TERS).

Potential/ Input from technique

Tip-enhanced Raman spectroscopy (TERS) has emerged as a powerful analytical technique providing high chemical sensitivity for surface molecular mapping with nanoscale spatial resolution under ambient conditions. In TERS, a metallic scanning probe microscopy (SPM) probe placed at the focal point of a laser undergoes localized surface plasmon resonance (LSPR), which together with the lightening rod effect leads to the enhancement and confinement of the electric field at the TERS probe apex. This effect simultaneously improves the sensitivity as well as the spatial resolution of Raman microscopy by enhancing the Raman signal from analyte molecules directly underneath the TERS probe. Furthermore, we take the surface characterization a step further by combining TERS with Kelvin probe force microscopy (KPFM) and thus demonstrate in situ topographical, chemical and electrical nanoscopy of a GO–COOH surface.

Starting point, what is known?

Carboxyl graphene oxide samples consist mostly of carbon and oxygen as well as different functional groups: C–O–C, C–O, C–CH3, C=O, COOH and C–H. With Raman spectroscopy the typical signature bands of graphitic material can be observed at ~ 1350 cm^{-1} (D band) and at ~ 1590 cm^{-1} (G band). Whereas the G band, representing the tangential stretch of the carbon atoms, is present in all graphitic substances, the D band appears only in the presence of defects. Thus, with D/G band intensity ratio (ID/IG) a relative defect concentration can be established. The differentiation of functional groups can be accomplished via specific band positions corresponding to different bonds (see Table 1 for detailed description).

Table 1. Tentative assignment of Raman bands from carbon-containing bonds.

Raman band position (cm^{-1})	Tentative assignment
1097	C–O (vs, C–O)
1179	C–O–C (vs, C–O–C)
1330	C–CH3 (δs, C–CH3)
1420	C–H (β, C–H)
1654	C=O (vs, C=O)
1747	COOH (vs, COOH)
vs: symmetric stretching mode, β: bending mode, δs: symmetric deformation mode	

Description of sample and measurement

The GO–COOH samples measured in this work by TERS were prepared by spin-coating GO–COOH (ACS Material, USA) on a Au coated glass substrate. A NanoRaman™ system combining an Atomic Force Microscope (SmartSPM, HORIBA Scientific) with a Raman spectrometer (XploRA, HORIBA Scientific) is used in side illumination/collection (objective lens ×100, NA=0.7). The *p*-polarized 638 nm laser light is focused onto the apex of the gold TERS tip, allowing simultaneous SPM and spectroscopic Raman measurements at the same location of the sample.

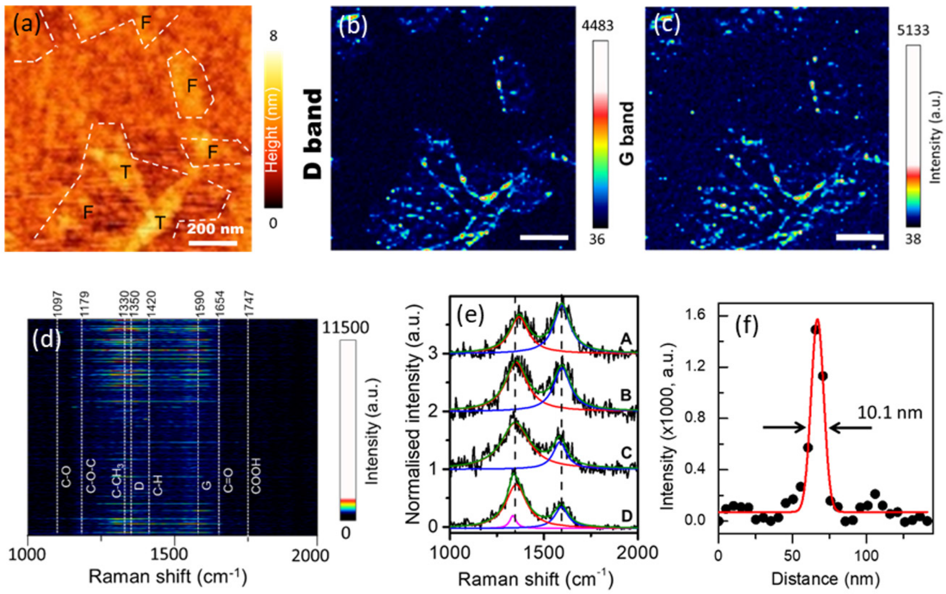

Figure 1. TERS mapping of GO-COOH flakes: topographic image with outlines of few layer (F) and thick layer (T) flakes (a), TERS maps of the D band (b) and G band (c), all measured TERS spectra are stacked with designated signature positions of the COOH functional groups (d), example of GO spectra with different ID/IG ratios (e), and example of spatial resolution D band profile across the edge of a flake (f).

To perform a detailed chemical analysis of the sample, a 1 × 1 μm^2 area was mapped. TERS spectra were collected 10 nm apart with acquisition time of 400 ms. Mapping of several flakes of carboxyl graphene oxide is presented in Fig. 1. The areas with few layer flakes that cannot be easy identified in the topographic image, become clearly visible in the TERS maps of D band and G band. Furthermore, analyzing all 10,000 TERS spectra helps to identify the functional carboxyl groups, and thus to spatially locate them at the nanometer scale with the TERS maps.

For further investigation, TERS mapping followed by Kelvin probe microscopy mapping was performed on an area of 2.5 x 1.7 μm^2 including a carboxyl graphene oxide flake. For TERS mapping the step size was 16.7 nm and acquisition time 75 ms. Fig. 2 displays the ID/IG ratio as well as the contact potential difference (CPD). The graph in Fig. 2 which plots CPD versus ID/IG ratio for a number of points in the mapped area highlights the inverse correlation between surface potential and ID/IG ratio. In other words high ID/IG relates with highly negative CPD.

Conclusion and perspectives

In summary, we have demonstrated nanoscale TERS mapping of structural defects and functional groups present on a GO–COOH surface with an unprecedented spatial resolution of ≈10 nm. Furthermore, we have pushed nanoscale surface characterisation a step forward by demonstrating in situ electrical and chemical nanoscopy of a GO–COOH sample by combining TERS with KPFM. This in situ multi-parameter measurement methodology greatly extends the capability of TERS allowing a direct correlation of local topography, chemical composition and electronic properties at the nanoscale not only in 2D materials but on almost any sample surface. In particular, we expect this work to open up the possibility of optimising optoelectronic devices based on novel 2D materials such as graphene, GO, single-layer MoS_2 via non-destructive, simultaneous and nanoscale multi-parameter characterisation of their surface properties even under operational conditions.

Bibliography

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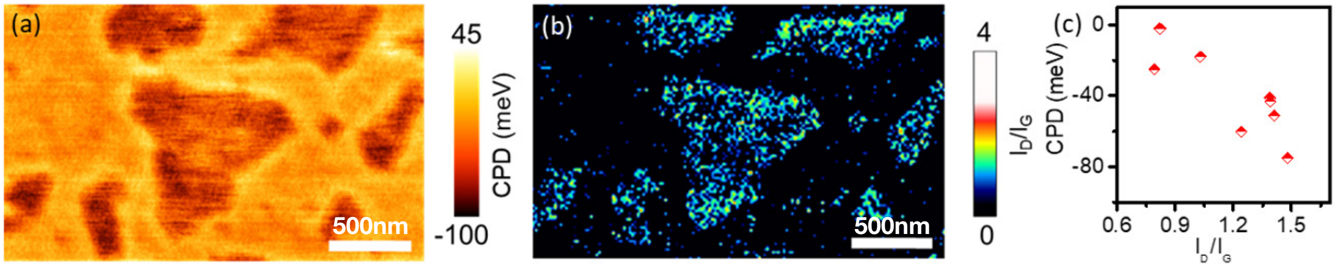

Figure 2 In-situ electrical and chemical TERS mapping of GO-COOH flakes: contact potential difference value (CPD) (a), TERS map of ID/IG ratio (b), and graph plotting CPD value as a function of corresponding ID/IG ratio for a selection of points in the mapped area (c).

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