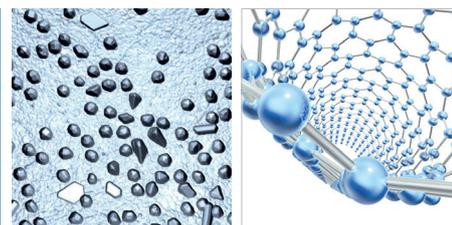# HORIBA Scientific

Characterization of Nanoparticles from Combustion Engine Emission using AFM-TERS

Ophélie Lancry[1], Jennifer Noble[1], Agnès Tempez[1], Sébastien Legendre[1], Marc Chaigneau[1], Philipp Kreutziger[2], Marcus Rieker[2], Cristian Focsa[3]

[1] HORIBA Scientific - HORIBA France SAS, Palaiseau, France. [2] HORIBA Automotive Test Systems - HORIBA Europe GmbH, Oberursel, Germany. [3] PhLAM Laboratory, Lille 1 University, Villeneuve d'Ascq, France.

Abstract: In the frame of the European PEMs4Nano project, nanoparticles from combustion engine emission have been deposited on gold substrates and imaged by AFM and its combined nano-resolution chemical TERS mode. Focus has been on sub-23 nm particles which are investigated for their health impact and are to be soon under regulation rules. Particles imaged by AFM are characterized by their size with a resolution of +/- 1 nm. Correlated TERS maps with a pixel size of 7 nm and below reveal the chemical complexity through the deconvoluted D and G band signatures. Using the D1 over (G+D2) band intensity ratio which is an indicator of the degree of order in soot structure, TERS is capable of distinguishing between combustion engine emitted nanoparticles of different structure.

Keywords: Nanoparticles, AFM-Raman, Tip-Enhanced Raman Spectroscopy (TERS), engine emission, combustion, carbon.

Context and issues

Particulate emissions from on-road motor vehicles are currently the focus of intensive research due to the impact of ambient particulate matter levels on climate and human health. Estimates of the health impact attributable to air pollution indicate that PM2.5 (particles with diameter below 2.5 µm) concentrations in 2012 were responsible for 432,000 premature deaths originating from long-term exposure in Europe (over 40 countries), of which 403,000 were in the EU-28. Although improvement in engine technology has led to a significant decrease in the number and mass of emitted particles a new concern is raised nowadays by even smaller particles.

Specifically, sub-23 nm particles can be produced, sometimes in high concentrations, in both diesel and gasoline direct-injection (GDI) engines [1]. Harmfulness of the particles has been shown to correlate better with surface area than with mass [2][3], which becomes important for ultrafine particles even though their residence time in the atmosphere is shorter. In addition, it has been estimated that the percentage of sub-23 nm solid particles fraction could reach 30-40% for gasoline vehicles utilizing direct injection and be potentially higher when alternative fuels are being used [4]. These nanoparticles are currently not measured by regulations in force (certification procedures have a cut-off size of 23 nm).

It becomes urgent to develop robust, reliable and reproducible measurement technology, supporting the engine development process as well as future certification procedures on the chassis dyno and during real driving emissions (RDE) measurements.

Existing regulation focuses on particle number and mass which are key to control the environmental impact. However, it is also critical to determine the chemical composition and especially the surface chemical composition of the nanoparticles to understand the potential reactivity with the environment including impact on human health.

Potential/ Input from technique

AFM can image combustion generated nanoparticles provided they are deposited on flat substrates and suitable scanning conditions are used. AFM images will allow characterization of their size and mechanical properties, both of which are critical

[1] Giechaskiel, B., et al., 2014. SAE International Journal of Fuels and Lubricants 7, 950–964.
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[3] Oberdörster, G., 1996. Inhalation Toxicology 8, 73–90.
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to determining how they are transported and how they can affect human health. However, no chemical information will be given by AFM. On the other hand, Raman spectroscopy is widely used for chemical characterization, but imaging is limited by a spatial resolution around 200 nm because of the diffraction limit. Tip-enhanced optical spectroscopies (Tip-Enhanced Raman Spectroscopy TERS, and Tip-Enhanced Photoluminescence TEPL) based on signal amplification from the nano-region under the tip will allow for actual chemical nano-characterization.

Starting point, what is known?

Raman spectroscopy has been demonstrated as an excellent chemical characterization tool for soot particles as it is sensitive not only to crystal structure but also to molecular structure (short range order). An example of a Raman spectrum of a soot particle is shown in Fig. 1 for the first order Raman region 800-2000 cm^{-1}). The five-peak deconvolution shown in Fig. 1 results from the curve fitting method of Sadezky procedure [5]. It contains two main features : the G band, derived from in-plane motion of carbon atoms and appearing at around 1580 cm^{-1}; and the D band, attributed to lattice motion away from the center of the Brillouin zone and appearing around 1270-1450 cm^{-1}, depending on the structural nature of the material. More details about the band characteristics and assignments are given in Table 1. This method allows distinguishing different types of soot according to their degree of graphitization.

Description of sample and measurement

Combustion-generated nanoparticles were produced using a generic single cylinder test engine in standard engine operating conditions and with gasoline fuel. The collection of size-selected particles of a wide size range from 10 μm to 10 nm was performed using a NanoMoudi II (model 125R, MSP, TSI company, PEMs4Nano consortium partner). The NanoMoudi is a cascade impactor Micro-Orifice Uniform-Deposit Impactor (MOUDI IITM), which combines aerodynamic design and micro-orifice nozzles to reduce jet velocity, pressure drop, particle bounce and entrainment during particle sampling (Fig. 2). Particles were collected on gold-coated silicon
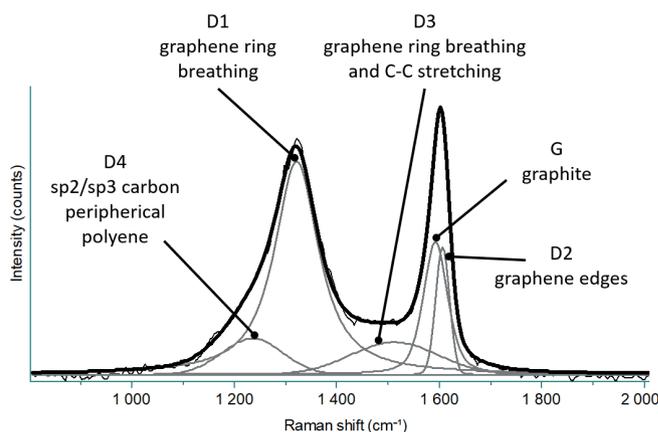

Figure 1. Typical Raman spectrum of carbon material , five-band fitting method, routinely applied to combustion soot.

wafers for 30-60 minutes, ensuring a smooth surface for AFM measurements and a low surface density. The smallest size bin, nominally containing particles with aerodynamic diameter 18-10 nm, was chosen for AFM-TERS studies.

A NanoRaman system from HORIBA Scientific combining

Figure 2. NanoMoudi particle size-selected collector.

an Atomic Force Microscope (SmartSPM) with a Raman spectrometer (LabRAM HR Evolution) is used in a reflection configuration for Tip-Enhanced Raman measurements (TERS). The incident laser (633 nm, *p*-polarised) is focused through the 100×, 0.7 NA, 7 mm long working distance objective lens (Mitutoyo) in side-illumination geometry with an angle of 60° with respect to the vertical axis. The collection of back-
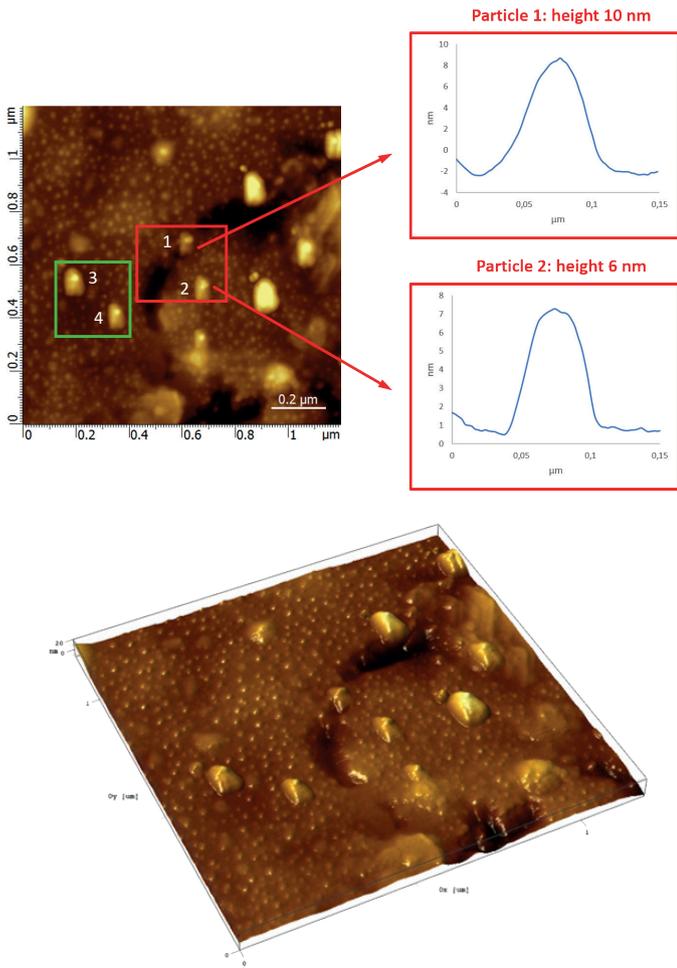
Table 1. First order Raman bands and vibrations reported for soot.

	Raman shift	Intensity	Vibrations	
D4	~1350 cm^{-1}	low	sp^3 carbon or polyene C=C or sp^{2}sp^3 CC	Disordered graphitic lattice
D3	~1500 cm^{-1}	medium	Defects (in place) or amorphous sp^3 C affecting C=C stretching	Amorphous carbon
D2	~1620 cm^{-1}	high	Aromatic C=C stretching from isolated graphene units	Disordered graphitic lattice
D1	~1350 cm^{-1}	very high	In-plane defects	Disordered graphitic lattice
G	~1580 cm^{-1}	high	sp^2 C=C stretching	Ideal graphite

[5] Sadezky, A, et al., 2005. Carbon 43, 1731-1742.

Particle 1: height 10 nm

Particle 2: height 6 nm

scattered signal is performed through the same objective. The probes used for AFM-TERS are cantilever-based silver TERS tips (Ag coated OMNI TERS probe, AppNano, manufactured only for HORIBA Scientific).

The size of single particles and their distribution were determined by AFM measurements. A 1.2×1.2 µm image (300×300 pixels) is displayed in Fig. 3 and exhibits two particles of 10 nm (particle 1) and 6 nm (particle 2) height. The diameter as measured by the FWHM (Full Width at Half Maximum) of particle 1 and particle 2 is respectively 48 nm and 43 nm. However, the lateral resolution is highly dependent on the tip used, especially when the radius dimension of the scanned object is close to the one of the tip (tip-sample convolution phenomenon). With a tip radius of 1 nm according to the manufacturer, the error on the particle diameter is +/- 1 nm.

Within this image, two smaller areas containing particles with diameters below 10 nm were defined and characterized by TERS to determine their chemical structure (Fig. 4) : the pixel size of zone 1 and zone 2 is respectively 7 nm and 5 nm, the acquisition time is 100 ms per pixel. The TERS maps (Fig. 4) correspond to the distribution of carbon material on the surface by monitoring the **G band** intensity (1500-1700 cm^{-1}, Fig. 4, Zone 1) and an overlay of the **G band** and **D1 band** (in green) intensities (1200-1700 cm^{-1}, Fig. 4, Zone 2). Three carbon particles identified by their TER spectra match perfectly with the particles highlighted on the topography image. The fourth one (particle 1) presents a feature related to the presence of amorphous carbon-based species. This signal originates from a crevice formed by the grain boundary between micro-crystals of the Au film (seen in the AFM image, Fig. 3).
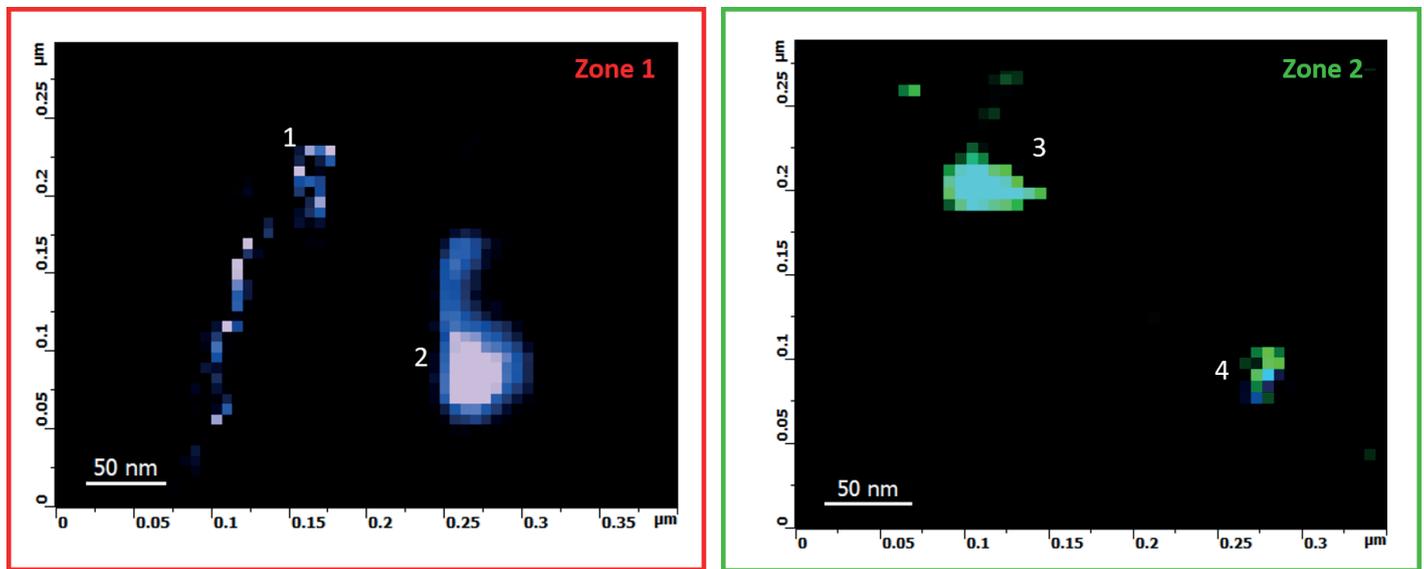
Figure 3. (top) AFM images of particles collected from the single cylinder test engine and their cross-section , (bottom) 3D AFM topographic image of the same area.

*Figure 4. TERS images of particles collected from the single cylinder test engine: (left) **G band** intensity map (Zone 1) and (right) **overlay of the G band and D1 band intensities** (Zone 2).*
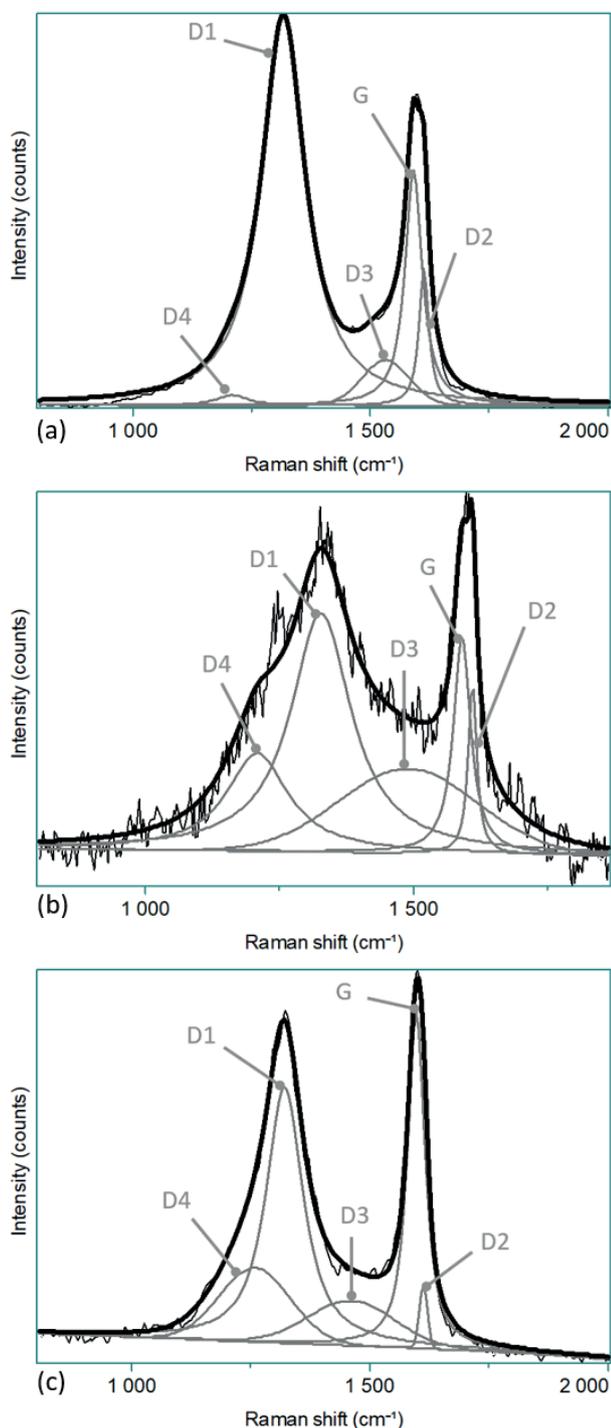
(a)

(b)

(c)

Figure 5. Five-band deconvolution applied to TERS spectra of particle 2 (a), particle 3 (b) and particle 4 (c).

Table 2. Deconvolution results.

Particle	Band	Position, cm⁻¹	Width, cm⁻¹	D1/(G+D2)
Particle 2	G D1 D2 D3 D4	1589.7 1315.5 1611.5 1530.7 1208.0	43.4 111.4 24.7 117.8 80.4	**3**
Particle 3	G D1 D2 D3 D4	1589.7 1315.5 1611.5 1530.7 1208.0	38.5 137.1 19.0 304.1 140.0	**2.5**
Particle 4	G D1 D2 D3 D4	1589.7 1315.5 1611.5 1530.7 1208.0	44.6 92.8 20.1 213.9 175.1	**1.5**

Average spectra of the three measured particles were extracted: they exhibit very different profiles indicating major structural differences between particles produced by the same engine regime and the same size bin. Five-band deconvolution analysis already applied to Raman spectra of soot particles [5] was used within Labspec 6 software. The fit results are presented in Fig. 5 and Table 2. The G, D1, D2 and D3 bands are fitted with a Lorentzian profile, whereas the D4 band is fitted with a Gaussian profile. The ratio of areas of the D1 on the (G+D2) bands is a strong indicator of the degree of order in soot structure [6]. This value increases from 1.5 (particle 4, Fig. 5c) to 2.5 (particle 3, Fig. 5b) and to 3 (particle 2, Fig. 5a), suggesting that particle 2 has much more disordered structure than the others. However, the presence of organic materials on the surface of the particles is indicated by higher D4 band intensity in the spectra of particles 3 and 4.

Conclusion and perspectives

This application note presents AFM-TERS results on combustion-generated nanoparticles for the first time. The combination of AFM and Raman through the NanoRaman platform enables morphological characterization (size distribution) and discrimination between the different particles on the surface (chemical information) at the nanoscale, revealing the diversity of carbon structures generated during gasoline combustion.

Acknowledgments

[5] Sadezky, A, et al., 2005. Carbon 43, 1731-1742.
[6] Carpentier, Y, et al. 2012. Astronomy & Astrophysics, 548, A40.