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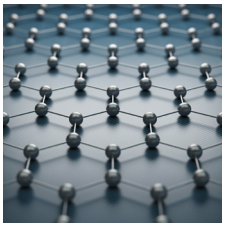
AFM-Raman

TERS Characterization of Explosive Nanoparticles



Application Note

Nanoparticles AFM20

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Abstract : This application note reports on TERS characterization of crystalline nanoparticles that are prepared by spray flash evaporation of two explosive organic coumpounds: CL-20 and HMX. The TERS surface sensitivity reveals that TER intensities of CL-20 and HMX band markers are inverted in comparison with their intensities in the bulk, which leads to the conclusion that the surface of the CL-20/HMX co-crystals nano-plates is HMX-terminated. This surface structure gives insights for an impact ignition mechanism and explains the close impact sensitivity values of HMX and CL-20/HMX co-crystals.

Keywords : Nanoparticles, nanocrystals, energetic materials, explosives, surface, Tip-Enhanced Raman spectroscopy.

Context and issues

The use of the remarkable surface driven properties of nanomaterials is now widespread with applications in medical, aerospace, microelectronics industries, and many other application areas.

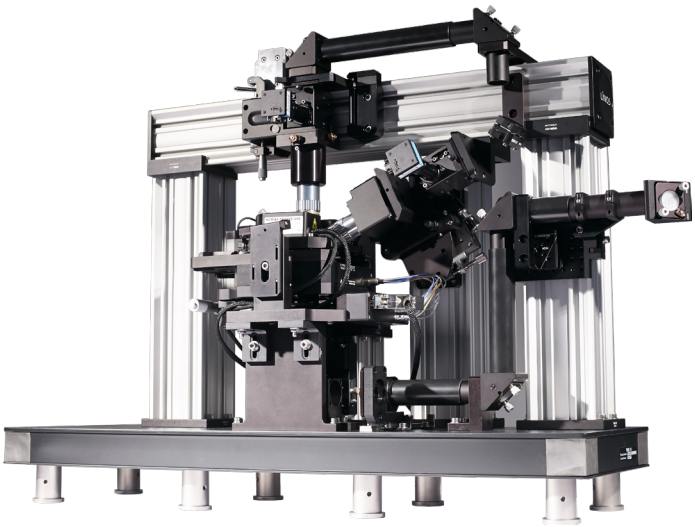
Co-crystals which consist in mixing two or more compounds in a crystalline manner are also applied to engineer materials with superior properties to single compound crystals. Co-crystals nanoparticles are used in the pharmaceutical industry to fabricate medicine with improved effects and in explosive industry to make highly energetic and safe materials.

For example, co-crystals made from a high energy/high friction sensitivity compound, 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0.0]dodecane (CL-20) and a lower energy/low friction sensitivity compound, 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) feature the “best of both worlds” : higher detonation velocity than pure HMX and lower impact sensitivity than CL-20 (close to that of HMX) [1, 2]. In addition, the nanosize of the co-crystals further improves the sensitivity characteristics, making it better than pure HMX [3].

So far it is not understood how co-crystallinity combined with nanostructuring leads to the enhanced behavior of these nanoparticles. Only a technique capable of probing single nanocrystals can bring answer about their observed pyrotechnical properties.

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. The higher electromagnetic field locally created at the apex of the irradiated tip enhances the Raman signal from the sample made in contact with or really close to the tip. The signal originates from the nanoregion underneath the tip, thus probing minute sample amount and ensuring nanometer lateral resolution. The strong field enhancement rapidly decays within a few nanometers which makes TERS ideal for nanoobjects observation but also makes it a highly surface sensitive technique.



TRIOS platform with its CombiScope AFM

In the case of energetic nanoparticles TERS offers the additional advantage of being a low input energy compared to electron microscopies in which the electron beam tends to induce the dissociation of energetic organic molecules.
TERS analysis also becomes crucial as the structural information given by single crystal XRD is bound to the ability to grow sufficient size crystals.

Starting point, what is known?

The AFM-TERS investigation of differently prepared energetic hexolite (i.e. a mixture of TNT [2,4,6-trinitrotoluene] and RDX [1,3,5-trinitro-1,3,5-triazine]) nanocomposites has led to the structure determination of RDX/TNT core/shell and patchy 15–20 nm sized nanoparticles[4].

Description of sample and measurement

The CL-20/HMX nanocrystals are prepared by spray flash evaporation: a pressurized solution of one or more compounds is sprayed through a heated cone nozzle into a reactor under vacuum. The strong pressure drop results in instantaneous evaporation of the solvent and subsequent

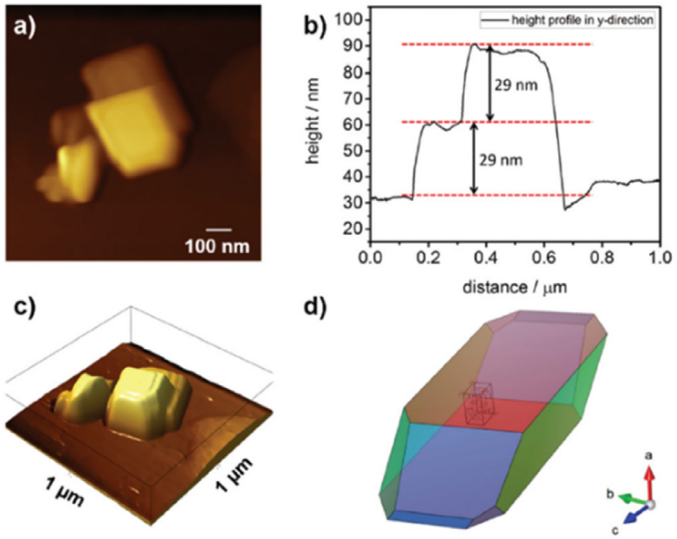


Fig. 1. (a) Topographic map of n-CL-20/HMX co-crystals; (b) height profile of particles shown in (a) along the the y-direction. (c) 3D image of (a); (d) crystal morphology simulated by using crystal faces.

formation of nanoparticles which are collected through a filter system. When the precursor solution contains more than one molecular compound, the formed nanosized products can be a mixture of single crystalline compounds, core shells particles and nano co-crystals. Here, as in Ref [1] (first synthesis of CL-20/HMX co-crystals) the precursor solution was prepared in a 2:1 CL-20:HMX molar ratio.

In this work, for AFM and TERS analysis, nanoparticles are applied onto glass cover slides by depositiong a spatula tip between two cover glasses. The sample is spread on the glass surface through pressureless rubbing of the two slides against each other.

TERS tips are AppNano Access-NC AFM probes coated with a 25 nm thick Silver layer on top of a 3 nm Titanium adhesion layer in an argon plasma sputtering system. SEM observation indicates the formation of a single silver nanoparticle at the apex of the tip.

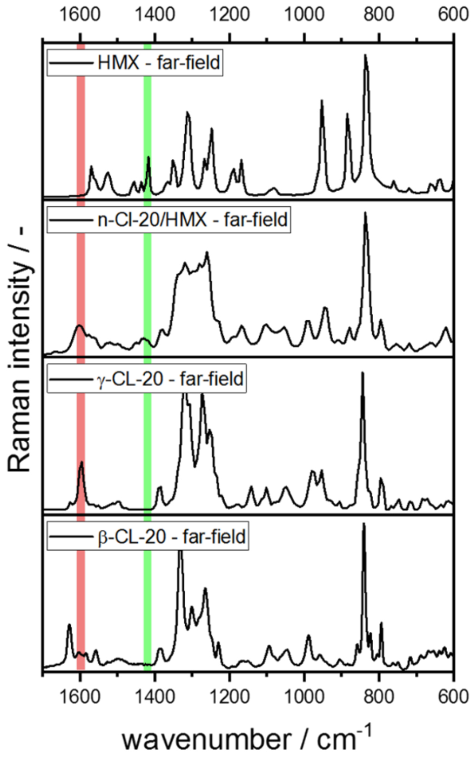


Fig. 2. Far-field Raman spectra of β-CL-20, γ-CL-20, n-CL-20/HMX nano co-crystals, and β-HMX between 1700 cm^{-1} and 600 cm^{-1}. Two Raman band markers are indicated: ***Red stripe*** *is the NO_2 asymetric stretching vibration of CL-20 at ~1600 cm^{-1}.* ***Green stripe*** *is the CH_2 out of plane wagging vibration of HMX at ~1416 cm^{-1}.*

Prior to TERS, X-ray powder diffraction (XRPD) reveals the monoclinic structure of the nanosize co-crystals in which layers of HMX alternate with bilayers of CL-20. XRPD gives the information about the complete conversion of the precursor mixture into CL-20/HMX co-crystals.
AFM topographic images (typical example shown in Fig. 1) of the nanoparticles acquired in non-contact mode confirm the crystalline morphoplogy of the particle with flat surfaces and sharp angles. The height of the angular plates of 29 nm is in line with the XRPD calculated coherence length in the [300] direction.

The µRaman spectrum acquired from the nano-particles is comparable to the signature spectrum obtained in the literature [2]. µRaman spectra were also collected from individual pure HMX and CL-20 crystalline particles to compare with the specific signature of the co-crystals. Such spectra comparison (Fig. 2) guides the selection of HMX and CL-20 marker bands making sure that no signal appears at these wavenumbers in the other pure crystalline compounds to monitor their spatial distribution of their contribution at the µscale but also at the nanoscale: the NO_2 asymmetric

stretching vibration at 1602 cm^{-1} (1595-1615 cm^{-1} integration interval) for CL-20 and the CH_2 out of plane wagging vibration at 1416 cm^{-1} (1404-1434 cm^{-1} integration interval) for HMX. These bands are present in the co-crystal signature but are broadened and shifted compared to pure individual compounds as a result of different chemical environments. The areal CL-20:HMX band marker ratio is 2.5:1 in the spectrum of the CL-20/HMX nanoparticles.

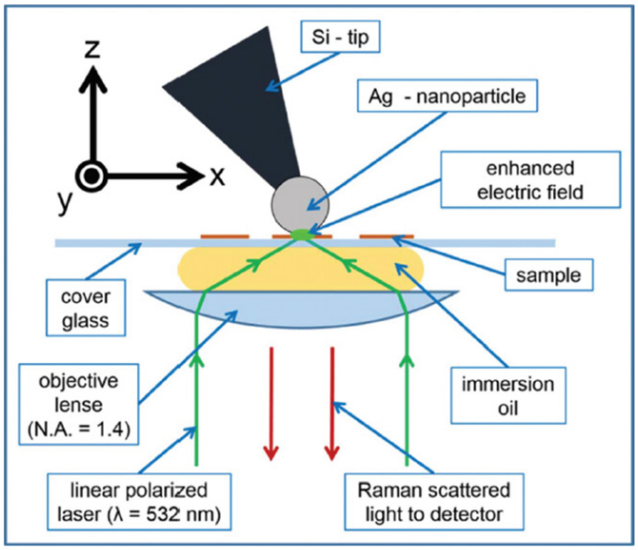


Fig. 3. Schematic diagram of the TERS experimental setup.

TERS measurements were performed using a NanoRaman system from HORIBA Scientific integrating an atomic force microscope (CombiScope™ SPM - TRIOS platform) and a Raman microscope (Labram HR Evolution) in bottom illumination mode (transmission mode). The 532 nm linearly polarized laser is precisely focused onto the TERS tips by a 100× 1.4 NA oil immersion objective by means of the piezo movement of the scanner on which the objective is mounted (Fig. 3). TERS maps are recorded in non-contact mode which means that the distance tip-sample surface varies constantly during the measurement. TERS images of two nanoparticles (with a pixel size of 50 nm) with their corresponding far-field and near-field spectra averaged over each entire particle are shown in Fig. 4. Each spectrum of the maps is recorded with an acquisition time of 0.2 s. A striking difference between the near-field and far-field spectra is the intensity inversion between the two CL-20:HMX markers: from a ratio of 2.5 to 1 in the far-fied to about 1 to 1.5 in the near-field spectra. This inversion could arise from a special arrangement of the oriented nano co-crystal particles toward the Raman scattering system. Fig. 5 shows additional data from three nanoparticles: the TERS maps have been acquired with higher resolution (20×20 nm^2 pixel area). Same observation can be made about the inversion ratio of the CL-20:HMX markers between far-field and near field spectra.

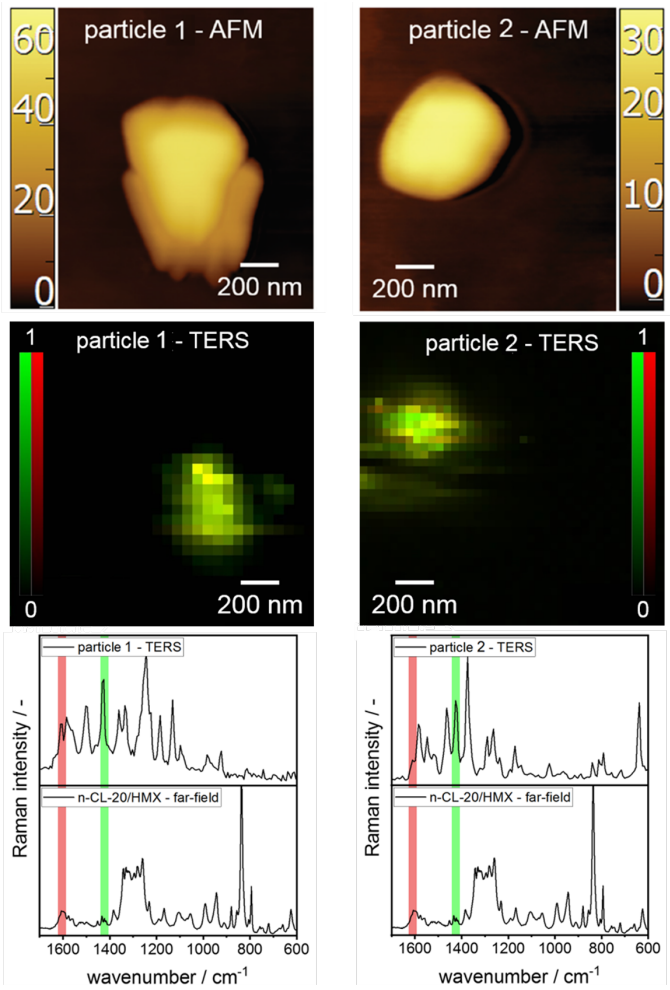


Fig. 4. AFM topographic images of two n-CL-20/HMX nanoparticles and their corresponding TERS maps and spectra. TERS spectra represent the average over all TER spectra on the particle surfaces.

However some approximated normal coordinate analysis leads to the conclusion that the CL-20 contribution should be three times the HMX contribution. As a result the intensity inversion observed in the near-field Raman spectra is very likely arising from a molecular HMX layer terminated surface. The HMX cyclic nitroamine may be more deformable than the CL-20 cage and thus be energetically more favorable to accommodate and form crystal free interface.

Conclusion and perspectives

This application note shows how TERS mapping is capable to characterize the crystalline nature, quality and orientation of single nano-particles prepared by co-crystallizing two explosive organic compounds (CL-20 and HMX) in a molar ratio of 2:1 under a spray evaporation process. Such sensitivity is appreciated when minute sample amount is available and other techniques like XRPD are limited.

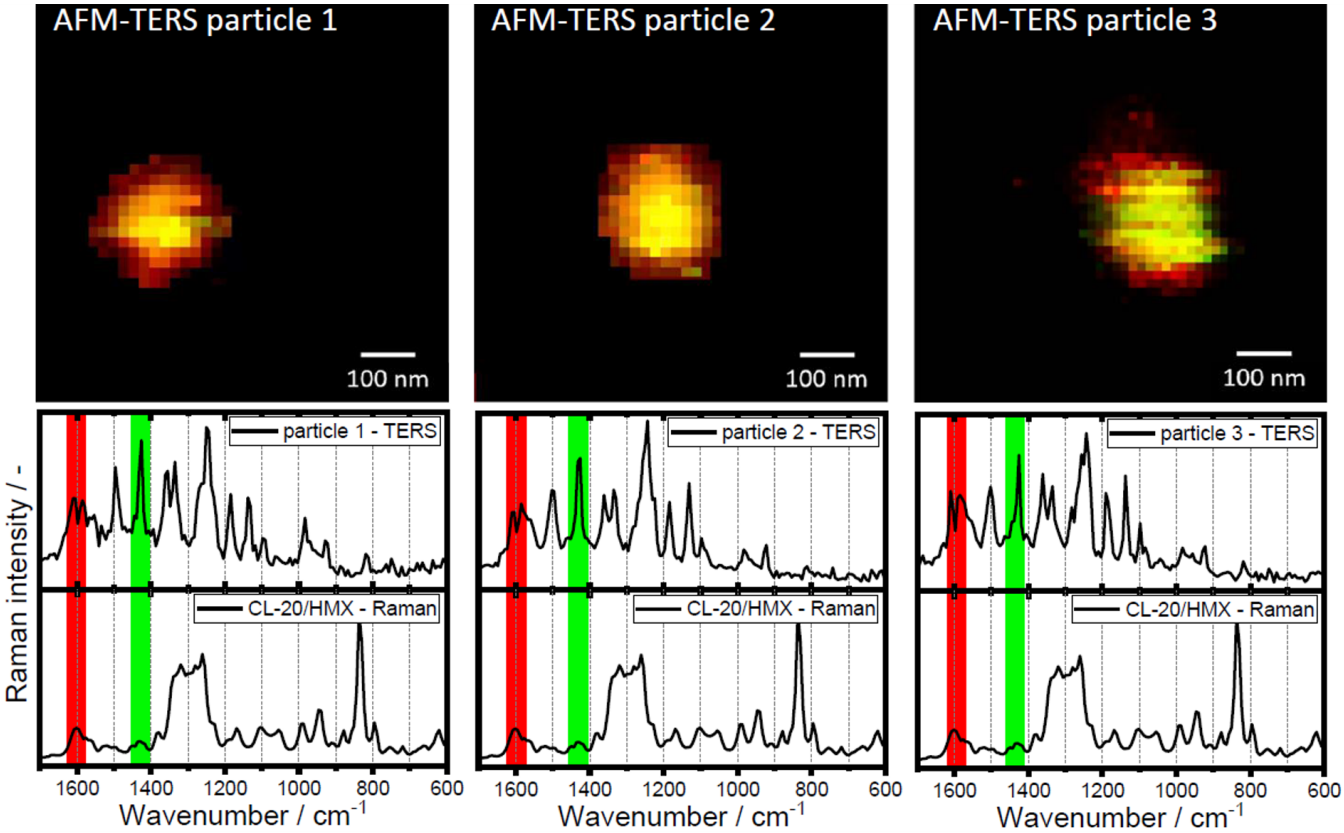


Fig. 5. TERS maps of three n-CL-20/HMX nanoparticles and their μRaman (far-field) and TER spectra. TERS spectra represent the average over all TER spectra on the particle surfaces.

Single nanoscale co-crystals imaged by AFM feature well defined flat faces and edges with step height of 29 nm and size of 100-400 nm. TERS images of single CL-20/HMX nanocrystals are collected with a spatial resolution down to 20 nm. The TER spectra feature a HMX/CL-20 contribution intensity ratio that is inverse with respect to the μRaman spectra which reveals a HMX molecular layer terminated surface. This finding allows to explain the mechanical sensitivity value of the co-crystal nanoparticles that is close to that of HMX (and much lower that CL-20). The HMX terminated surface also yields an impact mechanism proposal where ignition is spread from surfaces.

In conclusion, data in this note perfectly illustrate the surface sensitivity of TERS and its subsequent potential to give insights in the formation mechanism of co-crystal formation and to engineer co-crystals for dedicated applications.

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