application note

Lise-Meitner-Straße 6, D-89081 Ulm, Germany
Tel. +49 (0) 731 140 700, Fax. +49 (0) 731 140 70200
www.witec.de, info@witec.de

WITec
focus innovations

Confocal Raman Microscopy - Surface enhanced Raman Spectroscopy (SERS) on Ag-Nanoparticles coated with Dipicolinic Acid

Raman Spectroscopy is a powerful technique used to investigate the chemical states of the bonds in carbon materials.
Surface enhanced Raman spectroscopy (SERS), which enables the collection of Raman signals from even a single molecule,makes the technique more useful for analysis of molecules deposited onto metal surfaces.
Enhancement in Raman intensities of a factor up to 1014 may be observed with this technique. Two mechanisms are considered responsible for the enhancement:
The primary contribution is an enlargement of the local electromagnetic field, due to the excitation of a localised surface plasmon.
Another factor results from a charge transfer-state between the surface complex of the adsorbed molecule and the metal surface.

Due to its extreme sensitivity, the Confocal Raman Microscope alpha300 R is the ideal instrument to perform high resolution Raman imaging and SERS.

In this study, Ag-nanoparticles coated with organic dipicolinic acid were investigated to show the different arrangement of the particles and its corresponding chemical behaviour. The particles should have a diameter of about 20 nm and were agglomerated into groups of particles.
The alpha300 R was used in the Spectral Imaging Mode where a complete Raman spectrum was collected at every pixel of the image. 40 000 spectra (200 lines consisting of 200 pixels per line) with an integration time of 50 ms/spectrum were used to create the image in fig. 1. The total scan time was 35 minutes and the scan range was 50 µm x 50 µm. As is typical for SERS, not only one dedicated spectrum for the organic molecule, but many different spectra can be observed (Fig. 1 and Fig. 2).
This is due to the fact that the molecules are attached at different positions to the Ag-particle, which induces different proportions in the chemical bonds of the molecule to contribute to the SERS effect. As the field enhancement is confined to the near-field, only the parts of the molecules that are tightly bonded to the Ag-particle, show a strong Raman enhancement. In additon, the resonance enhancement depends also on the size and the shape of the Ag-particle.

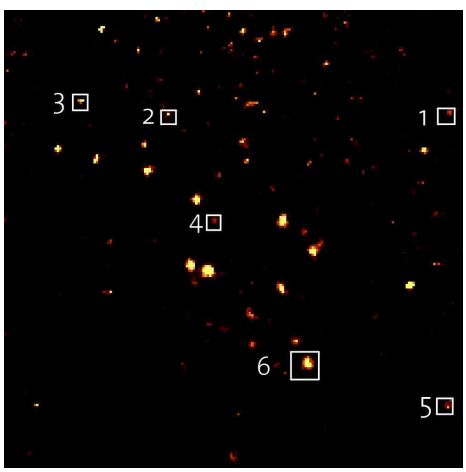

Fig. 1: Integral intensity of all Raman spectra acquired in the Spectral Imaging Mode. Scan range: 50 x 50 µm

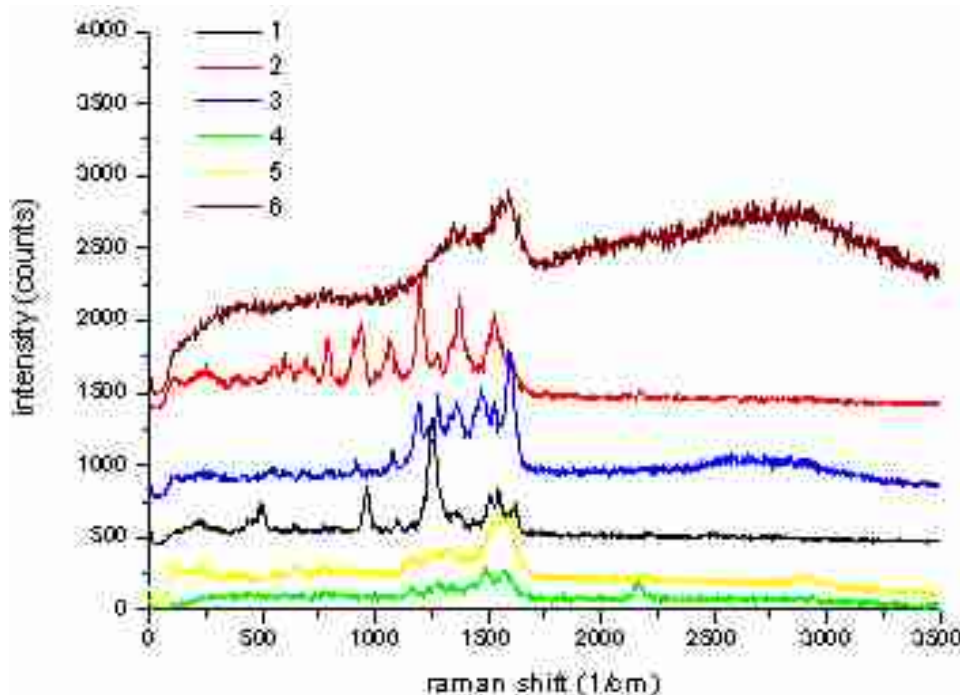

Fig. 2: Averaged Raman spectra of the marked regions in fig.1.

Lise-Meitner-Straße 6, D-89081 Ulm, Germany
Tel. +49 (0) 731 140 700, Fax. +49 (0) 731 140 70200
www.witec.de, info@witec.de

Time Series
For time series the Laser beam was positioned on a certain molecule and a series of 900 spectra with 200 ms integration time per spectrum was acquired (Fig.3).

The spectra can change completely within a fraction of a second. The spectra can be very stable for several seconds before suddenly changing dramatically within a few milliseconds. The reason for this behaviouur is that only a single molecule is involved in the Raman scattering process and that the bonding between the Ag-particle and the molecule changes due to thermal fluctuations and/or chemical reactions.

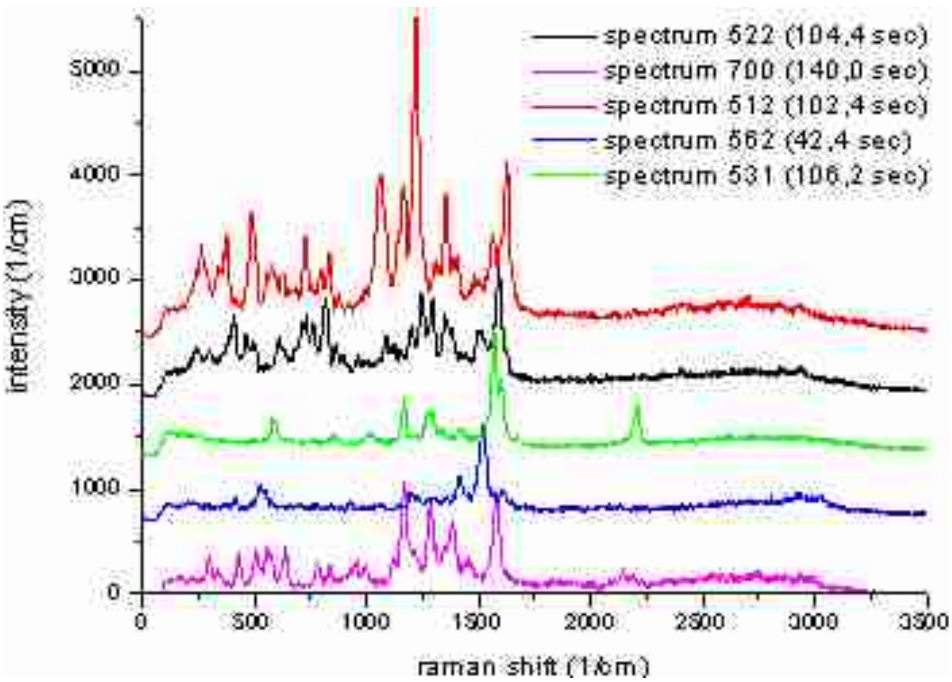

Fig. 3: Five spectra of a series of 900 spectra shown with an integration time of 200 ms for a single molecule.

Samples courtesy of Dr. Joseph Miragliotta, John Hopkins University, Baltimore, USA