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Publication date:
2015

Document Version
Peer reviewed version

Statistical analysis of large areas of Raman mapped DNA functionalized gold coated silicon nanopillar SERS substrates

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Keywords: SERS, area map, peak fitting, statistics, sensor

Detection of small molecules at low concentration by Surface Enhanced Raman Spectroscopy (SERS) has mostly been done using metal nanoparticles[1], where data is normally limited to a few measurements of different clusters. The emergence of SERS substrates with well-defined, uniform 2D layers of nanostructures has created an opportunity to increase the amount of data tremendously. The amount of data calls for new approaches for data processing and data visualization, especially when batches of large area maps are collected. However to our knowledge only limited statistical analysis on SERS maps have been published[2–4].

In this work we demonstrate new ways to analyze DNA and 6-mercapto-1-hexanol (MCH) surface functionalization of a uniform gold covered silicon nanopillar SERS substrate[5] (Figure 1; SEM images) by using a peak-fitting approach on 30x10 point area maps. Using the fitted model it is possible to observe behavior of peak creation and peak shifts during different functionalization steps. Direct characterization of a DNA and MCH functionalized SERS substrate is of high value for use in different diagnostic assays[3,6,7].

The analysis is carried out by jointly fitting a Voigt profile (a combination of Lorentzian and Gaussian shaped curve) and a linear baseline correction to a given spectral window (Figure 1; graph).

The gold heads of the SERS substrate were functionalized with thiolated 75-mer DNA. The remaining gold binding sites were subsequently blocked with the small molecule MCH (Figure 1; schematic). The SERS signal was then captured in a 30x10 point area map using a 780 nm laser with 0.1 mW power and a 50x objective.

By analyzing the large amount of data, it is possible to get a statistical view of the position of SERS peaks for a given surface functionalization. Current data shows the appearance of a specific DNA peak after 15 minutes incubation in thiolated DNA solution (data not shown). Incubation for longer time does not narrow the peak position distribution nor increase the intensity distribution of the peaks. Data on MCH backfilling show significant change in peak position of the DNA peak for different MCH concentrations (Figure 1; histogram). Smaller concentrations show only a slight shift of the DNA peak position, while the largest show only the MCH peak.

The statistical tool presented allows for direct inspection, interpretation and comparison of batches of SERS maps on uniform SERS substrates that would otherwise not be possible.

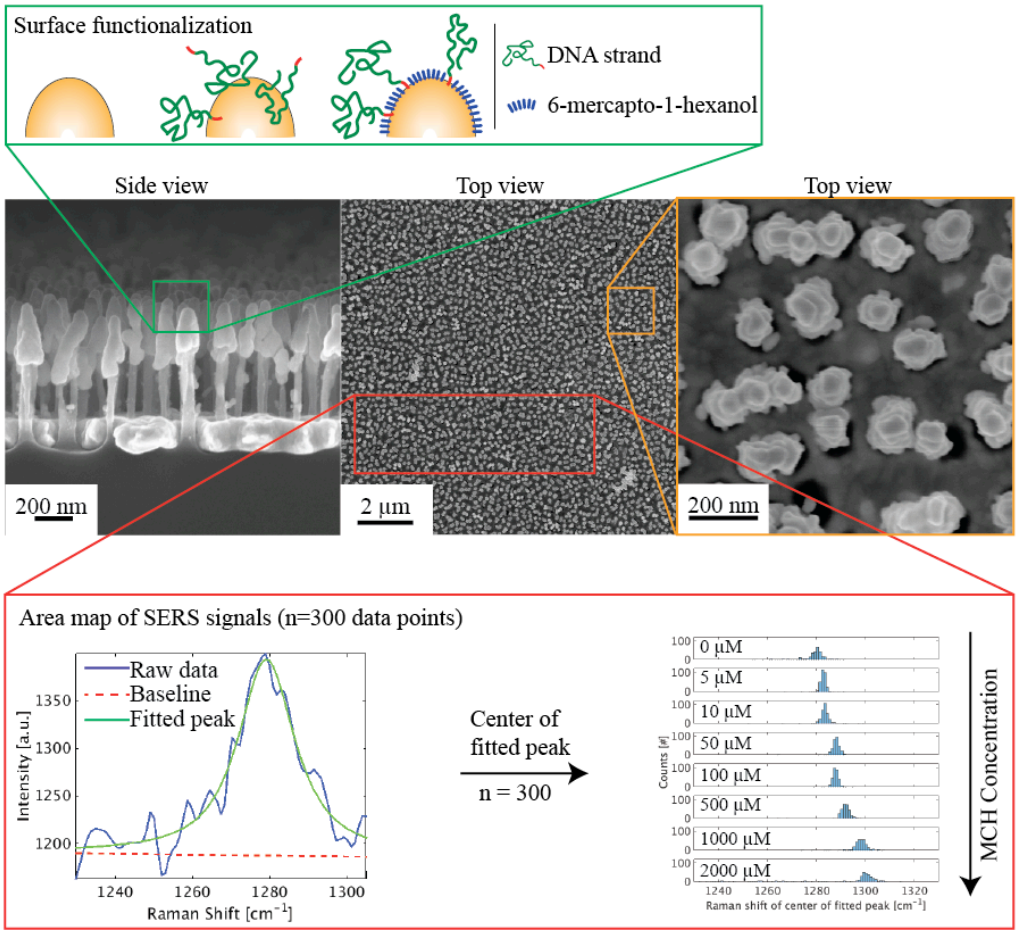

Figure 1. Top: schematic of the surface functionalization used in the experiments. Thiolated DNA was conjugated to the gold covered silicon nanopillar heads followed by backfilling with 6-mercapto-1-hexanol (MCH). Middle: SEM images of the SERS substrate seen from the side (left) and the top (middle and right). The gold heads of the silicon nanopillars are clearly seen. Bottom: overview of the peak-fitting model (left) used on 300 individual SERS spectra. The histogram (right) shows a clear shift of center peak position as a function of MCH concentration.

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