Hot spots contribution to overall SERS signal for SERS active dimers and trimers on various substrates

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The SERS (Surface enhancement Raman spectroscopy) is an increasingly active research field. SERS applications include sensing, spectroelectrochemistry, single molecule detection and detection of major health threats for humans (cancer, tuberculosis, viruses etc.). There are numerous advantages of this method as it is a very sensitive, label-free, humidity independent and rapid method with great capability of multiplexing.

One of the most versatile and perspective applications of SERS is in sandwich immunoassays, which provide high sensitivity and low Limit of Detection (LOD) for a detection of a variety of biotargets such as tuberculosis or cancer biomarkers. However, application of SERS sensors based on metal nanoparticles on metal films remain great challenge, due to low reproducibility, since various factors have an impact on sandwich SERS immunoassays, namely such as substrate composition, degree of NPs aggregation, pH, temperature and ionic strength of buffer solutions where immunoreactions occur.

We used combination of Raman microscopy, AFM and TEM to quantify the influence of dimerization on SERS signal for gold and silver nanoparticles on gold, silver, aluminum films and silicon wafer. Many published models predict high power inverse dependence of SERS enhancement on interparticle gap distance.

Formation of hot spots between two AuNPs or two Ag NPs modified with Raman reporters molecules increases mean SERS EF of the dimer relative to EF of a monomer by 15 – 30% per one particle, if this dimer is observed on the metal film of the same nature (AuNPs on Au film, AgNPs on Ag film). However dimers of AuNPs on Ag film and AgNPs on Au and Al films show higher EFs by 45 – 55% per one particle relative to EFs of monomer NPs on the same substrates. Overall increases in mean SERS EF upon dimerization (about 60% per one NP) and trimerisation (about 130% per one NP) of Au, Ag nanoparticles on the studied metal films are within factor of 2. All of the above mentioned data related to mean EFs values, although it was observed that the ratio of EFs for some dimers to mean EF of monomers can reach higher values up to 5.5 for Ag NPs on Au substrate.

To the contrary, for dimerization and trimerization of Au and Ag NPs on silicon, EF increase by 1 – 2 orders of magnitude relative to EF of single NPs. Therefore hot spots between gold nanoparticles over semiconductor substrate dominate SERS enhancement. The conclusion made for Raman reporters adsorbed on noble metal nanoparticles on plasmonic metal films is that all hot spot zones (e.g NP/NP and NP/metal film) generate on average SERS enhancement of the same order of magnitude.